



ADF Manual

Amsterdam Modeling Suite 2026.1

www.scm.com

Apr 02, 2026

CONTENTS

1	General	1
1.1	Introduction	1
1.1.1	ADF is an AMS Engine	2
1.1.2	Functionality	2
1.1.3	Applicability	2
1.1.4	Model Hamiltonian	2
1.1.5	Analysis	3
1.1.6	Technical	3
1.1.7	Fragments	3
	Basic atoms	4
	Automatic mode	4
1.1.8	Slater-type basis sets	4
1.2	What's new in ADF 2026.1	4
1.2.1	New features	4
1.3	Older releases	5
1.3.1	What's new in ADF 2025.1	5
	New features	5
	Input Changes	6
	Bug fixes	6
1.3.2	What's new in ADF 2024.1	6
	New features	6
	Removed features	6
1.3.3	What's new in ADF 2023.1	7
	New features	7
	Bug fixes	8
1.3.4	What's new in ADF 2022.1	8
	New features	8
1.3.5	What's new in ADF 2021.1	9
	New features	9
	New Defaults	9
1.3.6	What's new in ADF 2020.1	9
	New features	9
	New Defaults	10
1.3.7	ADF is an AMS Engine	10
1.4	AMSification of ADF in AMS2020	11
1.4.1	Restructuring of the input	11
1.4.2	Restructuring of input keys	12
1.4.3	Example shell script changes	13
1.4.4	Automatic tool for conversion of ADF2019 shell scripts	14
1.5	Input, execution and output	16

1.5.1	ADF specific files	16
1.6	Feature List	16
1.6.1	Model Hamiltonians	16
1.6.2	Structure and Reactivity	17
1.6.3	Spectroscopic properties	17
1.6.4	Charge transport properties	18
1.6.5	Analysis	18
1.6.6	Accuracy and Efficiency	19
1.7	Technical remarks, Terminology	19
1.7.1	Density functional theory	19
1.7.2	The Kohn-Sham MO model	20
1.7.3	Basis functions and orbitals	20
	Cartesian function sets, spurious components	20
	Frozen core: Core Orbitals and Core Functions	21
	Symmetry	21
	Orthonormal basis	21
	Fragments	21
	Summary of functions and orbitals	22
	Acronyms	22
1.7.4	Coulomb potential evaluation, density fitting	23
1.7.5	Three-step build-up of the bonding	23
1.7.6	Transition State procedure	24
2	Input, execution, and output	27
2.1	Input	27
2.1.1	General remarks on input structure and parsing	28
2.1.2	Keys	29
2.1.3	Blocks	30
2.1.4	Including an external file	31
2.1.5	Units	32
2.1.6	Title, comment	32
2.1.7	Amsification of ADF in ADF2020	33
2.1.8	Input parsing changes in ADF2018 and later	33
	ADF2018 syntax changes for a few keywords	33
	Strict parsing of input file	34
2.2	Execution	34
2.3	Structure of the Output	34
2.3.1	Job Characteristics on standard Output	35
2.3.2	Log file, adf.rkf, TAPE13	36
3	Coordinates, Basis sets, Fragments	37
3.1	Atomic coordinates	37
3.1.1	Cartesian	37
3.1.2	Z-Matrix	38
3.1.3	Orientation of Local Atomic Coordinates	38
3.1.4	Symmetry Key	39
3.2	Basis sets and atomic fragments	40
3.2.1	STO basis sets	40
3.2.2	Available basis sets	42
3.2.3	The Basis Key	44
3.2.4	Automatic mode	49
3.2.5	Create mode	50
3.2.6	Ghost Atoms, Non-standard Chemical Elements	51
	Automatic mode	51

3.2.7	Nuclear Model	52
3.3	Molecular fragments	53
3.3.1	Fragment mode	53
3.3.2	Fragment files	56
4	Model Hamiltonians	59
4.1	Electronic Configuration	59
4.1.1	Charge and Spin	59
	Spin: restricted vs. unrestricted	59
	Spin: unrestricted vs. restricted open-shell	61
	Unrestricted and Spin-Orbit Coupling	62
	Net Charge	64
4.1.2	Orbital occupations: electronic configuration, excited states	64
	Aufbau, smearing, freezing	64
	Explicit occupation numbers	66
	CHARGE and SPINPOLARIZATION vs. IRREPOCCUPATIONS	67
	Create mode	68
4.1.3	Frozen core approximation	68
4.1.4	Spin-polarized start-up potential	69
	Spin-flip method for broken symmetries	69
	Modify the starting potential	69
4.1.5	Unrestricted fragments	70
	Prepared for bonding	71
4.1.6	Simulated unrestricted fragments with key FRAGOCCUPATIONS	71
	Prepared for bonding	71
	FRAGOCCUPATIONS	71
4.1.7	Remove Fragment Orbitals	72
4.1.8	CDFT: Constrained Density Functional Theory	74
4.1.9	FOCDFT: Fragment Orbital Constrained DFT	78
4.2	Density Functionals (XC)	79
4.2.1	LDA	80
4.2.2	GGA	81
4.2.3	MetaGGA	84
4.2.4	Hartree-Fock	85
4.2.5	Hybrid	85
4.2.6	Meta-Hybrid	86
4.2.7	Range-separated hybrids	86
	RangeSep + XCFun: Yukawa range-separated hybrids	87
	Range-separated hybrids with LibXC	88
4.2.8	Notes on Hartree-Fock and (meta-)hybrid functionals	89
4.2.9	MP2, Double Hybrids, RPA	90
	Double Hybrid Functionals	90
	MP2	93
	RPA	94
	sigma-functional	95
	Spin-orbit coupling	96
4.2.10	Model Potentials	96
4.2.11	XCFun	97
4.2.12	LibXC	98
4.2.13	Dispersion corrections	99
	DFT-D4 functionals	99
	DFT-D3 functionals	100
	DFT-D functionals	102
	dDsC: density-dependent dispersion correction	103

	DFT-ulg	103
	DFT-MBD functionals	103
4.2.14	Post-SCF energy functionals	104
	GGA energy functionals	104
	Meta-GGA and hybrid energy functionals	105
	Post Hartree-Fock energy functionals	106
4.3	Relativistic effects	106
4.3.1	Pauli	109
4.3.2	ZORA	110
4.3.3	X2C and RA-X2C	110
4.3.4	Spin-Orbit coupling	111
	Partial ZORA	111
4.4	Solvents and other environments	111
4.4.1	COSMO: Conductor-like Screening Model	112
4.4.2	SM12: Solvation Model 12	119
4.4.3	Quild	122
4.4.4	Hybrid Engine (QM/MM, QM/QM')	122
4.4.5	DIM/QM: Discrete Interaction Model/Quantum Mechanics	122
	DRF	123
	Surface-enhanced response properties	124
	Input options	125
	DRF atomic parameters	129
	DIM atomic parameters	130
4.4.6	QM/FQ: Quantum Mechanics/Fluctuating Charges (and Fluctuating Dipoles)	134
	Gradients and geometry optimization	136
	Coupling with FDE	136
	Input options	136
4.4.7	QM/ ω FQ: Quantum Mechanics/Frequency-Dependent Fluctuating Charges (and Fluctuating Dipoles)	143
	Input options	144
4.4.8	FDE: Frozen Density Embedding	144
	Fragment-specific FDE options	146
	Kinetic energy approximants	148
	General FDE options	150
	Frozen Density Embedding with External Orthogonality	152
	FDE and (localized) COSMO	152
	FDE and QM/FQ(F μ)	153
	Subsystem TDDFT, coupled FDE	153
	Restrictions and pitfalls	155
4.4.9	3D-RISM: 3D Reference Interaction Site Model	155
4.5	Electric Field: Homogeneous, Point Charges, Polarizability	162
5	Structure and Reactivity	165
5.1	Single point calculations	165
5.2	Geometry optimization	165
5.3	Transition state search	165
5.4	Linear Transit, PES scan	166
5.5	Nudged Elastic Band (NEB)	166
5.6	Intrinsic Reaction Coordinate (IRC)	166
5.7	Excited state optimizations	166
5.8	Molecular dynamics	166
6	Gradients, Hessian, Thermodynamics	167
6.1	Gradients	167

6.2	Hessian	167
6.3	PES point character	167
6.4	Thermodynamics, gas phase Gibbs free energy	167
7	Spectroscopic properties	169
7.1	Vibrational Spectroscopy	169
7.1.1	IR frequencies and normal modes	169
	Analytical Hessian	169
7.1.2	(Resonance) Raman	172
7.1.3	VROA: (Resonance) vibrational Raman optical activity	173
7.1.4	VCD: Vibrational Circular Dichroism	173
7.1.5	Vibrational Polarizabilities	173
7.2	Time-dependent DFT	173
7.2.1	General remarks on the Response and Excitation functionality	174
7.2.2	Analysis options for TDDFT (excitation energies and polarizabilities)	176
7.2.3	Time-dependent Current DFT	177
	Magnetic properties within TDCDFT	178
7.3	Excitation energies: UV/Vis, X-ray, CD, MCD	179
7.3.1	Excitation energies, UV/Vis spectra	179
	Tamm-Dancoff approximation	181
	GW-Bethe-Salpeter equation (GW-BSE)	181
	Full XC kernel	182
	Plasmons in Molecules	183
	Transition dipole moments between excited states	183
	Accuracy and other technical parameters	183
7.3.2	Excitation energies for open-shell systems	184
	Unrestricted TDDFT	185
	ROKS TDA-DFT	186
	Spin-flip excitations: ALDA kernel	188
7.3.3	Select (core) excitation energies, X-ray absorption	189
	State selective optimization excitation energies	189
	Modify range of excitation energies	190
	Excitations as orbital energy differences	192
	Quadrupole intensities in X-ray spectroscopy	192
7.3.4	XES: X-ray emission spectroscopy	193
7.3.5	Excitation energies and Spin-Orbit coupling	194
	Perturbative inclusion of spin-orbit coupling	194
	ROKS-TDA-SOC	195
	Self-consistent spin-orbit coupling	196
	Highly approximate spin-orbit coupled excitation energies open shell molecule	197
7.3.6	CV(n)-DFT: Constricted Variational DFT	198
7.3.7	HDA, TD-DFT+TB, TDDFT-aas, sTDDFT	200
	HDA: Hybrid Diagonal Approximation	200
	TD-DFT+TB, TDA-DFT+TB	201
	TDDFT-aas	202
	sTDA, sTDDFT	203
7.3.8	CD spectra	205
7.3.9	MCD	205
7.3.10	Analysis	209
	NTO: Natural Transition Orbitals	209
	SFO analysis	209
	Charge-transfer descriptors	210
	ROSE or FOCDFDFT localized orbitals	210
7.4	Excited state (geometry) optimizations	211

7.4.1	Nuclear gradients only	213
7.5	Vibrationally resolved electronic spectra	214
7.5.1	AH-FC: Adiabatic Hessian Franck-Condon	214
7.5.2	VG-FC: Vertical Gradient Franck-Condon	214
7.6	(Hyper-)Polarizabilities, ORD, magnetizabilities, Verdet constants	214
7.6.1	RESPONSE: (Hyper-)Polarizabilities, ORD	214
	RESPONSE: Polarizabilities	214
	RESPONSE: Accuracy and convergence	216
	RESPONSE: Hyperpolarizabilities	216
	RESPONSE: Optical rotation dispersion (ORD)	217
7.6.2	AORESPONSE: Lifetime effects, (Hyper-)polarizabilities, ORD, magnetizabilities, Verdet constants	217
	AORESPONSE: Polarizabilities	217
	AORESPONSE: Technical parameters and expert options	218
	AORESPONSE: Damped First Hyperpolarizabilities	219
	AORESPONSE: Damped Second Hyperpolarizabilities	219
	AORESPONSE: ORD	220
	AORESPONSE: magnetizabilities, Verdet constants, Faraday B term	220
	AORESPONSE: Raman	221
	Applications of AORESPONSE	221
7.6.3	PolTDDFT: Damped Complex Polarizabilities	222
	UV/Vis spectra, CD spectra	223
	Reduced fit set	224
7.6.4	Van der Waals dispersion coefficients	225
	DISPER program: Dispersion Coefficients	225
7.7	Ligand Field and Density Functional Theory (LFDFT)	227
7.7.1	Introduction	227
7.7.2	Input description	228
	Average of Configuration run	228
	LFDFT atomic database	228
	LFDFT run	229
	EPR (ESR) g-tensor	230
	LFDFT intensities	230
	MCD	231
7.8	NMR	231
7.8.1	NMR Chemical Shifts	232
	Important notes	232
	Input options	234
7.8.2	Paramagnetic NMR Chemical Shifts	238
7.8.3	NMR spin-spin coupling constants	240
	Introduction	241
	Input file for CPL: adf.rkf	243
	Running CPL	244
	Practical Aspects	248
7.9	ESR/EPR	250
7.9.1	ESR/EPR g-tensor and A-tensor	250
7.9.2	ESR/EPR Q-tensor	253
7.9.3	ESR/EPR Zero-field splitting (D-tensor)	253
7.10	Nuclear Quadrupole Interaction (EFG)	254
7.11	Mössbauer spectroscopy	254
7.12	GW	255
7.12.1	General	255
7.12.2	Levels of self-consistency	257
	Eigenvalue-only self-consistent GW	257

	Quasiparticle self-consistent GW	258
	Convergence	258
7.12.3	Vertex corrections beyond GW	259
7.12.4	Embedding	261
7.12.5	Recommendations	261
	Basis sets	261
	Numerical aspects	262
	Choosing the KS reference	262
7.12.6	GW key	263
8	Transport properties	269
8.1	Charge transfer integrals (transport properties)	269
8.1.1	Charge transfer integrals with the TRANSFERINTEGRALS key	270
8.1.2	Charge transfer integrals with FDE	271
8.1.3	Charge transfer integrals with FOCDFT	274
8.2	Exciton transfer integrals	277
8.2.1	Exciton transfer integrals with FDE	277
8.2.2	Exciton transfer integrals with ROSE or FOCDFT	278
	ROSE localized orbitals	278
	FOCDFT localized orbitals	278
	Exciton transfer integrals	278
	ExcitonTransfer key	281
8.3	GREEN: Non-self-consistent Green's function calculation	284
8.3.1	Introduction	284
8.3.2	Wide-band-limit	286
8.3.3	Input options	286
8.3.4	Output	288
8.3.5	GREEN with ADF-GUI	289
9	Analysis	291
9.1	Molecules built from fragments	291
9.2	Bond energy analysis	292
9.2.1	Bond energy details	293
9.2.2	Notes on double-hybrid functionals and MP2	294
9.2.3	Total energy evaluation	294
9.2.4	Interacting Quantum Atoms (IQA)	295
9.3	Localized Molecular Orbitals	297
9.3.1	Boys-Foster and Pipek-Mezey localization	297
	Perturbed Localized Molecular Orbitals	299
9.3.2	Reduction of Orbital Space Extent (ROSE)	300
9.3.3	Natural Bond Orbitals (NBO)	303
9.4	Advanced charge density and bond order analysis	303
9.4.1	Charges, Populations	304
9.4.2	Bond orders	305
9.4.3	ETS-NOCV: Natural Orbitals for Chemical Valence	308
9.4.4	Adfnbo, gennbo: NBO analysis	309
	NBO analysis of EFG, NMR chemical shifts, NMR spin-spin coupling	311
9.4.5	QTAIM: Atoms in Molecules	315
	Local, atomic, and non-local properties	315
	ADF2AIM	317
	Aromaticity index with QTAIM	318
9.4.6	Conceptual DFT	319
	Global, atomic, and non-local descriptors	319
	Domains of the dual descriptor	321

9.4.7	adf2damqt: DAMQT interface	323
9.4.8	FOD: fractional orbital density	323
9.5	Controlling printed output	324
9.5.1	Print / NoPrint	324
9.5.2	Debug	327
9.5.3	EPrint	328
9.5.4	Eprint subkeys vs. Print switches	328
9.5.5	Other Eprint subkeys	333
9.5.6	Reduction of output	335
9.6	Results on Output	335
9.6.1	Electronic Configuration	336
9.6.2	Mulliken populations	336
9.6.3	Hirshfeld charges, Voronoi deformation density	336
9.6.4	Multipole derived charges	338
9.6.5	Charges Derived from the Electrostatic Potential	338
9.6.6	Charge model 5	338
9.6.7	Bond order analysis	338
9.6.8	Dipole moment, Quadrupole moment, Electrostatic potential	339
9.6.9	Fragments and Basis Functions	340
9.6.10	MO analysis	340
9.6.11	Bond energy analysis	341
9.7	Densf: Volume Maps	342
9.7.1	Input	342
	Input/Output files	343
	Grid	343
	Inline Grid	344
	Units	345
	Density	345
	Kinetic Energy Density and Electron Localization Function (ELF)	345
	Laplacian of the Density	346
	Gradient of the Density	346
	Hessian of the Density	346
	Potential	347
	Orbitals	347
	NOCV	348
	NOCV profile	350
	Generic orbitals	350
	NCI	350
	SEDD	351
	DualDescriptor	351
	PolTDDFT	352
9.7.2	Result: TAPE41	352
9.8	DOS: Density of States	357
9.8.1	Introduction	357
9.8.2	Mulliken population analysis	358
9.8.3	Density of states analyses based on Mulliken population analysis	359
9.8.4	Generalizations of OPDOS, GPDOS, PDOS	360
9.8.5	Input	360
9.9	VCD Analysis: VCDtools	363
9.10	PyFrag: Activation Strain Model Analysis	363
9.10.1	Requirements	363
9.10.2	Running PyFrag	363
9.10.3	Specifying the Trajectory	363
9.10.4	Molecular Fragments	364

9.10.5	ADF Options	364
9.10.6	Analysis Options	364
10	Accuracy and Efficiency	367
10.1	Precision and Self-Consistency	367
10.1.1	SCF	368
	Main options	368
	Energy-DIIS	371
	Augmented Roothaan-Hall (ARH)	372
10.1.2	Numerical Integration	373
	Becke Grid	374
	Voronoi grid (deprecated)	375
	Atomic radial grid	379
10.1.3	Density fitting	380
10.1.4	Hartree-Fock RI scheme	382
	Old Hartree-Fock RI scheme	383
10.1.5	MBPT scheme	384
	Recommended numerical settings	385
	MBPT input block	387
10.1.6	Dependency (basis set, fit set)	390
10.2	Basis Set Superposition Error (BSSE)	391
10.3	Control of Program Flow	392
10.3.1	Limited execution	392
10.3.2	Skipping	393
10.3.3	Ignore checks	393
10.4	Technical Settings	394
10.4.1	Memory usage	394
10.4.2	Direct SCF: recalculation of data	394
10.4.3	Vector length	394
10.4.4	Tails and old gradients	395
10.4.5	Linear scaling	395
10.4.6	All Points	397
10.4.7	Full Fock	397
10.4.8	Save info	397
11	Restarts	399
11.1	ADF Restart files	399
11.2	The restart key	400
11.3	Structure of the restart file	401
12	Recommendations and Troubleshooting	403
12.1	Recommendations	403
12.1.1	Precision	403
12.1.2	Electronic Configuration	404
	Spin-unrestricted versus spin-restricted, Spin states	404
12.1.3	What basis set should I use in ADF?	405
	ZORA or non-relativistic calculation?	405
	Large or small molecule?	405
	Frozen core or all-electron?	406
	Diffuse functions needed?	407
	Normal or even-tempered basis?	407
	Recommendations for Double-hybrids and MP2	408
	What accuracy do the basis sets give?	408
12.1.4	Relativistic methods	410

12.2	Troubleshooting	410
12.2.1	License file corrupt	410
12.2.2	Recover from Crash	411
12.2.3	Memory Management	411
12.2.4	SCF Convergence Guidelines for ADF	412
12.2.5	Geometry Optimization troubleshooting	414
	Very short bonds	415
12.2.6	Frequencies	416
	Imaginary Frequencies	416
	Geometry-displacement numbers in the logfile are not contiguous	417
12.2.7	Input ignored	417
12.2.8	SFO Populations	418
12.2.9	Error Aborts	418
12.2.10	Warnings	418
13	Appendices	419
13.1	Basis set file format	419
13.1.1	Sections	419
13.1.2	Example of a basis set file: Calcium	421
13.1.3	Extending a basis set	423
13.2	Elements of the Periodic Table	423
13.3	Multiplet States	426
13.3.1	Multiplet energies	427
13.4	Dirac program: relativistic core potentials	435
13.5	Symmetry	436
13.5.1	Schönflies symbols and symmetry labels	436
	TDDFT irrep labels	438
13.5.2	Molecular orientation requirements	439
	Molecular orientation conventions	439
13.6	Binary result files	439
13.6.1	ams.rkf	439
13.6.2	adf.rkf (TAPE21)	440
	adf.rkf: Added notes	440
13.6.3	TAPE10	441
13.6.4	TAPE13	442
13.6.5	TAPE15	442
13.6.6	TAPE41	442
13.6.7	Other binary files	442
13.7	Error messages	442
13.8	Warnings	443
14	Required Citations	457
14.1	General References	457
14.2	Feature References	458
14.2.1	Coordinates, basis sets, fragments	458
14.2.2	Geometry optimizations, transition states, and reaction paths	458
14.2.3	Model Hamiltonians	458
14.2.4	Relativistic Effects	459
14.2.5	Solvents and other environments	460
14.2.6	Frequencies, IR Intensities, Raman, VCD	461
14.2.7	Time-Dependent DFT	462
	Excitation Energies and Oscillator Strengths	462
	Excited state gradients	463
	Polarizabilities	464

	Hyperpolarizabilities	464
	CD, ORD, magnetizability, MCD, Verdet constants	464
	Dispersion Coefficients	465
14.2.8	LFDFT	465
14.2.9	NMR	466
	NMR Chemical Shifts	466
	NMR spin-spin coupling	466
14.2.10	ESR/EPR	467
	G-tensor: Zeeman interaction	467
	A-tensor: Nuclear magnetic dipole hyperfine interaction	468
14.2.11	Nuclear Quadrupole Interaction (EFG)	468
14.2.12	GW	468
14.2.13	Transport properties: Non-self-consistent Green's function	469
14.2.14	Analysis	469
14.2.15	Accuracy and efficiency	469
14.3	External programs and Libraries	470
15	Examples	471
15.1	Introduction	471
15.2	Model Hamiltonians	473
15.2.1	Special exchange-correlation functionals	473
	Example: r2SCAN-3c	473
	Example: Asymptotically correct XC potentials: CO	474
	Example: Meta-GGA energy functionals: OH	475
	Example: Hartree-Fock: HI	482
	Example: B3LYP: H2PO	485
	Example: Long-range corrected GGA functional LCY-BP: H2O	486
	Example: Range-separated functional CAMY-B3LYP: H2O	487
	Example: Single point MP2	488
	Example: Water Dimer SOS-AO-PARI-MP2	489
	Example: Single point B2GPPLYP	489
	Example: Water-MeOH - DODSCAN	493
	Example: unrestricted MP2: Li	494
	Example: RPA@PBE calculation: H2O	494
	Example: RPASOX@PBE0 calculation: H2O	495
	Example: Grimme Molecular Mechanics dispersion-corrected functionals (DFT-D3-BJ)	496
	Example: Density-Dependent Dispersion Correction (dDsC): CH4-dimer	500
	Example: DFT-ulg Dispersion Correction: Benzene dimer T-shaped	501
15.2.2	Relativistic effects: ZORA, X2C, spin-orbit coupling	502
	Example: ZORA Relativistic Effects: Au2	502
	Example: Spin-Orbit coupling: Bi and Bi2	503
	Example: Spin-Orbit unrestricted non-collinear: Tl	507
	Example: Excitation energies including spin-orbit coupling: AuH	511
	Example: ZORA, X2C and RA-X2C: HgI2 = Hg + I2	512
	Example: spin-orbit coupled MP2: atomization energy I2	514
	Example: Spin-Orbit spin-polarized start-up: Cr3	515
15.2.3	Solvents, other environments	516
	Example: COSMO: HCl	516
	Example: solvation model SM12: Acetamide	519
	Example: geometry optimization with SM12 using RESP charges	520
	Example: Electric Field: PtCO	521
	Example: Electric Field, Point Charge: N2	522
	Example: 3D-RISM: Glycine	523
	Example: 3D-RISM: Entropy	525

15.2.4	FDE: Frozen Density Embedding	527
	Example: FDE: H2O in water	527
	Example: FDE freeze-and-thaw: HeCO2	543
	Example: FDE energy: NH3-H2O	549
	Example: FDE energy: unrestricted fragments: Ne-H2O	553
	Example: FDE geometry optimization: H2O-Li(+)	555
	Example: FDE NMR shielding: Acetonitrile in water	557
	Example: FDE NMR spin-spin coupling: NH3-H2O	562
	Example: Subsystem TDDFT, coupled FDE excitation energies	566
	Example: FDE and COSMO: H2O-NH3	579
	Example: FDE and COSMO: H2O-NH3	582
15.2.5	QM/MM calculations	584
15.2.6	Quild: Quantum-regions Interconnected by Local Descriptions	584
15.2.7	DIM/QM: Discrete Interaction Model/Quantum Mechanics	584
	Example: DRF: H2O and H2O	584
	Example: DRF: hyperpolarizability H2O in water	585
	Example: DRF: scripting tool	595
	Example: DRF2: Polarizability N2 on Ag68 + H2O	596
	Example: CPIM: excitation energies N2 on silver cluster Ag68	604
	Example: CPIM: polarizability N2 on silver cluster Ag68	606
	Example: PIM: H2O on Ag2689	613
	Example: PIM: Polarizability with local fields	614
	Example: PIM: optimization N2 on silver cluster Ag68	616
	Example: PIM: polarizability N2 on silver cluster Ag68	619
	Example: PIM: Raman scattering N2 on silver cluster Ag68	625
	Example: PIM: SEROA calculation N2 on silver cluster Ag68	628
	Example: PIM: Multipole Method N2 on silver cluster Ag1415	631
15.2.8	QM/FQ(F μ): Quantum Mechanics / Fluctuating Charges (and Fluctuating Dipoles)	656
	Example: QM/FQ(F μ): 2-Methyloxirane (QM) in Water	656
	Example: QM/FQ(F μ): geometry optimization	682
	Example: QM/FQ(F μ): polarizability 2-Methyloxirane (AORESPONSE)	695
	Example: QM/FQ(F μ): polarizability 2-Methyloxirane (RESPONSE)	721
	Example: QM/FQ(F μ): excitations 2-Methyloxirane	747
	Example: QM/FDE/FQ: excitations of acrolein in water	773
	Example: QM/wFQ(F μ): 2-Methyloxirane (QM) with Sodium nanoparticle	789
	Example: QM/wFQ(F μ): 2-Methyloxirane (QM) on a carbon sheet	793
	Example: QM/wFQ(F μ): 2-Methyloxirane (QM) with Silver nanoparticle	798
	Example: QM/wFQ(F μ): 2-Methyloxirane (QM) with Gold nanoparticle	802
15.3	Structure and Reactivity	804
15.3.1	Geometry Optimizations	804
	Example: Geometry Optimization: H2O	804
	Example: Restraint Geometry Optimization: H2O	804
	Example: Constraint Geometry Optimization: H2O	806
	Example: Initial Hessian	810
	Example: Geometry optimization with an external electric field or point charges: LiF	812
15.3.2	Transition States, Linear Transits, Intrinsic Reaction Coordinates	814
	Example: LT, Frequencies, TS, and IRC: HCN	814
	Example: TS search using partial Hessian: C2H6 internal rotation	815
	Example: Relativistic ZORA TS search: CH4 + HgCl2 $\rightleftharpoons$ CH3HgCl + HCl	817
	Example: TS reaction coordinate: F- + CH3Cl	818
	Example: (non-)Linear Transit: H2O	819
15.3.3	Total energy, Multiplet States, S2, Localized hole, CEBE	820
	Example: Total Energy calculation: H2O	820
	Example: Multiplet States: [Cr(NH3)6]3+	824

Example: Calculation of S2: CuH+	829
Example: Localized Hole: N2+	831
Example: Broken spin-symmetry: Fe4S4	832
Example: Core-electron binding energies (CEBE): NNO	834
Example: CEBE 1s Iodine in HI	838
Example: Constrained DFT: H2O+ ... H2O	840
Example: ROKS: O2	841
Example: ROKS: SF	842
15.4 Spectroscopic Properties	843
15.4.1 IR Frequencies, (resonance) Raman, VROA, VCD	843
Example: Numerical Frequencies: NH3	843
Example: Numerical Frequencies, spin-orbit coupled ZORA: UF6	846
Example: Numerical Frequencies, accurate Hartree-Fock: H2O	848
Example: Analytic Frequencies: CN	849
Example: Analytic Frequencies: CH4	850
Example: Analytic Frequencies: HI	851
Example: Mobile Block Hessian (MBH): Ethanol	852
Example: Mobile Block Hessian: CH4	853
Example: Raman: NH3	854
Example: Raman: HI	857
Example: Resonance Raman, excited state finite lifetime: HF	862
Example: Vibrational Raman optical activity (VROA): H2O2	863
Example: Resonance VROA: H2O2	864
Example: Raman and VROA for approximate modes	865
Example: Vibrational Circular Dichroism (VCD): NHDT	867
Example: unrestricted VCD: CHFClBr	867
15.4.2 Excitation energies: UV/Vis spectra, X-ray absorption, CD, MCD	868
Example: Excitation energies and polarizability: Au2	868
Example: Excitation energies open shell molecule: CN	869
Example: Spin-flip excitation energies: SiH2	872
Example: TDHF excitation energies: N2	873
Example: excitation energies CAM-B3LYP: Pyridine	876
Example: CAMY-B3LYP excitation energies: H2O	877
Example: Full XC kernel in excitation energy calculation: H2O+	878
Example: Use of xcfun in excitation energy calculations: H2O	879
Example: Core excitation energies: TiCl4	880
Example: X-Ray Absorption and Emission Quadrupole Oscillator strengths at the Cl K-edge: TiCl4	885
Example: (Core) Excitation energies including spin-orbit coupling: Ne	888
Example: Excitation energies perturbative spin-orbit coupling: AgI	893
Example: ROKS-TDA-SOC: Cd+	894
Example: ROKS_TDA_SOC: NpF6	894
Example: Excitation energies including spin-orbit coupling for open shell: PbF	897
Example: Circular Dichroism (CD) spectrum: DMO	898
Example: CD spectrum with spin-orbit coupling: C2H3I	899
Example: CD spectrum, hybrid functional: Twisted ethene	900
Example: MCD: H2O	902
Example: MCD including zero-field splitting: H2O	903
Example: CV(n)-DFT excitation energies: Formamide	904
Example: HDA excitation energies: NH3	906
Example: HDA spin-orbit coupled excitation energies: H2O	907
Example: TD-DFT+TB excitation energies: beta-Carotene	908
Example: TDDFT-aas: Singlet excited state geometry optimization	910
Example: sTDA excitation energies: Adenine	911

Example: sTDDFT excitation energies: Adenine	913
Example: sTDA excitation energies RS functional: Bimane	914
Example: sTDA excitation energies wB97: TCNE-Benzene	915
15.4.3 Excited state (geometry) optimizations	917
Example: Excited state geometry optimization: N2	917
Example: Excited state geometry optimization with a constraint: CH2O	919
Example: Spin-flip excited state geometry optimization: CH2	920
Example: Numerical Frequencies of an excited state: PH2	922
Example: TD-DFT+TB: Singlet excited state geometry optimization	924
Example: TD-DFT+TB: Triplet excited state geometry optimization	925
Example: TD-DFT+TB: Open shell excited state geometry optimization	926
15.4.4 Vibrationally resolved (electronic) spectra	927
Example: Franck-Condon Factors: NO2	927
Example: Vibronic-Structure Tracking: Naphthalene	929
Example: Vibronic Density of States	931
15.4.5 (Hyper-)Polarizabilities, dispersion coefficients, ORD, magnetizabilities, Verdet constants	932
Example: Polarizabilities including spin-orbit coupling: AgI	932
Example: damped first hyperpolarizability: LiH	933
Example: damped second hyperpolarizability: LiH	935
Example: Verdet constants: H2O	938
Example: Dispersion Coefficients: HF	939
Example: Optical Rotation Dispersion (ORD): DMO	941
Example: ORD, lifetime effects (key AOESPONSE): DMO	942
Example: Polarizability: first order perturbed density	944
Example: Hyperpolarizabilities of He and H2	959
Example: Damped Verdet constants: Propene	961
Example: Static magnetizability: H2O	962
Example: Dynamic magnetizability: H2O	964
Example: Time-dependent current-density-functional theory: C2H4:	965
Example: Damped complex polarizabilities with POLTDDFT: Au10	966
Example: POLTDDFT with hybrid functional: NH3	967
Example: POLTDDFT with range-separated functional: C2F4-C2H2	968
15.4.6 Ligand Field DFT (LFDFT)	969
Example: Ligand Field DFT: Co 2+	969
Example: Ligand Field DFT: f-d transitions in Pr 3+	971
Example: LFDFT: g-tensor of Co(acacen)	973
Example: LFDFT: g-tensor of Cu(H2O)6	976
Example: LFDFT: XMCD 3d-4f transitions in Er 3+	977
15.4.7 NMR chemical shifts and spin-spin coupling constants	980
Example: NMR Chemical Shifts: HBr	980
Example: NMR Chemical Shifts: HgMeBr	982
Example: NMR Chemical Shifts, SAOP potential: CH4	985
Example: NMR Nucleus-independent chemical shifts (NICS): PF3	986
Example: NMR with B3LYP: PF3	987
Example: Partial ZORA analysis: NMR chemical shift	990
Example: open shell NMR (pNMR) shielding: O2	992
Example: NMR Spin-spin coupling constants: C2H2	994
Example: NMR Spin-spin coupling constants, hybrid PBE0: HF	998
Example: NMR Spin-spin coupling constants, finite nucleus: PbH4	999
15.4.8 ESR/EPR g-tensor, A-tensor, Q-tensor, ZFS	1001
Example: ESR g-tensor, A-tensor, Q-tensor, D-tensor: HfV	1001
Example: ESR g-tensor, A-tensor, self consistent spin-orbit coupling: VO	1003
Example: ESR g-tensor, A-tensor, perturbative spin-orbit coupling: HgF	1005
Example: ESR spin-restricted and spin-unrestricted: TiF3	1008

	Example: ESR, X2C and RA-X2C: PdH	1012
	Example: Zero-field splitting (ZFS), ESR D-tensor: NH	1014
	Example: ZFS D tensor, including direct electron spin-spin part: Phenylnitrene	1015
15.4.9	EFG, Mössbauer	1016
	Example: Mössbauer spectroscopy: Ferrocene	1016
	Example: Mössbauer with X2C: Hg compounds	1019
15.4.10	GW	1022
	Example: G_0W_0 @PBE calculation: H2O	1022
	Example: G_0W_0 @PBE0 calculation: O3	1023
	Example: G_0W_0 @PBE0 calculation: Phenol	1024
	Example: evGW@M06-2X calculation: H2O	1026
	Example: qsGW calculation: N2	1027
	Example: qsGW with frozen core: Br2	1028
	Example: G3W2 calculation: H2O	1029
	Example: GW with DRF: CH2O in Water	1030
15.5	Transport properties	1032
15.5.1	Charge and exciton transfer integrals	1032
	Example: Charge transfer integrals: AT base pair	1032
	Example: Charge transfer integrals with FDE: water dimer	1035
	Example: Charge transfer integrals with FOCDFE	1046
	Example: Charge Recombination Calculation of Toluene and TCNE	1051
	Example: XCDFT: Charge Separation of an ethylene dimer	1068
	Example: Exciton transfer integrals with FOCDFE	1080
15.5.2	Non-self-consistent Green's function calculation	1085
	Example: DOS and transmission: Aluminium	1085
	Example: Gold electrodes	1089
	Example: Benzenedithiol junction: Wide-Band-Limit	1095
	Example: Benzenedithiol junction	1100
15.6	Analysis	1108
15.6.1	Fragment orbitals, bond energy decomposition	1108
	Example: Compound Fragments: Ni(CO)4	1108
	Example: Fragments: PtCl4H2 2-	1110
	Example: Spin-unrestricted Fragments: H2	1112
	Example: Bond Energy analysis open-shell fragments: PCCP	1118
	Example: Analysis of NaCl using ionic fragments: Na+ and Cl-	1124
	Example: Electron Pair bonding in NaCl: open shell fragments	1126
	Example: Bond Energy analysis meta-GGA, (meta-)hybrids: Zn2, Cr2, CrH	1133
	Example: unrestricted EDA: Cu(C2H4)2	1138
	Example: unrestricted fragments: CH3I	1140
	Example: Spin-Orbit SFO analysis: TIH	1143
	Example: Activation Strain Model Analysis using PyFrag	1146
15.6.2	Localized orbitals, bond orders, charge analysis	1147
	Example: (Perturbed) localized molecular orbitals in twisted Ethene	1147
	Example: Rose localization and TD-DFT: C2F4-C2H4	1148
	Example: Charge model 5 (CM5)	1151
	Example: Bond Orders	1152
15.6.3	ETS-NOCV	1155
	Example: NOCV: ethylene – Ni-diimina	1155
	Example: NOCV: H+ – CO	1158
	Example: NOCV: CH2 – Cr(CO)5	1160
	Example: NOCV: CH3 – CH3	1162
15.6.4	QTAIM	1166
	Example: QTAIM Analysis	1166
	Example: QTAIM Reactivity	1167

Example: IQA/QTAIM analysis	1169
Example: QTAIM Aromaticity indices	1171
15.6.5 DOS: Density of states	1172
Example: Density of States: Cu ₄ CO	1172
15.6.6 Third party analysis software	1174
Example: adf2aim: convert an ADF adf.rkf to WFN format (for Bader analysis)	1174
Example: NBO analysis: adfnbo, gennbo	1175
Example: NBO analysis: EFG	1177
Example: NBO analysis: NMR chemical shift	1180
Example: NBO analysis: NMR spin-spin coupling	1183
Example: Multiple excited state gradients: H ₂ O	1186
Example: Calculation of overlap of primitive basis functions	1187
15.7 Accuracy and Efficiency	1188
15.7.1 BSSE, SCF convergence, Frequencies	1188
Example: Basis Set Superposition Error (BSSE): Cr(CO) ₅ + CO	1188
Example: Troubleshooting SCF convergence: Ti ₂ O ₄	1193
Example: Rescan frequencies: NH ₃	1201
15.7.2 Speed	1202
Example: Multiresolution	1202
15.8 Restarts	1204
15.8.1 Example: Restart analytical Hessian calculation	1204
15.9 Scripting	1206
15.9.1 Prepare an AMS job and generate a report	1206
Example: Single point for multiple xyz files: Bakerset	1206
Example: Basis set and integration accuracy convergence test: Methane	1206
Example: amsprep: Replace atom with ligand	1208
15.10 List of Examples	1208
16 Keywords	1211
16.1 Links to manual entries	1211
16.2 Summary of all keywords	1212
16.2.1 Engine ADF	1212
16.2.2 adfnbo	1365
16.2.3 cpl	1366
16.2.4 densf	1373
16.2.5 green	1378
16.2.6 lfdft	1380
16.2.7 lfdft_tdm	1382
16.2.8 nmr	1383
17 KF output files	1391
17.1 Accessing KF files	1391
17.2 Sections and variables on adf.rkf	1392
17.2.1 ActiveFrag	1392
17.2.2 ActiveFrag*	1404
17.2.3 All excitations	1407
17.2.4 All excitations *	1412
17.2.5 AMSResults	1416
17.2.6 AngularBoost	1426
17.2.7 AOMatrices	1427
17.2.8 AOESPONSE	1427
17.2.9 aoresponse_data	1427
17.2.10 atens	1427
17.2.11 Atyp*	1427

17.2.12	Basis	1431
17.2.13	BeckeGridConfig	1434
17.2.14	ConstrainedDFT	1436
17.2.15	ConstructPotential	1436
17.2.16	ConstructPotential_FunctionSet	1436
17.2.17	Core	1437
17.2.18	COSMO	1441
17.2.19	Critical Points	1444
17.2.20	CriticalPoints	1444
17.2.21	CSMRSP	1447
17.2.22	CurrentMatrix	1447
17.2.23	DIMQM	1447
17.2.24	Dipole velocity matrix	1447
17.2.25	EgoData	1447
17.2.26	Elec multipole ints OCCOCC	1447
17.2.27	Elec multipole ints OCCVIR	1447
17.2.28	ElstatEmbed	1448
17.2.29	Energy	1450
17.2.30	ETS	1459
17.2.31	Excitations SD *	1459
17.2.32	Excitations SO *	1466
17.2.33	Excitations SS *	1473
17.2.34	Excitations ST *	1479
17.2.35	FDE Energy	1486
17.2.36	FDEIntegrals	1486
17.2.37	Fit	1486
17.2.38	FitCoefficients	1486
17.2.39	FitFit	1486
17.2.40	FQQM	1486
17.2.41	Fragdepend	1488
17.2.42	Fragments	1488
17.2.43	Freq	1488
17.2.44	Freq Symmetry	1489
17.2.45	Ftyp*	1489
17.2.46	General	1489
17.2.47	GenptData	1495
17.2.48	Geometry	1495
17.2.49	GeoOpt	1502
17.2.50	Gradient	1502
17.2.51	gtens	1506
17.2.52	GW	1506
17.2.53	Hessian	1513
17.2.54	HFConfigADF	1514
17.2.55	HFdependency	1514
17.2.56	Irred dip vel matrix elem	1514
17.2.57	Irred magnetic matrix elem	1514
17.2.58	Irred matrix elements	1514
17.2.59	Irreducible CurrentMatrix	1514
17.2.60	Irreducible CurrentMatrix Factor	1514
17.2.61	KFDefinitions	1514
17.2.62	LF_diag	1515
17.2.63	LF_energies	1516
17.2.64	LF_excitations	1517
17.2.65	LF_input	1519

17.2.66	LibXCConfig	1520
17.2.67	LinearScaling	1522
17.2.68	LMO_P1	1522
17.2.69	LocOrb	1522
17.2.70	locpert_data	1522
17.2.71	Low Frequency Correction	1522
17.2.72	LqbasxLqfitx_xyznuc	1523
17.2.73	Magn multipole ints OCCOCC	1523
17.2.74	Magn multipole ints OCCVIR	1523
17.2.75	Magnetic moment matrix	1523
17.2.76	MCD Elements	1523
17.2.77	METAGGA bonding energies	1525
17.2.78	MetaGGAConfig	1525
17.2.79	Mobile Block Hessian	1525
17.2.80	Molecule	1527
17.2.81	MP2 energies	1531
17.2.82	MP2configADF	1532
17.2.83	Multipole matrix elements	1533
17.2.84	NBOs	1533
17.2.85	NLMOs	1534
17.2.86	NOCV	1535
17.2.87	Num Int Params	1537
17.2.88	OrbitalInfo	1537
17.2.89	OrbitalsCoulombInteraction	1547
17.2.90	Ort C energies	1548
17.2.91	Ort X energies	1548
17.2.92	Ort XC energies	1548
17.2.93	PartialZora	1548
17.2.94	Point_Charges	1549
17.2.95	POLTDDFT	1549
17.2.96	Properties	1549
17.2.97	QMFQ	1574
17.2.98	Reference Eigenvector	1576
17.2.99	Response Data	1577
17.2.100	ResponsePmats	1577
17.2.101	Rose Data	1578
17.2.102	RPA energies	1579
17.2.103	SCF	1580
17.2.104	sDFT Energy	1580
17.2.105	SFO popul	1582
17.2.106	SFO_Fock	1582
17.2.107	SFO_Overlap	1582
17.2.108	SFOs	1583
17.2.109	Spin operator matrix	1586
17.2.110	Spin_orbit	1586
17.2.111	SUB1!*	1587
17.2.112	SUB2!*	1587
17.2.113	SUBEXCI	1587
17.2.114	SUBRESP	1587
17.2.115	SumFrag C energies	1587
17.2.116	SumFrag X energies	1588
17.2.117	SumFrag XC energies	1588
17.2.118	SymFit	1588
17.2.119	Symmetry	1588

17.2.120Thermodynamics	1595
17.2.121Total C energies	1601
17.2.122Total Energy	1601
17.2.123Total X energies	1601
17.2.124Total XC energies	1601
17.2.125TransferIntegrals	1602
17.2.126VCDTools	1605
17.2.127Vibrations	1605
17.2.128XAS DATA	1611
17.2.129XCRangeSeparated	1611
17.2.130XES DATA	1613
17.2.131ZFS	1613
17.2.132ZlmFit_*	1614
17.2.133ZlmFitConfig	1614
18 FAQ	1617
18.1 My ADF input does not work in AMS2020?	1617
18.2 Can I use Gaussian type basis (6-31G*, TZVP, etc.) functions in ADF?	1617
18.3 Which basis set should I use?	1617
18.4 How do I calculate UV/VIS spectra with ADF?	1618
18.5 What settings are recommended for NMR calculations?	1619
18.6 Do you have tips on how to find a Transition State with ADF?	1619
18.7 What's the difference between COSMO and COSMO-RS? Do I need COSMO-RS to include solvent effects?	1620
18.8 What does a small, medium, or large frozen core mean?	1620
18.9 How did the keywords in ADF change from 2017 to 2018?	1620
18.10 How to do an EDA or ETS-NOCV calculation with open-shell fragments?	1621
18.11 Can ADF do restricted open shell Kohn-Sham (ROKS)?	1621
18.12 Can I use GPU acceleration in ADF?	1621
18.13 Where can I find the total energy in the output?	1621
18.14 How do I calculate atomization energies with ADF?	1622
18.15 I have problems with SCF convergence ("more iterations needed. not converged"). What to do?	1622
18.16 The geometry of my molecule is converged but when I do a frequency calculation, ADF finds one or more imaginary frequencies. Why?	1623
18.17 Are TDDFT calculations compatible with COSMO?	1623
18.18 Can I optimize excited states with TDDFT in ADF?	1623
18.19 Can I determine Raman intensities for open-shell systems?	1624
18.20 How do I calculate the frequency-dependent second hyperpolarizability, GAMMA?	1624
18.21 How can I do a spin restricted open-shell calculation for the calculation of the A-tensor?	1624
18.22 How do I read data from the binary KF files (adf.rkf, TAPE21, .runkf, .rkxf, .rkf or .t21 result files)? .	1625
18.23 I get the error: NO TRANSFORMATION FOUND in a fragment-based calculation. What to do? . . .	1626
18.24 What does the error message "BAD ETA INTEGRALS" mean?	1626
18.25 ADF will not start when the user's login name has non-ASCII characters in it. Sometimes a message "QUICKX terminates" is printed to the logfile.	1626
18.26 What does this error mean Int. Energy with ZlmFit+LargeFragment+VoronoiGrid not implemented. .	1627
Index	1629

1.1 Introduction

Since AMS2020 ADF is only accessible through the AMS driver program⁵. ADF (Amsterdam Density Functional) is an AMS engine for calculations on atoms and molecules (in gas phase or solution). It can be used for the study of such diverse fields as molecular spectroscopy, organic and inorganic chemistry, and pharmacochimistry. The AMS engine BAND is available for the study of periodic systems: crystals, surfaces, and polymers. The separate COSMO-RS program is used for calculating thermodynamic properties of (mixed) fluids.

The underlying theory is the Kohn-Sham approach to Density-Functional Theory (DFT). This implies a one-electron picture of the many-electron systems but yields, in principle, the exact electron density (and related properties) and the total energy.

If ADF is new for you we recommend that you carefully read the section *Technical remarks, Terminology* (page 19), which presents a discussion of a few ADF-typical aspects and terminology. This will help you understand the output of an ADF calculation.

ADF has been developed since the early 1970s (at that time called HFS, later AMOL, see also refs.¹²³⁵), mainly by the two theoretical chemistry groups of, respectively, the *Vrije Universiteit in Amsterdam* (<https://vu.nl/en/about-vu/more-about/theoretical-chemistry>) and the University of Calgary, Canada. Other researchers have also contributed. As a major research tool of these academic development groups, ADF is in continuous development and retains a firm basis in the academic world.

Maintenance and distribution of the commercial (export) version of the program is done by Software for Chemistry & Materials B.V. (SCM) (<https://www.scm.com>), a company based in Amsterdam, formally split off from the theoretical chemistry group in Amsterdam but practically still very much a part of it. Documentation such as user manuals, installation instructions, examples, and theoretical documents can be found at the SCM website.

Publications based on research with ADF should include appropriate references to the program. We recommend that references are made both to the program itself and to publications related to its development and structure. See the *Required Citations* (page 457).

The installation of the Amsterdam Modeling Suite (AMS) program package is explained in the *Installation manual*. This User's Guide describes how to use the program, how input is structured, what files are produced, and so on. Some special

⁵ E.J. Baerends, N.F. Aguirre, N.D. Austin, J. Autschbach, F.M. Bickelhaupt, R. Bulo, C. Cappelli, A.C.T. van Duin, F. Egidi, C. Fonseca Guerra, A. Förster, M. Franchini, T.P.M. Goumans, T. Heine, M. Hellström, C.R. Jacob, L. Jensen, M.V. Krykunov, E. van Lenthe, A. Michalak, M. Mitoraj, J. Neugebauer, V.P. Nicu, P.H.T. Philipsen, H. Ramanantoanina, R. Rüger, G. Schreckenbach, M. Stener, M. Swart, J.M. Thijssen, T. Trnka, L. Visscher, A.L. Yakovlev, S.J.A. van Gisbergen, *The Amsterdam Modeling Suite*, *Journal of Chemical Physics* 162, 162501 (2025) (<https://doi.org/10.1063/5.0258496>)

¹ E.J. Baerends, D.E. Ellis and P. Ros, *Self-consistent molecular Hartree-Fock-Slater calculations I. The computational procedure*, *Chemical Physics* 2, 41 (1973) ([https://doi.org/10.1016/0301-0104\(73\)80059-X](https://doi.org/10.1016/0301-0104(73)80059-X))

² E.J. Baerends and P. Ros, *Evaluation of the LCAO Hartree-Fock-Slater method: Applications to transition-metal complexes*, *International Journal of Quantum Chemistry* 14, S12, 169 (1978) (<https://doi.org/10.1002/qua.560140814>)

³ G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *Chemistry with ADF*, *Journal of Computational Chemistry* 22, 931 (2001) (<https://doi.org/10.1002/jcc.1056>)

applications of ADF are described in the [Examples](#) (page 471).

Where references are made to the operating system (OS) and to the file system on your computer, the terminology of UNIX-type OSs is used.

The AMS package is in continuous development to extend its functionality and applicability, to increase its efficiency and user-friendliness, and of course to correct errors. We appreciate comments and suggestions for improvement of the software and the documentation.

1.1.1 ADF is an AMS Engine

The most important change in AMS2020 is that ADF is only accessible via the AMS driver program. We recommend you first read the [General section of the AMS Manual](#). More details can be found in the section [AMSification of ADF](#) (page 11).

1.1.2 Functionality

- Computation of any electronic configuration
- Excitation energies, oscillator strengths, transition dipole moments, (hyper)polarizabilities, Van der Waals dispersion coefficients, CD spectra, ORD, MCD, VCD, magnetizabilities, Verdet constants, using Time-Dependent Density Functional Theory (TDDFT)
- ESR (EPR) g-tensors, A-tensors, NQCCs
- NMR chemical shifts and spin-spin coupling constants
- Mössbauer spectroscopy
- Transport properties: charge transfer integrals, NEGF
- Various other molecular properties
- Treatment of large systems and environment by the QM/MM (Quantum Mechanics / Molecular Mechanics) hybrid approach.

1.1.3 Applicability

All elements of the periodic table can be used ($Z = 1-120$). For each of the elements, basis sets of different sizes are available, ranging from minimal to high quality. Special basis sets are provided for relativistic calculations within the ZORA approach and for response calculations that require additional diffuse basis functions.

1.1.4 Model Hamiltonian

- A choice of Density Functionals, both for the Local Density Approximation (LDA), for the Generalized Gradient Approximation (GGA), for (range-separated) hybrid functionals (not for all properties available), and for meta-GGA functionals (not for all properties available) are available.
- Spin: restricted or unrestricted
- Relativistic effects: scalar approximation and spin-orbit (double-group symmetry), using the (now recommended) ZORA or the (previously used) Pauli formalism, X2C
- Environment: Solvent Effects, Homogeneous Electric Field, Point Charges (Madelung Fields), QM/MM method, FDE
- Constrained Density Functional Theory

1.1.5 Analysis

- Decomposition of the bond energy in ‘chemical’ components (steric interaction, Pauli repulsion, orbital interactions...)
- Natural orbitals for chemical valence (ETS-NOCV)
- Representation of data (Molecular Orbital coefficients, Mulliken Populations) in terms of the constituent chemical fragments in the molecule, along with the conventional representation in elementary basis functions
- Atomic charge determination by Hirshfeld analysis and by Voronoi analysis, multipole derived charges, along with the classical Mulliken populations, and Mayer bond orders
- QTAIM analysis based on local, atomic and non-local descriptors for bonding description.
- Conceptual DFT descriptors including global, atomic, non-local ones and a detailed analysis of the dual descriptor’s domains (predominantly electrophilic or nucleophilic regions).
- Bond energy decomposition based on the interacting quantum atoms (IQA) approach and using QTAIM real-space partition. Any atom-atom interaction can be evaluated and decomposed into electrostatic (ionic) and exchange (covalent) contributions.
- Localized molecular orbitals

1.1.6 Technical

- The implementation is based upon a highly optimized numerical integration scheme for the evaluation of matrix elements of the Fock operator, property integrals involving the charge density, etc. The code has been vectorized and parallelized.
- Basis functions are Slater-Type Orbitals (STOs). A database is available with several basis sets for each atom in the periodic table of elements.
- The Coulomb potential is evaluated via an accurate fitting of the charge density.
- A frozen core facility is provided for an efficient treatment of the inner atomic shells.
- Extensive use is made of point group symmetry. Most of the commonly encountered symmetry groups are available.
- Linear scaling techniques are used to speed up calculations on large molecules

1.1.7 Fragments

ADF has a fragment-oriented approach: the poly-atomic system to be computed is conceptually built up from fragments, the molecular one-electron orbitals are calculated as linear combinations of fragment orbitals, and final analyses of e.g. the bonding energy are in terms of fragment properties. The fragments may be single atoms or larger moieties.

When you compute a system in terms of its constituent fragments, these fragments must have been computed before and their properties must be passed on to the current calculation. This is done by attaching *fragment files*, which contain the necessary information. A fragment file is simply the standard result file of an ADF calculation on that fragment.

When using Basic Atoms as fragments, you do not need to create the fragment files yourself; ADF will create the required fragment files automatically. We therefore recommend this feature for starting ADF users.

Basic atoms

Obviously there must be a set of fundamental fragments that are not defined in terms of smaller fragments. Therefore ADF has two modes of execution: the normal mode, using fragments, and the create mode, in which a fundamental fragment is generated. Such a fundamental fragment *must* be a single atom, spherically symmetric and spin-restricted (i.e. spin- α and spin- β orbitals are spatially identical, they are equally occupied, and fractional occupations are applied, if necessary, to distribute the electrons equally over symmetry-degenerate states). Such a fundamental fragment is denoted a *basic atom*. The basic atoms are the smallest building blocks from which any ‘real’ calculations are started.

One should realize that the basic atoms are artificial objects that are convenient in the computational approach but that do not necessarily represent real atoms very well (in fact, usually not at all). The bonding energy of a molecule with respect to basic atoms, for instance, should be corrected for this discrepancy in order to get a decent comparison against experimental data. See ref.⁴ for a discussion and for examples of applicable values.

A basic atom is computed in the conventional way. The one-electron orbitals are determined as linear combinations of basis functions; the frozen core approximation may be applied for the inner atomic states; a particular type of density functional can be chosen, et cetera. You may have, for instance, different basic Copper atoms by using different basis sets, by choosing different levels of frozen core approximations, or by applying different density functionals.

Automatic mode

If you are using ‘Basic Atom’ fragments only, you do not need to prepare the corresponding fragment files yourself; ADF will generate all the required fragment files for you. This makes your job scripts and ADF inputs simpler, it ensures that consistent options for the create runs and molecular runs are used.

1.1.8 Slater-type basis sets

ADF uses Slater-Type Orbitals (STOs) as basis functions. Slaters can display the correct nuclear cusp and asymptotic decay.

$$f(\mathbf{r}) = Y_{lm} r^n e^{-\zeta r}$$

The center of the function is at a nucleus, the Y_{lm} are spherical harmonics, and the exponential factor ζ (zeta) determines the long-range decay of the function.

ADF comes with a database of thoroughly tested basis set files, ranging in quality from single-zeta to quadruple-zeta basis sets with various diffuse and polarization functions. All-electron and frozen-core basis sets are available for all elements, including lanthanides and actinides. The frozen-core approximation can be used to considerably reduce the computation time for systems with heavy nuclei, in a controlled manner.

1.2 What’s new in ADF 2026.1

1.2.1 New features

- Model Hamiltonians
 - *GW with embedding FQ(F μ)* (page 134)
 - *wFQ method for plasmonic spectroscopies* (page 143)
 - *SM12* (page 118) analytical gradients

⁴ E.J. Baerends, V. Branchadell and M. Sodupe, *Atomic reference-energies for density functional calculations*, Chemical Physics Letters 265, 481 (1997) ([https://doi.org/10.1016/S0009-2614\(96\)01449-2](https://doi.org/10.1016/S0009-2614(96)01449-2))

- *frozen core* (page 68) approximation with *LibXC* (page 98) XC functionals
 - * frozen cores can not be used with meta-XC functionals
- Spectroscopy
 - *ROKS-TDA* (page 186) and *ROKS-TDA-SOC* (page 195): inclusion of spin-flip down excited states
 - *excited state geometry optimizations for open-shell TD-DFT+TB* (page 210)
 - *NMR chemical shieldings* (page 232) with LibXC and/or range separated XC functionals
 - * NMR chemical shieldings cannot be calculated with meta-XC functionals
- Analysis
 - *added bond energy with respect to atoms also in case of non-atomic fragments* (page 292)
 - *Interacting Quantum Atoms (IQA)* (page 295) with ZORA
 - *PartialZORA: analysis of spin-orbit coupling* (page 111), expert option

1.3 Older releases

1.3.1 What's new in ADF 2025.1

New features

- Model Hamiltonians
 - Electronic Configuration
 - * *FOCDFT: fragment orbital constrained DFT* (page 78)
 - * *spin-orbit coupled spin-polarized start-up potential* (page 62)
 - Density Functional
 - * *Libxc updated library (libxc7.0.0)* (page 98)
 - * *sigma-functional parametrization optimized for Corr/TZ3P basis set* (page 94)
 - * *LAK: general purpose metaGGA* (page 84)
 - * *DFT-D3 update (s-dftd3 1.2.1)* (page 100) and *DFT-D4 update (dftd4 3.7.0)* (page 99)
 - inclusion of actinide parameters (Z = 87 (Fr) - 103 (Lr))
 - *QM/FQ gradients and geometry optimizations* (page 134)
- Spectroscopy
 - *ROKS-TDA: excited states for open-shell molecules with well-defined spin* (page 186)
 - *ROKS-TDA-SOC: ROKS-TDA with perturbative inclusion of spin-orbit coupling* (page 195)
 - *TDDFT-aas: excited states with TDDFT-approximate auxiliary s function* (page 202)
 - *PolTDDFT with range-separated CAMY-B3LYP* (page 222)
- Many-Body Perturbation Theory
 - *new vertex correction beyond GW* (page 255)
- Transport properties

- *exciton transfer integrals with ROSE* (page 278) or *FOCDFT* (page 278)
 - *charge transfer integrals with FOCDFT* (page 274)
- Analysis
 - *ROSE localized orbitals* (page 300)

Input Changes

- FDE: new key *FDEFRAGMENTS* (page 144) required, also for specifying fragment specific FDE options

Bug fixes

- *spin-orbit coupled excitations* (page 194): molecules with C(2h) symmetry can use full symmetry

1.3.2 What's new in ADF 2024.1

New features

- Simplified procedure for calculating *pNMR chemical shieldings* (page 238) of open-shell molecules
 - effects of ESR g-tensor and ESR A-tensor can be included, ESR D-tensor not
 - procedure contains a bug in AMS2024.101 - AMS2024.106, fixed in later releases
- Experimental combination of G_0W_0 (*GW* (page 255)) and embedding (*DRF* (page 123) or *COSMO* (page 111))
 - GW with embedding may yield inaccurate results

Removed features

- Solvation methods SCRF (Self-Consistent Reaction Field) and VSCRF no longer supported
 - see documentation in the ADF 2023 manual on *SCRF* (<https://www.scm.com/doc.2023/ADF/Input/SCRF.html>) and *VSCRF* (<https://www.scm.com/doc.2023/ADF/Input/VSCRF.html>)
- Old EPR/NMR program (\$AMSBIN/epr) is no longer supported
 - see the documentation in the *old ADF 2010 Properties document* (<https://downloads.scm.com/Doc/Doc2010/ADF/Properties/Properties.pdf>).
- Old FCF program (\$AMSBIN/oldfcf) is no longer supported
 - The new *FCF program* (\$AMSBIN/fcf) has replaced the old FCF program in AMS 2022
 - see documentation in the AMS 2021 manual on the *old FCF program* (https://www.scm.com/doc.2021/AMS/Utilities/FCF_module.html)

1.3.3 What's new in ADF 2023.1

New features

- Model Hamiltonians
 - *r2SCAN-3c* (page 85): composite DFT method: r2SCAN, mTZ2P, gCP, D4
 - * outperforms many hybrid/QZ approaches at a fraction of their cost
 - *sigma-functional* (page 94): New beyond-RPA method:
 - * outperforms RPA at the same cost.
 - *ROKS for high-spin open shell molecules* (page 61)
 - * work-in-progress, only single points calculations
 - *TASKCC metaGGA* (page 84) improves TASKxc atomization energies
 - Calculate entropies of solvation with *3D-RISM* (page 155)
- Spectroscopy
 - *GW-BSE: Bethe Salpeter equation* (page 181)
 - * G_0W_0 -BSE, evGW-BSE, qsGW-BSE
 - * spin-orbit coupled
 - *CD spectra with spin-orbit coupling* (page 205)
 - *excited state geometry optimizations for TD-DFT+TB* (page 210)
 - open shell excitation energies for *TD-DFT+TB*, *TDA-DFT+TB* (page 201), *sTDA*, *sTDDFT* (page 203)
 - open shell excitation energies with *Hybrid Diagonal Approximation (HDA)* (page 200)
 - *PolTDDFT with fitted HDA* (page 222)
 - Calculation of *vibrational polarizabilities* (page 173) under the harmonic approximation
- *Many-Body Perturbation Theory* (page 384)
 - *spin-orbit coupling with GW* (page 255): G_0W_0 , evGW, qsGW, G3W2
- Analysis
 - MBPT: *qsGW quasi particle orbitals in terms of SFOs* (page 255)
 - *NOCV* (page 308)
 - * T/V analysis of energy contributions
 - * NOCVs in terms of SFOs
 - * Mulliken population of the relaxation density in terms of primitive STOs
 - simplified calculation of site energies with *PRINT SFOSiteEnergies* (page 324)
 - *PolTDDFT* (page 222)
 - * analysis in terms of single orbital transitions
 - * fragment projection analysis using regions
 - *QTAIM* (page 315)
 - * source function for all BCPs and RCPs

- *IQA* (page 295)
 - * extended to open-shell systems
- Visualization with AMS-GUI
 - MBPT: GW quasi particle orbitals and energies
 - SFO site energies
 - *PolTDDFT*: TCM, ICM-OS, ICM-RS
- Performance
 - reduced disk usage for some files containing matrices (TAPE15, adf.rkf a.k.a. TAPE21), which also improves performance for some file systems (NFS, GPFS)
- New *AMS driver* features can be used in combination with ADF
 - what's new in the *AMS driver*

Bug fixes

- *GW* (page 255): AMS2023.102: bug fix GW. Incorrect Fermi energy was used. Also affects BSE.
- *LFDDFT analysis* (page 226): bug fix expectation values $\langle S^2 \rangle$, $\langle L^2 \rangle$, $\langle J^2 \rangle$

1.3.4 What's new in ADF 2022.1

New features

- Model Hamiltonians
 - *QM/FQ Quantum Mechanics/Fluctuating Charges* (page 134)
 - * extended to fluctuating dipoles (QM/FQF μ)
 - * can be combined with Frozen Density Embedding (FDE)
 - *3D-RISM* (page 155) revised implementation and additional functionality
 - *IQA Interacting Quantum Atoms* (page 295)
 - * intra-atomic terms
 - * parallelization
 - *MP2* (page 93) and *double hybrid* (page 90) in combination with *spin-orbit coupling* (page 106)
 - * in case of spin-orbit coupling approximate SS and OS contributions
- *Many-Body Perturbation Theory* (page 384)
 - *quasiparticle self-consistent GW: qsGW* (page 255)
 - *second-order self-energy GW: G3W2* (page 255)
 - improvements in stability of the MBPT results especially for larger basis sets
- New *AMS driver* features can be used in combination with ADF
 - what's new in the *AMS driver*
 - *FCF module* for the calculation of vibronic progressions and bandshapes improved

1.3.5 What's new in ADF 2021.1

New features

- Model Hamiltonians
 - *QM/FQ Quantum Mechanics/Fluctuating Charges* (page 134)
 - *r2SCAN-D4* (page 98) XC functional
- *Many-Body Perturbation Theory* (page 384)
 - *eigenvalue-only self-consistent GW: evGW* (page 255)
 - *Basis sets* (page 40) for use in *MBPT* (page 384)
 - * Corr/TZ3P
 - * Corr/QZ6P
- Spectroscopy
 - *LFDFT ESR (EPR) g-tensor doublets* (page 230)
 - *LFDFT MCD* (page 231)
 - *PolTDDFT: reduced fit sets for most elements for DZ, DZP, TZP basis sets* (page 222)
 - *unrelaxed dipole moment excited states* (page 179)
 - *transition dipole moment between excited states* (page 183)
- New **AMS driver** features can be used in combination with ADF. See the page [What's new in the AMS driver](#) for more details.

New Defaults

- *Perturbative inclusion of spin-orbit coupling for excitation energies* (page 194)
 - singlet ground state is included by default, keyword GSCORR now subkey of SOPERT
 - improved way to calculated transition dipole moment

1.3.6 What's new in ADF 2020.1

New features

- *Many-Body Perturbation Theory* (page 384)
 - *GW approximation* (page 255): G_0W_0
 - *RPA* (page 94)
- Spectroscopy
 - *VCD for open shell molecules* (page 173)
 - *Hybrid diagonal approximated (HDA) excitation energies* (page 200)
 - *Hybrid functionals with PolTDDFT* (page 222)
- STO basis sets
 - *STO basis sets for Uue (Z=119) and Ubn (Z=120) added* (page 40)

- PES point character (see [AMS driver](#))
 - without calculating the full Hessian, characterize a PES point
- Symmetry (see [AMS driver](#))
 - ADF does not symmetrize coordinates anymore
 - AMS can symmetrize coordinates, but that is not the default
 - more symmetries possible with irreducible representations whose characters are complex, like C(3), S(4)
 - labels for vibrational normal modes for these symmetries
 - remark: not more symmetries can be used for electronic states
- Speed
 - double parallelization (see [AMS driver](#)) possible for numerical calculation of IR frequencies

New Defaults

- *Scalar relativistic ZORA* (page 106) (instead of non-relativistic)
- AMS does not symmetrize coordinates by default, which ADF used to do. See also [AMS driver system definition](#) and *symmetry section of ADF* (page 436).
- \$AMSHOME/atomicdata/ADF directory with ADF basis sets (instead of \$ADFHOME/atomicdata)

1.3.7 ADF is an AMS Engine

Starting from AMS2020 ADF is only accessible via the AMS driver program. The standalone program ‘adf’ does not exist anymore. The job of the AMS driver is to handle all changes in the geometry, e.g. during a geometry optimization, using so-called engines like ADF for the calculation of energies and forces.

Important: In the AMS2020 release ADF is an AMS engine. We recommend you to first read the [General section of the AMS Manual](#)

If you use ADF exclusively via the Graphical User Interface (GUI), this change should not create any issues. If, on the other hand, you create input files by hand (or you use ADF via [PLAMS](#)), then you should be aware that shell scripts for ADF2019 and previous versions are not compatible with ADF2020 and have to be adjusted to the new setup (see also *Automatic tool for conversion of ADF2019 shell scripts* (page 14)).

Some of the changes:

- environment variables AMSHOME, AMSBIN (instead of ADFHOME, ADFBIN)
- ams (instead of adf)
- major restructuring of input and input keys
- output files in separate directory
- ams.rkf new binary output file, contains mainly geometry related data
- adf.rkf binary output file (instead of TAPE21), contains mainly single point related data
- AMS does not symmetrize coordinates by default, which ADF used to do. See also [AMS driver system definition](#) and *symmetry section of ADF* (page 436).
- QM/MM, QM/QM, Quilid with the Hybrid engine

- \$AMSHOME/atomicdata/ADF directory with ADF basis sets (instead of \$ADFHOME/atomicdata)
- scalar relativistic ZORA is the default (instead of non-relativistic)

See also:

More details this can be found in the section *AMSification of ADF* (page 11)

1.4 AMSification of ADF in AMS2020

1.4.1 Restructuring of the input

The input for the following features belongs (mostly) to the *AMS driver* part of the input:

- *Geometry, System definition*
 - Geometry
 - Total charge
 - Masses of atoms (isotopes)
 - Electric field, point charges
 - Regions
- *Structure and Reactivity, Molecular Dynamics*
 - Geometry Optimizations
 - Linear Transit (LT), Transition States (TS), Nudged Elastic Band (NEB), TSRC
 - Intrinsic Reaction Coordinate (IRC)
 - Constraints, restraints
 - Excited state optimizations
 - Molecular Dynamics
- *Gradients, Hessian, Thermodynamics*
 - Nuclear gradients, Hessian, PES point character
 - Thermodynamics, gas phase Gibbs free energy
- *Vibrational Spectroscopy*
 - IR frequencies and intensities
 - Mobile Block Hessian (MBH), Mode Scanning, Mode Refinement, Mode Tracking
 - (Resonance) Raman, vibrational Raman optical activity (VROA)
 - Vibrational Circular Dichroism (VCD)
- *Vibrationally resolved electronic spectra*
 - Vibrational resolved absorption, emission, phosphorescence, ionization
 - Adiabatic Hessian Franck-Condon
 - Vertical Gradient Franck-Condon

The input for QM/MM, QM/QM, and Quild calculations uses the Hybrid engine.

- Model Hamiltonians

– QM/MM, QM/QM, QuilD

The input for most other features belongs to the ADF engine part of the input.

1.4.2 Restructuring of input keys

ADF2019 key / feature	ADF2020 key / AMS2020 key / comments
\$ADFBIN	\$AMSBIN
\$ADFHOM	\$AMSHOME
\$ADFRESOURCES	\$AMSRESOURCES=\$AMSHOME/atomicdata
\$ADFHOM/atomicdata	\$AMSHOME/atomicdata/ADF. Directory with ADF basis sets.
\$ADFHOM/atomicdata/ZORA	\$AMSHOME/atomicdata/ADF/ZORA. Directory with ADF ZORA basis sets.
'ANALYTICALFREQ'	subkey 'NormalModes' of key 'Properties' in AMS driver .
'AOESPONSE'	subkey 'FreqRange' and 'Frequency' removed. Use new subkey 'Frequencies'.
'ATOMPROPS'	key removed. See alternative elements (page 51).
'ATOMS'	subkey 'Atoms' of key 'System' in AMS driver .
... f=fragtype/n	... adf.f=fragtype n.
... R=CosmoRadius	... adf.R=CosmoRadius.
'CHARGE'	subkey 'Charge' of key 'System' in AMS driver . key 'SpinPolarization' in ADF.
'CONSTRAINTS'	key 'Constraints' in AMS driver .
'COLLINEAR'	subkey 'SpinOrbitMagnetization Collinear' in key 'Relativity' in ADF.
'CRDFILEXYZ'	key removed.
'CRDFILEMOL'	key removed.
EField	subkey 'ElectroStaticEmbedding%ElectricField' of key 'System' in AMS driver .
fcf	program 'fcf' documented in AMS driver
'GEOMETRY'	key 'Task' and key 'Properties' in AMS driver .
Geometry optimization	key 'Task GeometryOptimization' in AMS driver .
'GEOVAR'	key removed.
'GRADIENT'	subkey 'Gradients' of key 'Properties' in AMS driver .
'HESSDIAG'	key removed.
'HESSTEST'	key removed.
Initial Hessian	subkey 'InitialHessian' of key 'GeometryOptimization' in AMS driver .
Intrinsic Reaction Coordinate	key 'Task IRC' in AMS driver .
IR frequencies	subkey 'NormalModes' of key 'Properties' in AMS driver .
... Mobile Block Hessian	subkey 'Displacements Block' of key 'NormalModes' in AMS driver .
... symmetric displacements	subkey 'Displacements Symmetric' of key 'NormalModes' in AMS driver .
'IRCSTART'	key removed.
'ISOTOPICSHIFT'	key removed.
Linear Transit	key 'Task PESScan' in AMS driver .
'LINEARCONSTRAINTS'	key removed.
MBH	subkey 'Displacements Block' of key 'NormalModes' in AMS driver .
'MP2'	key 'MBPT'.
'NONCOLLINEAR'	subkey 'SpinOrbitMagnetization NonCollinear' in key 'Relativity' in ADF.
Nudged Elastic Band	key 'Task NEB' in AMS driver .
Partial Hessian	subkey 'SelectedRegionForHessian' and 'NormalModes' of key 'Properties' in AMS driver .
'POINTCHARGES'	subkey 'ElectroStaticEmbedding%MultipolePotential' of key 'System' in AMS driver .
'POLTDDFT'	subkey 'NFreq' and 'NGrid' added.
'QMMM'	Hybrid engine .
QM/MM; QM/QM; QuilD	Hybrid engine .
Raman	subkey 'Raman' of key 'Properties' in AMS driver .
'RELATIVISTIC'	block key 'Relativity' in ADF.

continues on next page

Table 1.1 – continued from previous page

ADF2019 key / feature	ADF2020 key / AMS2020 key / comments
'RESPONSE'	subkey 'FrqBeg', 'FrqEnd', and 'NFreq' removed. Use new subkey 'Frequencies'.
'RESTRAINT'	key 'Restrains' in AMS driver .
'Restart'	The file should be specified in 'EngineRestart' in AMS driver .
'SYMMETRY'	both in ADF and AMS driver .
symmetrization	ADF does not symmetrize anymore. Subkey 'Symmetrize' of key 'System' in AMS driver .
'THERMO'	key 'Thermo' in AMS driver .
Transit State search	key 'Task TransitionStateSearch' in AMS driver .
'UNITS'	key removed. Possibility added to add units for many keys.
VCD	subkey 'VCD' of key 'Properties' in AMS driver .
vcdtools	program 'vcdtools' documented in AMS driver
VIBRON module	VIBRON module removed. For resonance Raman application see AMS driver .
VROA	subkey 'VROA' of key 'Properties' in AMS driver .

1.4.3 Example shell script changes

The example below shows how a shell script for ADF2019 is converted to ADF2020 (see also *Automatic tool for conversion of ADF2019 shell scripts* (page 14)).

ADF2019 shell script (obsolete):

```
#!/bin/sh

# This is a shell script for ADF2019 which will not work for ADF2020

$ADFBIN/adf <<eor
  Title WATER Geometry Optimization
  Atoms
    O          0.000000    0.000000    0.000000
    H          0.000000   -0.689440   -0.578509
    H          0.000000    0.689440   -0.578509
  End
  Geometry
    Converge grad=1e-4
  End
  Basis
    Type TZP
  End
  XC
    GGA PBE
  End
eor
```

ADF2020 shell script:

```
#!/bin/sh

# This is a shell script for ADF2020

# You should use '$ADFBIN/ams' instead of '$ADFBIN/adf'

$ADFBIN/ams <<eor
  # Input options for the AMS driver:
```

(continues on next page)

(continued from previous page)

```

System
  Atoms
    O      0.000000    0.000000    0.000000
    H      0.000000   -0.689440   -0.578509
    H      0.000000    0.689440   -0.578509
  End
End
Task GeometryOptimization
GeometryOptimization
  Convergence gradients=1e-4
End

# The input options for ADF, which are described in this manual,
# should be specified in the 'Engine ADF' block:

Engine ADF
  Basis
    Type TZP
  End
  XC
    GGA PBE
  End
EndEngine
eor

```

1.4.4 Automatic tool for conversion of ADF2019 shell scripts

The executable `$AMSBIN/adf` no longer performs ADF calculations. Instead, it will call an **input-conversion tool**¹ which will automatically convert an ADF2019 input into an ADF2020 input.

For example, if you save and execute the following script (note that the `$AMSBIN/adf` executable is used):

```

#!/bin/sh

# This is a shell scripts of an ADF2019 calculation, which will not work for ADF2020
# If you execute this script, the ADF2019 input will be converted into an ADF2020
↪input.

$AMSBIN/adf <<eor
  Atoms
    O      0.000000    0.000000    0.000000
    H      0.000000   -0.689440   -0.578509
    H      0.000000    0.689440   -0.578509
  End

  Basis
    Type TZP
  End
eor

```

no ADF calculation will actually be performed. Instead, the input conversion tool will be called, and you will obtain the new shell script for ADF2020 (note the `$AMSBIN/ams` executable):

¹ You can find the actual python script that performs the ADF2019 to ADF2020 conversion in `$AMSHOME/Utils/adf_to_ams_input_converter.py`.

```

# =====
# IMPORTANT
# =====

# Starting from AMS2020, ADF can only be used through the AMS driver program.
# Many input options for ADF have changed since the 2019 version.
# Below you will find an automatically-converted input script for AMS2020.
# The automatic conversion is not 100% accurate, so double check your input!

#
# =====
# Automatic conversion of ADF-2019 input to AMS-2020
# =====

# === NOTES ===
# - "TAPE21" is now called "adf.rkf" and is located in AMS results folder (by default
  ↳ "ams.results")
# - Unlike ADF2019, AMS does not symmetrize the structure by default. See "System ->
  ↳ Symmetrize" in the AMS driver manual.
# - The AMS default symmetrization tolerance is larger than the ADF2019 one. See
  ↳ "Symmetry -> SymmetrizeTolerance" in the AMS driver manual.
# - Scalar relativistic effects (ZORA) are included by default in the 2020 version of
  ↳ ADF.

$AMSBIN/ams << eor
System
  Atoms
    O      0.0000000000      0.0000000000      0.0000000000
    H      0.0000000000     -0.6894400000     -0.5785090000
    H      0.0000000000      0.6894400000     -0.5785090000
  End
  Symmetrize True
End

Symmetry
  SymmetrizeTolerance 0.001
End

Engine ADF
  Relativity
    Level None
  End

  Basis
    Type TZP
  End
EndEngine

eor

```

The conversion tool might raise WARNINGS. Make sure to address them before using the converted the script!

1.5 Input, execution and output

See the AMS driver documentation:

- [Input, execution and output section of the AMS driver manual](#)

1.5.1 ADF specific files

The ADF engine may generate several output / result files, along that ADF writes part of the standard output file. The most important one is `adf.rkf` (previously ADF<=2019 known as TAPE21 or as a `.t21` file), the general result file. The `adf.rkf` contains relevant information about the outcome of the calculation. It is a binary file that contains a lot of information about the calculation, such as the one-electron orbitals expressed in the basis functions. It can be used as a fragment file for subsequent calculations, or can be used as input to a property program, like NMR, CPL, or LFDFT.

Files attached to the job, such as fragment files, are by default also assumed to exist in the directory where you start AMS. You must take care to move or copy required files to that directory before starting the calculation, or to provide via input adequate information to the program where to find the files. In many cases you can specify a complete path to the file.

Most files that are generated by the program, in particular the standard result file that can be used as a fragment file in other calculations, are *binary* files. A binary file should usually not be moved from one machine to another, i.e. it may not be readable by another machine than the one that generated the file, unless the two machines are of the same type. The ADF package provides utilities to convert the ADF binary result files from binary to ASCII, and vice versa, so that you don't have to regenerate your fragment libraries when going to another machine. See the [Scripting Section](#) for further details regarding such aspects.

ADF is an engine that lends itself particularly well for chemical analysis. This is a direct result of the fragment-based approach, where properties of the molecule are related to the properties of the constituent fragments, which is precisely how the chemist thinks. Molecular Orbitals are (optionally) analyzed extensively as how they are composed from occupied and virtual fragment orbitals. This inherently implies a large amount of output. Even computations on small molecules may produce startlingly many pages of output. This is not necessarily so because you can regulate the production of output in detail. Obviously, some kind of *default* production of output had to be implemented. The field of ADF users is so wide and diverse that it is hard to satisfy everybody as regards this default level of output. Depending on your purposes the automatic settings, which determine how much output is generated without instructions to the contrary, may yield boringly many numbers that you just skip through in search for the one value you're interested in, or it may be widely insufficient. Therefore, take notice of the possibilities to regulate output.

Above all, however get familiar with the analysis tools that ADF provides to see in what ways these may help to interpret your results. In a later chapter a global description of output is given as it is normally produced. The chapter below gives an introduction in some of the essential features of ADF, which may be sufficiently different from what you are used to in other Quantum Chemistry codes to deserve your attention.

1.6 Feature List

1.6.1 Model Hamiltonians

- *XC energy functionals and potentials* (page 79)
 - *LDA* (page 80), *GGA* (page 81), *meta-GGA* (page 84), *model potentials* (page 96)
 - *(meta-)hybrid* (page 85), *range-separated* (page 86), *double-hybrids* (page 90)
 - *dispersion corrected* (page 99), *r2SCAN-3c* (page 85)
- *Many-Body Perturbation Theory* (page 384)

- *MP2* (page 93), *RPA* (page 94)
- *GW approximation* (page 255): G_0W_0 , evGW, qsGW, G3W2
- *Relativistic effects* (page 106)
 - scalar relativity, spin-orbit coupling
 - ZORA, X2C
- Solvents and other environments
 - *COSMO* (page 111), *SM12* (page 118), *DIM/QM* (page 122), *QM/FQ* (page 134), *FDE* (page 144), *3D-RISM* (page 155)
 - Quild, QM/MM, QM/QM (see the [Hybrid engine](#))
- Homogeneous electric field and point charges (see [AMS driver](#))

1.6.2 Structure and Reactivity

- Geometry optimizations (see [AMS driver](#))
- Linear transit, PES scan, Transition state search, Nudged Elastic Band (NEB) (see [AMS driver](#))
- Intrinsic Reaction Coordinate (IRC) (see [AMS driver](#))
- *Excited state optimizations with TDDFT gradients* (page 210) (see also [AMS driver](#))

Optimizations can be done in Cartesian and delocalized coordinates. Various restraints and constraints can be imposed. Hessians are available analytically for most GGAs, and numerically otherwise. Preoptimization is possible, for example, with DFTB.

1.6.3 Spectroscopic properties

- Vibrational Spectroscopy (see [AMS driver](#))
 - IR frequencies and intensities (see [AMS driver](#))
 - Mobile Block Hessian (MBH), Vibrational Circular Dichroism (VCD) (see [AMS driver](#))
 - Raman intensities (see [AMS driver](#))
 - Resonance Raman frequency-dependent polarizabilities or excited state gradients (see [AMS driver](#))
 - vibrational Raman optical activity (VROA) (see [AMS driver](#))
 - Franck-Condon Factors (see [AMS driver](#))
- *Excitation energies: UV/Vis spectra, X-ray absorption, CD, MCD* (page 179)
 - *UV/Vis spectra, oscillator strengths* (page 179), *open shell excitations* (page 184), *spin-orbit coupled excitations* (page 194), *GW-BSE* (page 181)
 - *core excitations* (page 188), *Quadrupole oscillator strengths* (page 192), *XES* (page 193)
 - *TD-DFT+TB* (page 201), *TDDFT-aas* (page 202), *sTDA*, *sTDDFT* (page 203)
 - vibrationally resolved electronic spectra (see [AMS driver](#))
 - *excited state optimizations* (page 210) (see also [AMS driver](#))
 - *CD spectra* (page 205), *MCD* (page 205)
 - *LFDFT* (page 226)

- (Hyper-)Polarizabilities, dispersion coefficients, ORD, magnetizabilities, Verdet constants (page 214)
 - frequency-dependent (hyper)polarizabilities (page 214), lifetime effects (page 217)
 - PolTDDFT (page 222)
 - van der Waals dispersion coefficients (page 225)
 - optical rotatory dispersion (ORD) (page 217)
 - magnetizability (page 217)
 - Verdet constants, Faraday terms (page 217)
- NMR
 - chemical shifts (page 232)
 - spin-spin couplings (page 240)
- ESR (EPR)
 - g-tensors (g-factor) (page 250)
 - A-tensor (hyperfine interaction) (page 250)
 - zero-field splitting (ZFS, D-tensor) (page 250)
- Nuclear quadrupole interaction (EFG), ESR Q-tensor (page 254)
- Mössbauer (page 254), NRVS (page 255)

1.6.4 Charge transport properties

- charge transfer integrals (page 269)
- exciton transfer integrals (page 277)
- Non-self-consistent Green's function calculation (page 284)

1.6.5 Analysis

- Fragments (page 3)
- Bond energy decomposition (page 23), ETS-NOCV (page 308)
- Advanced charge density and MO analysis
 - Mulliken (page 336), Multipole-derived charges (page 338)
 - Hirshfeld charges, Voronoi deformation density (page 336), CM5 charges (page 338), FOD (page 323)
 - bond orders: Mayer, Nalewajski-Mrozek (page 338)
 - Bader (QT-AIM) (page 315), Conceptual DFT (page 319)
 - Localized molecular orbitals (page 297), ROSE (page 300)
 - NBO 6.0 (page 309)
 - (partial) DOS (page 357)
- Molecular symmetry (page 21), Schönflies symbols and symmetry labels (page 436)

1.6.6 Accuracy and Efficiency

- *Slater-type basis sets* (page 20)
 - *Z = 1 to 120, all electron, frozen-core, non-relativistic and relativistic* (page 40)
 - *SZ, DZ, DZP, TZP, TZ2P, QZ4P, even-tempered, diffuse* (page 40)
- *Integration scheme* (page 373)
- Parallelization (see [AMS driver](#))
- *Linear scaling / distance cut-offs* (page 395)
- *Density fit* (page 380) and *frozen core approximation* (page 20)
- SCF convergence: *simple damping, DIIS, EDIIS, ADIIS, LISTi, ARH* (page 368)

1.7 Technical remarks, Terminology

A few words about ADF as regards its technical setup and the names and abbreviations used in this manual. References to these will be made in the discussion of output and print switches.

1.7.1 Density functional theory

The underlying theory of the ADF engine is the Kohn-Sham approach to the Density-Functional Theory (DFT). Kohn-Sham DFT is an important first-principles computational method to predict chemical properties accurately and to analyze and interpret these in convenient and simple chemical terms.

The reasons for its popularity and success are easy to understand. In the first place, the DFT approach is in principle exact. In particular, the Kohn-Sham method implies a one-electron picture of the many-electron systems but yields in principle the exact electron density (and related properties) and the total energy. The exact exchange-correlation (XC) functional is unknown, but the currently available XC functionals provide in most cases already a ‘chemical’ accuracy of a few kcal/mol for binding energies. Moreover, the quest for more accurate ones based on a more detailed understanding of their essential properties is continuing.

In the past decades, computational chemistry has evolved from a curiosity of theoreticians into a mainstream tool used by all types of chemists, physicists and engineers who have an interest in research and development. In that time Density Functional Theory has become the dominant method for modeling chemistry at the molecular level.

In the second place, it preserves at all levels of approximation the appealing one-electron molecular orbital (MO) view on chemical reactions and properties. The computed orbitals are suitable for the typical MO-theoretical analyses and interpretations. The KS method effectively incorporates all correlation effects.

In the third place, it is a relatively efficient computational method, and its fundamental scaling properties do not deteriorate when methodological precision is increased, in particular, when a more accurate XC functional is applied. Recent research paves the way to implementations that scale only linearly with the system size. This brings within reach the treatment by fundamental quantum chemical methods of systems with hundreds, maybe even thousands of atoms.

DFT gives superior accuracy to Hartree-Fock theory and semi-empirical approaches, and it is well suited for molecules containing metal atoms. In contrast to conventional ab initio methods (MP2, CI, CC), it enables accurate treatment of systems with several hundreds of atoms (or several thousands with QM/MM).

Text is mostly taken from: *Chemistry with ADF*, G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *Journal of Computational Chemistry* 22, 931 (2001) (<https://doi.org/10.1002/jcc.1056>)

1.7.2 The Kohn-Sham MO model

The basic postulate in Kohn-Sham DFT is that we can apply a one-electron formulation to the system of N interacting electrons by introducing a suitable local potential $V_{\text{XC}}(r)$, in addition to any external potentials $V_{\text{ext}}(r)$ and the Coulomb potential of the electron cloud $V_{\text{C}}(r)$, and solving:

$$[T + V_{\text{ext}}(r) + V_{\text{C}}(r) + V_{\text{XC}}(r)]\phi_i(r) = \epsilon_i\phi_i(r)$$

Here T is the kinetic energy operator. The potential $V_{\text{XC}}(r)$ is the functional derivative with respect to the density ρ of $E_{\text{XC}}[\rho]$, the exchange-correlation energy functional. The one-electron molecular orbitals (MOs) ϕ_i with corresponding orbital energies ϵ_i define the exact electronic charge density and give, in principle, access to all properties because these are expressible as functional of the density, in particular the energy. Moreover, they provide an intuitively appealing view of the system as being built from independent-electron orbitals with all ensuing interpretations. The exact form of the exact energy density $E_{\text{XC}}(r)$, representing and incorporating all exchange and correlation (XC) effects is unknown. From general principles one can formulate conditions on what $E_{\text{XC}}(r)$ should look like, and several, more and more advanced expressions have been advocated for it in the literature. Their application to real systems has been impressively successful, and it seems likely that a further increase of accuracy is a matter of time.

1.7.3 Basis functions and orbitals

Let us make a clear distinction between (basis) *functions* and *orbitals*, even where these phrases are sometimes mixed up in the traditional terminology. Orbitals are always specific combinations of the basis functions. Orbitals are related to the computed eigenfunctions of some Fock operator or Hamiltonian occurring in the run or in a related preceding calculation. Functions are merely the elementary mathematical entities in which the orbitals are expressed. A Slater Type Orbital (STO), for instance is a function, not an orbital.

The physical meaning of one-electron orbitals in DFT has often been questioned. We believe that they are useful quantities for interpretation, just like the HF orbitals. For a discussion see ref.¹.

See also

- ADF-GUI tutorial: [basis set effects](#)

Cartesian function sets, spurious components

ADF employs Slater-type exponential basis functions centered on the atoms. Such a function consists of an exponential part $\exp(-ar)$ and a polynomial pre-factor $r^{kr} x^{kx} y^{ky} z^{kz}$. A function *set* is characterized by its radial behavior (the exponential part and the power of r , kr) and by its angular momentum quantum number l . The functions in such a set consist of all possible combinations $x^{kx} y^{ky} z^{kz}$, such that $kx+ky+kz=l$. These are denoted the *Cartesian* spherical harmonics.

The Cartesian function sets are very suitable for computational manipulations, but they have a drawback. By inspection it is easily verified that a d -set consists of 6 Cartesian functions, while there can of course be only 5 true d -type functions among them: one (linear combination) of them is in fact an s -type function ($x^2+y^2+z^2$). Similarly, there are 10 f -type Cartesian functions, 3 of which are in fact p -functions. And so on. In ADF all such lower- l (combinations of) functions are projected out of the basis and not employed. As a consequence the basis set *size* in the sense of the number of degrees of freedom and hence the number of possible eigenfunctions of the Fock operator is smaller than the number of expansion coefficients that refer to the primitive (Cartesian) basis functions.

The abbreviation BAS is used for references to the elementary Cartesian basis functions.

¹ F.M. Bickelhaupt and E.J. Baerends, *Kohn-Sham DFT: Predicting and Understanding Chemistry*, in *Reviews in Computational Chemistry*, D.B. Boyd and K.B. Lipkowitz, Editors. 2000, Wiley-VCH: New York. p. 1-86.

Frozen core: Core Orbitals and Core Functions

To speed up the computation the innermost atomic shells are kept frozen. The frozen Core Orbitals (CO), which are solutions of a large-basis all-electron calculation on the isolated atom, are expressed in an auxiliary set of (Slater-type) basis functions *cor-bas*, distinct from the valence set. The core basis set and the COs expansion coefficients are stored in the basis set files.

Orthogonality of the valence Molecular Orbitals (MO) to the COs is achieved with the help of so-called Core Functions (CF). These functions are included in the valence set but they are not additional degrees of freedom. Each of the normal valence functions is combined with a linear combination of all CFs in the molecule in such a way that the transformed function (*cbas*) is orthogonal to all frozen COs in the molecule. There are exactly as many CFs as COs so the orthogonality condition for all valence basis functions amounts to the solution of a linear system where the number of conditions equals the number of parameters.

This aspect once more increases the discrepancy between the number of expansion coefficients of an MO and the number of MOs: the expansion coefficients in the most elementary *bas* representation run over all *bas* functions, including the CFs among them. At some places there may, alternatively, be expansions in the core-orthogonalized *BAS* functions, *CBAS*, where the CFs do not count anymore: they are included implicitly in the *cbas* functions.

Symmetry

The Overlap and Fock matrices become block-diagonal by using symmetry-adapted combinations of the (C)*BAS* functions, such that each such function transforms under the symmetry operators as one of the subspecies of the irreducible representations (*irrep*) of the symmetry group. Symmetry adapted functions are denoted (C)*SBAS*.

For a given *irrep* and subspecies not all elementary basis functions can participate in the symmetry adapted combinations. For instance, for an atom in a reflection plane a basis function that is anti-symmetric with respect to the reflection cannot be part of any symmetric combination of functions. In particular for higher symmetries the number of *BAS* functions that are relevant for a subspecies may be considerably smaller than the total number of *BAS* functions. This is used to cut down expansion lengths, both as used internally in the computation and construction of the Fock matrix, and in printed output. The printed expansion coefficients (in the *bas* representation) refer only to the participating *BAS* functions. A defining list of them is printed at an early stage of the run for each of the subspecies.

Orthonormal basis

It is often computationally convenient to use an orthonormal basis. This is constructed from the *CSBAS* basis by a Lowdin orthogonalization procedure. The resulting symmetry-adapted orthonormal basis is denoted *low*.

The MOs are computed by diagonalization of the Fock matrix in the *LOW* representation. The resulting eigenvectors are easily transformed back to any other representation whenever suitable, such as for instance to the primitive Cartesian *bas* representation (including the CFs).

Fragments

Except in Create mode, where a *basic atom* is constructed, the system is built up from fragments and the corresponding fragment files are attached to the run. The ADF engine reads from the files the fragment MOs and these are used as (compound) *basis functions* for the molecular calculation. The fragment MOs are called Fragment Orbitals (FO).

FOs belong, of course, to one of the symmetry representations of the fragment, but not necessarily to a symmetry representation of the new molecule. The FOs are therefore combined into symmetry-adapted combinations, *SFOs*, to serve as a symmetry-adapted basis in the molecule. These combinations may involve one or more FOs from the same fragment and/or from different fragments. In the latter case the fragments must be symmetry related by one of the operators of the molecule. Symmetry related fragments must of course be identical, apart from their spatial location: they must be of the same fragment *type*.

FOs are naturally orthogonal to the Core Orbitals of their own fragment, but not necessarily to COs of other fragments. By a suitable combination of the SFOs with all CFs in the molecule we obtain the core-orthogonalized symmetry-adapted CSFOs.

The CSFOs can be transformed to an orthonormal basis by a Lowdin transformation. The resulting basis is called low, as above.

Summary of functions and orbitals

In Create mode the (conceptual) approach is:

BAS $\rightarrow$ (core-orthogonalization) $\rightarrow$ CBAS $\rightarrow$ (symmetry) $\rightarrow$ CSBAS $\rightarrow$ (orthonormality) $\rightarrow$ LOW $\rightarrow$ (Fock diagonalization) $\rightarrow$ MO

In Fragment mode:

FO (=MO from fragment file) $\rightarrow$ (symmetry) $\rightarrow$ SFO $\rightarrow$ (core-orth.) $\rightarrow$ CSFO $\rightarrow$ (orthonormality) $\rightarrow$ LOW $\rightarrow$ (Fock diagonalization) $\rightarrow$ MO

Acronyms

BAS

Elementary Cartesian basis functions, consisting of a radial part (exponential factor and power of r) and an angular part (Cartesian spherical harmonic). The complete BAS set contains spurious lower- l combinations; these combinations are projected out and not used in the calculation. The BAS set contains also Core Functions.

SBAS

Symmetry-adapted combination of BAS functions.

CF

Core Function, part of the bas set. The CFs do not represent degrees of freedom in the basis set but serve only to ensure orthogonalization of the valence space to all frozen Core Orbitals.

CBAS

Core-orthogonalized elementary basis functions: the true valence (not-CF) BAS functions transformed by adding a suitable combination of the CFs. The total number of CBAS + the total number of CFs equals the total number of BAS.

CSBAS

Symmetry-adapted combination of cbas functions.

CO

Frozen Core Orbitals, expressed as linear combinations of an auxiliary corbas basis set. The corbas set plays no role in the further discussion. The corbas functions are *not* the CFs.

The number of COs equals the number of CFs.

LOW

Lowdin orthonormalized symmetry-adapted core-orthogonalized basis. In Create mode they are derived directly from the BAS functions, in Fragment mode from the Fragment Orbitals, which are themselves of course expressible in the BAS set.

FO

Fragment Orbital: the MO of a fragment calculation, now used as a *basis function* in the molecule of which the fragment is part.

SFO

Symmetry adapted combination of FOs.

CSFO

Core-orthogonalized SFO.

1.7.4 Coulomb potential evaluation, density fitting

Using Slater-type basis functions yields awkward multi-center integrals in the evaluation of the Coulomb potential. We therefore first need to find an approximate density-representation for which the Coulomb integral can be evaluated efficiently. This procedure is commonly referred to as density fitting. The default density fitting procedure in ADF is described in Ref.².

One of the most important properties of a molecule is its energy, or its bonding energy with respect to the constituent fragments. The approximate nature of the fitting procedure introduces two types of errors. The first is that, since the Coulomb potential is only approximated, the SCF solution itself, i.e. the set of self-consistent Molecular Orbitals and their energy eigenvalues may be slightly wrong, yielding an error in the charge density and hence in the energy. Since the energy is to first order stable with respect to changes in the mo coefficients this error in the energy can be assumed very small. The second type of error derives from the computation of the energy from the (self-consistent) charge density, via the Coulomb potential. Let

$$\rho \equiv \rho_{exact}(r) = \rho_{fit}(r) + \delta(r)$$

and

$$V_{fit}(r) = \int \rho_{fit}(r')/|r - r'|dr'$$

For the Coulomb energy of the charge density we have

$$\begin{aligned} 2E_{Coul} &= \iint \rho(r)\rho(r')/|r - r'|drdr' = \int \rho(r)V_{fit}(r)dr + \iint \rho(r)\delta(r)/|r - r'|drdr' \\ &= \int V_{fit}(r)(\rho(r) + \delta(r))dr + \iint \delta(r)\delta(r')/|r - r'|drdr' \end{aligned}$$

from which we see that the fit error is corrected to first order (by adding the fit deficiency $\delta(r)$ to the exact charge density when integrating against the fit potential) and that only a second order term remains that cannot be evaluated, the last term in the right-hand-side of the last equation.

A fair impression of the fit quality and the importance of the second order error term is obtained by checking

- the size of the first order correction term $\int V_{fit}(r)\delta(r)dr$ and
- the norm of the deficiency function, $\int \delta^2(r)dr$.

Both are printed in standard output, at the end of the output of the SCF procedure computational report. They are usually very small, which gives some confidence that the second order fit error can be ignored.

1.7.5 Three-step build-up of the bonding

The approach of ADF is based on fragments. This applies not only in the analysis at the end of the computation but also in the set-up of the ADF engine. The computation of the molecule from its constituent fragments takes place in three steps, and these are reflected in the analysis of bond energy components.

First, the (free, unrelaxed) fragments are placed at their positions in the molecule. This implies an *electrostatic* interaction: for each fragment the Coulomb interaction of its undisturbed charge density with the fields of the other fragments.

² M. Franchini, P.H.T. Philipsen, E. van Lenthe, L. Visscher, *Accurate Coulomb Potentials for Periodic and Molecular Systems through Density Fitting*, *Journal of Chemical Theory and Computation* 10, 1994 (2014) (<https://doi.org/10.1021/ct500172n>)

Next, the Pauli exclusion principle is applied. Even without considering self-consistency the one-electron orbitals of the combined fragments cannot represent a correct one-determinant wave function because the orbitals of different fragments are not orthogonal to one another. The ADF engine performs an orthonormalization of the occupied Fragment Orbitals to obtain an antisymmetrized product. This implies a change in the total molecular charge density from the sum-of-fragments to what is called the sum-of-*orthogonalized*-fragments. The corresponding (repulsive) energy term is evaluated separately and is called *Exchange* repulsion, or alternatively *Pauli* repulsion. The phrase *orthogonal(ized) fragments*, if you find it elsewhere in this manual or in the source code of ADF, refers to this aspect. The sum of Pauli repulsion and electrostatic interaction is called the *steric interaction*.

The third phase is the relaxation to self-consistency, with of course the ensuing contributions to the bond energy.

1.7.6 Transition State procedure

This phrase stands for an analysis method described in ref.⁴ and has no relation to transition states in chemical reactions. An extensive discussion of bond energy analysis by ADF is given in ref.^{5,6}.

The energy associated with a change in charge density, say the relaxation to self-consistency from the sum-of-orthogonal-fragments, can be computed by subtracting final and initial energies, each obtained from the corresponding charge density. For purposes of analysis the change in energy dE can be reformulated as

$$dE = \int dr \left((\rho_{\text{final}}(r) - \rho_{\text{initial}}(r)) \int_{\rho_{\text{initial}}}^{\rho_{\text{final}}} d\rho F[\rho(r)] \right) \quad (1.2.8)$$

$F(\rho)$ is the Fock operator belonging to the charge density ρ

By writing the density difference $\rho_{\text{final}} - \rho_{\text{initial}}$ a summation over contributions from the different irreducible representations Γ of the molecular symmetry group, an expression is obtained that lends itself for a decomposition of the bond energy into terms from the different symmetry representations:

$$dE = \sum_{\Gamma} \int dr \left(\Delta\rho^{\Gamma}(r) \int_{\rho_{\text{initial}}}^{\rho_{\text{final}}} d\rho F[\rho(r)] \right) \quad (1.2.9)$$

The integral of the Fock operator over the charge density is now approximated by a weighted summation (in fact, a Simpson integration):

$$\int_{\rho_{\text{initial}}}^{\rho_{\text{final}}} d\rho F[\rho(r)] \approx \frac{1}{6} F[\rho_{\text{initial}}] + \frac{2}{3} F[\rho_{\text{average}}] + \frac{1}{6} F[\rho_{\text{final}}] \quad (1.2.10)$$

where

$$\rho_{\text{average}} = \frac{1}{2}(\rho_{\text{initial}} + \rho_{\text{final}}) \quad (1.2.11)$$

The term with the Fock operator due to the average charge density has given rise to the phrase *transition state*. To avoid confusion we will often refer to it as to the *transition field*.

The approximate integral (1.2.10) involves two errors. The first, rather obvious, is the approximation of the exact integral in (1.2.9) by the weighted sum in (1.2.10). Except in pathological cases this approximation is highly accurate.

The second error comes from the fact that the Coulomb and XC potentials in the Fock operator are computed from the *fit* density. This is only an approximation to the true density, while in the original bond-energy expression (energy due to the final density minus energy due to the initial density) no potentials occur and the *exact* charge density can be used.

⁴ T. Ziegler and A. Rauk, *On the calculation of Bonding Energies by the Hartree Fock Slater method. I. The Transition State Method*, *Theoretica Chimica Acta* 46, 1 (1977) (<https://doi.org/10.1007/BF00551648>)

⁵ P.J. van den Hoek, A.W. Kleyn and E.J. Baerends, *What is the origin of the repulsive wall in atom-atom potentials*, *Comments Atomic and Molecular Physics* 23, 93 (1989)

⁶ E.J. Baerends, *Pauli repulsion effects in scattering from and catalysis by surface*, in *Cluster models for surface and bulk phenomena*, ISBN13: 9780306441028, G. Puccchiori, P.S. Bagus and F. Parmigiani, Editors. 1992, Springer: New-York. p. 189-207.

As mentioned before, these fit-related errors are usually small. For the XC potential the true density can be used if one includes the keyword EXACTDENSITY.

All such errors in the total bonding energy are easily corrected by comparing the summation over the Γ s with the correct value for the total bonding interaction term. The difference is simply added to the total bond energy, so no true error remains. We only have a (correction) term that can't be split in contributions from the distinct symmetry representations. In the printed bond energy analysis such small corrections are 'distributed' over the other terms by scaling the other terms such that their sum is the correct total value.

INPUT, EXECUTION, AND OUTPUT

2.1 Input

The input options for ADF are specified in a text file consisting of a series of key-value pairs, possibly nested in blocks. Much of the general remarks about input for ADF apply also to related property and analysis programs, which are also described in this document. The input for the description of the system, structure and reactivity, vibrational spectroscopy, belongs (mostly) to the [AMS driver](#) part of the input.

- [Input, execution, and output section of the AMS manual](#)

The input is usually embedded in an executable shell script. This is the content of a typical shell script for running an ADF calculation:

```
#!/bin/sh

$AMSBIN/ams <<eor
# This is the beginning of the input.
# The input consists of key-value pairs and blocks.
# Here we define the input option for the AMS driver:

Task GeometryOptimization

System
  Atoms
    H 0.0 0.0 0.0
    H 0.9 0.0 0.0
  End
End

# Next comes the ADF "Engine" block. The input options for ADF, which are
# described in this manual, should be specified in this block:

Engine ADF
  Basis
    Type DZP
  End

  XC
    GGA PBE
  End
EndEngine
eor
```

To run the calculation above from the command line, you should:

1. Create a text file called, for example, `test.run` and copy and paste the content of the script above.
2. Make the script executable by typing in your shell `chmod u+x test.run`.
3. Execute the script and redirect the output to a file: `./test.run > out`.

The program will create a directory called `ams.results`. Inside it, you will find the *log file* `ams.log` (which can be used to monitor the progress of the calculation) and the binary results files `ams.rkf` and `adf.rkf`. After the calculation is completed, you can examine the output file `out`. For more details, see

- [Input, execution and output section of the AMS manual](#)

See also:

The [Examples](#) (page 471) section contains a large number of input examples.

Important: Most options described in this manual should be specified in the ADF Engine block:

```
# All ADF keywords should be specified inside the 'Engine ADF' block
Engine ADF
  Basis
    Type DZP
  End

  XC
    GGA PBE
  End
EndEngine
```

2.1.1 General remarks on input structure and parsing

- Most keys are optional. Defaults values will be used for keys that are not specified in the input
- Keys/blocks can either be *unique* (i.e. they can appear in the input only once) or *non-unique*. (i.e. they can appear multiple times in the input)
- The order in which keys or blocks are specified in the input does not matter. Possible exceptions to this rule are a) the content of non-standard blocks b) some non-unique keys/blocks)
- Comments in the input file start with one of the following characters: `#`, `!`, `::`:

```
# this is a comment
! this is also a comment
:: yet another comment
```

- Empty lines are ignored
- The input parsing is **case insensitive** (except for string values):

```
# this:
UseSymmetry false
# is equivalent to this:
USESMMETRY FALSE
```

- Indentation does not matter and multiple spaces are treated as a single space (except for string values):

```
# this:
    UseSymmetry      false
# is equivalent to this:
UseSymmetry false
```

- Environment variables in the input will be replaced by their value. We only support simple substitution of variables (optionally surrounded by `{}`). All other [parameter expansion features of the POSIX shell](https://pubs.opengroup.org/onlinepubs/9699919799/utilities/V3_chap02.html#tag_18_06_02) (https://pubs.opengroup.org/onlinepubs/9699919799/utilities/V3_chap02.html#tag_18_06_02) (e.g. default values) are **not** supported. Expansion of a variable can be prevented by prefixing the leading dollar (`$`) with a backslash (`\`). Note that variables which are not set will expand to an empty string, just like in a shell:

```
File $SOME_DIRECTORY/file.txt
File ${SOME_DIRECTORY}_BACKUP/file.txt
Key  \ $WILL_NOT_EXPAND
```

2.1.2 Keys

Key-value pairs have the following structure:

```
KeyName Value
```

Possible types of keys:

bool key

The value is a single Boolean (logical) value. The value can be `True` (equivalently `Yes`) or `False` (equivalently `No`). Not specifying any value is equivalent to specifying `True`. Example:

```
KeyName Yes
```

integer key

The value is a single integer number. Example:

```
KeyName 3
```

float key

The value is a single float number. For scientific notation, the E-notation is used (e.g. -2.5×10^{-3} can be expressed as `-2.5E-3`). The decimal separator should be a dot (`.`), and **not** a comma (`,`). Example:

```
KeyName -2.5E-3
```

Note that fractions (of integers) can also be used:

```
KeyName 1/3      (equivalent to: 0.3333333333...)
```

string key

The value is a string, which can include white spaces. Only ASCII characters are allowed. Example:

```
KeyName Lorem ipsum dolor sit amet
```

multiple_choice key

The value should be a single word among the list options for that key (the options are listed in the documentation of the key). Example:

```
KeyName SomeOption
```

integer_list key

The value is list of integer numbers. Example:

```
KeyName 1 6 0 9 -10
```

Note that one can also specify ranges of integers by specifying the interval and (optionally) the step size separated by colons:

```
KeyName 1:5      (equivalent to: 1 2 3 4 5)
KeyName 2:10:2    (equivalent to: 2 4 6 8 10)
KeyName 20:10:-2  (equivalent to: 20 18 16 14 12 10)
```

Note also that ranges can be freely combined with individual numbers:

```
KeyName 1:5 10 20 (equivalent to: 1 2 3 4 5 10 20)
```

float_list key

The value is list of float numbers. The convention for float numbers is the same as for Float keys. Example:

```
KeyName 0.1 1.0E-2 1.3
```

Float lists can also be specified as a range with equidistant points, by specifying the interval's boundaries (inclusive) as well as the number of desired subintervals separated by colons:

```
KeyName 1.0:1.5:5 (equivalent to: 1.0 1.1 1.2 1.3 1.4 1.5)
```

Range specifications can be freely combined with each other and single numbers:

```
KeyName 0.0 1.0:1.5:5 2.0:3.0:10
```

2.1.3 Blocks

Blocks give a hierarchical structure to the input, grouping together related keys (and possibly sub-blocks). In the input, blocks generally span multiple lines, and have the following structure:

```
BlockName
  KeyName1 value1
  KeyName2 value2
  ...
End
```

Headers

For some blocks it is possible (or necessary) to specify a *header* next to the block name:

```
BlockName someHeader
  KeyName1 value1
  KeyName2 value2
  ...
End
```

Compact notation

It is possible to specify multiple key-value pairs of a block on a single line using the following notation:

```
# This:
BlockName KeyName1=value1 KeyName2=value2

# is equivalent to this:
BlockName
  KeyName1 value1
  KeyName2 value2
End
```

Notes on compact notation:

- The compact notation cannot be used for blocks with headers.
- Spaces (blanks) between the key, the equal sign and the value are ignored. However, if a value itself needs to contain spaces (e.g. because it is a list, or a number followed by a unit), the entire value must be put in either single or double quotes:

```
# This is OK:
BlockName Key1=value Key2 = "5.6 [eV]" Key3='5 7 3 2'
# ... and equivalent to:
BlockName
  Key1 value
  Key2 5.6 [eV]
  Key3 5 7 3 2
End

# This is NOT OK:
BlockName Key1=value Key2 = 5.6 [eV] Key3=5 7 3 2
```

Non-standard Blocks

A special type of block is the *non-standard block*. These blocks are used for parts of the input that do not follow the usual key-value paradigm.

A notable example of a non-standard block is the `Atoms` block (in which the atomic coordinates and atom types are defined).

2.1.4 Including an external file

You can include an external ASCII file in the input with the `@include` directive:

```
@include FileName.in
@include "file name with spaces.in"
```

The file name should include the path, either absolute or relative to the run-directory. The content of the file is included in the input at the point where the `@include` directive occurs. The `@include` directive may occur any number of times in the input.

The `@include` feature makes it easy to pack your preferred settings in one file and use them in every run with minimum input-typing effort.

2.1.5 Units

Some keys have a default unit associated (not all keys have units). For such keys, the default unit is mentioned in the key documentation. One can specify a different unit within square brackets at the end of the line:

```
KeyName value [unit]
```

For example, assuming the key `EnergyThreshold` has as default unit `hartree`, then the following definitions are equivalent:

```
# Use defaults unit:
EnergyThreshold 1.0

# use eV as unit:
EnergyThreshold 27.211 [eV]

# use kcal/mol as unit:
EnergyThreshold 627.5 [kcal/mol]

# hartree is the atomic unit of energy:
EnergyThreshold 1.0 [hartree]
```

Available units:

- **Energy:** hartree, joule, eV, kJ/mol, kcal/mol, cm1, MHz
- **Forces:** hartree/bohr, eV/bohr, hartree/angstrom, eV/angstrom, kcal/mol/angstrom, kJ/mol/angstrom
- **Length:** bohr, angstrom, meter
- **Angles:** radian, degree
- **Mass:** el, proton, atomic, kg
- **Pressure:** atm, pascal, GPa, a.u., bar, kbar
- **Electric field:** V/angstrom, V/meter, a.u.

2.1.6 Title, comment

```
TITLE Title
```

Title may be any string. The program combines it (that is, the first approximately 50 characters) with date and time of the job to construct the *job identification*. The job identification is used to stamp an identification on result files, which will be read and printed if such a file is used again, for instance as a fragment file.

The job identification will also be echoed in the output header to identify the current run. By default the date and time are combined with a dummy string. In Create mode the title is first read from the data file that supplies the basis functions, etc., and can then be overwritten via input.

Note that, contrary to some other programs, ADF does *not* take the first input record as a title.

You can put more remarks in the input file to be echoed in the standard output file; these will not become part of the job identification:

```
COMMENT
text
```

(continues on next page)

(continued from previous page)

```
...
End
```

The text records are copied to the output header, directly after the job identification.

The key COMMENT may occur any number of times; all text blocks are printed in the output header with a blank line between any two text blocks.

2.1.7 Amsification of ADF in ADF2020

The standalone program `adf` does not exist anymore in ADF2020. The job of the AMS driver is to handle all changes in the geometry, e.g. during a geometry optimization, using so-called engines like ADF for the calculation of energies and forces. Details of this change can be found in the section on the

- [AMSification of ADF](#) (page 11)

2.1.8 Input parsing changes in ADF2018 and later

The input file parsing for ADF and its properties programs has changed from the 2017 version to the 2018 version.

ADF2018 syntax changes for a few keywords

In order to adapt ADF to the new (more strict) input format, the syntax of a few keywords had to be changed. The following table contains the list of keywords that have changed in ADF2018. Note that some keywords changed in AMS2020 again, see the [section on ADF amsification](#) (page 11). Note also that the block key DEFINE was removed.

key in ADF2017 and before	key in ADF2018 and later / comments
CorePotentials	<i>CorePotentials</i> (page 68) is now a block (and not a <i>general</i> key/block)
Define	removed
Dependency	<i>Dependency</i> (page 391) is now a block (and not a key)
EField	ADF2020: key 'System%ElectroStaticEmbedding' in <i>AMS driver</i>
ETSNOCV	<i>ETSNOCV</i> (page 309) is now a block (and not a key)
Excitations -> Davidson	<i>Excitations -> Davidson</i> (page 179) is now a block (and not a key)
Excitations -> Exact	<i>Excitations -> Exact</i> (page 179) is now a block (and not a key)
Geometry	ADF2020: key 'Task' and key 'Properties' in <i>AMS driver</i>
Integration Value	<i>Integration -> Accint Value</i> (page 375)
LinearScaling	<i>LinearScaling</i> (page 396) is now a block (and not a <i>general</i> key/block)
ModifyStartPotential	<i>ModifyStartPotential</i> (page 69) is now a block (and not a <i>general</i> key/block)
Occupations	Split into <i>Occupations</i> (page 64) and <i>IrrepOccupations</i> (page 66)
Relativistic	ADF2020: block key <i>Relativity</i> (page 106)
Restart -> Value	<i>Restart -> File -> Value</i> (page 400)
Response -> Units	Removed optional units for <i>FrqBeg</i> and <i>FrqEnd</i> in <i>Response</i> block
SCF -> ADIIS	<i>SCF -> ADIIS</i> (page 368) is now a block (and not a key)
SCF -> ARH	<i>SCF -> ARH</i> (page 372) is now a block (and not a key)
SCF -> DIIS	<i>SCF -> DIIS</i> (page 368) is now a block (and not a key)
SlaterDeterminants	<i>SlaterDeterminants</i> (page 426) is now a block (and not a <i>general</i> key/block)
SOPert	<i>SOPert</i> (page 194) is now a block (and not a key)
Thermo	ADF2020: key 'Thermo' in <i>AMS driver</i>

Strict parsing of input file

In ADF2018 and later **exact keyword matching** is used, meaning that **keyword abbreviations (or extensions) are not allowed**. In ADF2017 (and previous versions) the parsing of the input file was *tolerant* and it would allow for abbreviations and extensions of keywords.

In the example below, only the first version is allowed in ADF2018 and later, while the second and third versions will trigger an input syntax error:

```
# This is the proper input syntax:
SCF
  Converge 1.0E-7
End

# In ADF2017 you could (for some keywords) use abbreviations. e.g.:
SCF
  Conv 1.0E-7
End

# or extensions. e.g.:
SCF
  Convergence 1.0E-7
End

# Keyword abbreviations and extensions are NOT ALLOWED in ADF2018 and later.
```

2.2 Execution

See

- [Input, execution and output section of the AMS manual](#)

2.3 Structure of the Output

AMS produces two ASCII files: standard output and the ams.log file. ADF writes part of these files. See also

- [Input, execution and output section of the AMS manual](#)

The ams.log file is a very concise summary of the calculation's progress during the run. Furthermore, ADF produces and reads binary data files. Most of these files have the so-called KF format. KF stands for Keyed File: KF files are keyword oriented, which makes them easy to process by simple procedures. KF files are Direct Access binary files. Consult the [Scripting Section](#) for information about how to use some standard utilities for processing KF files.

The graphical user interface ADF-GUI provides graphical representations of calculated data fields:

See also:

[GUI overview tutorials](#)
[ADF-GUI tutorials](#)

2.3.1 Job Characteristics on standard Output

Input Echo, Output Header

- Header with the program name, the release number and a copyright statement.
- AMS part of the output file with the geometry
- Copy of the ADF engine part of the input file
- Title and any comments that may have been supplied via input (key COMMENT).

Main Job Characteristics

- The Model Parameters such as the Density Functional and relativistic options.
- A list of attached files: restart data files and fragment files.
- (Initial) geometric data: atomic positions, atom types, defined fragments, and the inter-atomic distance matrix.
- The point group symmetry, with a list of the irreducible representations and subspecies.
- The electronic configuration: occupation numbers (if specified), their distribution over spin- α and spin- β , and the net charge of the molecule.

Build Info: Fragments and Function Sets

- Correspondence between fragments in the molecule and the corresponding *master* fragments on the pertaining fragment file. (This output is by default off)
- SFOs: the Symmetry combinations of Fragment Orbitals. The SFOs are the basic conceptual entities for the analysis of MOs and other results.
- The elementary basis functions and the frozen-core levels of the atoms.

Technical Parameters

- Parallelization and vectorization characteristics.
- Update strategy parameters for the SCF procedure.
- General precision settings for numerical integration and neglect-of-small function values (in integral evaluations).

Computational Report

- Numerical integration parameter(s) and the number of generated (symmetry unique) integration points, and partitioning of the points in blocks.
- SCF procedure, at each cycle: for each irreducible representation: the one-electron orbital energies and the occupation numbers for a contiguous sequence of orbitals.
- Gross atomic charges, computed from a Mulliken population analysis.
- Property-specific output, like spectroscopic properties.
- AMS part of the output

Exit Procedure

- Normal termination or an error message.

2.3.2 Log file, **adf.rkf**, **TAPE13**

The `ams.log` file (logfile) is generated during the calculation and flushed after (almost) each message that is sent to it by the program. Consequently, the user can inspect it and see what is going on without being delayed by potentially large system I/O buffers. Each message contains the date and time of the message plus additional info.

A major part of the messages simply states the name of a procedure. Such messages are sent when the procedure is entered. During the SCF procedure, the SCF errors, which are a measure for non-self-consistency, are written at every cycle. In calculations where the geometry is changing (optimization, frequencies...) each set of new coordinates is sent to the log file (Cartesian, in Angstrom and also Z-matrix, if a Z-matrix structure was provided in the input file). Other messages should be self-explanatory.

Be alert to error messages. Take them seriously: inspect the standard output carefully and try to understand what has gone wrong. Be also alert to warnings. They are not necessarily fatal but you should understand what they are about before being satisfied with the results of the calculation. Do not ignore them just because the program has not aborted: in some cases the program may not be able to determine whether or not you really want to do what appears to be wrong or suspicious. If you believe that the program displays erratic behavior, then the standard output file may contain more detailed information. Therefore, in such cases save the complete standard output file, together with the log file, in case we need these files for further analysis.

adf.rkf

`adf.rkf` is the general result file of an ADF calculation. It is a KF file: direct-access, binary, and keyword driven. It contains information about the calculation. You can use it as a fragment file in a subsequent calculation on a bigger molecule, where the current one may be a part, or in an analysis or property program. For more information on `adf.rkf`, see [Appendix on `adf.rkf`](#) (page 439).

TAPE13

TAPE13 is the checkpoint file for restarts after a crash. It is a concise version of `adf.rkf`, containing only the data the program uses for restarting the calculation. See the `RESTART` keyword. Like `adf.rkf`, TAPE13 is a binary, keyword-driven KF file, see [Appendix on TAPE13](#) (page 441).

COORDINATES, BASIS SETS, FRAGMENTS

See also:

ADF-GUI tutorial: [building molecules](#) , [basis set effects](#) , [fragments](#)

3.1 Atomic coordinates

See also

- [Geometry, System definition section of the AMS manual](#)

3.1.1 Cartesian

You can define the input atomic coordinates in the `Atoms` sub-block key of the `System` key in AMS. Note that in AMS you cannot add an integer by which the atoms are numbered.

```
System
  Atoms
    AtomType Coords {adf.F=Fragment}
    ...
  End
End
```

AtomType

The name of an *atom type*. It must begin with the standard one- or two-character symbol for the chemical element (e.g. H, He, Li,...). Optionally it may be appended by `.text`, where `text` is any string (not containing delimiters). Examples: H, Mn.3, Cu.dz-new.

Note: *Atom type* is not identical to *chemical element*. An atom type is defined by all characteristics of the basic atom to which it in fact refers: the nuclear charge, the basis functions, the frozen core, the density functional and any other features that were applied in generating that basic atom.

Coords

The xyz coordinates of the atom. Example:

```
ATOMS
  O  0.000000  0.000000  0.000000
  H  0.758602  0.000000  0.504284
  H  0.758602  0.000000 -0.504284
END
```

adf.F=Fragment

Specifies that the atom belongs to a particular fragment. The fragment name must be of the form `fragtype|n`, where `fragtype` is the name of one of the types of fragments in the molecule. The integer `n`, after the pipe `|`, counts the individual fragments of that type. The numbering suffix `|n` is not required if there is only one fragment of that type.

When `adf.f=Fragment` is omitted altogether, the fragment type is taken to be the *atom type* that was specified earlier on the same line. (The numbering `|n` is then added automatically by the program, by counting the number of times that this single-atom fragment type occurs in the list of atoms).

Note: Input items are generally case insensitive. Exceptions are the names of files and directories. Since (to be discussed below) the name of the fragment type as it is defined under atoms (explicitly with the `adf.f=Fragment` option, or implicitly as the name of the atom type) might also directly indicate the fragment file, the specification of fragment types is in principle case-sensitive. Errors may occur if you are sloppy in this respect. However, you must not give different fragment type names that differ only by case: at various places in the program fragment type names are compared in a case-insensitive way.

3.1.2 Z-Matrix

It is possible to specify the input geometry as a Z-Matrix.

```
System
  Atoms Z-Matrix
    C
    H  1 1.089000
    H  1 1.089000  2 109.4710
    H  1 1.089000  2 109.4710  3 120.0000
    H  1 1.089000  2 109.4710  3 -120.0000
  End
End
```

Only the first atom may be a dummy atom in a Z-matrix. Use the chemical symbol `XX` for the dummy atom.

3.1.3 Orientation of Local Atomic Coordinates

As discussed before, the atomic positions are input with the key `ATOMS`. One option has thus far not been mentioned: the possibility to redefine the local coordinate frame of an atom.

```
ATOMS {type of coordinates}
  AtomType coordinates {adf.F=fragment} {Z="xx yy zz"} {X="xx yy zz"}
  ...
End
```

Except for the `z=` option, all aspects have been examined already before.

z="xx yy zz"

Defines a reorientation of the local atomic z-axis; it is interpreted as a direction vector with components `(xx,yy,zz)` pointing away from the atom. In the local, reoriented frame the local atomic x-axis will be rotated to the plane defined by the directions of the molecular z-axis and the local atomic z-axis. This feature can be used only for single-atom fragments (otherwise it is ignored). Its purpose is to give more flexibility in the analysis of the final molecular orbitals in terms of the atomic orbitals. In such a case it may be very helpful to redefine the orientation of the p-orbitals of an atom. For instance, you may orient all p-orbitals towards the origin by specifying for each atom `z= -x -y -z` (with `x,y,z` the coordinates of that atom). By default the local and molecular z-axes are identical.

x="xx yy zz"

Defines a reorientation of the local atomic x-axis; it is interpreted as a direction vector with components `(xx,yy,zz)`

pointing away from the atom. Together with the z vector this defines the xz plane. The y-axis is then given by the vector product $\vec{z} \times \vec{x}$. This is used for analysis (see orientation of the z-axis).

3.1.4 Symmetry Key

Note that this is a specification of the `Symmetry` key in the Engine ADF part of the input. You can use the `System%Symmetrize` key in the AMS part of the input, such that AMS will symmetrize the coordinates. ADF will not adjust coordinates. Thus input atomic coordinates that are off from their correct positions, even if they are only slightly off, are not adjusted by ADF. There exists a `System%Symmetry` key in the AMS part of the input, which can be used with the `System%Symmetrize` key to symmetrize coordinates. Note that the symmetry used in AMS does not have to be the same as is used in ADF.

The point group symmetry and symmetry tolerance can be supplied.

```
Symmetry [AUTO | NOSYM | ATOM | C(LIN) | D(LIN) | C(I) | C(S) | C(2) | C(2V) | C(3V) |
↪ | C(4V) |
      C(5V) | C(6V) | C(7V) | C(8V) | C(2H) | D(2) | D(3) | D(4) | D(5) | D(6) | ↪
↪ D(7) |
      D(8) | D(2D) | D(3D) | D(4D) | D(5D) | D(6D) | D(7D) | D(8D) | D(2H) | ↪
↪ D(3H) |
      D(4H) | D(5H) | D(6H) | D(7H) | D(8H) | O(H) | T(D) ]
```

Symmetry

Type

Multiple Choice

Default value

AUTO

Options

[AUTO, NOSYM, ATOM, C(LIN), D(LIN), C(I), C(S), C(2), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), O(H), T(D)]

Description

Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. Coordinates must be symmetric within SymmetryTolerance.

```
SymmetryTolerance float
```

SymmetryTolerance

Type

Float

Default value

1e-07

Description

Tolerance used to detect symmetry in the system. If symmetry Schoenflies symbol is specified, the coordinates must be symmetric within this tolerance.

The point group symmetry specified in input with a Schönflies type symbol puts restrictions on the orientation of the atomic system. If symmetry is specified, you must take care of supplying the *Cartesian* coordinates in the appropriate orientation.

3.2 Basis sets and atomic fragments

See also:

- *What basis set should I use in ADF?* (page 405)
- *Basis set file format* (page 419)

3.2.1 STO basis sets

The basis functions used in ADF are commonly known as Slater-type Orbitals (STOs). The ADF package comes with a database of STO basis sets. The basis sets are simple ASCII files and they are located in the directory `$AMSHOME/atomicdata/ADF`. A description of the basis set file format can be found in the appendix *Basis set file format* (page 419).

A basis set can roughly be characterized by its size (single-, double-, triple-zeta; with or without polarization) and by the level of frozen core approximation. The standard basis sets available in ADF are:

- **SZ** Minimal basis sets: single-zeta without polarization. The exponents of the functions correspond to the standard STO-3g basis sets used in programs that employ Gaussian-type basis functions. Type-SZ files are provided only for the lighter elements, up to Kr.
- **DZ** Double-zeta basis sets without polarization functions. A triple-zeta set is used for the 3d shells of the first row transition metals, the 4f shells of the lanthanides, and the 5f shells of the actinides. In all these cases a double-zeta set provides a rather poor expansion basis for the true (numerically computed) atomic orbital.
- **DZP** Double-zeta polarized basis. The basis sets in DZP are derived from DZ, extended with a polarization function. This type of basis set is thus far provided only for the elements up to Ar, and for the 4p series Ga through Kr.
- **TZP** Triple-zeta basis sets. A polarization function is added for H through Ar and for Ga through Kr (from DZP).
- **TZ2P** Triple-zeta with two polarization functions, for H through Ar and Ga through Kr (from DZP). Note that the TZ2P basis set files are provided only for the lighter elements, up to Kr. The ZORA/TZ2P basis set files are provided for all elements. Typically for all elements one polarization function is added compared to the corresponding TZP basis set. Note, however, that TZ2P will not always give you extra basis functions for most lanthanide and actinide frozen core basis sets.

In addition to the standard basis sets, the database contains directories with special basis sets:

- **TZ2P+** For transition metals Sc-Zn and lanthanides (ZORA) only: as TZ2P, but with extra d-STO (3d metals), and extra f-STO (lanthanides, ZORA).
- **ZORA** contains basis sets designed for *ZORA relativistic calculations* (page 106) (relativistic calculations have special basis set requirements, especially in the core region). ZORA basis sets with frozen core should be used **exclusively** in relativistic calculations with the ZORA approach, while all-electron ZORA basis sets can be used for both relativistic and non-relativistic calculations. The ZORA/QZ4P basis set can be loosely described as core triple zeta, valence quadruple zeta, with four sets of polarization functions.
- **ET** contains several even-tempered basis sets which enable one to go to the basis set limit, such as ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE. The accuracy of the smallest basis set in this directory can loosely be described as quadruple zeta in the valence with three polarization functions added. This directory also contains basis sets with extra diffuse functions. In response calculations one should use such large basis sets in case of small molecules. Very diffuse functions are absolutely necessary to get good results for excitation energies corresponding to high-lying orbitals (Rydberg states).
- **AUG** contains several augmented standard basis sets which enable one to get reasonable results for excitation energies with relatively small basis sets, such as AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P.

- **Corr** contains several extended all-electron ZORA basis sets, especially useful in MBPT (MP2, GW, BSE) calculations, Corr/TZ3P and Corr/QZ6P. For MBPT larger basis sets are needed to achieve the same accuracy as in a standard DFT calculation.

Furthermore, in `$AMSHOME/atomicdata/ADF` you will find:

- **Special/AE** contains non-relativistic basis sets for all-electron calculations. However, these files cannot be used as such, because they do not contain any fit sets. They serve as a starting point for the development of (new) basis sets. For some of the all-electron sets appropriate fit sets have already been generated. The corresponding database files can be found in the appropriate sub-directories SZ, DZ, DZP, et cetera.
- **Special/Vdiff** contains non-relativistic basis sets that include very diffuse functions. These were recommended for response calculations. Very diffuse functions are absolutely necessary to get good results for excitation energies corresponding to high-lying orbitals. Recommendation: use the even-tempered basis sets in the ET directory, since these basis sets are better.
- **Special/MDC** contains non-relativistic basis sets with optimized fit functions especially useful for accurate multipole-derived charges. These are available only for a limited number of basis sets.

The directory `$AMSHOME/atomicdata/Dirac` contains the input files for the DIRAC auxiliary program (see the RELATIVITY keyword).

Frozen core

Multiple occurrences of one chemical element in the same basis set sub-directory correspond to different levels of the *frozen core approximation* (page 20). Manganese, for instance, may have a basis set for an atom with a frozen 2p shell and another one with a frozen 3p shell. The file names are self-explanatory: Mn.2p stands for a data file for Manganese with frozen core shells up to the 2p level. An all-electron basis set would correspond to a file that has no frozen-core suffix in its name.

Electronic configurations specific basis sets

Another type of multiple occurrence of one element in one basis set directory may be found when basis sets have been developed for different electronic configurations: the Slater-type basis sets are fitted to numerical orbitals from runs with different occupation numbers. Currently this applies only for Ni (in `$AMSHOME/atomicdata/ADF DZ, TZP and TZ2P`), where basis sets are supplied for the d8s2 and the d9s1 configurations respectively. Since in earlier releases only the d8s2 variety was available, the names of the basis set files are Ni.2p (for d8s2) and Ni_d9.2p, and likewise Ni.3p and Ni_d9.3p.

References on basis sets

- E. van Lenthe and E.J. Baerends, *Optimized Slater-type basis sets for the elements 1-118*. *Journal of Computational Chemistry* 24, 1142 (2003) (<https://doi.org/10.1002/jcc.10255>)
- D.P. Chong, E. van Lenthe, S.J.A. van Gisbergen and E.J. Baerends, *Even-tempered Slater-Type orbitals revisited: From Hydrogen to Krypton*. *Journal of Computational Chemistry* 25, 1030 (2004) (<https://doi.org/10.1002/jcc.20030>)
- D.P. Chong, *Augmenting basis set for time-dependent density functional theory calculation of excitation energies: Slater-type orbitals for hydrogen to krypton*. *Molecular Physics* 103, 749 (2005) (<https://doi.org/10.1080/00268970412331333618>)

Older references for STO basis sets are Refs.¹²³. See also the paper by Raffennetti on design and optimization of even-tempered STO basis sets⁴. The paper by Del Chong describes completeness profiles as a visual tool in estimating the

¹ E. Clementi, C. Roetti, *Roothaan-Hartree-Fock atomic wavefunctions: Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms, $Z \leq 54$* , Atomic Data and Nuclear Data Tables 14, 177 (1974) ([https://doi.org/10.1016/S0092-640X\(74\)80016-1](https://doi.org/10.1016/S0092-640X(74)80016-1))

² A.D. McLean, R.S. McLean, *Roothaan-Hartree-Fock atomic wave functions Slater basis-set expansions for $Z = 55-92$* , Atomic Data and Nuclear Data Tables 26, 197 (1981) ([https://doi.org/10.1016/0092-640X\(81\)90012-7](https://doi.org/10.1016/0092-640X(81)90012-7))

³ J.G. Snijders, P. Vernooijs, E.J. Baerends, *Roothaan-Hartree-Fock-Slater atomic wave functions: Single-zeta, double-zeta, and extended Slater-type basis sets for 87 Fr-103 Lr*, Atomic Data and Nuclear Data Tables 26, 483 (1981) ([https://doi.org/10.1016/0092-640X\(81\)90004-8](https://doi.org/10.1016/0092-640X(81)90004-8))

⁴ R.C. Raffennetti, *Eventempered atomic orbitals. II. Atomic SCF wavefunctions in terms of eventempered exponential bases*, Journal of Chemical Physics 59, 5936 (1973) (<https://doi.org/10.1063/1.1679962>)

completeness of a basis set⁵. Finally, Zeiss and coworkers⁶ describe field-induced polarization functions for STOs. These are useful for defining basis sets with diffuse functions for (hyper)polarizability and other property calculations.

The procedure for the usage and optimization of fit functions is described by Baerends et al.⁷.

For documentation on how to make custom even-tempered basis/fit sets, see the [old ADF 2014 documentation](https://downloads.scm.com/Doc/Doc2014/ADF/ADFUsersGuide/ADFUsersGuide.pdf) (<https://downloads.scm.com/Doc/Doc2014/ADF/ADFUsersGuide/ADFUsersGuide.pdf>).

3.2.2 Available basis sets

ADF has optimized STO basis sets for the whole periodic table ($Z=1-120$).

The next tables give an indication which all electron (ae) and frozen core (fc) standard basis sets are available for the different elements in ADF.

Table 3.1: Available standard basis sets for non-relativistic (non-rel) and ZORA calculations H-Kr ($Z=1-36$)

Element	ae or fc	SZ, DZ	DZP	TZP, TZ2P	TZ2P+	QZ4P, ET	AUG
H-He ($Z=1-2$)	ae	Yes	Yes	Yes		Yes	Yes
Li-Ne ($Z=3-10$)	ae	Yes	Yes	Yes		Yes	Yes
	.1s	Yes	Yes	Yes			non-rel
Na-Ar ($Z=11-18$)	ae	Yes	Yes	Yes		Yes	Yes
	.1s .2p	Yes	Yes	Yes			non-rel
K-Ca ($Z=19-20$)	ae	Yes	Yes	Yes		Yes	Yes
	.2p .3p	Yes	Yes	Yes			non-rel
Sc-Zn ($Z=21-30$)	ae	Yes		Yes	Yes	Yes	Yes
	.2p .3p	Yes		Yes	Yes		non-rel
Ga-Kr ($Z=31-36$)	ae	Yes	Yes	Yes		Yes	Yes
	.3p .3d	Yes	Yes	Yes			non-rel

Table 3.2: Available standard basis sets for non-relativistic calculations Rb-Cm ($Z=37-96$)

Element	fc	DZ, TZP
Rb-Sr ($Z=37-38$)	.3p .3d .4p	Yes
Y-Cd ($Z=39-48$)	.3d .4p	Yes
In-Ba ($Z=49-56$)	.4p .4d	Yes
La-Lu ($Z=57-71$)	.4d .5p	Yes
Hf-Hg ($Z=72-80$)	.4d .4f	Yes
Tl-Rn ($Z=81-86$)	.4d .4f .5p .5d	Yes
Fr-Ra ($Z=87-88$)	.5p .5d	Yes
Ac-Cm ($Z=89-96$)	.5d	Yes

⁵ D.P. Chong, *Completeness profiles of one-electron basis sets*, *Canadian Journal of Chemistry* 73, 79 (1995) (<https://doi.org/10.1139/v95-011>)

⁶ G.D. Zeiss, W.R. Scott, N. Suzuki, D.P. Chong, S.R. Langhoff, *Finite-field calculations of molecular polarizabilities using field-induced polarization functions: second- and third-order perturbation correlation corrections to the coupled Hartree-Fock polarizability of H₂O*, *Molecular Physics* 37, 1543 (1979) (<https://doi.org/10.1080/00268977900101121>)

⁷ E.J. Baerends, D.E. Ellis and P. Ros, *Self-consistent molecular Hartree-Fock-Slater calculations I. The computational procedure*, *Chemical Physics* 2, 41 (1973) ([https://doi.org/10.1016/0301-0104\(73\)80059-X](https://doi.org/10.1016/0301-0104(73)80059-X))

Table 3.3: Available standard basis sets for ZORA calculations Rb-Og (Z=37-120)

Element	ae or fc	DZ, TZP, TZ2P	TZ2P+	QZ4P
Rb-Sr (Z=37-38)	ae	Yes		Yes
	.3p .3d .4p	Yes		
Y-Cd (Z=39-48)	ae	Yes		Yes
	.3d .4p	Yes		
In-Ba (Z=49-56)	ae	Yes		Yes
	.4p .4d	Yes		
La-Yb (Z=57-70)	ae	Yes	Yes	Yes
	.4d .5p	Yes	Yes	
Lu (Z=71)	ae	Yes		Yes
	.4d .5p	Yes		
Hf-Hg (Z=72-80)	ae	Yes		Yes
	.4d .4f	Yes		
Tl (Z=81)	ae	Yes		Yes
	.4d .4f .5p	Yes		
Pb-Rn (Z=82-86)	ae	Yes		Yes
	.4d .4f .5p .5d	Yes		
Fr-Ra (Z=87-88)	ae	Yes		Yes
	.5p .5d	Yes		
Ac-Lr (Z=89-103)	ae	Yes		Yes
	.4f .5d	Yes		
Rf-Cn (Z=104-112)	ae	Yes		Yes
	.4f .5d .5f	Yes		
Nh-Og (Z=113-118)	ae	Yes		Yes
	.5d .5f	Yes		
Uue-Ubn (Z=119-120)	ae	Yes		Yes
	.5f	Yes		

For heavier elements, from Rb on, the non-relativistic all electron basis sets are missing. In the ZORA basis sets directory you will find all-electron basis sets for all elements ($Z = 1-120$), which also could be used in non-relativistic calculations. Note, however, that these basis sets were optimized for ZORA calculations, which means that non-relativistic calculations will not always give you the expected accuracy. Non-relativistically optimized basis sets for the heavier elements are provided in a separate directory AE, which contains basis sets of single-, double- and triple-zeta quality indicated respectively by suffixes ‘sz’, ‘dz’, and ‘tz’. The files in Special/AE/ are not complete basis set files, because they don’t contain fit sets (the usage and relevance of fit functions is explained later).

Basis sets directories

Basis sets can be found in the directory \$AMSHOME/atomicdata/ADF, for non-relativistic calculations in the sub-directories SZ, DZ, DZP, TZP, TZ2P, TZ2P+, for ZORA calculations in ZORA/SZ, ZORA/DZ, ZORA/DZP, ZORA/TZP, ZORA/TZ2P, ZORA/TZ2P+, ZORA/TZ2P-J, ZORA/QZ4P, ZORA/QZ4P-J, the augmented basis sets can be found in AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, the even tempered basis sets in ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, the basis sets for MBPT calculations in Corr/TZ3P, Corr/QZ6P. All electron basis sets can be used in non-relativistic and ZORA calculations.

Basis sets acronyms

- SZ: single zeta
- DZ: double zeta
- DZP: double zeta + 1 polarization function

- TZP: valence triple zeta + 1 polarization function
- TZ2P: valence triple zeta + 2 polarization function
- TZ2P+: = TZ2P + extra d (3d metals) or extra f (lanthanides)
- QZ4P: valence quadruple zeta + 4 polarization function, relativistically optimized
- ET: even tempered
 - pVQZ, QZ3P: valence quadruple zeta + 3 polarization function, even tempered
 - QZ3P-nD: = QZ3P + n diffuse sets of s, p, d, and f functions, even tempered
- AUG: augmented
 - ASZ, ADZ, ADZP, ATZP, ATZ2P: augmented for use in TDDFT
- Corr: for use in MBPT
 - TZ3P: = all electron (Z=1-54) ZORA/TZ2P + extra tight polarization function
 - QZ6P: = all electron (Z=1-118) ZORA/QZ4P + extra tight polarization functions
- TZ2P-J, QZ4P-J: for use in ESR hyperfine or NMR spin-spin couplings
 - TZ2P or QZ4P + extra tight (mainly 1s) functions

All electron or frozen core

- element name (without suffix): all electron
- .1s frozen: 1s
- .2p frozen: 1s 2s 2p
- .3p frozen: 1s 2s 2p 3s 3p
- .3d frozen: 1s 2s 2p 3s 3p 3d
- .4p frozen: 1s 2s 2p 3s 3p 3d 4s 4p
- .4d frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d
- .4f frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f
- .5p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 5s 5p (La-Lu)
- .5p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p (other)
- .5d frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d
- .6p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 6s 6p (Ac-Lr)
- .5f frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 5f 6s 6p

3.2.3 The Basis Key

The basis set can be specified in the input via the `Basis` key block. The most important subkeys `Type` and `Core`. Description of all subkeys:

```
Basis
  Type [...]
  Core [None | Small | Large]
End
```

Basis

Type

Block

Description

Definition of the basis set

Type**Type**

Multiple Choice

Default value

DZ

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

GUI name

Basis set

Description

Select the basis set to use.

SZ: Single Z

DZ: Double Z

DZP: Double Z, 1 polarization function

TZP: Triple Z, 1 polarization function

TZ2P: Triple Z, 2 polarization functions

QZ4P: Quad Z, 4 pol functions, all-electron

AUG: Augmented (extra diffuse functions)

ET: Even tempered all electron basis sets

J: Extra tight functions

These descriptions are meant to give an indication of the quality,

but remember that ADF uses Slater type functions.

For standard calculations (energies, geometries, etc.) the relative quality is:

SZ < DZ < DZP < TZP < TZ2P < ET-pVQZ < QZ4P

The basis set chosen will apply to all atom types in your molecule. If no matching basis set is found, ADF will try to use a basis set of better quality.

For TDDFT applications and small negatively charged atoms or molecules, use basis sets with extra diffuse functions.

J: TZ2P-J, QZ4P-J: for use in ESR hyperfine or NMR spin-spin couplings.

Use the Basis panel to select a basis set per atom type, and to see what basis set actually will be used.

Core**Type**

Multiple Choice

Default value

Large

Options

[None, Small, Large]

GUI name

Frozen core

Description

Select the size of the frozen core you want to use.

Small and Large will be interpreted within the basis sets available (of the selected quality), and might refer to the same core in some cases.

If you specify 'None' you are guaranteed to have an all-electron basis set.

Warning: Do not include the *Corepotentials* (page 68) keys when using the Basis key. Typically one should not include both the the Basis key and the *Fragments* (page 53) key.

Description of the other Basis subkeys:

```
Basis
  CreateOutput Yes/No
  Path string
  PerAtomType
    Core [None | Small | Large]
    File string
    Symbol string
    Type [...]
  End
  PerRegion
    Core [None | Small | Large]
    File string
    Region string
    Type [...]
  End
  FitType [...]
End
```

Basis**CreateOutput****Type**

Bool

Default value

No

Description

If true, the output of the atomic create runs will be printed to standard output. If false, it will be saved to the file CreateAtoms.out in the AMS results folder.

Path**Type**

String

Description

The name of an alternative directory with basis sets to use. ADF looks for appropriate basis sets only within this directory. Default \$AMSRESOURCES/ADF.

PerAtomType**Type**

Block

Recurring

True

Description

Defines the basis set for all atoms of a particular type.

Core**Type**

Multiple Choice

Options

[None, Small, Large]

Description

Size of the frozen core.

File**Type**

String

Description

The path of the basis set file (the path can either absolute or relative to \$AMSRESOURCES/ADF). Note that one should include ZORA in the path for relativistic calculations, for example 'ZORA/QZ4P/Au'. Specifying the path to the basis file explicitly overrides the automatic basis file selection via the Type and Core subkeys.

Symbol**Type**

String

Description

The symbol for which to define the basis set.

Type**Type**

Multiple Choice

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

Description

The basis sets to be used.

PerRegion**Type**

Block

Recurring

True

Description

Defines the basis set for all atoms in a region. If specified, this overwrites the values set with the Basis%Type and Basis%PerAtomType keywords for atoms in that region. Note that if this keyword is used multiple times, the chosen regions may not overlap.

Core**Type**

Multiple Choice

Default value

Large

Options

[None, Small, Large]

Description

Size of the frozen core.

File**Type**

String

Description

The path of the basis set file (the path can either absolute or relative to \$AMSRESOURCES/ADF). Note that one should include ZORA in the path for relativistic calculations, for example 'ZORA/QZ4P/Au'. Specifying the path to the basis file explicitly overrides the automatic basis file selection via the Type and Core subkeys.

Region**Type**

String

Description

The identifier of the region for which to define the basis set. Note that this may also be a region expression, e.g. 'myregion+myotherregion' (the union of two regions).

Type**Type**

Multiple Choice

Default value

DZ

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

Description

The basis sets to be used.

FitType**Type**

Multiple Choice

Default value

Auto

Options

[Auto, SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE]

GUI name

STO fit set

Description

Expert option.

Select the auxiliary fit to be used for STOfit or old Hartree-Fock RI scheme.

The fit set for a given atom is taken from the all-electron basis set file for the specified choice, for the same element as the atom.

By default (Auto) the fit set is taken from the original basis set file.

An example where you can use regions to define basis sets for parts of your system, see [Example: Multiresolution](#) (page 1202).

3.2.4 Automatic mode

The following input will run a geometry optimization on water, using a (almost) minimal input:

```
"$AMSBIN/ams" <<eor
  Task GeometryOptimization
  System
    Atoms
      O 0 0 0
      H 1 1 0
      H -1 1 0
    End
    Symmetrize Yes
  End

  Engine ADF
    Basis
      Type TZP
    End
  EndEngine
eor
```

- The `ATOMS` subblock key in the `System` block key specifies the geometry of the system;
- the `Task GeometryOptimization` key instructs AMS to perform a geometry optimization;
- the `Basis` block key instructs ADF to run the *create runs* automatically, using a TZP basis sets.

The *automatic mode* will be used when the `Basis` key is present in the input, or if no `Fragments` block key is present.

In *automatic mode* ADF will first create fragment files for all the basic atom fragments found in the `Atoms` block. Normally this means that for each atom type in your molecule a fragment file will be created.

You may have different fragments with the same atom: add a dot and a name (without spaces) after the name of the element. For example: `H.1` and `H.2`. In this example two fragment files will be created: one for the `H.1` fragment and one for the `H.2` fragment. Using the `PerAtomType` subkey you may assign different basis sets to these fragments. Another consequence is that the `H.1` and `H.2` atoms will never be symmetry equivalent to each other.

In case of a relativistic calculation, the DIRAC program will also be run automatically, and the create runs will include the correct relativistic key and corresponding basis sets. For **ZORA** calculations, ADF first tries to locate a special ZORA basis set. If this does not succeed it will use a normal basis set if the required basis set does not use a frozen core.

3.2.5 Create mode

Expert option. In Create mode the input file is relatively simple. First, the geometry is trivial: one atom at the origin.

Second, the problem is computationally so simple that default settings for precision aspects, such as convergence criteria and levels of numerical integration accuracy, are internally defined to be much more stringent than in normal calculations. These aspects don't have to be looked after. Also one should specify the wanted XC functional. If you use the Basis key all this will be handled automatically.

In Create mode you need an input file of the following form:

```
System
  Atoms
    Atomtype 0 0 0
  End
end
Task SinglePoint
Engine ADF
  CREATE Atomtype Datafile
EndEngine
```

Create

is the keyword. The remainder of the record (atomtype datafile) is the argument.

Atomtype

is a name for the basic atom that you want to create. The program reads and interprets this name. Therefore, the name must begin with the standard chemical symbol (H, He, Li, ...) of the element to be created. Optionally the name may have an suffix of the form .text. The suffix begins with a period (.); the part after the period (text) is at your discretion as long as it does not contain a delimiter. A few examples:

Table 3.4: Examples of appropriate and inappropriate atom type names used with the keyword create.

appropriate names	inappropriate names
K	Si-with-core (no period after the chemical symbol)
Li.newbasis	\$HOME/atomicdata/ADF/C.dzp (not beginning with the chemical symbol)
P.1992_Feb.30	Ga.nocore,smallbasis (contains a comma (a delimiter))
	Sodium.2s (Sodium is not the <i>symbol</i> for this element (Na))

Datafile

specifies the data file that contains the basis set and related items. It may contain a full path if the file does not reside in the working directory of the job. The datafile part is optional. If you omit it, ADF assumes that the file name is identical to the atom type name, i.e. Create Atomtype is equivalent to and interpreted as Create Atomtype Atomtype In view of the restrictions that apply to the atom type name, the option to use the short form can only be used if the file name has the appropriate format. To make the input file easier to understand for a human reader you may, for Datafile, also type file=Datafile, where file= must be typed as such, and datafile is the name of the file.

So you could have a simple calculation as follows (the 'creation' of a Carbon atom);

```
$AMSBIN/ams << eor
System
  Atoms
```

(continues on next page)

(continued from previous page)

```

      C 0 0 0
    End
  end
  Task SinglePoint
  Engine ADF
    Create C $AMSHOME/atomicdata/ADF/DZ/C.1s
  EndEngine
eor

```

The presence of the keyword `create` sets the computational mode of ADF to: *create a basic atom*. Here a basis set file is located in `$AMSHOME/atomicdata/ADF`, where the file 'C.1s' in the sub-directory DZ/ (this contains basis sets of double-zeta quality). Examine logfile and out to check that everything has gone well.

A considerable number of basis set files are included in the ADF. You can also create basic atoms corresponding to so-called *Alternative Elements*, with for instance a non-integer nuclear charge or a different mass. See the next section.

3.2.6 Ghost Atoms, Non-standard Chemical Elements

The atom type names used under atoms (and in the create record) must begin with the standard chemical element symbol (H, He, Li...). The program uses this to deduce the nuclear charge and other elemental properties.

For the standard elements one can redefine the atomic mass (for instance to define a suitable isotope). Masses are specified by adding the desired mass (in Dalton) at the end of the atom's line (`mass=`).

It is also possible to define an artificial chemical element with user-specified properties. Such new elements are denoted *Alternative Elements*; and may for instance have a non-integer nuclear charge.

The chemical symbol of for a (ghost) atom that has zero nuclear charge is Gh. The `BASIS` key recognizes elements denoted with Gh.atom in the `ATOMS` key as being ghost atoms. If one does not specifically select a basis set for this ghost atom, the all electron basis set for the atom is selected in the creation of the ghost atom using the type of basis set chosen with the `BASIS` key. The atom name must begin with the standard one- or two-character symbol for the chemical element: Gh.H, Gh.He, Gh.Li, and so on. Optionally it may be appended by .text, where text is any string (not containing delimiters). Examples: Gh.H, Gh.Mn.3, Gh.Cu.dz-new. See also the [Basis set superposition error \(BSSE\) tutorial](#).

For other alternative elements, for instance that have a non-integer nuclear charge, one should use one of the standard chemical symbols. The `BASIS` key will use this chemical symbol for selecting the basis set for this alternative element. Nuclear charges are specified by adding the nuclear charge at the end of the atom's line (`nuclear_charge=`).

You can create Gh-type basic atoms and other alternative elements and use them subsequently as fragments in a molecule.

Automatic mode

AMS allows to set user-defined masses for particular atoms. This can be used to simulate isotopes of different atoms. Masses are specified by adding the desired mass (in Dalton) at the end of the atom's line.

Example: three different hydrogen isotopes:

```

System
  Atoms
    N      0.000000    0.000000    0.010272
    H     -0.471582   -0.816803    0.407861
    H      0.943163    0.000000    0.407861 mass=2.014101778
    H     -0.471582    0.816803    0.407861 mass=3.01604927
  End
End

```

Use as fragment

Alternative basic atoms can be used like any other basic atoms to build up larger fragments and molecules. Gh can be considered just one more chemical symbol along with the other traditional ones. For other alternative elements one should define the nuclear charge, and possibly the nuclear mass.

You may have different alternative elements in a molecule, with different nuclear charges for instance.

Example: ghost atoms:

```
System
atoms
  Gh.O  -0.525330      -0.050971      -0.314517
  Gh.H  -0.942007      0.747902       0.011253
  Gh.H   0.403697      0.059786     -0.073568
  O      2.316633      0.045501      0.071858
  H      2.684616     -0.526577      0.749387
  C      2.781638     -0.426129     -1.190301
  H      2.350821      0.224965     -1.943415
  H      3.867602     -0.375336     -1.264613
  H      2.453296     -1.445999     -1.389381
end
end
```

Example: alternative elements:

```
System
Atoms
  Mg 0.0  0.0  0.0
  F  1.0  1.0  1.0  nuclear_charge=9.5
  F  1.0 -1.0 -1.0  nuclear_charge=9.5
  F -1.0  1.0 -1.0  nuclear_charge=9.5
  F -1.0 -1.0  1.0  nuclear_charge=9.5
End
End
```

3.2.7 Nuclear Model

By default in ADF a point charge model is used for the nuclear charge distribution. Alternatively, one can use a spherical Gaussian nuclear charge distribution model, see Ref.⁸. Nuclear finite size effects can have large effects on hyperfine interactions (ESR A-tensor, NMR spin-spin coupling) if heavy atoms like, for example, Mercury (Hg), are involved. In Ref.^{Page 52, 8} it was asserted that the isotropic J-couplings (parameters in NMR spin-spin coupling) are typically reduced in magnitude by about 10 to 15 % for couplings between one of the heaviest NMR nuclei and a light atomic ligand, and even more so for couplings between two heavy atoms. This Ref.⁸ gives more details on the parameters used in the Gaussian nuclear charge distribution model. Note that one needs basis sets with very tight functions to see any effect of using a finite size of the nucleus instead of a point nucleus. Such basis sets can be found for all elements in \$AMSRESOURCES/ZORA/TZ2P-J and \$AMSRESOURCES/ZORA/QZ4P-J, and for some elements in \$AMSRESOURCES/ZORA/jcpl, which are basis sets especially designed for ESR hyperfine and NMR spin-spin coupling calculations.

```
NuclearModel [PointCharge | Gaussian]
```

NuclearModel

⁸ J. Autschbach, *Magnitude of Finite-Nucleus-Size Effects in Relativistic Density Functional Computations of Indirect NMR Nuclear Spin-Spin Coupling Constants*, *ChemPhysChem* 10, 2274 (2009) (<https://doi.org/10.1002/cphc.200900271>)

Type

Multiple Choice

Default value

PointCharge

Options

[PointCharge, Gaussian]

Description

Model for the nuclear charge distribution.

To see effects from your choice you will need to use a basis set with extra steep functions. For example you can find these in the ZORA/TZ2P-J basis directory.

In the ADF output parameters will be shown for the Gaussian nuclear charge distribution if one includes in the input for ADF:

```
PRINT Nuclei
```

Starting from ADF2013 ADF also uses a finite distribution of the nuclear magnetic dipole moment for the calculation of the A-tensor.

3.3 Molecular fragments

3.3.1 Fragment mode

In Fragment mode you must specify: (1) the atomic positions and (2) how the total system is built up from fragments. You may also specify (3) the point group symmetry.

Example of an input file for the C₂H₄ molecule:

```
System
  Atoms
    C  0      0      0.668
    C  0      0     -0.668
    H  0.927  0     -1.203
    H -0.927  0     -1.203
    H  0.927  0      1.203
    H -0.927  0      1.203
  End
End

Engine ADF
  Fragments
    C C_dzp.results/adf.rkf
    H H_dzp.results/adf.rkf
  End

  Symmetry D(2h)
EndEngine
```

The *Atoms block key* (page 37) is in the AMS driver part of the input. Two keys are used in the engine ADF part: *fragments* (page 56) and *symmetry* (page 39).

atoms

Defines the atomic positions: each record in the data block contains the chemical symbol of an atom followed by its Cartesian coordinates in angstroms (Z-matrix type input of atomic positions is also possible).

fragments

Lists the fragment files. Each record contains a fragment *type* followed by the corresponding fragment *file*. In the example the files are *local* files. Files in other directories are addressed by giving the complete (relative) file path. Note: if a *parallel* calculation is performed, be sure that each 'kid' finds the specified fragment files. This will usually require that the files are *not* local to the job, but first be moved to some shared volume, and that the references to the fragment files in the input contain the full path.

symmetry

Specifies the point group symmetry by a Schönflies type symbol. *Symmetry* (page 436) contains a complete list of all Schönflies symbols that are recognized by ADF. If no symmetry is specified, ADF will use the true symmetry of the nuclear frame. If (*electric*) *fields* (page 162) are used, see later, symmetry will be NOSYM. Note that the computed symmetry may not occur in the list of allowed symmetries (see *Symmetry* (page 436)), in which case ADF should automatically use a (lower) point group symmetry. If a different or specific symmetry is wanted, then one should specify the point group symmetry.

The atomic coordinates must conform to the point group symmetry; the program will check this and abort if the atomic system does not have the specified symmetry. It is allowed, however, to specify a *lower* symmetry than what is actually present in the set of atomic positions. The *specified* symmetry determines how results are analyzed and how irreducible representations and subspecies are labeled. It also determines various algorithmic aspects: the program runs more efficiently with the highest possible symmetry.

The spatial orientation of the molecular coordinate system is not arbitrary. ADF requires for each point group symmetry a specific standard orientation. In axial groups, for instance, the main rotation axis must be the z-axis. This implies a restriction on how you can define the atomic coordinates under atoms. The orientation requirements for all point groups are listed in *Symmetry* (page 436). If the specified symmetry equals the true symmetry of the nuclear frame, ADF will adjust the input orientation of the molecule to the requirements (if necessary). If you have specified a subgroup of the true nuclear symmetry, no such orientation adjustment is carried out and the user has to make sure that the input data yield the correct orientation, lest an error occur.

Restrictions apply to the symmetry (as specified) of the molecule, related to the symmetries of the fragments as they were stipulated in the preceding fragment calculations. All symmetry operators of the molecule that internally rotate or reflect a fragment but leave it at the same position in the molecule, must also be operators of the symmetry group in which the fragment has been computed. Furthermore, two fragments must not be symmetry-equivalent in the molecule only by an improper rotation. The implied internal reflection of the fragment must be one of the symmetry operators in the point group symmetry that is used in the fragment calculation *and* the molecular symmetry group must also contain a proper rotation that maps the two fragments onto each other.

You can use the System%Symmetrize key in the AMS part of the input to symmetrize the coordinates. It can be used in combination with the System%Symmetry key, see the [symmetry discussion in the AMS manual](#).

The example of the C₂H₄ molecule implicitly assumes that all fragments are *single-atom* fragments. When the fragments are larger the data records in the atoms key have to be extended: you must specify which atoms belong together in one fragment.

```
System
  Atoms
    Ni  0      0      0
    C  -1.06 -1.06  1.06 adf.f=CO|1
    C  -1.06  1.06 -1.06 adf.f=CO|2
    C  -1.06  1.06 -1.06 adf.f=CO|3
    C   1.06 -1.06 -1.06 adf.f=CO|4
    O   1.71  1.71  1.71 adf.f=CO|1
    O  -1.71 -1.71  1.71 adf.f=CO|2
    O  -1.71  1.71 -1.71 adf.f=CO|3
    O   1.71 -1.71 -1.71 adf.f=CO|4
  End
End
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  Fragments
    CO CO_yesterday.results/adf.rkf
    Ni Ni_dzp.results/adf.rkf
  End

  Symmetry T(D)
EndEngine

```

Another sample input file uses a single-atom Ni fragment and four molecular CO fragments. The keys symmetry and fragments operate as before. Again we have two types of fragments (here: Ni and CO); for each of them, the fragment file is specified.

Under the key ATOMS the chemical symbols and the nuclear coordinates are listed. Added is the `adf.f=...` part; f stands here for fragment and tells the program that the carbon and oxygen atoms belong to CO fragments. The last part in `adf.f=CO|n` enumerates the individual CO fragments: here you define which C and O belong together in one CO fragment.

The record for Ni contains no `adf.f=` part, implying the *default* for this atom: it is a fragment on its own. In the C₂H₄ example before the default applied to all atoms.

Note that one should use the `adf.f=` part for symmetry-equivalent fragments. In the next example, ADF assumes the fragments CO1, CO2, CO3, and CO4, to be of different fragment types, even though they are coming from the same `adf.rkf` (TAPE21). Therefore ADF will assume symmetry NOSYM in the next calculation, and will not run in T(D) symmetry.

```

System
  Atoms
    Ni 0      0      0
    C -1.06 -1.06  1.06 adf.f=CO1
    C -1.06  1.06 -1.06 adf.f=CO2
    C -1.06  1.06 -1.06 adf.f=CO3
    C  1.06 -1.06 -1.06 adf.f=CO4
    O  1.71  1.71  1.71 adf.f=CO1
    O -1.71 -1.71  1.71 adf.f=CO2
    O -1.71  1.71 -1.71 adf.f=CO3
    O  1.71 -1.71 -1.71 adf.f=CO4
  End
End

Engine ADF
  Fragments
    CO1 CO_yesterday.results/adf.rkf
    CO2 CO_yesterday.results/adf.rkf
    CO3 CO_yesterday.results/adf.rkf
    CO4 CO_yesterday.results/adf.rkf
    Ni Ni_dzp.results/adf.rkf
  End
End

```

There are more possibilities with the keys atoms and fragments. This is described later. The purpose of this section was to provide a quick and easy start.

3.3.2 Fragment files

The `adf.rkf` (TAPE21) result files from the ADF computations on the fragments that constitute a molecule completely characterize these fragments. The fragment `adf.rkf` (TAPE21) files must be attached as *fragment files*. This is achieved with the key `FRAGMENTS`. See also the next section for the relation between Atom type, Fragment type and Fragment file names.

```

Fragments {Directory}
  FragType FragFile
  FragType FragFile
end

```

FragType

One of the fragment *types* defined under atoms, either explicitly (`adf.f=fragtype|n`) or implicitly (fragment `type=atom type`, if the `adf.f=` option is not used).

FragFile

The fragment file: the standard `adf.rkf` (TAPE21) result file from the computation of that fragment. The file name must contain the complete path relative to `Directory` (the argument of the key). By default, when no `Directory` is specified, this is the local directory where the job runs. You may therefore omit the directory and give simple (local) file names if all the files are present in the working directory of the job.

Obviously, `FragFile` is **case-sensitive**. However, `FragType` is also treated as case-sensitive; see also the [ATOMS key](#) (page 37) discussion (`adf.f=` option). The reason is that there are shortcuts possible to the effect that the `FragType` name (in the atoms block) is immediately interpreted as the name of the fragment file.

The key `FRAGMENTS` may be used any number of times in the input file. This is convenient if you employ a sizable number of fragment files, with subsets located in different directories. You can then use the key separately for each directory, to avoid typing long path names for all the files. `Fragtypes` that occur in the fragments block(s), but that are not referred to by atoms are ignored. No fragment files must be specified for dummy atoms (`xx`).

It is allowed to use the same fragment file for different fragment types. Example:

```

ATOMS
  C.1 x1 y1 z1
  C.2 x2 y2 z2
end

Fragments
  C.1 C.results/adf.rkf
  C.2 C.results/adf.rkf
end

```

Two different atom types (and fragment types) `C.1` and `C.2` are defined. The properties of the two fragment types are now identical since they are characterized by the same fragment file, but from the program's point of view they are different and can therefore not be symmetry equivalent.

The reason you may want to specify different atom types will usually be related to analysis, in particular symmetry aspects. If you know in advance that the two atom types are not symmetry equivalent, or more generally, that they play a rather different role in the molecule, it can enhance clarity of printed output to assign different atom type names to them. However, see the notes below.

If you want your fragment file to be the result file of a spin-unrestricted calculation, you should use the [UNRESTRICTEDFRAGMENTS](#) (page 70) key. You can also analyze a molecule in terms of simulated unrestricted fragments, in which spin-restricted fragment files are used and the key [FRAGOCCUPATIONS](#) (page 71) is specified.

Suppose that you have done a calculation on a molecule *mol*, in which you have defined two different atom types for atoms of the same chemical element. Suppose furthermore, that you want to use that molecule now as a fragment in a new calculation.

You list under atoms all atoms of the molecule and you specify which atoms belong to the various fragments, among which the molecular fragment *mol*. The program will then have a problem deciding which atoms in your system are associated with the different atom types in the fragment. Normally, ADF analyzes this by comparing the chemical elements. That is not sufficient here because one chemical element corresponds with more than one type of atom in the *mol fragment* type. In such a case it is imperative to use *the same atom type names* in your new calculation as you used in the generation of the fragment. These names are stored in the fragment file, and they are printed in the output file of the calculation of *mol*.

The names of three items may be related to each other, depending on how you specify input: the *atom type*, the *fragment type*, and the *fragment file*.

The atom type is defined in the data block to atoms.

The fragment type is also defined in the data block to atoms: with the *adf.f=* option. For records in the data block that do not have the *adf.f=* option, the fragment type name is by definition identical to the atom type name.

The fragment file is defined in the data block to fragments, each record consisting of a fragment *type* name, followed by the fragment *file*. If a fragment type is not listed in the data block to fragments, so that no fragment file name is specified, the fragment *file* is by definition identical to the fragment *type* name.

MODEL HAMILTONIANS

See also:

[spin-orbit coupling](#)

Examples: [special XC functionals](#) (page 473), [relativistic effects](#) (page 502), [solvents, other environments](#) (page 516)

4.1 Electronic Configuration

The next few keys can be used to specify the electronic configuration. If you don't specify any such keys, certain defaults will apply. In principle, the program will (by default) attempt to find the lowest-energy spin-restricted (one-determinant) state. If SCF convergence is problematic, the program may wind up at an excited state, by which (in this context) we mean a one-determinant state with a higher energy than some other one-determinant state with the same net spin polarization. In worse cases, the program may fail to converge to any state at all. It is good practice to *always* verify which configuration you actually have computed.

When you specify a particular configuration and/or net charge and/or net spin-polarization of the system, the program will try to compute accordingly, even if the requested configuration has no physical or chemical meaning. The program has no knowledge about the existence of materials and will simply try to carry out what you tell it to do.

4.1.1 Charge and Spin

Spin: restricted vs. unrestricted

Unrestricted Yes/No

Unrestricted

Type

Bool

Default value

No

Description

By default, a spin-restricted calculation is performed where the spin alpha and spin beta orbitals are spatially the same.

SpinPolarization float

SpinPolarization**Type**

Float

Description

The spin polarization of the system, which is the number of spin- α electrons in excess of spin- β electrons. Specification is only meaningful in a spin-unrestricted calculation. However, specification is not meaningful in an unrestricted Spin-Orbit coupled calculation using the (non-)collinear approximation.

In an `unrestricted` calculation, spin- α and spin- β MOs may be spatially different and may have different occupation numbers. In the case of Spin-Orbit coupling, it means that Kramers' symmetry does not have to be satisfied, in which case the key `UNRESTRICTED` should be used in combination with the subkey `SpinOrbitMagnetization NONCOLLINEAR` or `SpinOrbitMagnetization COLLINEAR` of the key `Relativity`.

The unrestricted mode roughly doubles the computational effort. The actual numbers of spin- α and spin- β electrons respectively are controlled by the keys `SpinPolarization` and `OCCUPATIONS` (page 64). Note carefully that using *only* the keyword `unrestricted`, without either `SpinPolarization` or `Occupations` (or both), will not result in any spin polarization. This implies that you would effectively perform a spin-restricted calculation, but with increased computational effort. Therefore, the program will check that in an unrestricted calculation at least one of the keys `SpinPolarization` or `Occupations` is applied.

The unrestricted feature is equivalent, in *ab initio* terminology, to (spin-)unrestricted Hartree-Fock (UHF); the N-particle wave function is a single determinant and not necessarily an eigenfunction of the spin operator S^2 .

A *restricted* calculation implies that the (spatial) orbitals *and* the occupation numbers are identical for spin- α and spin- β .

An unrestricted calculation with `SpinPolarization 0.0` (for instance by not specifying the spin polarization at all) is, if one does not break the spin symmetry, in fact a restricted run: it should give exactly the same as the restricted calculation, but it will use more CPU time. If one does break the spin symmetry, for example with the key `MODIFYSTARTPOTENTIAL` or the `SPINFLIP` option in the key `RESTART` (page 400), the solution may also be a broken spin symmetry solution. For example, you may want to start a calculation in broken symmetry with spin- α density on one fragment and spin- β density on another, e.g. in a spin-unrestricted calculation of H_2 at large separation.

The Fock operator, both in an unrestricted and in a restricted run, commutes with the spin operator S_z , but not (unless accidentally) with S^2 . The obtained one-determinant wave function may for instance be a mixture of a singlet and a triplet state.

In an unrestricted calculation the expectation value of S^2 is computed in ADF (note 29 in Ref.¹). The implementation of an evaluation of S^2 is not quite trivial. DFT is essentially a one-particle formalism, so the S-operator for the n-particle system has to be written out in single-particle operators². The equations used in ADF to calculate the expectation value of S^2 can be found in Szabo and Ostlund³. Note that the so-called exact value $(S_{\text{exact}})^2$, which is printed in the ADF output, is defined as $(S_{\text{exact}})^2 = (N_a - N_b / 2)(N_a - N_b / 2 + 1)$, where N_a and N_b are the number of spin- α and spin- β electrons, respectively. The expectation value of S^2 is not calculated in a Spin-Orbit coupled calculation.

If one includes the `UNRESTRICTEDFRAGMENTS` (page 70) key, molecules that have been calculated using the spin-unrestricted formalism can be employed as fragments. In this case, the calculation on the full complex also needs to use the spin-unrestricted formalism. See also the examples *Example: unrestricted fragments: CH3I* (page 1140) and *Example: unrestricted EDA: Cu(C2H4)2* (page 1138).

A fair approximation to a computation with spin-unrestricted fragments can be achieved with the key `FRAGOCCUPATIONS` (page 71), which uses spin-restricted fragments, but allows for spin-unrestricted fragment occupations. See also

¹ R.E. Buló, A.W. Ehlers, S. Grimme and K. Lammertsma, *Vinylphosphirane.Phospholene Rearrangements: Pericyclic [1,3]-Sigmatropic Shifts or Not?* *Journal of the American Chemical Society* 124, 13903 (2002) (<https://doi.org/10.1021/ja027925u>)

² R. Pauncz, *Spin Eigenfunctions*, ISBN13: 9780306401411, 1979, New York: Plenum Press

³ A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry*, ISBN13: 9780070627390, 1st ed. revised ed. 1989: McGraw-Hill

the examples *Example: Spin-unrestricted Fragments: H2* (page 1112), *Example: Bond Energy analysis meta-GGA, (meta-)hybrids: Zn2, Cr2, CrH* (page 1133) and *Example: Bond Energy analysis open-shell fragments: PCCP* (page 1118).

Spin: unrestricted vs. restricted open-shell

In unrestricted calculations the spin- α and spin- β orbitals, energies and occupations may differ. In restricted open shell calculations the spin- α and spin- β orbitals and energies should be identical, only the occupations may differ. In ADF2023, a restricted open-shell method is implemented for high-spin open-shell molecules (ROSCF), similar to Ref.¹¹, in which case the one-determinant wave function is an eigenfunction of S_z and S^2 . The implementation of the method is work in progress. At the moment, it is only valid for single-point calculations. This method cannot be used with spin-orbit coupling or for many other properties. In ADF2025, ROSCF can be used to calculate excitation energies of open-shell molecules, including a method to include spin-orbit coupling perturbatively.

The method implemented in ADF needs integer occupation numbers and a positive spin polarization. It requires the subkey ROSCF of the key SCF, the keyword UNRESTRICTED, and the key SPINPOLARIZATION. Part of the input could look like:

```
Occupations IntegerAufbau
Unrestricted Yes
SpinPolarization 2
SCF
  ROSCF
  End
End
```

The ROSCF options are:

```
SCF
  ROSCF
    Alpha float_list
  End
End
```

SCF

ROSCF

Type

Block

Description

Settings for the ROSCF method.

Alpha

Type

Float List

Default value

[0.5, 0.5, 0.5]

Description

Coefficients to build the alpha-spin orbital contribution to the diagonal closed-, open-, and virtual-shell blocks of the Fock matrix. The beta-spin orbital contributions are 1.0 minus the alpha ones.

¹¹ P. Ramos, M. Pavanello, *Constrained subsystem density functional theory*, *Physical Chemistry Chemical Physics* 18, 21172 (2016) (<https://doi.org/10.1039/C6CP00528D>)

Unrestricted and Spin-Orbit Coupling

In the case of spin-orbit coupling there are two ways to do spin-polarized calculations, either using the collinear approximation or the non-collinear approximation⁴⁵. Using the unrestricted feature to assign different numbers of electrons to α and β spin cannot be applied as such when spin-orbit coupling is included, since the electrons are not directly associated with spin- α and spin- β . For the collinear and non-collinear approximations, you should use `Symmetry NOSYM` (see *Symmetry key* (page 39)), and each level can allocate 1 electron. Do not specify the spin polarization.

Collinear approximation

```
Unrestricted Yes
Symmetry NOSYM
Relativity
  Level Spin-Orbit
  SpinOrbitMagnetization COLLINEAR
End
```

The `SpinOrbitMagnetization` subkey is only relevant in the case of Spin-Orbit coupling.

In the collinear approximation, in each point in space the spin polarization has the same direction (default is in the direction of the z-axis). Kramers' symmetry does not have to be satisfied. Symmetry should be NOSYM. The default direction of the spin polarization can be overridden using as argument `COLLINEARX` for spin polarization only in the direction of the x-axis, or as argument `COLLINEARY` for spin polarization only in the direction of the y-axis.

Noncollinear approximation

```
Unrestricted Yes
Symmetry NOSYM
Relativity
  Level Spin-Orbit
  SpinOrbitMagnetization NONCOLLINEAR
End
```

In the non-collinear approximation, in each point in space the spin polarization can have a different direction. Kramers' symmetry does not have to be satisfied. Symmetry should be NOSYM.

Spin-orbit coupled spin-polarized start-up potential

In the collinear and non-collinear approach, by default ADF uses in the first SCF cycle an artificial magnetic field in the z-direction that only affects spin (spin-Zeeman term). With the `SpinOrbitMagnetization` key you can use an artificial magnetic field that can have a different orientation in different regions. This is similar to using a spin-polarized start-up potential, however, the usage is different and with the key `SpinOrbitMagnetization` you can also choose an arbitrary magnetization direction. Note that a different orientation is typically only useful in the non-collinear approach.

Remark: keys `MODIFYSTARTPOTENTIAL` and `RESTART%spinflip` cannot be used in spin-orbit coupled calculations. The key `SpinOrbitMagnetization` should be used instead.

```
SpinOrbitMagnetization
  PerRegion
    Direction float_list
    Region string
    Strength float
  End
  Strength float
End
```

⁴ H. Eschrig and V.D.P. Servedio, *Relativistic density functional approach to open shells*, Journal of Computational Chemistry 20, 23 (1999) ([https://doi.org/10.1002/\(SICI\)1096-987X\(19990115\)20:1%3C23::AID-JCC5%3E3.0.CO;2-N](https://doi.org/10.1002/(SICI)1096-987X(19990115)20:1%3C23::AID-JCC5%3E3.0.CO;2-N))

⁵ C. van Wüllen, *Spin densities in two-component relativistic density functional calculations: Noncollinear versus collinear approach*, Journal of Computational Chemistry 23, 779 (2002) (<https://doi.org/10.1002/jcc.10043>)

SpinOrbitMagnetization**Type**

Block

Description

Starting artificial spin-orbit magnetization at first SCF cycle

PerRegion**Type**

Block

Recurring

True

Description

Defines the starting spin-polarization direction for all atoms in a region. Note that if this keyword is used multiple times, the chosen regions may not overlap.

Direction**Type**

Float List

Default value

[0.0, 0.0, 1.0]

Description

The starting spin-polarization direction for a region.

Region**Type**

String

Description

The identifier of the region for which to define the starting spin-polarization direction.

Strength**Type**

Float

Default value

0.2

Unit

Hartree

Description

Strength of artificial spin-polarization in this region

Strength**Type**

Float

Default value

0.2

Unit

Hartree

Description

Strength of artificial spin-polarization at first SCF cycle

Net Charge

The net charge of the molecule can be controlled with the key **CHARGE** in the **System** block in the **AMS** part of the input:

```
System header
  Charge float
End
```

System**Charge****Type**

Float

Default value

0.0

GUI name

Total charge

Description

The system's total charge in atomic units.

4.1.2 Orbital occupations: electronic configuration, excited states

With the keys **OCCUPATIONS** and **IRREPOCCUPATIONS** you can specify in detail the assignment of electrons to MOs.

Aufbau, smearing, freezing

```
OCCUPATIONS Options
```

Options

May contain IntegerAufbau, Keeporbitals, ElectronicTemperature, Smear, Freeze, or Steep:

IntegerAufbau

Electrons are assigned to MOs according to the Aufbau principle, trying to use integer occupations, also in case of degeneracy at the Fermi level. ADF normally may use fractional occupation numbers in that case. Note that for multi-dimensional irreps, using the subkey IntegerAufbau may still not prevent fractional occupation numbers to be used.

Keeporbitals=NKeep

Until SCF cycle Nkeep electrons are assigned to MOs according to the Aufbau principle, using at each cycle the then current orbital energies of the MOs. Thereafter the KeepOrbitals feature is applied. As soon as this is activated the program will on successive SCF cycles assign electrons to the MOs that maximally resemble - in spatial form - those that were occupied in a 'reference cycle number'. The default for Nkeep is 20, except:

- When orbital occupations for MOs are specified explicitly in the data block of the occupations key, these apply throughout.
- In a Create run fixed occupations are derived from a database in the program.

- c) When electron smearing is explicitly turned on by the user (see the Smear option below) Nkeep is by default 1,000,000 so the program will ‘never’ compare the spatial forms of MOs to determine the occupation numbers. The ‘reference cycle number’ is by default the previous cycle, which will suppress jumps in the spatial occupations during the SCF development while at the other hand allowing the system to let the more-or-less-frozen configuration relax to self-consistency.

Freeze

Occurrence of this word in the option list specifies that the ‘reference cycle number’ will be the cycle number on which the KeepOrbitals feature is activated: during all subsequent SCF cycles the program will assign electrons to MOs that resemble the MOs of that specific SCF cycle. This may be used when the MOs of that cycle are already reasonably close to the final ones, and it will suppress unwanted step-by-step charge-transfers from occupied to empty orbitals that are very close in energy. By default this option is not active.

ElectronicTemperature=T

Invokes orbital population using the Fermi-Dirac distribution with temperature T (in Kelvin). This may be used to achieve SCF convergence in an otherwise problematically converging system. Note that the default SCF acceleration method A-DIIS is not compatible with non-aufbau orbital occupations so it is disabled automatically and the classical Pulay DIIS scheme is used. For this reason it is strongly recommended to use either MESA or one of the methods from the LIST family in combination with ElectronicTemperature or Smear.

Smear=Smear1[, Smear2, Smear3, . . . , Smear10]

Another form of specifying the electronic temperature (in Hartree). The smearing parameter SmearN is related to the ElectronicTemperature in such a way that the occupation number for any orbital outside the smearing interval will deviate from an integer value (0 and 1 for spin-unrestricted, 0 and 2 for spin-restricted) by no more than 1% (0.01 electron for spin-unrestricted, 0.02 for spin-restricted). More precisely, a smearing value of 1 Hartree is equivalent to an electronic temperature of 34285 Kelvin. When a comma-delimited list of values is specified, the next value from the list is picked after SCF has converged, and the SCF is continued. This way one can specify a list of gradually decreasing values to get sort of annealing effect. NOTE: No spaces are allowed when specifying the list of values for Smear.

Steep=Lambda[, Nmax]

The occupation number for each orbital is updated according to a steepest-descent method (Ref: F. W. Averill and G. S. Painter, Phys. Rev. B **46**, 2498 (1992)). During an SCF cycle, the occupation number for each new orbital is initially determined by decomposing the old charge density with new orbitals. Then, the occupation numbers are modified so that the total energy of the system decreases. The Lambda parameter gives the coefficient for the charge transfer in 1/au units. The second parameter, Nmax, is an additional limit for the amount of charge transfer. Nmax would be useful for early cycles when the Lambda parameter gives too large a charge transfer. Too small an Nmax results in irregular behavior in SCF convergence. In the case of difficult SCF convergence, you should make mixing and Lambda smaller. From our experience, Nmax=0.1 or 0.2 is usually OK. This method should be used with the DIIS method turned off (DIIS N=0), and the choice of the mixing parameter in the SCF cycle is also important. This option is especially useful for systems with many quasi-degenerate orbitals around the Fermi level. For instance, cluster models of surface systems usually suffer from dangling bonds and should be converged with this method. Note though that slow convergence is an intrinsic feature of this method, so one should specify a large limit for the number of SCF cycles, say 500 or even 1000, depending on the cluster size.

OptimizeSpin=Delta, OptimizeSpinRound=Delta

The spin polarization can be optimized by minimizing the difference between Fermi level values for spin-alpha and spin-beta MOs. This method works reliably only when a reasonably large finite electron temperature is used (300K is found to be sufficiently large for small transition metal clusters). The polarization value is optimized up to a specified tolerance Delta (fractional values are allowed) by step-wise reduction of the root-bracketing interval for the objective function $f = \text{FermiLevel}(\alpha) - \text{FermiLevel}(\beta)$. The SCF procedure is converged for each spin polarization. When the interval becomes smaller than Delta the optimization is considered converged. After that the SCF may optionally be repeated with the spin polarization set to the nearest even or odd number (depending on the total number of electrons in the system) or, in other words, with

the total number of electrons per spin rounded to the nearest integer. The method is invoked using either the `OptimizeSpin` or the `OptimizeSpinRound` Occupation option. As mentioned above, it must be used together with the `ElectronicTemperature` option. The `OptimizeSpin` and `OptimizeSpinRound` argument specifies the tolerance value. The `OptimizeSpinRound` option specifies that after polarization has converged the SCF must be completed with the total number of electrons per spin rounded to the nearest integer. It should be noted that, as usual, the `Unrestricted` and `SpinPolarization` keys must be specified as for any other spin-unrestricted calculation. The argument of the `SpinPolarization` key sets the initial spin polarization value from which the optimization is started. The result of the optimization may depend on the initial value because the objective function may have more than one root.

Notes about the occupations options:

- When occupation numbers are explicitly defined via the block `IRREPOCCUPATIONS` (see next section), the `Smear` option cannot be used.
- The Aufbau principle does not determine or adjust the distribution of electrons over spin- α versus spin- β in an unrestricted calculation. This aspect is controlled by the key `SpinPolarization` and by any explicit occupations in the data block of occupations.
- Smearing cannot be used in combination with the `KeepOrbitals` option.

Explicit occupation numbers

```
IrrepOccupations
  irrep orbitalnumbers
  irrep orbitalnumbers
  ...
End
```

irrep

The name of one of the irreducible representations (not a subspecies) of the point group of the system. See the [Symmetry](#) (page 436) for the irrep names as they are used in ADF.

orbitalnumbers

A series of one or more numbers: the occupation numbers for one-electron *valence* orbitals in that irrep. The orbitals are ordered according to their energy eigenvalue; higher states than those listed get an occupation number zero.

For degenerate representations such as the 2-dimensional E-representations or the 3-dimensional T-representations, you must give the *total* occupation, i.e. the sum over the partner representations; ADF assigns each partner an occupation equal to the appropriate fraction of what appears here.

In an unrestricted calculation, two sequences of numbers must be specified for each irrep; the sequences are separated by a double slash (`//`). The first set of numbers is assigned to the spin- α orbitals, the second set to the spin- β orbitals. Example unrestricted calculation in symmetry NOSYM with two unpaired electrons:

```
IrrepOccupations
  A 28 // 26
End
SpinPolarization 2
Symmetry NOSYM
```

Note that this is not meaningful in an unrestricted Spin-Orbit coupled calculation using the (non-)collinear approximation, where one should use one sequence of occupation numbers for each irrep.

Notes about the occupations data block:

- When specifying electron configurations, all valence electrons in the calculation must be explicitly assigned to MOs and the IRREPOCCUPATIONS keyword must be used. In this context the concept *valence electrons* and hence *valence orbitals* is not necessarily identical to what you may normally assume to be the valence space of an atom or molecule. The meaning of *valence* is here strictly defined as whatever electrons are outside the frozen core. It depends therefore on the level of frozen core approximation applied in the calculation. This traces back to the Create runs in which the basic atoms were generated that are now used to build the molecule.
- When for some irrep there is a rather long list of occupation numbers, corresponding to *consecutive fully occupied* states, you can combine these numbers and enter their sum instead: ADF knows the maximum occupation for an irrep, and when you put a larger number the program will split it up. For instance, if you give for the *p*-representation (in a single atom calculation):

```
P 17 3
```

ADF will interpret this as:

```
P 6 6 5 3
```

i.e. the occupation number 17 is interpreted as denoting two fully occupied p-shells and the remaining five electrons in the next higher shell. This example also illustrates how to specify an excited state: here we have defined a hole in the third p-shell.

- Fractional occupation numbers in input are allowed. For a discussion of the interpretation of fractional occupation numbers see ref.⁶. The program even allows you (technically) to use a non-integer total number of electrons, whatever the physical meaning of such a calculation is.
- The data block of occupations is not parsed (see the section *Input* (page 27)). The program does not replace expressions by their value and it does not recognize constants or functions defined with the define key.
- In a numerical frequencies run (without symmetric displacements) the symmetry used internally in the program is NOSYM, irrespective of any Schönflies symbol in the input file. As a consequence the program will recognize only the A representation (the only irrep in nosym), but not the representations belonging to the input point group symmetry. (The symmetry in the equilibrium geometry, defined by the input Schönflies symbol, is used to enhance efficiency and stability in the construction of the matrix of Force constants).

CHARGE and SPINPOLARIZATION vs. IRREPOCCUPATIONS

The contents of the data block of IRREPOCCUPATIONS, if used, defines the total number of valence electrons and hence the net total charge. In an unrestricted run it also defines the net spin polarization. If the keys CHARGE and SPINPOLARIZATION are also used, the program will check that the specifications are consistent.

We strongly recommend that you always specify the net total charge and spin polarization with CHARGE whenever explicit occupation numbers are supplied with IRREPOCCUPATIONS, so that the program can check that your occupation numbers result in the total charge and spin polarization you intend.

⁶ S.G. Wang and W.H.E. Schwarz, *Simulation of nondynamical correlation in density functional calculations by the optimized fractional orbital occupation approach: Application to the potential energy surfaces of O₃ and SO₂*, *Journal of Chemical Physics* 105, 4641 (1996) (<https://doi.org/10.1063/1.472307>)

Create mode

In Create mode occupation numbers are predefined (see Appendix *Elements of the Periodic Table* (page 423)), and these are applied unless you specify occupations in the input yourself. Conceivably this may result in a non-Aufbau configuration. In Create mode the program always operates as if the occupations were set in the input.

4.1.3 Frozen core approximation

Frozen core vs. pseudopotentials

Pseudopotentials are not supported. The frozen core approximation is automatic in a normal (Fragment mode) calculation and is defined by the basic atomic fragments. The data file used in the Create run specifies the frozen core for the atom, which is then used in all molecules that incorporate that atomic fragment.

Core Potentials

In the standard approach the Coulomb potential and the charge density due to the atomic frozen core are computed from the frozen one-electron orbitals. ADF stores the computed core density and core potential for each atom type in the molecule on a file TAPE12. Alternatively, you may attach a file with (core) potentials and densities. The file must have the same structure as the standard TAPE12. It should contain one or more sections, each with the core information for one type of atom. With the block COREPOTENTIALS you specify the core file and (optionally) which sections pertain to the distinct atom types in the molecule.

```
COREPOTENTIALS corefile
  {atomtype index}
  {atomtype index}
  ...
end
```

corefile

The file with core potentials and charge densities. The name may contain a path.

atomtype

One of the atom type names as defined by atoms.

index

Points to the core section on the attached file that applies to the atom type. Different atom types may use the same section. A non-positive index tells the program that the atoms of that type don't have a frozen core. If the information on the corresponding fragment file (or data file in Create mode) indicates the contrary the program will abort with an error message.

If the key is used as a simple key (specifying only the core file) the sections on the file are associated with the atom types in order: the first section is used for the first atom type, et cetera. This is overruled by applying the block form. However, since the key *must* have the core file as argument, the block form requires that you apply the continuation symbol: an ampersand (&), separated from the core file name by at least one blank.

If you omit an atom type from the data block it gets a zero index (no core).

The attached file may contain more sections than used in the calculation, and the indices specified in the data block don't have to be in ascending order, consecutive, or cover a specific interval.

When a file with non-standard (e.g. relativistic) cores is attached and used in the calculation of an atom or molecule, and the result is used as a fragment in a subsequent calculation, you should attach and use the same core potentials again. Otherwise, the program will internally compute the standard core potentials and hence implicitly employ a different fragment than you may think, i.e. a fragment with other properties. ADF will not check anything in this respect and COREPOTENTIALS should therefore be handled with great care.

The primary application of the corepotentials option is to include (scalar) relativistic corrections in the (frozen core part of the) Fock operator. The relativistic core potentials can be computed with the auxiliary program `dirac` (see the RELATIVITY keyword).

4.1.4 Spin-polarized start-up potential

The Fock matrix for the first SCF cycle is built by combining the Fock matrices from the fragment files. When performing a *Restart* (page 400), the initial Fock Matrix may be read from the specified `adf.rkf` file.

Spin-flip method for broken symmetries

It is possible to exchange alpha and beta electrons for selected atoms when performing a restart from a previous spin-unrestricted calculation. Note that for spin-orbit coupled calculations one should look at the section on how to make a *spin-orbit coupled spin-polarized start-up potential* (page 62).

In many cases, one wishes to perform a calculation of a low-spin complex where spin-density is positive on some atoms and negative on the others. It is usually very difficult to achieve SCF convergence if one starts from scratch. Sometimes, the `ModifyStartPotential` feature (see next section) helps with this problem but sometimes it does not. A more robust way is to first perform a high-spin calculation and then modify the resulting `adf.rkf` file by “flipping” the spin on some atoms. This file then can be used to restart a subsequent low-spin calculation.

Such a “flipping” can be performed during restart by specifying the `SpinFlip` keyword in the *Restart* (page 400) input block as shown below:

```
Restart
  File HighSpin.results/adf.rkf
  ! SpinFlip keyword is followed by the indices of the
  ! atoms for which the flipping will be performed
  SpinFlip 1
End
```

See also:

The example *Broken spin-symmetry: Fe4S4* (page 832) and the AMS-GUI tutorial *Spin Coupling in Fe4S4 Cluster* demonstrate the use of the spin-flip option.

Modify the starting potential

In some applications you may want to modify the initial potential (from the restart file or the fragment files), see also the previous section. This is achieved with the block `ModifyStartPotential`. It allows you to scale the potential so as to represent user-chosen amounts of spin- α and spin- β density on some or all of the fragments. This will adjust the spin- α and spin- β initial potentials. In spin-orbit coupled calculations the `ModifyStartPotential` key cannot be used; see instead the section on how to make a *spin-orbit coupled spin-polarized start-up potential* (page 62).

The `ModifyStartPotential` option applies only to *unrestricted* calculations, of course. It may be used to help the program find a particular state. This might, for instance, be hard to find otherwise due to the alpha-beta symmetry in the start-up situation. It may also be useful to speed up the SCF convergence in case you know what the final distribution of spin- α and spin- β density over the molecule will approximately be.

```
ModifyStartPotential {specification}
{ frag alfa // beta
  frag alfa // beta
  ...}
end
```

specification

Must be *two numbers*, ASPIN and BSPIN, if provided at all. They specify the (relative) amounts of spin- α and spin- β fit density to define the spin-dependent potential at the first SCF cycle. The coefficients retrieved from the fragment files (or from the restart file in case of a SCF restart) are scaled accordingly. This will not affect the *total* amount of fit density: the absolute values of ASPIN and BSPIN play no role, only their ratio. In case of a restart run the restart file must have been generated in a *restricted* calculation, while the continuation run must be an *unrestricted* one.

If no argument is given, a data block must be supplied with records frag alfa // beta. This is very much similar to the main option with ASPIN and BSPIN: you specify ASPIN and BSPIN now separately for each fragment. This involves somewhat more input but increases the possibilities for tuning the initial potential. Again, this can be applied only in an unrestricted calculation. It cannot be used in a restart: the affected fit coefficients are those from the fragment files, while in an SCF restart run these are ignored and replaced by the coefficients on the adf.rkf (TAPE21) restart file.

Each line specifies a frag with its corresponding ASPIN and BSPIN fit partitioning. If frag is the name of a fragment *type*, the specified ASPIN-BSPIN is applied to all individual fragments of that type. Alternatively an *individual* fragment can be specified, using the format fragtype/n, where *n* is an index between one and the total number of fragments of that type. In such a case the ASPIN-BSPIN data applies only to that particular fragment while different values may be supplied for the other fragments of the same type.

It is allowed to specify for certain fragment types individual fragments and for other fragment types only the type. Duplicate specifications are not allowed; an individual fragment must not be specified if its fragment type is also specified as a whole. If the data block form is used, only the fit coefficients of the referenced fragments are affected. For the unreferenced fragments the fit densities are used as they are defined on the corresponding fragment files.

The SCF convergence of a spin-unrestricted calculation usually improves when you start with potentials that correspond to the correct ratio of spin- α and spin- β electrons. By default ASPIN=BSPIN=0.5, as implied by the spin-restricted start density of the fragments or restricted molecule.

The total amount of fit density used on the first iteration is defined by the sum-of-fragment densities (or the density on the restart file). This may be different from the total number of electrons in the actual calculation. On the second SCF cycle the fit density will internally be normalized so as to represent the correct number of electrons.

The block-form of the key makes the start-up of broken symmetry calculations easy. For example, one may want to start a calculation in broken symmetry with spin- α density on one fragment and spin- β density on another, e.g. in a spin-unrestricted calculation of H₂ at large separation. It is particularly useful for larger systems, e.g. for magnetic coupling between spin-polarized magnetic centers, as in Fe-S complexes⁷: start with oppositely polarized Fe centers, but with, for instance, the remaining bridge and terminal ligands unpolarized.

See also:

The example *Localized Hole: N2+* (page 831) demonstrates the use of the ModifyStartPotential option.

4.1.5 Unrestricted fragments

In ADF you can use spin-unrestricted fragments if the key UNRESTRICTEDFRAGMENTS is used.

```
UNRESTRICTEDFRAGMENTS
UNRESTRICTED
```

If spin-unrestricted fragments are used, the full complex must also be calculated spin-unrestricted, which means that the key UNRESTRICTED is required, and in addition the SPINPOLARIZATION key and/or the IRREPOCCUPATIONS block key must be included. The key FRAGOCCUPATIONS should not be included. The spin- α and spin- β occupations are read from the spin-unrestricted fragment files. For spin-restricted fragments the spin- α and spin- β occupations will be set equal and sum to the spin-restricted occupation numbers.

⁷ L. Noodleman, and E.J. Baerends, *Electronic Structure, Magnetic Properties, ESR, and Optical Spectra for 2-Fe Ferredoxin Models by LCAO-Xa Valence Bond Theory*, *Journal of the American Chemical Society* 106, 2316 (1984) (<https://doi.org/10.1021/ja00320a017>)

The unrestricted fragments can be self-consistent: different numbers of spin- α and spin- β electrons usually result in different spatial orbitals and different energy eigenvalues for spin- α and spin- β when you go to self-consistency.

Prepared for bonding

Typically an unrestricted electron configuration for the fragments is used, such that the Pauli repulsion between the fragments is minimal, which means that the fragments are so-called “prepared for bonding.” For example, if one has two fragments that both have one unpaired electron, one would put the unpaired electron of the first fragment in the spin- α orbital and the unpaired electron of the second fragment in the spin- β orbital. If one wants to calculate the electron pair bonding separately, see key [REMOVEALLFRAGVIRTUALS](#) (page 72).

4.1.6 Simulated unrestricted fragments with key FRAGOCCUPATIONS

In the method that simulates unrestricted fragments with the key FRAGOCCUPATIONS, the fragments from which the molecule is built must be spin-restricted, that is, the fragment files must be result files of spin-restricted calculations. For purposes of analysis, however, it may be desirable in some applications to build your molecule from fragments that have an *unrestricted* electronic configuration. This can be simulated as follows.

You tell ADF that you want to *treat* the fragments as if they were unrestricted; this causes the program to duplicate the one-electron orbitals of the fragment: one set for spin- α and one set for spin- β . You can then specify occupation numbers for these spin-unrestricted fragments, and occupy spin- α orbitals differently from spin- β orbitals.

Of course, the unrestricted fragments that you use in this way are not self-consistent: different numbers of spin- α and spin- β electrons usually result in different spatial orbitals and different energy eigenvalues for spin- α and spin- β when you go to self-consistency, while here you have spatially identical fragment orbitals. Nevertheless it is often a fair approximation which gives you a considerable extension of analysis possibilities.

Prepared for bonding

Typically an unrestricted electron configuration for the fragments is used, such that the Pauli repulsion between the fragments is minimal, which means that the fragments are so-called “prepared for bonding.” For example, if one has two fragments that both have one unpaired electron, one would put the unpaired electron of the first fragment in the spin- α orbital and the unpaired electron of the second fragment in the spin- β orbital. If one wants to calculate the electron pair bonding separately, see key [REMOVEALLFRAGVIRTUALS](#) (page 72).

FRAGOCCUPATIONS

```
FRAGOCCUPATIONS
  fragtype
    irrep spin-a // spin-b
    irrep spin-a // spin-b
    ...
  subend
  fragtype
    irrep spin-a // spin-b
    ...
  subend
end
```

fragtype

One of the fragment types and functions as a (block type) subkey. The data block for the subkey ends with the standard end code for block type subkeys (subend).

irrep

One of the irreducible representations (irreps) for the point group symmetry that was used in the computation of that fragment.

spin-a // spin-b

Two sequences of occupation numbers, which will be applied to the spin- α and spin- β versions of the Fragment Orbitals. The sequences must be separated by a double slash (/).

The sum of spin- α and spin- β occupations must, for each fragment orbital in each irrep separately, be equal to the total (restricted) occupation of that orbital as it is stored on the fragment file. In other words: you can only change the distribution over spin- α and spin- β electrons within one orbital.

(Without this restriction the spatial distribution of the total (sum over spins) fragment charge density would be changed, leading to an incorrect bonding energy analysis after the calculation).

Be aware that in more-dimensional irreps (E, T) the number of electrons in a fully occupied orbital is input as the dimension of the irrep times the one-electron orbital occupation. Compare the key IRREPOCCUPATIONS.

For irreps that are not mentioned in this input block, and hence for all irreps of fragment types that are not mentioned at all, the spin- α and spin- β occupations will be set equal, which is of course what they in fact are on the (restricted) fragment file.

For an example of applying this option see ref.⁸.

4.1.7 Remove Fragment Orbitals

By default all fragment orbitals (the MOs of the fragment computation), which are stored on the fragment file, are used as basis functions for the overall molecule. You can remove one or more of these fragment orbitals from the basis set of the molecule. This may be useful for special analyses, like calculating the electron pair bonding in case one has open-shell fragments, or for instance to study the effect of deleting all virtual MOs of a particular fragment (CSOV analysis, Constrained Space Orbital Variation). It may also enhance the efficiency since you effectively reduce the size of the basis set, but you should be aware of the potential effects on the results.

The pure orbital interaction effect of forming electron pair bonding between open-shell molecules can approximately be calculated with a bond energy analysis in which all virtual orbitals are removed from the fragments, see Ref.⁹. For calculating the effect of electron pair bonding, it is best to specify an unrestricted electron configuration for the fragments, such that the Pauli repulsion is minimal. Removing all virtuals from an open-shell fragment that is calculated spin-restricted means that all fragment orbitals with zero occupation are removed. Thus, for example, a singly occupied fragment orbital will not be removed. This singly occupied fragment orbital will result in a spin- α and a spin- β fragment orbital. In combination with other singly occupied fragment orbitals they may form an electron pair bonding combination, but also an antibonding combination. In practice this means that the orbital interaction calculated with a bond energy analysis in which all virtual orbitals are removed from open-shell fragments might be due to more than electron pair bonding. The situation is not much different if one uses unrestricted fragments, because technically always the same number of spin- α and spin- β orbitals must be removed, and the removed orbitals must all have zero occupation.

If one wants to remove all virtual fragment orbitals, use the key REMOVEALLFRAGVIRTUALS.

REMOVEALLFRAGVIRTUALS

If one wants to remove all virtual fragment orbitals except on the first fragment, use the key REMOVEOTHERFRAGVIRTUALS.

⁸ F.M. Bickelhaupt, N.M. Nibbering, E.M. van Wezenbeek and E.J. Baerends, *The Central Bond in the Three CN Dimers NC-CN, CN-CN, and CN-NC: Electron Pair Bonding and Pauli Repulsion Effects**, *Journal of Physical Chemistry* 96, 4864 (1992) (<https://doi.org/10.1021/j100191a027>)

⁹ F.M. Bickelhaupt, M. Solà, C. Fonseca Guerra, *Highly polar bonds and the meaning of covalency and ionicity – structure and bonding of alkali metal hydride oligomers*, *Faraday Discussions* 135, 451 (2007) (<https://doi.org/10.1039/B606093E>)

REMOVEOTHERFRAGVIRTUALS

If one does not want to remove all virtual fragment orbitals, then one should use the block key REMOVEFRAGORBITALS.

```
REMOVEFRAGORBITALS
  fragtype
    subspecies nremove
    subspecies nremove
    ...
  subend
  fragtype
    subspecies nremove
    ...
  subend
  ...
  (etc.)
  ...
end
```

fragtype

One of the fragment types in the system. Any subset of the available fragment types can be used here as subkey. The subkeys are block type keys; their data blocks end with subend.

subspecies

One of the subspecies of the irreducible representations of the point group symmetry that was used in the calculation of the fragment itself. This requires of course that one knows the symmetry that has been used for the fragment calculation.

nremove

The number of fragment orbitals of the pertaining representation that will not be used as basis functions for the overall system. The *highest* (in energy eigenvalue) nremove orbitals are discarded. You must not remove *occupied* fragment orbitals.

By default (omission of the key) all fragment orbitals are used in the basis set for the system.

Important Note

It is imperative that any removal of fragment orbitals will not break the symmetry of the molecule. This consideration is relevant when, for instance, two different subspecies of a fragment irrep contribute to different partner subspecies in one of the irreps of the molecule. In such a case, when one removes an orbital in such a fragment subspecies, its partner orbital should also be removed. If this is violated an error may occur or the results will simply be wrong. Quite likely, the program will detect the error, but this may occur only in the final (analysis) stage of the calculation so that a lot of CPU time may have been wasted.

Example: consider a single-atom fragment, computed in atom symmetry, used as fragment in a c(lin) molecule and assume that the p:x and p:y fragment orbitals contribute to respectively the pi:x and pi:y subspecies of the molecule. Then, when you remove one or more p:x fragment orbitals, you should also remove the same number of p:y fragment orbitals. Practical cases may be more complicated and whenever you use this key, make sure that you've fully analyzed and understood how the fragment irreps combine into the molecular symmetry representations. Hint: run the molecule, without removing any fragment orbitals, and stop at an early stage after the program has computed and printed the build-up of the molecular SFOs from the fragment orbitals. To control early aborts via input, use the key STOPAFTER.

4.1.8 CDFT: Constrained Density Functional Theory

CDFT is a tool for carrying out DFT calculations in the presence of a constraint. The nature of the constraint is general in theory; however, in the current implementation the user can constrain the charges or the spins of a set of moieties (as identified by sets of atoms) to be a specific real number given in the input. Note that the use of CDFT as implemented in ADF is an **expert option**, and it is a **work in progress**. Implemented in ADF by M. Pavanello and P. Ramos^{Page 61, 11}, based on the method described in Ref.¹⁰. At the moment SYMMETRY NOSYM and an all-electron basis set are required.

Warning: CDFT is an expert option that may not work for your system or the specific constraint you had in mind.

The simplest way to run CDFT is using the following keyword combination

```
CDFT
  NCONSTRAINTS 1
  NATOMSPERSET N
  THEATOMS atom1 atom2 ... atomN
  CONSTRAINTS charge
END
```

All the CDFT block key options are:

```
CDFT
  AllAtoms Yes/No
  AnalyticalHessian integer
  ChargeAndSpin Yes/No
  Constraints float_list
  DoNotOptimize Yes/No
  ExcitedCDFT Yes/No
  InitialMultipliers float_list
  MaxIter integer
  Metric Yes/No
  NAtomsPerSet integer_list
  NConstraints integer
  OnlyCharge Yes/No
  OnlySpin Yes/No
  PopType [yukawalike | fuzzyvoronoibecke | fuzzyvoronoifermi]
  Print [low | medium | high]
  SelfConsistent Yes/No
  StepSize float
  TheAtoms integer_list
  Threshold float
End
```

CDFT

Type
Block

Description
CDFT is a tool for carrying out DFT calculations in the presence of a constraint.

AllAtoms

Type
Bool

¹⁰ Q. Wu, T. Van Voorhis, *Direct optimization method to study constrained systems within density-functional theory*, Physical Review A 72, 024502 (2005) (<https://doi.org/10.1103/PhysRevA.72.024502>)

Default value

No

Description

If AllAtoms is true, then TheAtoms is overridden and all the atoms in the active fragment are included in the set.

AnalyticalHessian**Type**

Integer

Default value

0

Description

This will calculate the analytical derivative of the energy w.r.t. the Lagrange multiplier up to the specified SCF iteration. This key is not recommended due to the high computational cost that comes with it. The calculation is equivalent to a ground state Hessian, and it is carried out with the full sum-over-states formula.

ChargeAndSpin**Type**

Bool

Default value

No

Description

will constrain both the charge and the spin

Constraints**Type**

Float List

Description

The values of the constraints. If CHARGEANDSPIN, constraints to the alpha and beta electrons need to be specified sequentially. One more electron => CONSTRAINTS -1.0. One less electron => CONSTRAINTS 1.0. If the CDFT type is EXCITEDCDFT, CONSTRAINTS=1.0 is recommended. Other values are technically possible but have not been tested yet.

DoNotOptimize**Type**

Bool

Default value

No

Description

If true, the multipliers chosen in INITIALMULTIPLIERS will not be optimized and will be constant throughout the entire SCF procedure.

ExcitedCDFT**Type**

Bool

Default value

No

Description

will generate an excited state with CONSTRAINTS number of ALPHA electrons constrained to occupy the virtual space of a ground state reference calculation. This is the essence of the eXcited Constrained DFT (XCDFT) method (P. Ramos, M. Pavanello, Low-lying excited states by constrained DFT, Journal of Chemical Physics 148, 144103 (2018) <https://doi.org/10.1063/1.5018615>) for the calculation of low-lying single excitations. XCDFT is found to correctly reproduce the energy surface topology at conical intersections between the ground state and the first singly excited state and can also account for the condensed phase effects in solvated chromophores where typical Delta SCF methods variationally collapse.

InitialMultipliers**Type**

Float List

Description

If available, a guess for the Lagrange multipliers can be entered.

MaxIter**Type**

Integer

Default value

200

Description

Maximum number of CDFT iterations. CDFT carries out a loop nested inside the SCF cycle.

Metric**Type**

Bool

Default value

No

Description

Relevant for XCDFT. In the XCDFT method orthogonality is not imposed between the KS-orbitals of ground and excited states. If METRIC is specified, the degree of mixing of the single excited state with the ground state or high-order excitations is calculated. Three parameters are calculated: p, m and d. The parameters p and m will give information about the amount of mixing with the ground state, while parameter d will determine the mixing with high order excitations. Additional information about the origin of these parameters can be found in the literature (P. Ramos, M. Pavanello, Low-lying excited states by constrained DFT, Journal of Chemical Physics 148, 144103 (2018) <https://doi.org/10.1063/1.5018615>)

NAtomsPerSet**Type**

Integer List

Description

The number of atoms in each moiety (set).

NConstraints**Type**

Integer

Default value

1

Description

This specifies the number of sets of atoms to be considered. For example, if the user wishes to constrain a positive charge on one part of the system, and a negative charge on another part, NCONSTRAINTS should be set to two. There is no limit on the number of constraints. However, SCF convergence becomes an issue with more than 2 constraints. Note: NCONSTRAINTS>1 is untested.

OnlyCharge**Type**

Bool

Default value

Yes

Description

Will constrain only the charge, letting spin relax (and potentially delocalize)

OnlySpin**Type**

Bool

Default value

No

Description

Will constrain only the spin

PopType**Type**

Multiple Choice

Default value

yukawalike

Options

[yukawalike, fuzzyvoronoibecke, fuzzyvoronoifermi]

Description

The population analysis chosen for determining the constraint.

Print**Type**

Multiple Choice

Default value

low

Options

[low, medium, high]

Description

Print level and debugging.

SelfConsistent**Type**

Bool

Default value

No

Description

Self-Consistent CDFT

StepSize**Type**

Float

Default value

0.5

Description

The amount of the Lagrange multipliers step taken in each CDFT iteration

TheAtoms**Type**

Integer List

Description

The atom numbers of the moieties in the input geometry order. If NCONSTRAINTS is larger than 1, the sets of atoms are entered as a single list.

Threshold**Type**

Float

Default value

1e-10

Description

The threshold for convergence of the CDFT constraints. The tighter the SCF convergence criteria, the tighter the THRESHOLD should be.

4.1.9 FOCDF: Fragment Orbital Constrained DFT

ADF has a fragment-oriented approach. FOCDF is a fragment-orbital-based method for constraining (integer) charges and/or spins on fragments. In practice this method works best if there are no covalent bonds, or if one does not want covalent bonds between the fragments. FOCDF uses the so-called Löwdins that ADF creates at the start of an SCF calculation on the whole complex. These Löwdins are reasonably localized orbitals, such that one can assign a fragment to each Löwdin. Next, these Löwdins are used to constrain charges and/or spins on fragments.

Symmetry can be used in FOCDF, although one typically should not use symmetry-equivalent fragments. FOCDF gradients cannot be calculated. FOCDF is not implemented for spin-orbit coupled calculations.

To better understand the method it is relevant how the Löwdins are made in ADF. The fragment MOs are called fragment orbitals (FO) in ADF. If there are symmetry-equivalent fragments ADF generates symmetry combinations of the FOs and uses the symmetrized fragment orbitals (SFOs) as basis functions. In case of FOCDF one typically should not use symmetry-equivalent fragments, which means that in that case there is no distinction between SFOs and FOs. The so-called Löwdins are Löwdin orthonormalized core-orthogonalized fragment orbitals. This Löwdin orthonormalization is done in several steps. In case of frozen core calculations the fragment orbitals are first orthogonalized on the frozen core orbitals on the other fragment(s). In case of an all electron calculation this step is skipped. Next the (core orthogonalized) occupied fragment orbitals are orthonormalized. The occupied-occupied part of the overlap matrix in terms of (core orthogonalized) occupied fragment orbitals is diagonalized. The results are used to do a Löwdin orthonormalization ($S^{-1/2}$) of the (core orthogonalized) occupied fragment orbitals. Next the (core orthogonalized) valence fragment orbitals are Gram-Schmidt orthogonalized on the Löwdin orthonormalized (core orthogonalized) occupied fragment orbitals, and the overlap between these functions is calculated and a Löwdin orthonormalization of these virtuals is done. In practice the Löwdins coming from the Löwdin orthonormalized (core orthogonalized) occupied fragment orbitals resemble the

occupied fragment orbitals quite well. The other Löwdins (that have more virtual fragment character) may differ more from the virtual fragment orbitals they originate from, especially if the basis set is larger. Note that the number of virtual fragment orbitals increases if the basis set increases, whereas the number of occupied fragment orbitals remains constant.

In FOCDFT the Fock matrix is calculated on the basis of the Löwdins. The off-diagonal part of the Fock matrix between Löwdins on one fragment and Löwdins on another fragment is set to zero, such that a block diagonal Fock matrix is constructed. Due to this block structure each eigenfunction of the Fock matrix will be a linear combination of Löwdins on one fragment. This means that the eigenfunctions are automatically localized on a fragment. By occupying the orbitals with the lowest eigenvalues on each fragment, it is very easy to constrain (integer) charge and/or spin on such a fragment.

Usage:

```
FOCDFT
  Charge float_list
  SpinPolarization float_list
End
```

FOCDFT

Type

Block

Description

Localize orbitals on fragments and constrain charge and spin polarization on fragments.

Charge

Type

Float List

Description

Constrain charge on fragments. Number of charges should be the same as number of fragments, and sum should add up to total charge.

SpinPolarization

Type

Float List

Description

Constrain spin polarization on fragments. Number of spin polarization values should be the same as number of fragments, and sum should add up to total spin polarization. Calculation should be spin unrestricted.

The list of fragment charges and spin should be given in the same order as the fragments in the [FRAGMENTS](#) (page 56) key. Especially if one includes charge constraints, the resulting electron configuration may not be Aufbau.

FOCDFT can be used in the calculation of [charge transfer integrals](#) (page 274) and [exciton transfer integrals](#) (page 278).

4.2 Density Functionals (XC)

The Density Functional, also called the exchange-correlation (XC) functional, can include an LDA part, a GGA part, a Hartree-Fock exchange part (hybrids), and a meta-GGA part (meta-GGA or meta-hybrid). Possibly, it also depends on virtual Kohn-Sham orbitals through the inclusion of an orbital-dependent correlation (double-hybrids). LDA stands for the Local Density Approximation, which implies that the XC functional at each point in space depends only on the (spin) density at that point. GGA stands for Generalized Gradient Approximation and extends the LDA part, by including terms that depend on derivatives of the density. A hybrid GGA (for example B3LYP) is a combination of a standard GGA with a fraction of Hartree-Fock exchange. A meta-GGA (for example TPSS) has a GGA part, but also depends on the kinetic energy density. A meta-hybrid (for example TPSSh) has a GGA part, a fraction of Hartree-Fock exchange, and a part

that depends on the kinetic energy density. For these terms, ADF supports a large number of formulas advocated in the literature. For post-SCF energies only, ADF also supports various other meta-GGA functionals and additional hybrid functionals. A double-hybrid has a hybrid or a meta-hybrid part, but also contains a contribution from second-order Møller-Plesset perturbation theory (MP2). Here, only the hybrid (meta-hybrid) part is evaluated self-consistently; the MP2 part is evaluated post-SCF and added to the hybrid (meta-hybrid) energy.

The key that controls the Density Functional is XC. All subkeys are optional.

```
XC
{LDA LDA {Stoll}}
{GGA GGA}
{MetaGGA metagga}
{Model MODEL POT [IP]}
{HartreeFock}
{HYBRID hybrid {HF=HFpart}}
{MetaHYBRID metahybrid}
{DOUBLEHYBRID doublehybrid}
{RPA {option}}
{XCFUN}
{RANGESEP {GAMMA=X} {ALPHA=a} {BETA=b}}
{LibXC functional}
{DISPERSION [s6scaling] [RSCALE=r0scaling] [Grimme3] [BJDAMP] [PAR1=par1]
→[PAR2=par2] [PAR3=par3] [PAR4=par4]}
{Dispersion Grimme4 {s6=...} {s8=...} {a1=...} {a2=...}}
{DISPERSION dDsC}
{DISPERSION UFF}
end
```

If the XC key is omitted, the program will use the Local Density Approximation (no GGA terms). The chosen LDA form is then VWN.

4.2.1 LDA

```
XC
  LDA {functional} {Stoll}
End
```

LDA

Defines the LDA part of the XC functional. If `functional` is omitted, VWN will be used (even if LYP is specified in the GGA part).

Available LDA functionals:

- **Xonly**: The pure-exchange electron gas formula. Technically, this is identical to the Xalpha form (see next) with a value 2/3 for the X-alpha parameter.
- **Xalpha**: The scaled (parametrized) exchange-only formula. When this option is used, you may (optionally) specify the X-alpha *parameter* by typing a numerical value after the string Xalpha (separated by a blank). If omitted, this parameter takes the default value 0.7.
- **VWN**: The parametrization of electron gas data given by Vosko, Wilk, and Nusair (ref¹, formula version V). Among the available LDA options, this is one of the more advanced ones, including correlation effects to a fair extent.

¹ S.H. Vosko, L. Wilk and M. Nusair, *Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis*, Canadian Journal of Physics 58 (8), 1200 (1980) (<https://doi.org/10.1139/p80-159>)

- **Stoll**: For the VWN variety of the LDA form, you may include Stoll's correction² by typing Stoll on the same line, after the main LDA specification. You must not use Stoll's correction in combination with the Xonly or the Xalpha form for the Local Density functional. The Stoll formula is considered to be a *correlation* correction to the *Local Density Approximation*. It is conceptually not correct to use the Stoll correction *and* apply gradient (GGA) corrections to the correlation. It is the user's responsibility, in general and also here, to avoid using options that are not solidly justified theoretically.
- **PW92**: The parametrization of electron gas data given by Perdew and Wang (ref³).

4.2.2 GGA

```
XC
    GGA functional
End
```

GGA

Specifies the GGA part of the XC functional (formerly often called the 'non-local' correction to the LDA part of the density functional). It uses derivatives (gradients) of the charge density.

Available GGA functionals:

- **BP86**: Exchange: Becke, Correlation: Perdew
- **PW91**: Exchange: pw91x, Correlation: pw91c
- **mPW**: Exchange: mPWx, Correlation: pw91c
- **PBE**: Exchange: PBEx, Correlation: PBEC
- **RPBE**: Exchange: RPBEx, Correlation: PBEC
- **revPBE**: Exchange: revPBEx, Correlation: PBEC
- **mPBE**: Exchange: mPBEx, Correlation: PBEC
- **PBEsol**: Exchange: PBEsolx, Correlation: PBEsolc
- **HTBS**: Exchange: HTBSx, Correlation: PBEC
- **BLYP**: Exchange: Becke, Correlation: LYP
- **OLYP**: Exchange: OPTX, Correlation: LYP
- **OPBE**: Exchange: OPTX, Correlation: PBEC⁴
- **BEE**: Exchange: BEEEx, Correlation: PBEC
- **XLYP**: Exchange: XLYPx⁵ (exchange, not available separately from LYP) + LYP
- **SSB-D**: Dispersion corrected functional by Swart-Solà-Bickelhaupt^{65,66}. The SSB-D functional by definition already includes a dispersion correction by Grimme (factor 0.847455). There are some numerical issues with

² H. Stoll, C.M.E. Pavlidou, and H. Preuss, *On the calculation of correlation energies in the spin-density functional formalism*, *Theoretica Chimica Acta* 49, 143 (1978) (<https://doi.org/10.1007/BF00553794>)

³ J.P. Perdew and Y. Wang, *Accurate and simple analytic representation of the electron-gas correlation energy*, *Physical Review B* 45, 13244 (1992) (<https://doi.org/10.1103/PhysRevB.45.13244>)

⁴ M. Swart, A.W. Ehlers and K. Lammertsma, *Performance of the OPBE exchange-correlation functional*, *Molecular Physics* 2004 102, 2467 (2004) (<https://doi.org/10.1080/0026897042000275017>)

⁵ X. Xu and W.A. Goddard III, *The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties*, *Proceedings of the National Academy of Sciences* 101, 2673 (2004) (<https://doi.org/10.1073/pnas.0308730100>)

⁶⁵ M. Swart, M. Solà and F.M. Bickelhaupt, *A new all-round DFT functional based on spin states and SN2 barriers*, *Journal of Chemical Physics* 131, 094103 (2009) (<https://doi.org/10.1063/1.3213193>)

⁶⁶ M. Swart, M. Solà and F.M. Bickelhaupt, *Switching between OPTX and PBE exchange functionals*, *Journal of Computational Methods in Science and Engineering* 9, 69 (2009) (<https://doi.org/10.3233/JCM-2009-0230>)

the GGA implementation in ADF of SSB-D (Ref. ^{Page 81, 65}^{Page 81, 66}) for some systems. Because of this, the GGA SSB-D option is only available for single-points calculations (and NMR). Geometry optimizations (etc.) are still possible by using instead:

```
XC
  METAGGA SSB-D
END
```

This METAGGA implementation requires an all-electron basis set. Use GGA SSB-D for NMR calculations.

- **S12g**: Dispersion corrected (Grimme-D3) functional by Swart, successor of SSB-D⁶.
- **LB94**: By Van Leeuwen and Baerends⁷.
- **KT1**: By Keal and Tozer⁸.
- **KT2**: By Keal and Tozer⁸.

If only a GGA part is specified (omitting the LDA subkey), the LDA part defaults to VWN, except when the LYP correlation correction is used: in that case the LDA default is Xonly: pure exchange. The reason for this is that the LYP formulas assume the pure-exchange LDA form, while, for instance, the Perdew-86 correlation correction is a correction to a *correlated* LDA form. The precise form of this correlated LDA form assumed in the Perdew-86 correlation correction is not available as an option in ADF, but the VWN formulas are fairly close to it.

Separate choices can be made for the GGA exchange correction and the GGA correlation correction. Both specifications must be typed (if at all) on the same line after the GGA subkey.

For the **exchange** part the options are:

- **Becke**: Becke (1988)¹⁰.
- **PW86x**: Perdew-Wang (1986)¹¹.
- **PW91x**: Perdew-Wang (1991)¹².
- **mPWx**: Modified PW91 by Adamo-Barone (1998)¹³.
- **PBEx**: Perdew-Burke-Ernzerhof (1996)¹⁴.
- **RPBEx**: Revised PBE by Hammer-Hansen-Norskov (1999)¹⁵.
- **revPBEx**: Revised PBE by Zhang-Wang (1998)¹⁶.
- **mPBEx**: Modified PBE by Adamo-Barone (2002)¹⁷.

⁶ M. Swart, *A new family of hybrid density functionals*, *Chemical Physics Letters* **580**, 166 (2013) (<https://doi.org/10.1016/j.cplett.2013.06.045>)

⁷ R. van Leeuwen and E.J. Baerends, *Exchange-correlation potential with correct asymptotic behavior*, *Physical Review A* **49**, 2421 (1994) (<https://doi.org/10.1103/PhysRevA.49.2421>)

⁸ T.W. Keal and D.J. Tozer, *The exchange-correlation potential in Kohn-Sham nuclear magnetic resonance shielding calculations*, *Journal of Chemical Physics* **119**, 3015 (2003) (<https://doi.org/10.1063/1.1590634>)

¹⁰ A.D. Becke, *Density-functional exchange-energy approximation with correct asymptotic behavior*, *Physical Review A* **38**, 3098 (1988) (<https://doi.org/10.1103/PhysRevA.38.3098>)

¹¹ J.P. Perdew and Y. Wang, *Accurate and simple density functional for the electronic exchange energy: generalized gradient approximation*, *Physical Review B* **33**, 8822 (1986) (<https://doi.org/10.1103/PhysRevB.33.8800>)

¹² J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Sing and C. Fiolhais, *Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation*, *Physical Review B* **46**, 6671 (1992) (<https://doi.org/10.1103/PhysRevB.46.6671>)

¹³ C. Adamo and V. Barone, *Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models*, *Journal of Chemical Physics* **108**, 664 (1998) (<https://doi.org/10.1063/1.475428>)

¹⁴ J.P. Perdew, K. Burke and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, *Physical Review Letters* **77**, 3865 (1996) (<https://doi.org/10.1103/PhysRevLett.77.3865>)

¹⁵ B. Hammer, L.B. Hansen, and J.K. Norskov, *Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals*, *Physical Review B* **59**, 7413 (1999) (<https://doi.org/10.1103/PhysRevB.59.7413>)

¹⁶ Y. Zhang and W. Yang, *Comment on "Generalized Gradient Approximation Made Simple"*, *Physical Review Letters* **80**, 890 (1998) (<https://doi.org/10.1103/PhysRevLett.80.890>)

¹⁷ C. Adamo and V. Barone, *Physically motivated density functionals with improved performances: The modified Perdew-Burke-Ernzerhof model*, *Journal of Chemical Physics* **116**, 5933 (1996) (<https://doi.org/10.1063/1.1458927>)

- **PBEsolx**: Perdew-Ruzsinszky-Csonka-Vydrov-Scuseria (2008)¹⁸.
- **HTBSx**:¹⁹.
- **OPTX**: Handy-Cohen (2001)²⁰.
- **BEEEx**: Mortensen-Kaasbjerg-Frederiksen-Nørskov-Sethna-Jacobsen (2005)²¹.

For the **correlation** part the options are:

- **Perdew**: Perdew (1986)²².
- **PBEc**: Perdew-Burke-Ernzerhof (1996)¹⁴.
- **PBEsolc**: The PBEsol correlation correction by Perdew-Ruzsinszky-Csonka-Vydrov-Scuseria (2008)¹⁸.
- **PW91c**: Perdew-Wang (1991), see [Page 82, 12](#).
- **LYP**: Lee-Yang-Parr (1988) correlation correction^{67,68,69}.

The string GGA must contain at most one exchange option and at most one correlation option. If options are applied for both, they must be separated by a blank or a comma. Example:

```
XC
  GGA Becke Perdew
End
```

is equivalent to

```
XC
  GGA BP86
End
```

It is questionable to apply gradient corrections to the *correlation* while not doing so at the same time for the exchange. Therefore, the program will check this and stop with an error message. This check can be overridden with the key ALLOW.

¹⁸ J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, *Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces*, *Physical Review Letters* 100, 136406 (2008) (<https://doi.org/10.1103/PhysRevLett.100.136406>)

¹⁹ Ph. Haas, F. Tran, P. Blaha, and K.H. Schwartz, *Construction of an optimal GGA functional for molecules and solids*, *Physical Review B* 83, 205117 (2011) (<https://doi.org/10.1103/PhysRevB.83.205117>).

²⁰ N.C. Handy and A.J. Cohen, *Left-right correlation energy*, *Molecular Physics* 99, 403 (2001) (<https://doi.org/10.1080/00268970010018431>)

²¹ J.J. Mortensen, K. Kaasbjerg, S.L. Frederiksen, J.K. Nørskov, J.P. Sethna, and K.W. Jacobsen, *Bayesian Error Estimation in Density-Functional Theory*, *Physical Review Letters* 95, 216401 (2005) (<https://doi.org/10.1103/PhysRevLett.95.216401>)

²² J.P. Perdew, *Density-functional approximation for the correlation energy of the inhomogeneous electron gas*, *Physical Review B* 33, 8822 (1986) (<https://doi.org/10.1103/PhysRevB.33.8822>) Erratum: J.P. Perdew, *Physical Review B* 34, 7406 (1986) (<https://doi.org/10.1103/PhysRevB.34.7406>)

⁶⁷ C. Lee, W. Yang and R.G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density*, *Physical Review B* 37, 785 (1988) (<https://doi.org/10.1103/PhysRevB.37.785>)

⁶⁸ B.G. Johnson, P.M.W. Gill and J.A. Pople, *The performance of a family of density functional methods*, *Journal of Chemical Physics* 98, 5612 (1993) (<https://doi.org/10.1063/1.464906>)

⁶⁹ T.V. Russo, R.L. Martin and P.J. Hay, *Density Functional calculations on first-row transition metals*, *Journal of Chemical Physics* 101, 7729 (1994) (<https://doi.org/10.1063/1.468265>)

4.2.3 MetaGGA

```
XC
  MetaGGA functional
End
```

MetaGGA

Specifies that a meta-GGA should be used during the SCF. **All-electron basis sets should be used** (see *Basis key* (page 44)).

Available meta-GGA functionals:

- **M06-L**: Functional by Yan-Truhlar^{61,62}.
- **TPSS**: Functional by Tao-Perdew-Staroverov-Scuseria^{63,64}.
- **revTPSS**: Revised TPSS functional²⁴.
- **SSB-D**: Dispersion corrected GGA functional by Swart-Solà-Bickelhaupt^{Page 81, 65Page 81, 66}. Use GGA SSB-D for NMR calculations.
- **MVS**: Functional by Sun-Perdew-Ruzsinszky²⁵.
- **MS0**: Functional by Sun et al.²⁶.
- **MS1**: Functional by Sun et al.²⁷.
- **MS2**: Functional by Sun et al.²⁷.
- **SCAN**: Functional by Sun et al.²⁸.
- **TASKxc**: Functional by Aschebrock et al.³⁴, intended for charge transfer systems.
- **TASKCC**: Functional by Lebeda et al.³⁶, improves TASKxc atomization energies.
- **r2SCAN-3c**: Composite DFT method by Gasevic et al.³⁵.
- **LAK**: Functional by Lebeda and coworkers⁹. It is a general-purpose functional.

⁶¹ Y. Zhao and D.G. Truhlar, *A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions*, *Journal of Chemical Physics* 125, 194101 (2006) (<https://doi.org/10.1063/1.2370993>)

⁶² Y. Zhao and D.G. Truhlar, *The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals*, *Theoretical Chemical Accounts* 120, 215 (2008) (<https://doi.org/10.1007/s00214-007-0310-x>)

⁶³ J. Tao, J.P. Perdew, V.N. Staroverov and G.E. Scuseria, *Climbing the Density Functional Ladder: Nonempirical MetaGeneralized Gradient Approximation Designed for Molecules and Solids* *Physical Review Letters* 91, 146401 (2003) (<https://doi.org/10.1103/PhysRevLett.91.146401>)

⁶⁴ V.N. Staroverov, G.E. Scuseria, J. Tao and J.P. Perdew, *Comparative assessment of a new non empirical density functional: Molecules and hydrogen-bonded complexes* *Journal of Chemical Physics* 119, 12129 (2003) (<https://doi.org/10.1063/1.1626543>)

²⁴ J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, and J. Sun, *Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry*, *Physical Review Letters* 103, 026403 (2009) (<https://doi.org/10.1103/PhysRevLett.103.026403>).

²⁵ J. Sun, J.P. Perdew, and A. Ruzsinszky, *Semilocal density functional obeying a strongly tightened bound for exchange*, *Proceedings of the National Academy of Sciences* 112, 685 (2015) (<https://doi.org/10.1073/pnas.1423145112>)

²⁶ J. Sun, B. Xiao, A. Ruzsinszky, *Communication: Effect of the orbital-overlap dependence in the meta generalized gradient approximation*, *Journal of Chemical Physics* 137, 051101 (2012) (<https://doi.org/10.1063/1.4742312>).

²⁷ J. Sun, R. Haunschild, B. Xiao, I.W. Bulik, G.E. Scuseria, J.P. Perdew, *Semilocal and hybrid meta-generalized gradient approximations based on the understanding of the kinetic-energy-density dependence*, *Journal of Chemical Physics* 138, 044113 (2013) (<https://doi.org/10.1063/1.4789414>).

²⁸ J. Sun, A. Ruzsinszky, J.P. Perdew, *Strongly Constrained and Appropriately Normed Semilocal Density Functional*, *Physical Review Letters* 115, 036402 (2015) (<https://doi.org/10.1103/PhysRevLett.115.036402>).

³⁴ T. Aschebrock, and S. Kümmel, *Ultranonlocality and accurate band gaps from a meta-generalized gradient approximation*, *Phys. Rev. Research* 1, 033082 (2019) (<https://doi.org/10.1103/PhysRevResearch.1.033082>)

³⁶ T. Lebeda, T. Aschebrock, and S. Kümmel, *First steps towards achieving both ultranonlocality and a reliable description of electronic binding in a meta-generalized gradient approximation*, *Phys. Rev. Research* 4, 023061 (2022) (<https://doi.org/10.1103/PhysRevResearch.4.023061>)

³⁵ T. Gasevic, J.B. Stückerath, S. Grimme, and M. Bursch, *Optimization of the r2SCAN-3c Composite Electronic-Structure Method for Use with Slater-Type Orbital Basis Sets*, *Journal of Physical Chemistry A* 126, 3826 (2022) (<https://doi.org/10.1021/acs.jpca.2c02951>)

⁹ T. Lebeda, T. Aschebrock, and S. Kümmel, *Balancing the contributions to the gradient expansion: Accurate binding and band gaps with a nonempirical meta-GGA*, *Phys. Rev. Letters*, 023061 (2024) (accepted for publication) (<https://journals.aps.org/prl/accepted/d2072Y38Fff15b8b58146dd51ea85cccaf9f3dc>)

The r2SCAN-3c composite method³⁵ uses the r^2 SCAN (r2SCAN) exchange-correlation functional, in combination with a tailor-made all-electron polarized basis set (mTZ2P), the semiclassical London dispersion correction (D4), and a geometrical counterpoise (gCP) correction. NumericalQuality should be set to Good, and ZORA should be used. Note that LibXC will be used internally for the r2SCAN functional, and the D4 and gCP corrections will be included automatically. The STO-optimized r2SCAN-3c outperforms many conventional hybrid/QZ approaches in most common applications at a fraction of their cost.

The M06-L functional needs high integration accuracy (at least *BeckeGrid quality good* (page 373)) for reasonable gradients. For TPSS, moderate integration accuracy is sufficient for reasonable gradients. For heavier elements ($Z > 36$), and if one uses the M06-L functional, it is also necessary to include the following keyword

```
FragMetaGGAToten
```

Using this FRAGMENTAGGATOTEN key, the difference in the meta-hybrid or meta-GGA exchange-correlation energies between the molecule and its fragments will be calculated using the molecular integration grid, which is more accurate than the default but is much more time-consuming. By default, the meta-GGA exchange-correlation energies for the fragments are calculated on the numerical integration grid of the fragments.

4.2.4 Hartree-Fock

```
XC
  HartreeFock
End
```

HartreeFock

Specifies that the Hartree-Fock exchange should be used during the SCF.

4.2.5 Hybrid

```
XC
  HYBRID functional {HF=HFpart}
End
```

HYBRID

Specifies that a hybrid functional should be used during the SCF.

Available hybrid functionals:

- **B3LYP**: ADF uses VWN5 in the B3LYP functional (20% HF exchange) by Stephens-Devlin-Chabrowski-Frisch²⁹.
- **B3LYP***: Modified B3LYP functional (15% HF exchange) by Reiher-Salomon-Hess³⁰.
- **B1LYP**: Functional (25% HF exchange) by Adamo-Barone³¹.
- **KMLYP**: Functional (55.7% HF exchange) by Kang-Musgrave³².
- **O3LYP**: Functional (12% HF exchange) by Cohen-Handy³³.

²⁹ P.J. Stephens, F.J. Devlin, C.F. Chabalowski and M.J. Frisch, *Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields*, *Journal of Physical Chemistry* 98, 11623 (1994) (<https://doi.org/10.1021/j100096a001>)

³⁰ M. Reiher, O. Salomon and B.A. Hess, *Reparameterization of hybrid functionals based on energy differences of states of different multiplicity*, *Theoretical Chemistry Accounts* 107, 48 (2001) (<https://doi.org/10.1007/s00214-001-0300-3>)

³¹ C. Adamo and V. Barone, *Toward reliable adiabatic connection models free from adjustable parameters*, *Chemical Physics Letters* 274, 242 (1997) ([https://doi.org/10.1016/S0009-2614\(97\)00651-9](https://doi.org/10.1016/S0009-2614(97)00651-9))

³² J.K. Kang and C.B. Musgrave, *Prediction of transition state barriers and enthalpies of reaction by a new hybrid density-functional approximation*, *Journal of Chemical Physics* 115, 11040 (2001) (<https://doi.org/10.1063/1.1415079>)

³³ A.J. Cohen and N.C. Handy, *Dynamic correlation*, *Molecular Physics* 99, 607 (2001) (<https://doi.org/10.1080/00268970010023435>)

- **X3LYP**: Functional (21.8% HF exchange) by Xu-Goddard^{Page 81, 5}.
- **BHandH**: 50% HF exchange, 50% LDA exchange, and 100% LYP correlation.
- **BHandHLYP**: 50% HF exchange, 50% LDA exchange, 50% Becke88 exchange, and 100% LYP correlation.
- **B1PW91**: Functional (25% HF exchange) by Adamo-Barone^{Page 85, 31}.
- **mPW1PW**: Functional (25% HF exchange) by Adamo-Barone^{Page 82, 13}.
- **mPW1K**: Functional (42.8% HF exchange) by Lynch-Fast-Harris-Truhlar³⁷.
- **PBE0**: Functional (25% HF exchange) by Ernzerhof-Scuseria³⁸ and by Adamo-Barone³⁹, hybrid form of PBE.
- **OPBE0**: Functional (25% HF exchange) by Swart-Ehlers-Lammertsma^{Page 81, 4}, hybrid form of OPBE.
- **S12H**: Dispersion corrected (Grimme-D3) functional (25% HF exchange) by Swart^{Page 82, 6}.

HFpart

Specifies the amount of HF exchange to use instead of the default HF exchange fraction for the given hybrid.
Example HF=0.25 means 25% Hartree-Fock exchange.

4.2.6 Meta-Hybrid

```
XC
  MetaHYBRID functional
End
```

MetaHYBRID

Specifies that a meta-hybrid functional should be used during the SCF.

Available meta-hybrid functionals:

- **M06**: Functional (27% HF exchange) by Yan-Truhlar^{Page 84, 61Page 84, 62}.
- **M06-2X**: Functional (54% HF exchange) by Yan-Truhlar^{Page 84, 61Page 84, 62}.
- **M06-HF**: Functional (100% HF exchange) by Yan-Truhlar^{Page 84, 61Page 84, 62}.
- **TPSSH**: Functional (10% HF exchange) by Tao-Perdew-Staroverov-Scuseria^{Page 84, 63Page 84, 64}.

4.2.7 Range-separated hybrids

In ADF, there are two (mutually exclusive) ways of specifying range-separated hybrid functionals:

- Through the `RANGESEP` and `XCFUN` keys. This will use the Yukawa potential as switching function, see Ref.⁴⁰;
- By specifying a range-separated functional via the `LibXC` key.

See also the advanced tutorial: [Tuning the range separation in LC-wPBE for organic electronics](https://www.scm.com/news/tuning-range-separation-lc-wpbe-organic-electronics/) (<https://www.scm.com/news/tuning-range-separation-lc-wpbe-organic-electronics/>).

³⁷ B.J. Lynch, P.L. Fast, M. Harris and D.G. Truhlar, *Adiabatic Connection for Kinetics*, *Journal of Physical Chemistry A* 104, 4811 (2000) (<https://doi.org/10.1021/jp000497z>)

³⁸ S. Grimme, *Accurate description of van der Waals complexes by density functional theory including empirical corrections*, *Journal of Computational Chemistry* 25, 1463 (2004) (<https://doi.org/10.1002/jcc.20078>)

³⁹ M. Ernzerhof and G. Scuseria, *Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional*, *Journal of Chemical Physics* 110, 5029 (1999) (<https://doi.org/10.1063/1.478401>)

⁴⁰ M. Seth and T. Ziegler, *Range-Separated Exchange Functionals with Slater-Type Functions*, *Journal of Chemical Theory and Computation* 8, 901 (2012) (<https://doi.org/10.1021/ct300006h>)

RangeSep + XCFun: Yukawa range-separated hybrids

RANGESEP {GAMMA=X} {ALPHA=a} {BETA=b}

If RANGESEP is included, by default a long-range corrected (LC) functional is created with a range separation parameter GAMMA of 0.75. In this case, the switching function is the Yukawa potential, see Ref.⁴⁰. Range-separated functionals require XCFUN and are limited to GGA, meta-GGA, and CAMY-B3LYP. The CAMY-B3LYP functional is not the same as the CAM-B3LYP functional, since a different switching function is used. No other hybrids or meta-hybrids are supported. The special CAMY-B3LYP functional is defined by three parameters, ALPHA, BETA, and the attenuation parameter GAMMA. For CAMY-B3LYP, by default ALPHA is 0.19, BETA is 0.46, and GAMMA is 0.34.

Range-separated functionals make use of a modified form of the Coulomb operator that is split into pieces for exact exchange and DFT. In this case, the switching function is the Yukawa potential, see Ref.^{Page 86, 40}. Global hybrids can be thought of as a special case of a range-separated functional where the split is independent of the inter-electronic distance and is a simple X exact and 1-X DFT in all space.

In a general RS-functional, the split depends on the inter-electronic distance. How the split is achieved depends on the functional in question, but it is achieved using functions that smoothly go from 1 to 0. In practical terms, this means that a range-separated functional looks very much like a hybrid (or meta-hybrid) functional but with additional integrals over the attenuated interaction with fit functions on the exact exchange side and a modified functional on the DFT side.

DFT part of RS-functionals

Using Hirao's approach for creating RS-functionals, the RS form of a given exchange functional is created by multiplying the standard energy density by a factor that depends on the energy density. The factor is the same for all functionals and the only difference is introduced by the individual energy densities.

The range separation comes in at the level of the integrals over the operator with fit functions. They are very similar to the standard Coulomb integrals.

RS-functionals

An RS-functional is described by a series of regions describing each of the pieces of the Coulomb operator. The total function is built up by looping over the regions and adding up all the pieces. Currently, simple LC functionals can be defined where the exact exchange goes from 0 to 1 as the inter-electronic distance increases, and the DFT part does the reverse. In addition, CAMY-B3LYP type functionals can be defined. More general functionals are not possible with XCFun.

Functionality and limitations

RS functionals with XCFUN are limited to the GGA and meta-GGA functionals and one hybrid CAMY-B3LYP. The following functionals can be evaluated with range separation at the present time:

- LDA: VWN5, X-ALPHA PW92
- GGA exchange: Becke88, PBEX, OPTX, PW91X, mPW, revPBEX
- GGA correlation: LYP, Perdew86, PBEC
- MetaGGA: TPSS, M06L, B95
- Hybrids: CAMY-B3LYP

The following functionality has been tested: XC potential, energy, ground state geometry, and TDDFT. Starting from ADF2018, singlet-triplet excitation calculations and excited state geometry optimizations are possible. For possible limitations in excitation calculations or excited state geometry optimizations, see the corresponding part of the ADF manual.

Numerical stability

The range-separated implementation requires that the range separation parameter is not too close to the exponent of a fit function. In practice, this means that values of the separation parameter between 1.0 and 50 can cause numerical problems. Typical useful values are in the range 0.2 to 0.9, so this should not be too serious a limitation.

```
XC
  XCFUN
  RANGESEP {GAMMA=X} {ALPHA=a} {BETA=b}
END
```

Range separation is activated by putting RANGESEP in the XC block. Inclusion of XCFUN is required; see the [XCFUN description](#) (page 97). By default, a long-range corrected (LC) functional is created with a range separation parameter of 0.75. The parameter can be changed by modifying X in GAMMA=X in the RANGESEP card. Range separation is typically used in combination with a GGA or METAGGA functional.

Range separation cannot be included with a hybrid or meta-hybrid, with one exception: the special RS functional CAMY-B3LYP. This is entered as HYBRID CAMY-B3LYP and must be used in combination with XCFUN (see [XCFUN description](#) (page 97)) and RANGESEP. The CAMY-B3LYP functional is defined by three parameters, ALPHA, BETA, and the attenuation parameter GAMMA. The GAMMA parameter can be modified as for the LC functionals. For CAMY-B3LYP it defaults to 0.34. The ALPHA and BETA parameters can be modified through ALPHA=a and BETA=b in the RANGESEP card. They default to 0.19 and 0.46, respectively.

```
XC
  HYBRID CAMY-B3LYP
  XCFUN
  RANGESEP GAMMA=0.34 ALPHA=0.19 BETA=0.46
END
```

List of the most important functionals for which one can use range separation:

```
LDA VWN
GGA BLYP
GGA BP86
GGA PBE
HYBRID CAMY-B3LYP
```

Range-separated hybrids with LibXC

You can simply specify a range-separated hybrid functional in the [LibXC](#) (page 98) key, *e.g.*:

```
XC
  LibXC CAM-B3LYP
End
```

See the [LibXC](#) (page 98) section for a list of available range-separated hybrid functionals.

For the HSE03 and HSE06 short range-separated hybrids, you can (optionally) specify the switching parameter omega, *e.g.*:

```
XC
  LibXC HSE06 omega=0.1
End
```


4.2.8 Notes on Hartree-Fock and (meta-)hybrid functionals

If a functional contains a part of Hartree-Fock exchange, then the LDA, GGA, meta-GGA, or MODEL key should not be used. You should specify only one of HartreeFock, HYBRID, or MetaHYBRID. Dispersion can be added. Note that it is not recommended to use (part of the) Hartree-Fock exchange in combination with frozen cores, since the frozen core orbitals are currently not included in the Hartree-Fock exchange operator. In ADF, one can do unrestricted Hartree-Fock (or hybrid or meta-hybrid) calculations, as long as one has integer occupation numbers. The default implementation in ADF for unrestricted Hartree-Fock calculations is UHF. In case of a high-spin electron configuration, one can do ROHF; see [ROKS for high-spin open shell molecules](#) (page 61). You need to use the same XC potential in the create run of the atoms, which is done automatically if you use the BASIS key.

Starting from ADF2009.01, the meta-hybrids M06, M06-2X, M06-HF, and TPSSH can be used during the SCF. Also starting from ADF2009.01, Hartree-Fock and the (meta-)hybrid potentials can be used in combination with geometry optimization, TS, IRC, LT, and numerical frequencies; hybrids can be used in calculating [NMR chemical shift](#) (page 232); PBE0 can be used in calculating [NMR spin-spin coupling](#) (page 240); Hartree-Fock and (meta-)hybrid can be used in calculating excitation energies, in which the kernel consists of the Hartree-Fock percentage times the Hartree-Fock kernel plus one minus the Hartree-Fock percentage times the ALDA kernel (thus no (meta-)GGA kernel). Hartree-Fock and the (meta-)hybrid potentials still cannot (or should) not be used in combination with analytical frequencies, the (AO)RESPONSE key, EPR/ESR g-tensor, and frozen cores. Starting from ADF2010, it is possible to use Hartree-Fock and hybrids to calculate CD spectra.

In ADF, one can do unrestricted Hartree-Fock (or hybrid or meta-hybrid) calculations (UHF, UKS) as long as the occupation numbers are integers. For a high-spin electron configuration, one can use ROHF or ROKS; see [ROKS for high-spin open shell molecules](#) (page 61).

It is possible to change the amount of HF exchange in the input for hybrids (not for meta-hybrids and Hartree-Fock). For many hybrid functionals, the sum of the amount of Hartree-Fock exchange and the amount of LDA exchange (or GGA exchange) is one. If that is the case, then if one changes the amount of Hartree-Fock exchange in the input, the amount of LDA exchange (or GGA exchange) will also be changed such that the sum remains one. Example:

```
XC
  Hybrid B3LYP HF=0.25
END
```

In this case, the amount of Hartree-Fock for the B3LYP functional will be changed to 25% (instead of 20%), and the amount of LDA exchange to 75% (instead of 80%). The LDA correlation and GGA exchange and correlation part will be left unaltered.

An accuracy issue is relevant for some of the meta-GGA functionals, in particular the M06 functionals. These need high integration accuracy (at least BeckeGrid quality good) for reasonable gradients. For TPSSH, moderate integration accuracy is sufficient for reasonable gradients. For heavier elements ($Z > 36$), and if one uses one of the M06 functionals, it is also necessary to include the following keyword

```
FragMetaGGAToten
```

Using this key FRAGMETAGGATOTEN, the difference in the meta-hybrid or meta-GGA exchange-correlation energies between the molecule and its fragments will be calculated using the molecular integration grid, which is more accurate than the default but is much more time-consuming. By default, the meta-hybrid or meta-GGA exchange-correlation energies for the fragments are calculated on the numerical integration grid of the fragments.

For benchmark calculations, one would like to use a large basis set, like the QZ4P basis set. In such cases it is recommended to use a good numerical quality. Thus, for accurate hybrid calculations of **small** molecules, one could use:

```
basis
  type QZ4P
end
AddDiffuseFit
```

(continues on next page)

(continued from previous page)

```
Dependency bas=1e-4
NumericalQuality good
```

4.2.9 MP2, Double Hybrids, RPA

To treat correlation energies beyond DFT, ADF offers MP2 and random-phase approximation (RPA) based methods. In addition, ADF offers a large number of modern double-hybrid functionals that combine MP2 correlation with a hybrid functional.

ADF implements canonical MP2 using density fitting. Additionally, ADF implements RPA and direct MP2 using an efficient atomic-orbital-based algorithm. The algorithm is described in Ref.⁹². The algorithm has been continuously improved over the last few years and currently allows single-point calculations for systems with up to 1000 atoms on a single modern compute node. Many of the most accurate double-hybrid functionals use direct MP2 only.

Double Hybrid Functionals

```
XC
  DOUBLEHYBRID functional
End
```

DOUBLEHYBRID

Specifies that a double-hybrid functional⁷¹ should be used.

See also:

The paper [Double hybrid DFT calculations with Slater type orbitals](https://doi.org/10.1002/jcc.26209) (https://doi.org/10.1002/jcc.26209) and the page [Double hybrids: recommendations for accurate thermochemistry and kinetics](https://www.scm.com/highlights/double-hybrids-recommendations-for-accurate-thermochemistry-kinetics/) (https://www.scm.com/highlights/double-hybrids-recommendations-for-accurate-thermochemistry-kinetics/) contain useful recommendations for Double Hybrid calculations in ADF.

Double hybrids usually yield considerably better energies than (meta-)GGA and (meta-)hybrid functionals for (main group) thermochemistry and kinetics, transition metal chemistry, and non-covalent interactions. For an overview of the capabilities of double-hybrids implemented in ADF, we refer to a review.⁷²

The MP2 correlation energy consists of two terms,

$$E_{MP2} = \frac{1}{2}(E_{\text{direct}} - E_{\text{ex}})$$

$$E_{\text{direct}} = \sum_{ij} \sum_{ab} \frac{(ia|jb)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$E_{\text{ex}} = \sum_{ij} \sum_{ab} \frac{(ia|jb)(ib|ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$(ia|jb) = \iint \phi_i^\dagger(1)\phi_a(1) \frac{1}{r_{12}} \phi_j^\dagger(2)\phi_b(2) d1d2$$

⁹² A. Förster, M. Franchini, E. van Lenthe, L. Visscher, *A Quadratic Pair Atomic Resolution of the Identity Based SOS-AO-MP2 Algorithm Using Slater Type Orbitals*, *Journal of Chemical Theory and Computation* 16, 875 (2020) (https://doi.org/10.1021/acs.jctc.9b00854)

⁷¹ S. Grimme, *Semiempirical hybrid density functional with perturbative second-order* *J. Chem. Phys.* 2006, 124, 034108 (https://doi.org/10.1063/1.2148954)

⁷² A. Förster, L. Visscher, *Double hybrid DFT calculations with Slater type orbitals*, *Journal of Computational Chemistry* 41 1660–1684 (2020) (https://doi.org/10.1002/jcc.26209)

For a closed-shell system, the MP2 correlation energy can also be partitioned as

$$E_{MP2} = E_{OS} + E_{SS}$$

$$E_{OS} = E_{\text{direct}}$$

$$E_{SS} = E_{\text{direct}} - E_{\text{ex}}$$

Here, OS (opposite spin) denotes the contribution to the correlation energy from electrons with unpaired spins, and SS (same spin) denotes the contribution to the correlation energy from electrons with paired spins. In case of spin-orbit coupling, *approximate SS and OS contributions* (page 96) are calculated.

There are three classes of double-hybrid functionals:

- Opposite-spin-only functionals (only the OS term is used and scaled by an empirical factor)
- Spin-component-scaled functionals (both the OS and SS components are individually scaled by empirical factors)
- Standard double-hybrid functionals (both the OS and SS components are scaled by the same empirical factor)

We recommend using opposite-spin-only functionals for large systems (50-100 atoms and larger), since they are computationally more efficient than the other functionals, which also include the same-spin contribution. **An opposite-spin-only functional calculation is always feasible when a hybrid calculation is feasible too!**

For additional technical details of the algorithm and how to tweak the technical parameters, see *the MBPT section* (page 387).

Opposite-spin-only Double Hybrids

Currently, ADF supports the following opposite-spin-only Double Hybrid functionals:

- **SOS1-PBE-QIDH**: 1-parameter functional with PBE exchange, PBE correlation (69 % HF, 44 % OS-MP2)⁷³
- **rev-DOD-BLYP**: B88 exchange, LYP correlation, Grimme3 dispersion (71 % HF, 62.2 % OS-MP2)⁷⁴
- **rev-DOD-BLYP-D4**: B88 exchange, LYP correlation, Grimme4 dispersion (71 % HF, 63.5 % OS-MP2)^{Page 91, 74}
- **rev-DOD-PBE**: PBE exchange, PBE correlation, Grimme3 dispersion (68 % HF, 61.3 % OS-MP2)⁷⁴
- **rev-DOD-PBE-D4**: PBE exchange, PBE correlation, Grimme4 dispersion (68 % HF, 61.8 % OS-MP2)⁷⁴
- **rev-DOD-PBEP86**: PBE exchange, P86 correlation, Grimme3 dispersion (69 % HF, 60.6 % OS-MP2)⁷⁴
- **rev-DOD-PBEP86-D4**: PBE exchange, P86 correlation, Grimme4 dispersion (69 % HF, 61.2 % OS-MP2)⁷⁴
- **DOD-SCAN**: SCAN exchange and correlation, Grimme3 dispersion (66 % HF, 63.0 % OS-MP2)⁷⁴
- **rev-DOD-SCAN-D4**: SCAN exchange and correlation, Grimme4 dispersion (66 % HF, 63.4 % OS-MP2)⁷⁴

Except for **SOS1-PBE-QIDH**, all functionals include dispersion correction by default which cannot be switched off.

Standard Double Hybrids

Currently, ADF supports the following standard double-hybrid functionals:

- **B2PLYP**: B88 exchange and LYP correlation (53 % HF, 27 % MP2)^{Page 90, 71}
- **B2PIPLYP**: B88 exchange and LYP correlation (60 % HF, 27 % MP2), parametrized for pi-pi interactions⁷⁵
- **ROB2PLYP**: B88 exchange and LYP correlation (59 % HF, 28 % MP2), restricted-open-shell version of B2PLYP⁷⁶

⁷³ Js. Garcia, E. Bremond, M. Savarese, A.J. Perez-Gimenez, C. Adamo, *Partnering dispersion corrections with modern parameter-free double-hybrid density functionals* Phys. Chem. Chem. Phys., 19, 13481 (2017) (<https://doi.org/10.1021/acs.jctc.8b01203>)

⁷⁴ G. Santra, N. Sylvetsky, and J.M.L. Martin, *Minimally Empirical Double-Hybrid Functionals Trained against the GMTKN55 Database: revDSD-PBEP86-D4 revDOD-PBE-D4, and DOD-SCAN-D4* J. Chem. Phys. 2019, 123, 5129 (<https://doi.org/10.1021/acs.jpca.9b03157>)

⁷⁵ J.C. Sancho-García, A.J. Pérez-Jiménez, *Assessment of double-hybrid energy functionals for PI-conjugated systems* J. Chem. Phys. 2009, 131, 084108 (<https://doi.org/10.1063/1.3212881>)

⁷⁶ D.C. Graham, A.S. Menon, L. Goerigk, S. Grimme, L. Radom *Optimization and basis-set dependence of a restricted-open-shell form of B2-PLYP double-hybrid density functional theory* J. Phys. Chem. A 2009, 113, 9861 (<https://doi.org/10.1021/jp9042864>)

- **B2TPLYP**: B88 exchange and LYP correlation (60 % HF, 31 % MP2), parametrized for thermodynamics⁷⁷
- **B2GPPLYP**: B88 exchange and LYP correlation (65 % HF, 36 % MP2), ‘General Purpose’ parametrization⁷⁸
- **B2KPLYP**: B88 exchange and LYP correlation (72 % HF, 42 % MP2), parametrized for kinetics^{Page 92, 77}
- **B2NCPLYP**: B88 exchange and LYP correlation (70 % HF, 49 % MP2), parametrized for non-covalent interactions⁷⁹
- **mPW2PLYP**: mPW exchange and LYP correlation (55 % HF, 25 % MP2)⁸⁰
- **mPW2KPLYP**: mPW exchange and LYP correlation (72 % HF, 42 % MP2)⁷⁷
- **mPW2NCPLYP**: mPW exchange and LYP correlation (42 % HF, 49 % MP2)⁷⁹
- **DH-BLYP**: 1-Parameter functional with B88 exchange and LYP correlation (65 % HF, 42 % MP2)⁸¹
- **PBE0-DH**: 1-Parameter functional with PBE exchange and PBE correlation (50 % HF, 13 % MP2)⁸²
- **PBE-QIDH**: 1-parameter functional with PBE exchange and PBE correlation (69 % HF, 33 % MP2)^{Page 91, 73}
- **LS1-DH**: 1-Parameter functional with PBE exchange and PBE correlation (75 % HF, 42 % MP2)⁸³
- **PBE0-2**: 1-Parameter functional with PBE exchange and PBE correlation (79 % HF, 50 % MP2)⁸⁴
- **LS1-TPSS**: 1-Parameter functional with TPSS meta-GGA (85 % HF, 61 % MP2)⁸⁵
- **DS1-TPSS**: 1-Parameter functional with TPSS meta-GGA (73 % HF, 53 % MP2)⁸⁵

Empirical dispersion corrections can be requested in the XC block in the usual way. Some functionals can be combined with Grimme’s D4 empirical dispersion correction with optimized parameters: B2PLYP, B2GPPLYP, mPW2PLYP, PBE0-DH, PBE0-2. All functionals in this category can be combined with Grimme’s D3(BJ) empirical dispersion correction with optimized parameters. Note that for Grimme’s D3(BJ) the parameters for B2PIPLYP, ROB2PLYP, B2TPLYP, B2KPLYP, mPW2PLYP, mPW2KPLYP, DH-BLYP, LS1-DH, PBE0-2, and DS1-TPSS are modified B2PLYP parameters, see Ref.^{Page 90, 72}. If no optimized empirical dispersion parameters exist for a certain functional, default parameters are used, which may not give the expected results.

Spin-component-scaled functionals

Currently, ADF supports the following spin-component scaled Double Hybrid functionals:

- **DSD-BLYP**: B88 exchange and LYP correlation, Grimme3 dispersion (69 % HF, 46 % OS-MP2, 37 % SS-MP2)⁸⁶
- **rev-DSD-BLYP**: revised version of DSD-BLYP, Grimme3 dispersion (71 % HF, 54.7 % OS-MP2, 19.8 % SS-MP2)^{Page 91, 74}

⁷⁷ A. Tarnopolsky, A. Karton, R. Sertchook, D. Vuzman, J.M.L. Martin, *Double-hybrid functionals for thermochemical kinetics* J. Phys. Chem. A 2008, 112, 3 (<https://doi.org/10.1021/jp710179r>)

⁷⁸ A. Karton, A. Tarnopolsky, J.F. Lamere, G.C. Schatz, J.M.L. Martin, *Highly accurate first-principles benchmark data sets for the parametrization and validation of density functional and other approximate methods. Derivation of a robust, generally applicable, double-hybrid functional or thermochemistry and thermochemical kinetics.* J. Phys. Chem. A 2008, 112, 12868 (<https://doi.org/10.1021/jp801805p>)

⁷⁹ Y. Feng, *Double-Hybrid Density Functionals Free of Dispersion and Counterpoise Corrections for Non-Covalent Interactions* J. Phys. Chem. A 2014, 118, 3175 (<https://doi.org/10.1021/jp5005506>)

⁸⁰ T. Schwabe, S. Grimme, *Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects.* Phys. Chem. Chem. Phys. 2006, 8, 4398 (<https://doi.org/10.1039/B608478H>)

⁸¹ K. Sharkas, J. Toulouse, A. Savin, *Double-hybrid density-functional theory made rigorous* J. Chem. Phys. 2011, 134, 064113 (<https://doi.org/10.1063/1.3544215>)

⁸² E. Bremond, C. Adamo, *Seeking for parameter-free double-hybrid functionals: The PBE0-DH model* J. Chem. Phys. 2011, 135, 024106 (<https://doi.org/10.1063/1.3604569>)

⁸³ J. Toulouse, K. Sharkas, E. Bremond, C. Adamo, *Rationale for a new class of double-hybrid approximations* J. Chem. Phys. 2011, 135, 101102 (<https://doi.org/10.1063/1.3640019>)

⁸⁴ J.D. Chai, S.P. Mao, *Seeking for reliable double-hybrid density functionals without fitting parameters: the PBE0-2 functional* Chem. Phys. Lett. 2012, 538, 121 (<https://doi.org/10.1016/j.cplett.2012.04.045>)

⁸⁵ S.O. Souvi, K. Sharkas and J. Toulouse, *Double-hybrid density functional theory with meta-generalized gradient approximations* J. Chem. Phys. 2014, 140, 084107 (<https://doi.org/10.1016/j.cplett.2012.04.045>)

⁸⁶ S. Kozuch, D. Gruzman, J.M.L. Martin, *DSD-BLYP: a general purpose double hybrid density functional including spin component scaling and dispersion correction* J. Phys. Chem. C 2010, 114, 20801 (<https://doi.org/10.1021/jp1070852>)

- **rev-DSD-BLYP-D4**: revised version of DSD-BLYP, Grimme4 dispersion (71 % HF, 55.9 % OS-MP2, 19.7 % SS-MP2)^{Page 91, 74}
- **DSD-PBEP86**: PBE exchange and P86 correlation (69 % HF, 52 % OS-MP2, 22 % SS-MP2)⁸⁷
- **rev-DSD-PBEP86**: revised version of DSD-PBEP86 (69 % HF, 57.9 % OS-MP2, 8 % SS-MP2)^{Page 91, 74}
- **rev-DSD-PBEP86-D4**: PBE exchange and P86 correlation, Grimme4 dispersion (69 % HF, 59.2 % OS-MP2, 6.4 % SS-MP2)^{Page 91, 74}
- **DSD-PBE**: PBE exchange and PBE correlation, Grimme3 dispersion (68 % HF, 55 % OS-MP2, 13 % SS-MP2)⁸⁷
- **rev-DSD-PBE**: revised version of DSD-PBE, Grimme3 dispersion (68 % HF, 58.5 % OS-MP2, 7 % SS-MP2)^{Page 91, 74}
- **rev-DSD-PBE-D4**: revised version of DSD-PBE, Grimme4 dispersion (68 % HF, 60 % OS-MP2, 4.2 % SS-MP2)^{Page 91, 74}
- **rev-DSD-SCAN-D4**: based on SCAN meta-GGA (66 % HF, 63.2 % OS-MP2, 1.3 % SS-MP2)^{Page 91, 74}
- **SD-SCAN69**: Based on SCAN meta-GGA, no dispersion correction (69 % HF, 62 % OS-MP2, 26 % SS-MP2)^{Page 91, 74}

Except for **SD-SCAN69**, all functionals include dispersion correction by default which cannot be switched off.

MP2

```
XC
  MP2
  EmpiricalScaling {NONE|SOS|SCS|SCSMI}
END
```

In addition to double-hybrids, ADF also implements MP2 including some popular spin-scaled variants. Technically, they are not distinct from double-hybrids; however, they all rely on an HF instead of a DFT calculation. The following variants are supported.

- **SOS-MP2**: pure HF reference (100 % HF, 130 % OS-MP2)⁸⁸
- **MP2**: pure HF reference (100 % HF, 100 % MP2 correlation)
- **SCS-MP2**: pure HF reference (100 % HF, 120 % OS-MP2, 33 % SS-MP2)⁸⁹
- **SOS-MI-MP2**: pure HF reference (100 % HF, 40 % OS-MP2, 129 % SS-MP2)⁹⁰

In case of spin-orbit coupling, *approximate SS and OS contributions* (page 96) are calculated.

The spin-scaling variant can be requested in the XC block together with the MP2 keyword:

```
XC
  MP2
  EmpiricalScaling SOS
END
```

⁸⁷ S. Kozuch, J.M.L. Martin, *DSD-PBEP86: In search of the best double-hybrid DFT with spin-component scaled MP2 and dispersion corrections* Phys. Chem. Chem. Phys. 2011, 13, 20104 (<https://doi.org/10.1039/C1CP22592H>)

⁸⁸ Y. Jung, R.C. Lochan, A. D. Dutoi, M. Head-Gordon, *Scaled opposite-spin second order Møller-plesset correlation energy: An economical electronic structure method*. Journal of Chemical Physics 2004, 121, 9793 (<https://doi.org/10.1063/1.1809602>)

⁸⁹ S. Grimme, *Improved second-order Møller-Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies*. Journal of Chemical Physics 2003, 118, 9095 (<https://doi.org/10.1063/1.1569242>)

⁹⁰ R.C. Lochan, Y. Jung, M. Head-Gordon, *Scaled opposite spin second order Møller-Plesset theory with improved physical description of long-range dispersion interactions* Journal of Physical Chemistry A 2005, 109, 7598 (<https://doi.org/10.1021/jp0514426>)

requests an SOS-MP2 calculation.

For additional technical details of the algorithm and how to tweak parameters, see [the MBPT section](#) (page 387).

RPA

Note: In AMS2022, the keyword for RPA+SOX was RPASOX.

The RPA goes beyond MP2 by accounting explicitly for the polarizability of the system, which screens the electron-electron interaction. It can therefore be applied to large systems for which MP2 typically diverges.⁹³ The following RPA-based methods are available.

- **RPA** : Standard (direct) RPA without exchange
- **RPA + SOX** : Standard RPA plus statically screened second-order exchange⁹⁴
- **RPA + SOSEX**: Standard RPA plus dynamically screened second-order exchange⁹⁵

A detailed overview of the RPA algorithm in ADF and a detailed assessment of the performance of second-order exchange corrections can be found in⁹⁷.

An RPA calculation is requested in the XC block:

```
XC
  RPA {NONE|DIRECT|SOSEX|SOSSX|SIGMA}
End
```

An RPA calculation needs to be combined with an XC functional. For instance,

```
XC
  hybrid pbe0
  RPA DIRECT
End
```

will perform a PBE0 calculation followed by a direct RPA calculation. RPA and all of its variants can be used in conjunction with LDA, GGAs, hybrid, and RSH functionals.

For additional technical details of the algorithm and how to tweak parameters, see [the RPA section](#) (page 387).

⁹³

B. D. Nguyen, G. P. Chen, M. M. Agee, A. M. Burow, M. P. Tang, F. Furche, *Divergence of Many-Body Perturbation Theory for Noncovalent Interactions of Large Molecules*, *Journal of Chemical Theory and Computation* 16(4), 2258-2273 (2020) (<https://doi.org/10.1021/acs.jctc.9b01176>)

⁹⁴ A. Förster, L. Visscher, *Exploring the statically screened G3W2 correction to the GW self-energy : Charged excitations and total energies of finite systems*, *Physical Review B* 105, 125121 (2022) (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.105.125121>)

⁹⁵ X. Ren, P. Rinke, G.E. Scuseria, M. Scheffler, *Renormalized second-order perturbation theory for the electron correlation energy: Concept, implementation, and benchmarks*, *Physical Review B* 88(3), 035120 (2013) (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.88.035120>)

⁹⁷ A. Förster, *Assessment of the second-order statically screened exchange correction to the random phase approximation for correlation energies*, *Journal of Chemical Theory and Computation* 18(10), 5948-5965 (2022) (<https://doi.org/10.1021/acs.jctc.2c00366>)

sigma-functional

Starting from AMS2023, the sigma-functional by Görling and coworkers is implemented.⁹⁶ In this method, the correlation kernel is calculated from the adiabatic fluctuation-dissipation theorem. In addition to the direct RPA (Hartree) kernel, higher-order contributions to the kernel are included by the so-called sigma-kernel, which is fitted to relative energies. Sigma-functionals are as fast as RPA.

ADF features a σ -functional implementation which is specifically parametrized for STO-type basis sets²³. In particular, for the Corr/TZ3P basis one should use the S1re parametrization of the σ -functional, preferably with the PBE0 functional.

Like an RPA calculation, a sigma-functional calculation needs to be combined with an XC functional. For instance,

```
XC
  hybrid pbe0
  RPA sigma
End
```

requests to use the sigma-functional with the W1 parametrization for PBE0.⁹⁸ Sigma-functionals can only be used with a limited number of exchange-correlation functionals, since they need to be explicitly parametrized for each functional. Currently, the sigma-functional can be used in conjunction with the GGA PBE, and the hybrids PBE0 and B3LYP. The available parametrizations for each functional are listed in the following table:

functional	available parametrizations ⁹⁸⁹⁹²³
PBE	W1 S1 S1re S2
PBE0	W1 S1 S1re S2 W2
B3LYP	W1

Note that S1re is the default value for the parametrization, which is optimized for the Corr/TZ3P basis set (all-electron). The parametrization can be changed in the MBPT block, see *the MBPT block* (page 387). For instance:

```
MBPT
  SigmaFunctionalParametrization S1
End
```

⁹⁶ E. Trushin, A. Thierbach, A. Görling *Toward chemical accuracy at low computational cost: Density-functional theory with sigma-functionals for the correlation energy*, *The Journal of Chemical Physics* 154, 014104 (2021) (<https://doi.org/10.1063/5.0026849>)

²³ S.Fauser, A. Förster, L. Redeker, C. Neiss, J. Erhard, E. Trushin, A. Görling, *Basis Set Requirements of σ -Functionals for Gaussian-and Slater-Type Basis Functions and Comparison with Range-Separated Hybrid and Double Hybrid Functionals*, *Journal of Chemical Theory and Computation* 20 (6), 2404-2422 (2024) (<https://doi.org/10.1021/acs.jctc.3c01132>).

⁹⁸ S.Fauser, E. Trushin, C. Neiss, A. Görling *Chemical accuracy with sigma-functionals for the Kohn-Sham correlation energy optimized for different input orbitals and eigenvalues*, *The Journal of Chemical Physics* 155, 034111 (2021) (<https://doi.org/10.1063/5.0059641>)

⁹⁹ J.Erhard, S. Fauser, E. Trushin, A. Görling *Scaled sigma-functionals for the Kohn-Sham correlation energy with scaling functions from the homogeneous electron gas*, *The Journal of Chemical Physics* 157, 114105 (2022) (<https://doi.org/10.1063/5.0101641>)

Spin-orbit coupling

In case of spin-orbit coupling, approximate SS and OS contributions are calculated, which is relevant for open shell molecules with double hybrids or MP2 variants that use different scaling factors for these contributions:

$$\begin{aligned}(ia|jb) &= \iint \phi_i^\dagger(1)\phi_a(1)\frac{1}{r_{12}}\phi_j^\dagger(2)\phi_b(2)d1d2 \\ m_{ij} &= \int \phi_i^\dagger(1)\vec{\sigma}\phi_i(1)d1 \cdot \int \phi_j^\dagger(2)\vec{\sigma}\phi_j(2)d2 \\ E_2^{SS} &= -\sum_{ijab} \frac{(1+m_{ij})(ia|jb)(ai|bj)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{ijab} \frac{2(ia|jb)(aj|bi)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ E_2^{OS} &= -\sum_{ijab} \frac{(1-m_{ij})(ia|jb)(ai|bj)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}\end{aligned}$$

with, i, j occupied spinors, a, b virtual spinors, ϵ spinor energies, $\vec{\sigma}$ Pauli spin matrices. Note that with pure α and β orbitals, $m_{i\alpha j\alpha} = m_{i\beta j\beta} = 1$, $m_{i\alpha j\beta} = m_{i\beta j\alpha} = -1$, one has the familiar SS and OS energy expressions.

4.2.10 Model Potentials

Several asymptotically correct XC potentials have been implemented in ADF, such as the (now somewhat outdated) LB94 potential^{Page 82, 7}, the gradient-regulated asymptotic correction (GRAC)⁴¹, and the statistical average of orbital potentials (SAOP)^{44,42}. These can currently be used only for response property calculations, not for geometry optimizations. For spectroscopic properties, they usually give results superior to those obtained with LDA or GGA potentials (see Ref.⁴³ for applications to (hyper)polarizabilities Cauchy coefficients, etc. of small molecules). This is particularly true if the molecule is small and the (high-lying) virtual orbitals are important for the property under study.

It was also shown that, simply using the orbital energies of the occupied Kohn-Sham orbitals of a SAOP calculation, quite good agreement with experimental vertical ionization potentials is obtained. This is true not only for the HOMO orbital energy, which should be identical to (minus) the experimental ionization potential with the exact XC potential, but also for lower-lying occupied orbital energies. The agreement becomes worse for deep-lying core orbital energies. A theoretical explanation and practical results are given in Ref.⁴⁵.

```
XC
  Model ModelPotential [IP]
End
```

MODEL

Specifies that one of the less common XC potentials should be used during the SCF. These potentials specify both the exchange and the correlation part. No LDA, GGA, MetaGGA, HartreeFock, HYBRID, or MetaHYBRID key should be used in combination with these keys. It is also not advised to use any energy analysis in combination with these potentials. For energy analysis, we recommend using one of the GGA potentials. It is currently not possible to perform a Create run with these potentials. It is possible to do a one-atom regular ADF calculation with these

⁴¹ M. Grüning, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *Shape corrections to exchange-correlation Kohn-Sham potentials by gradient-regulated seamless connection of model potentials for inner and outer region*, *Journal of Chemical Physics* 114, 652 (2001) (<https://doi.org/10.1063/1.1327260>)

⁴⁴ O.V. Gritsenko, P.R.T. Schipper and E.J. Baerends, *Approximation of the exchange-correlation Kohn-Sham potential with a statistical average of different orbital model potentials*, *Chemical Physics Letters* 302, 199 (1999) ([https://doi.org/10.1016/S0009-2614\(99\)00128-1](https://doi.org/10.1016/S0009-2614(99)00128-1))

⁴² P.R.T. Schipper, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *Molecular calculations of excitation energies and (hyper)polarizabilities with a statistical average of orbital model exchange-correlation potentials*, *Journal of Chemical Physics* 112, 1344 (2000) (<https://doi.org/10.1063/1.480688>)

⁴³ M. Grüning, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *On the required shape correction to the LDA and GGA Kohn Sham potentials for molecular response calculations of (hyper)polarizabilities and excitation energies*, *Journal of Chemical Physics* 116, 9591 (2002) (<https://doi.org/10.1063/1.1476007>)

⁴⁵ D.P. Chong, O.V. Gritsenko and E.J. Baerends, *Interpretation of the Kohn-Sham orbital energies as approximate vertical ionization potentials*, *Journal of Chemical Physics* 116, 1760 (2002) (<https://doi.org/10.1063/1.1430255>)

potentials, though, using a regular `adf.rkf` (TAPE21) file from an LDA or GGA potential as input. Available model potentials:

- **LB94**: This refers to the XC functional of Van Leeuwen and Baerends^{Page 82, 7}. There are no separate entries for the exchange and correlation parts of LB94. Usually the GRAC or SAOP potentials give results superior to LB94.
- **GRAC**: The gradient-regulated asymptotic correction, which in the outer region closely resembles the LB94 potential^{Page 96, 41}. It requires a further argument: the ionization potential [IP] of the molecule, in Hartree units. This should be estimated or obtained externally, or calculated in advance from two GGA total energy calculations.
- **IP**: Should be supplied only if GRAC is specified.
- **SAOP**: The statistical average of orbital potentials^{Page 96, 44}^{Page 96, 42}. It can be used for all-electron calculations only. It will be expensive for large molecules, but requires no further parameter input.

The LB94, GRAC, and SAOP functionals have only an SCF (= potential) implementation, but **no Energy** counterpart.

The LB94, GRAC, and SAOP forms are density functionals specifically designed to get the correct asymptotic behavior. This yields much better energies for the highest occupied molecular orbital (HOMO) and better excitation energies in a calculation of response properties (time-dependent DFT). Energies for lower-lying orbitals (sub-valence) should improve as well (in case of GRAC and SAOP, but not LB94). The energy expression underlying the LB94 functional is very inaccurate. This does not affect the response properties, but it does imply that the energy and its derivatives (gradients) should not be used because LB94-optimized geometries will be wrong; see, for instance,⁴⁶. The application of the LB94 functional in a runtime that involves the computation of energy gradients is disabled in ADF. You can override this internal check with the key `ALLOW` (page 393).

In a GRAC calculation, the user should be aware that the potential in the outer region is shifted up with respect to the usual level. In other words, the XC potential does not tend to zero in the outer region in this case. The size of the shift is the difference between the HOMO orbital energy and the IP given as input. In order to compare to regular GGA orbital energies, it is advisable to subtract this amount from all orbital energies. Of course, orbital energy differences, which enter excitation energies, are not affected by this shift in the potential.

4.2.11 XCFun

Any publication employing calculations carried out with XCFun needs to cite Ref. [U. Ekström, L. Visscher, R. Bast, A.J. Thorvaldsen, and K. Ruud, *J. Chem. Theory Comput.* 6, 1971 (2010) (<https://doi.org/10.1021/ct100117s>)]⁴⁷.

XCFUN

XCFun is a library of approximate exchange-correlation functionals, see Ref.⁴⁷, for which functional derivatives can be calculated automatically. For example, with XCFUN the full (non-ALDA) kernel can be evaluated and this has been implemented in the calculation of TDDFT excitations. The full kernel cannot be used in combination with symmetry or excited state geometry optimizations. The following functionals can be evaluated with XCFUN at the present time:

- LDA: VWN5, X-ALPHA, PW92
- GGA exchange: Becke88, PBEX, OPTX, PW91X, mPW, revPBEX
- GGA correlation: LYP, Perdew86, PBEC
- MetaGGA: TPSS, M06L, B95
- Meta-hybrids: M06, M05, M062X, M06HF

⁴⁶ R. Neumann, R.H. Nobes and N.C. Handy, *Exchange functionals and potentials*, *Molecular Physics* 87, 1 (1996) (<https://doi.org/10.1080/00268979600100011>)

⁴⁷ U. Ekström, L. Visscher, R. Bast, A.J. Thorvaldsen, and K. Ruud, *Arbitrary-Order Density Functional Response Theory from Automatic Differentiation*, *Journal of Chemical Theory and Computation* 6, 1971 (2010) (<https://doi.org/10.1021/ct100117s>)

- Hybrids: PBE0, B3LYP, BHandH, B1LYP, B3LYP*, PBEFALFX
- Yukawa range-separated hybrids: CAMY-B3LYP and more, see *Yukawa RS hybrids with XCFUN* (page 87)

Here, MetaGGA B95 means Becke88 exchange + B95c correlation. The meta-hybrids PW6B95 and PWB6K have been removed from this list, since they do not agree with the LibXC implementation.

4.2.12 LibXC

Any publication employing calculations carried out with LibXC needs to cite the current literature reference of LibXC, which is at the moment Ref. [S. Lehtola, C. Steigemann, M.J.T. Oliveira, M.A.L. Marques, *SoftwareX* 7, 1 (2018) (<https://doi.org/10.1016/j.softx.2017.11.002>)]⁴⁹. Benchmark papers employing functionals from LibXC should especially include a reference to the employed DFT library, since as discussed in Ref. [S. Lehtola, M.A.L. Marques, *J. Chem. Phys.* 159, 114116 (2023) (<https://doi.org/10.1063/5.0167763>)]⁵⁴, the implementations of a given functional in various program packages may not lead to the same result, even at the complete basis set limit.

LibXC functional

LibXC is a library of approximate exchange-correlation functionals, see Ref.⁴⁸Page 98, 49. **All-electron basis sets should be used** (see *Basis key* (page 44)). LibXC version 7.0.0 is used. The following functionals can be evaluated with LibXC (incomplete list):

- LDA: LDA, PW92, TETER93
- GGA: AM05, BCGP, B97-GGA1, B97-K, BLYP, BP86, EDF1, GAM, HCTH-93, HCTH-120, HCTH-147, HCTH-407, HCTH-407P, HCTH-P14, PBEINT, HTBS, KT2, MOHLYP, MOHLYP2, MPBE, MPW, N12, OLYP, PBE, PBEINT, PBESOL, PW91, Q2D, SOGGA, SOGGA11, TH-FL, TH-FC, TH-FCFO, TH-FCO, TH1, TH2, TH3, TH4, XLYP, XPBE, HLE16
- MetaGGA: M06-L, M11-L, MN12-L, MS0, MS1, MS2, MVS, PKZB, RSCAN, R2SCAN, REVSCAN, SCAN, TPSS, HLE17
- Hybrids: B1LYP, B1PW91, B1WC, B3LYP, B3LYP*, B3LYP5, B3LYP5, B3P86, B3PW91, B97, B97-1 B97-2, B97-3, BHANDH, BHANDHLYP, EDF2, MB3LYP-RC04, MPW1K, MPW1PW, MPW3LYP, MPW3PW, MPWLYP1M, O3LYP, OPBE, PBE0, PBE0-13, REVB3LYP, REVPBE, RPBE, SB98-1A, SB98-1B, SB98-1C, SB98-2A, SB98-2B, SB98-2C, SOGGA11-X, SSB, SSB-D, X3LYP
- MetaHybrids: B86B95, B88B95, BB1K, M05, M05-2X, M06, M06-2X, M06-HF, M08-HX, M08-SO, MPW1B95, MPWB1K, MS2H, MVSH, PW6B95, PW86B95, PWB6K, REVSCAN0, SCAN0, REVTPSSH, TPSSH, X1B95, XB1K
- Range-separated: CAM-B3LYP, CAMY-B3LYP, HJS-PBE, HJS-PBESOL, HJS-B97X, HSE03, HSE06, LRC-WPBE, LRC-WPBEH, LCY-BLYP, LCY-PBE, M06-SX, M11, MN12-SX, N12-SX, TUNED-CAM-B3LYP, WB97, WB97X

One can use one of the acronyms in the list above or one can use the functionals described at the LibXC website <https://libxc.gitlab.io/functionals> (where one should include XC_ at the beginning). Example usage for the BP86 functional:

```
XC
  LibXC BP86
End
```

Alternative

⁴⁹ S. Lehtola, C. Steigemann, M.J.T. Oliveira, M.A.L. Marques, *Recent developments in LibXC – A comprehensive library of functionals for density functional theory*, *SoftwareX* 7, 1 (2018) (<https://doi.org/10.1016/j.softx.2017.11.002>)

⁵⁴ S. Lehtola, M.A.L. Marques, *Reproducibility of density functional approximations: how new functionals should be reported*, *Journal of Chemical Physics* 159, 114116 (2023) (<https://doi.org/10.1063/5.0167763>)

⁴⁸ M.A.L. Marques, M.J.T. Oliveira, and T. Burnus, *Libxc: a library of exchange and correlation functionals for density functional theory*, *Computer Physics Communications* 183, 2272 (2012) (<https://doi.org/10.1016/j.cpc.2012.05.007>)


```
XC
  LibXC XC_GGA_X_B88 XC_GGA_C_P86
End
```

When using LibXC, the ADF output will provide the reference for the selected functional, see also the LibXC website <https://libxc.gitlab.io/functionals>.

Do not use any of the subkeys LDA, GGA, METAGGA, MODEL, HARTREEFOCK, HYBRID, METAHYBRID, XCFUN, or RANGESEP in combination with the subkey LIBXC. One can use the DISPERSION key with LIBXC. For many XC functionals the optimized dispersion parameters will then be used automatically, please check the output in this case. Note that in many cases you have to include the DISPERSION key and include the correct dispersion parameters yourself.

Note that ADF cannot calculate VV10 dispersion-dependent LibXC functionals, like VV10, LC-VV10, B97M-V, WB97X-V, WB97M-V. Before ADF2025, ADF would stop if one tried to calculate a VV10 dispersion dependent functional. Starting from ADF2025, ADF will not stop if one includes another dispersion method (with the DISPERSION key), in which case the VV10 dispersion-dependent part of the functional will be replaced with the other dispersion method that is specified.

Starting with AMS2026 many of the LibXC functionals can be used with frozen cores, NMR calculations, the (AO)RESPONSE key, or the EPR/ESR g-tensor. However, meta-XC functionals, like meta-GGA or meta-hybrid XC functionals cannot be used with frozen cores, NMR calculations, the (AO)RESPONSE key, or the EPR/ESR g-tensor. Note also that the kernel in (range-separated) hybrids in case of the (AO)RESPONSE key may be incorrect. Most LibXC functionals can be used in combination with geometry optimization, TS, IRC, LT, numerical frequencies, and excitation energies (ALDA kernel used). For a few GGA LibXC functionals, analytical frequencies can be calculated, and one can use the full kernel in the calculation of excitation energies (if FULLKERNEL is included as subkey of the key EXCITATIONS). In case of LibXC (meta-)hybrids and calculating excitation energies, the kernel consists of the Hartree-Fock percentage times the Hartree-Fock kernel plus one minus the Hartree-Fock percentage times the ALDA kernel (thus no (meta-)GGA kernel). For the LibXC range-separated functionals, like CAM-B3LYP, starting from ADF2016.102, the kernel consists of range-separated ALDA plus the kernel of the range-separated exact exchange part. In ADF2016.101, the kernel for LibXC range-separated functionals, like CAM-B3LYP, used a 100% ALDA plus range-separated exact exchange kernel (the ALDA part was not range-separated corrected). For the range-separated functionals WB97 and WB97X, one can use the full kernel in the calculation of excitation energies.

4.2.13 Dispersion corrections

DFT-D4 functionals

Grimme's dispersion correction, D4(EEQ)⁵⁰, was added in AMS 2019.3 and updated in AMS 2025.1. In contrast to the earlier D3 dispersion correction, in D4(EEQ) the atomic coordination-dependent dipole polarizabilities are scaled based on atomic partial charges obtained from an electronegativity equilibrium model (EEQ). Compared to D3, the introduced charge dependence improves thermochemical properties, especially for systems containing metals. The authors recommend D4(EEQ) as a physically improved and more sophisticated dispersion model in place of D3. In ADF2025, parameters for Grimme4 were updated according to version 3.7.0 of dftd4 (<https://github.com/dftd4/dftd4>).

Dispersion Grimme4 {s6=...} {s8=...} {a1=...} {a2=...}

If Dispersion Grimme4 is present in the XC block, the D4(EEQ) dispersion correction (with the electronegativity equilibrium model) by the Grimme group^{Page 99, 50} will be added to the total bonding energy, gradient, and second derivatives, where applicable.

Version 3.7.0 of dftd4 is used (<https://github.com/dftd4/dftd4>), which includes parameters for actinides. For elements for which no parameters are present ($103 < Z < 112$, $Z > 118$), the parameters for the element $Z'=Z-32$ will be used.

⁵⁰ E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, S. Grimme, *A Generally Applicable Atomic-Charge Dependent London Dispersion Correction Scheme*, *ChemRxiv* 7430216 v2 (<https://doi.org/10.26434/chemrxiv.7430216>)

The D4(EEQ) model has four general parameters: s_6 , s_8 , a_1 , and a_2 , and their value should depend on the XC functional used. For many functionals the D4(EEQ) parameters are **predefined**, for example: B1B95, B3LYP, B3PW91, BLYP, BP86, CAM-B3LYP, HartreeFock, OLYP, OPBE, PBE, PBE0, PW6B95, REVPBE, RPBE, TPSS, TPSSH. For these functionals it is enough to specify `Dispersion Grimme4` in the input block. E.g.:

```
XC
  GGA BLYP
  Dispersion Grimme4
END
```

For many other functionals you should explicitly specify the D4(EEQ) parameters in the `Dispersion` key (otherwise the PBE parameters will be used). For example, for the PW91 functional you could use the following input (although this is not necessary, since the parameters for PW91 are predefined):

```
XC
  GGA PW91
  Dispersion Grimme4 s6=1.0 s8=0.7728 a1=0.3958 a2=4.9341
END
```

The D4(EEQ) parameters for many functionals can be found in the supporting information of the following paper:⁵⁰, see also <https://github.com/dftd4/dftd4>.

For double hybrids, see the *Double Hybrid Functionals* (page 90) section of the user manual.

DFT-D3 functionals

The D3 dispersion correction by Stefan Grimme is available in ADF, and updated in ADF2025.1. Grimme and his coworkers at the Universität Münster outlined the parametrization of this correction, dubbed DFT-D3, in Ref.⁵³. A slightly improved version with a more moderate BJ damping function appeared later, and was called DFT-D3-BJ.⁵¹ The authors list the advantages of this method as the following:

- It is less empirical, i.e., the most important parameters are computed from first principles by standard Kohn-Sham (KS)-(TD)DFT.
- The approach is asymptotically correct with all DFs for finite systems (molecules) or nonmetallic infinite systems. It gives the almost exact dispersion energy for a gas of weakly interacting neutral atoms and smoothly interpolates to molecular (bulk) regions.
- It provides a consistent description of all chemically relevant elements of the periodic system (nuclear charge $Z = 1-94$).
- Atom pair-specific dispersion coefficients and cutoff radii are explicitly computed.
- Coordination number (geometry) dependent dispersion coefficients are used that do not rely on atom connectivity information (differentiable energy expression).
- It provides similar or better accuracy for “light” molecules and a strongly improved description of metallic and “heavier” systems.

Parametrizations are available for: B3LYP, TPSS, BP86, BLYP, revPBE, PBE, PBEsol, RPBE, and many more functionals, and will be automatically set if one of these functionals is used. Otherwise, PBE parameters will be used. The parameters can be set manually; see the XC key block. In ADF2025, parameters for Grimme3 and Grimme3 BJDAMP were updated according to version 1.2.1 of s-dftd3 (<https://github.com/dftd3/simple-dftd3>).

⁵³ S. Grimme, J. Anthony, S. Ehrlich, and H. Krieg, *A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu*, *Journal of Chemical Physics* 132, 154104 (2010) (<https://doi.org/10.1063/1.3382344>).

⁵¹ S. Grimme, S. Ehrlich, and L. Goerigk, *Effect of the Damping Function in Dispersion Corrected Density Functional Theory*, *Journal of Computational Chemistry* 32, 1457 (2011) (<https://doi.org/10.1002/jcc.21759>).

DISPERSION Grimme3 BJDAMP

If DISPERSION Grimme3 BJDAMP is present, a dispersion correction (DFT-D3(BJ)) by Grimme⁵¹ will be added to the total bonding energy, gradient, and second derivatives, where applicable.

Version 1.2.1 of s-dftd3 for DFT-D3(BJ) is used (<https://github.com/dftd3/simple-dftd3>), which includes parameters for actinides. For elements for which no parameters are present ($Z > 103$), the parameters for the element $Z' = Z - 32$ will be used.

For many XC functionals, parametrizations are implemented e.g. for B3LYP, TPSS, BP86, BLYP, PBE, PBEsol, RPBE, and SCAN. For example, this is the input block for specifying the PBE functional with Grimme3 BJDAMP dispersion correction (PBE-D3(BJ)):

```
XC
  GGA PBE
  DISPERSION Grimme3 BJDAMP
End
```

The D3(BJ) dispersion correction has four general parameters that depend on the XC functional. One can override the default parametrization by using $PAR1=.$, $PAR2=.$, etc. In the table, the relation is shown between the parameters and the real parameters in the Dispersion correction.

variable	variable on Bonn website	(https://www.chemie.uni-bonn.de/grimme/de/software/dft-d3/bj_damping)
PAR1	s6	
PAR2	a1	
PAR3	s8	
PAR4	a2	

For example, this is the input block for specifying the PBE-D3(BJ)-GP parametrization by Proppe et al.⁹¹ (i.e. $a_1 = 0$, $s_8 = 0$, $a_2 = 5.6841$):

```
XC
  GGA PBE
  DISPERSION Grimme3 BJDAMP PAR2=0 PAR3=0 PAR4=5.6841
End
```

DISPERSION Grimme3

If DISPERSION Grimme3 is present, a dispersion correction (DFT-D3) by Grimme^{Page 100, 53} will be added to the total bonding energy, gradient, and second derivatives, where applicable.

Version 1.2.1 of s-dftd3 for DFT-D3 is used (<https://github.com/dftd3/simple-dftd3>), which includes element-specific parameters for actinides. For elements for which no parameters are present ($Z > 103$), the parameters for the element $Z' = Z - 32$ will be used.

Parametrizations are available for many XC functionals, e.g. for B3LYP, TPSS, BP86, BLYP, revPBE, PBE, PBEsol, RPBE, and SCAN, and many more, and will be automatically set if one of these functionals is used. There are also parameters directly recognized for S12g and S12h. For other functionals, PBE-D3 parameters are used as default. You can explicitly specify the three parameters.

variable	variable on Bonn website	(https://www.chemie.uni-bonn.de/grimme/de/software/dft-d3/zero_damping)
PAR1	s6	
PAR2	sr,6	
PAR3	s8	

⁹¹ J. Proppe, S. Guglerb and M. Reiher, *Gaussian Process-Based Refinement of Dispersion Corrections* <https://arxiv.org/pdf/1906.09342.pdf>

DFT-D functionals

An implementation of dispersion corrections, called DFT-D is available in ADF. Like DFT-D3, this implementation is easy to use and is also supported by the GUI.

This DFT-D implementation is based on the paper by Grimme^{Page 86, 38} and is extremely easy to use. The correction is switched on by specifying *DISPERSION*, possibly with parameters, in the XC input block. See *description of the XC input block* (page 80) for details about the *DISPERSION* keyword.

Post-SCF energies for different DFT-D or GGA-D functionals are also included in the table printed when the METAGGA keyword is specified. These include: BLYP-D, PBE-D, BP86-D, TPSS-D, B3LYP-D, and B97-D. NOTE: this option does not require specifying a *DISPERSION* keyword in the XC block and thus there is **no correction added to the energy gradient** in this case. Please also note that although the original B97 functional includes HF exchange (and is thus a hybrid functional), the B97-D is a pure GGA. B3LYP-D is, however, a hybrid functional. The following functional-dependent global scaling factors s_6 are used: 1.2 (BLYP-D), 0.75 (PBE-D), 1.05 (BP86-D), 1.0 (TPSS-D), 1.05 (B3LYP-D), and 1.25 (B97-D). These are fixed and cannot be changed.

Regarding performance of different functionals, testing has shown that BLYP-D gives good results for both energies and gradients involving VdW interactions. Post-SCF energy-only calculations at fixed geometries showed that B97-D also gives good binding energies compared to high-level reference data. Thorough comparison of different DFT-D functionals can be found in Ref.⁷⁰.

Note: The original paper by Grimme included parameters for elements H throughout Xe. In ADF2009.01 values for dispersion parameters for DFT-D functionals for heavier elements (Cs-Rn) have been added. These newer values have not been tested extensively. Thus, in this implementation, no dispersion correction is added for interactions involving atoms heavier than Radon.

DFT-D is invoked with the XC block, for example:

```
XC
  GGA BLYP
  Dispersion
END
```

DISPERSION {s6scaling} {RSCALE=r0scaling}

If the *DISPERSION* keyword is present (without the argument Grimme3), a dispersion correction (DFT-D) by Grimme^{Page 86, 38} will be added to the total bonding energy, gradient, and second derivatives, where applicable. The global scaling factor with which the correction is added depends on the exchange-correlation functional used at SCF, but it can be modified using the *s6scaling* parameter. The following scaling factors are used (with the XC functional in parentheses): 1.20 (BLYP), 1.05 (BP), 0.75 (PBE), 1.05 (B3LYP). In all other cases a factor 1.0 is used unless modified via the *s6scaling* parameter. The SSB-D functional includes the dispersion correction (factor 0.847455) by default.

The van der Waals radii used in this implementation are hard coded in ADF. However, it is possible to modify the global scaling parameter for them using the *RSCALE=r0scaling* argument. The default value is 1.1 as proposed by Grimme^{Page 86, 38}.

⁷⁰ S. Grimme, J. Antony, T. Schwabe and C. Mück-Lichtenfeld, *Density Functional Theory with Dispersion Corrections for Supramolecular Structures, Aggregates, and Complexes of (Bio)Organic Molecules*, *Organic & Biomolecular Chemistry* 5, 741 (2007) (<https://doi.org/10.1039/B615319B>)

dDsC: density-dependent dispersion correction

The DISPERSION dDsC key invokes the density-dependent dispersion correction⁵⁵, which has been parametrized for the functionals BLYP, PBE, BP, revPBE, B3LYP, PBE0, and BHANDHLYP.

```
XC
  GGA BLYP
  Dispersion dDsC
END
```

For other functionals, one can set the dDsC parameters ATT0 and BTT0 with

```
XC
  ...
  DISPERSION dDsC ATT0=att0 BTT0=btt0
END
```

The dispersion dDsC in ADF cannot be used with fragments larger than one atom. The reason is that ADF uses the Hirshfeld partitioning on fragments for dDsC, which is only correct if the fragments are atoms.

DFT-ulg

The DISPERSION UFF key invokes the universal correction of density functional theory to include London dispersion (DFT-ulg)⁵⁶, which has been parametrized for all elements up to Lr (Z=103), and for the functional PBE, PW91, and B3LYP. For other functionals, the PBE parameters will be used. Example:

```
XC
  GGA PBE
  Dispersion UFF
END
```

DFT-MBD functionals

The DISPERSION MBD key invokes the MBD@rsSCS method⁵⁷, which is designed to accurately describe long-range correlation (and thus dispersion) in finite-gap systems, including at the same time a description of the short-range interactions from the underlying DFT computation of the electronic structure. The MBD (many-body dispersion) method⁵⁸ obtains an accurate description of van der Waals (vdW) interactions that includes both screening effects and treatment of the many-body vdW energy to infinite order. The revised MBD@rsSCS method^{Page 103, 57} employs a range separation (rs) of the self-consistent screening (SCS) of polarizabilities and the calculation of the long-range correlation energy. It has been parametrized for the elements H-Ba, Hf-Rn, and for the functional PBE and PBE0. Note that the MBD@rsSCS method depends on Hirshfeld charges. In calculating forces the dependence of the Hirshfeld charges on the actual geometry is neglected. The MBD method is implemented in case the BeckeGrid is used for the numerical integration. Example for PBE MBD@rsSCS:

⁵⁵ S.N. Steinmann, and C. Corminboeuf, *Comprehensive Benchmarking of a Density-Dependent Dispersion Correction*, *Journal of Chemical Theory and Computation* 7, 3567 (2011) (<https://doi.org/10.1021/ct200602x>).

⁵⁶ H. Kim, J.-M. Choi, W.A. Goddard, *Universal Correction of Density Functional Theory to Include London Dispersion (up to Lr, Element 103)*, *Journal of Physical Chemistry Letters* 3, 360 (2012) (<https://doi.org/10.1021/jz2016395>).

⁵⁷ A. Ambrosetti, A.M. Reilly, Robert A. DiStasio Jr., A. Tkatchenko, *Long-range correlation energy calculated from coupled atomic response functions*, *Journal of Chemical Physics* 140, 18A508 (2014) (<https://doi.org/10.1063/1.4865104>).

⁵⁸ A. Tkatchenko, R.A. DiStasio Jr., R. Car, M. Scheffler *Accurate and Efficient Method for Many-Body van der Waals Interactions*, *Physical Review Letters* 108, 236402 (2012) (<https://doi.org/10.1103/PhysRevLett.108.236402>).

```
XC
  GGA PBE
  Dispersion MBD
END
```

One can use user-defined values with:

```
XC
  Dispersion MBD {RSSCS|TS} {BETA=beta}
END
```

MBD {RSSCS|TS} {BETA=beta}

The default method for MBD is MBD@rsSCS. Optionally, one can use MBD@TS or change the used parameter β with setting beta.

4.2.14 Post-SCF energy functionals

GGA energy functionals

In principle, you may specify different functionals to be used for the *potential*, which determines the self-consistent charge density, and for the *energy* expression that is used to evaluate the (XC part of the) energy of the charge density. To be consistent, one should generally apply the same functional to evaluate the potential and energy, respectively. Two reasons, however, may lead one to do otherwise:

- The evaluation of the GGA part in the *potential* is more time-consuming than LDA. The effect of the GGA term in the potential on the self-consistent charge density is often not very large. From the point of view of computational efficiency, it may therefore be attractive to solve the SCF equations at the LDA level (i.e. not including GGA terms in the potential), and to apply the full expression, including GGA terms, to the energy evaluation *a posteriori* (post-SCF).
- A particular XC functional may have only an implementation for the potential, but not for the energy (or vice versa). This is a rather special case, intended primarily for fundamental research of Density Functional Theory, rather than for routine production runs.

One possibility is to calculate a whole list of post-SCF energy functionals using the METAGGA keyword; see the next section. For some functionals the next possibility is enough. One has to specify different functionals for potential and energy evaluations respectively, using:

```
XC
  {LDA {Apply} LDA {Stoll}}
  {GGA {Apply} GGA}
end
```

Apply

States whether the functional defined on the corresponding line will be used self-consistently (in the SCF-potential), or only post-SCF, i.e. to evaluate the XC energy corresponding to the charge density. The value of `Apply` must be SCF or Energy. A value `postSCF` will also be accepted and is equivalent to Energy. A value `Potential` will also be accepted and is equivalent to SCF. For each record separately, the default (if no `Apply` value is given in that record) is SCF. For each of the two terms (LDA, GGA) in the functional: if no record with Energy specification is found in the data block, the evaluation of the XC energy will use the same functional as is applied for the potential.

LDA, GGA

See the XC potential section for all possible values.

Meta-GGA and hybrid energy functionals

The post-SCF energy calculation is an easy and cheap way to get a reasonable guess for the bond energies for different XC functionals at the same time. Note that post-SCF energy calculations for a certain XC functional will not be so accurate if the functional form of the XC functional used in the SCF is very different from the XC functional used post-SCF. The relative accuracy of post-SCF energies may not be so high if one looks at small energy differences. For accurate energy calculations it is recommended to use the same XC functional during the SCF as for the energy.

The calculation of a large, pre-specified list of LDA, GGA, and meta-GGA energy functionals is invoked by specifying

```
METAGGA
```

as a separate keyword. The following (incomplete) list gives an idea of the (meta-)GGA density functionals that will then be calculated (the t-MGGA functional is the θ -MGGA functional of Ref.⁵⁹):

```
BP, PW91, mPW, BLYP, PBE, RPBE, revPBE, mPBE, OLYP, OPBE, KCIS, PKZB, VS98, FT97,   
→BLAP3,   
HCTH, tau-HCTH, BmTau1, BOP, OLAP3, TPSS, KT1, KT2, B97, M06-L, t-MGGA.
```

The hybrid GGA and hybrid meta-GGA energy functionals are calculated if in addition to the METAGGA key, the key

```
HARTREEFOCK
```

is included. The following (incomplete) list gives an idea of the extra hybrid (meta-)GGA density functionals that will then be calculated:

```
B3LYP, B3LYP*, B1LYP, KMLYP, O3LYP, X3LYP, BHandH, BHandHLYP, B1PW91, MPW1PW, MPW1K,   
PBE0, OPBE0, TPSSh, tau-HCTH-hybrid, B97, M05, M05-2X, M06, M06-2X.
```

The keys METAGGA and HARTREEFOCK can be used in combination with any XC potential. Note that at the moment hybrid functionals cannot be used in combination with frozen cores. Also most METAGGA functionals will give wrong results if used in combination with frozen cores. Thus it is best to use an all-electron basis set if one of the keywords METAGGA or HARTREEFOCK is used. One should include the HARTREEFOCK keyword also in the create runs of the atoms. In ADF, the hybrid energies only make sense if the calculation is performed with completely filled orbitals. In case of a high-spin electron configuration, one can do ROKS; see [ROKS for high-spin open shell molecules](#) (page 61).

The Examples document describes an application to the OH molecule for the METAGGA option. More output, on the total XC energy of the system, can be obtained by specifying

```
PRINT METAGGA
```

This latter option is intended for debugging purposes mainly and is not recommended for general use.

The implementation calculates the total XC energy for a system and writes it to a file. This is always done in Create runs. If the basic fragments are atoms, the keyword

```
ENERGYFRAG   
  ATOM [filename]   
  ATOM [filename]   
  ...   
END
```

specifies that different atomic fragment files are to be used in the meta-GGA energy analysis than the regular atomic fragment files from the create runs. This keyword cannot be used for molecular fragment files. In order to compare meta-GGA energy differences between molecular fragments and the total molecule, results from the various calculations need to be combined by hand.

⁵⁹ P. de Silva and C. Corminboeuf, *Communication: A new class of non-empirical explicit density functionals on the third rung of Jacob's ladder*, *Journal of Chemical Physics* 143, 111105 (2015) (<https://doi.org/10.1063/1.4931628>)

In such situations, it is advisable to use a somewhat higher integration accuracy than one would normally do, at least for the smaller fragments, as there is no error cancellation as in a regular ADF bond energy analysis.

A general comment is that some functionals show a more stable behavior than others (at least in our current implementation). In general, the functionals which are dependent on the Laplacian of the density may display a large variation with respect to basis set changes or different numerical integration accuracy. For this reason we currently recommend FT97 in favor of FT98. Similarly, the results with the BmTau1 functional should still be carefully checked. In our test calculations on the G2 set of molecules, the VS98 showed best performance, both for the average error and for the maximum error. The G2 set consists only of small molecules with elements up to Cl. The relative performance for transition metals and heavy elements is unknown and may well be very different from the ordering for the G2 set.

Post Hartree-Fock energy functionals

This section is largely adapted from text by the authors of Ref. ^{Page 106, 60}:

In the early days of DFT, non-self-consistent Kohn-Sham energy was often evaluated on Hartree-Fock (HF) densities as a way to test new approximations. This method was called HF-DFT. It has been discovered that in some cases, HF-DFT actually gave more accurate answers when compared to self-consistent DFT calculations. In Ref. ⁶⁰, it was found that DFT calculations can be categorized into two different types of calculations. The error of an approximate functional can be decomposed into two parts: error from the functional (functional error), and error from the density (density-driven error). For most calculations, functional error is dominant, and here self-consistent DFT is usually better than non-self-consistent DFT on more accurate densities (called density-corrected DFT (DC-DFT)). Unlike these 'normal' calculations, there is a class of calculations where the density-driven error is much larger, so DC-DFT gives a better result than self-consistent DFT. These calculations can be classified as 'abnormal'. HF-DFT is a simple implementation of DC-DFT, and a small HOMO-LUMO gap is an indicator of an 'abnormal' calculation, thus HF-DFT would perform better in such cases.

In ADF, one can do HF-DFT with:

```
XC
  HartreeFock
END
MetaGGA
```

This will produce a large, pre-specified list of LDA, GGA, meta-GGA, hybrid, and meta-hybrid energy functionals.

4.3 Relativistic effects

Scalar relativistic effects using the ZORA formalism are included by default in ADF calculations. Different relativistic options, such as spin-orbit coupling, can be included using the `Relativity` key.

Note: Starting from the 2020 version, ZORA scalar relativistic effects are included by default. In 2019.3 and previous versions of ADF, relativistic effects were **not** included by default.

```
Relativity
  Formalism [Pauli | ZORA | X2C | RA-X2C]
  Level [None | Scalar | Spin-Orbit]
  Potential [MAPA | SAPA]
  SpinOrbitMagnetization [NonCollinear | Collinear | CollinearX | CollinearY | ↵
↵CollinearZ]
End
```

⁶⁰ M.-C. Kim, E. Sim, and K. Burke, *Understanding and Reducing Errors in Density Functional Calculations*, *Physical Review Letters* 111, 2073003 (2013) (<https://doi.org/10.1103/PhysRevLett.111.073003>)

Relativity**Type**

Block

Description

Options for relativistic effects.

Formalism**Type**

Multiple Choice

Default value

ZORA

Options

[Pauli, ZORA, X2C, RA-X2C]

Description

Note that if Level is None, no relativistic effects are taken into account, irrespective of the chosen formalism.

Pauli stands for the Pauli Hamiltonian.

ZORA means the Zero Order Regular Approximated Hamiltonian, recommended.

X2C and RA-X2C both stand for an exact transformation of the 4-component Dirac equation to 2-components.

X2C is the modified Dirac equation by Dyll.

RA-X2C is the regular approach to the modified Dirac equation.

Level**Type**

Multiple Choice

Default value

Scalar

Options

[None, Scalar, Spin-Orbit]

GUI name

Relativity

Description

None: No relativistic effects.

Scalar: Scalar relativistic.

This option comes at very little cost.

Spin-Orbit: Spin-orbit coupled.

This is the best level of theory, but it is (4-8 times) more expensive than a normal calculation. Spin-orbit effects are generally quite small, unless there are very heavy atoms in your system, especially with p valence electrons (like Pb).

See also the SpinOrbitMagnetization subkey.

Potential

Type

Multiple Choice

Default value

MAPA

Options

[MAPA, SAPA]

Description

Starting from ADF2017 instead of SAPA (the Sum of neutral Atomic potential Approximation) MAPA is used by default for ZORA. The MAPA (the Minimum of neutral Atomic potential Approximation) at a point is the minimum of the neutral Atomic potentials at that point. Advantage of MAPA over SAPA is that the gauge dependence of ZORA is reduced. The ZORA gauge dependency is small for almost all properties, except for the electron density very close to a heavy nucleus. The electron density very close to a heavy nucleus can be used for the interpretation of isomer shifts in Mossbauer spectroscopy.

SpinOrbitMagnetization**Type**

Multiple Choice

Default value

CollinearZ

Options

[NonCollinear, Collinear, CollinearX, CollinearY, CollinearZ]

Description

Relevant only for spin-orbit coupling and if unrestricted key has been activated.

Most XC functionals have as one ingredient the spin polarization in case of unrestricted calculations. Normally the direction of the spin quantization axis is arbitrary and conveniently chosen to be the z-axis.

However, in a spin-orbit calculation the direction matters, and it is arbitrary to put the z-component of the magnetization vector into the XC functional. There is also the exotic option to choose the quantization axis along the x or y axis.

It is also possible to plug the size of the magnetization vector into the XC functional. This is called the non-collinear approach.

- NonCollinear: the non-collinear method.
- CollinearXYZ: use the x, y, or z component as spin polarization for the XC functional.
- Collinear: the same as CollinearZ.

MAPA and SAPA

The SAPA method is described in Ref.¹ for the BAND program. The same potential was used in the ADF program. However, starting from ADF2017, instead of SAPA (the Sum of neutral Atomic Potential Approximation) MAPA is used by default for ZORA. The MAPA (the Minimum of neutral Atomic Potential Approximation) at a point is the minimum of the neutral atomic potentials at that point. The advantage of MAPA over SAPA is that the gauge dependence of ZORA is reduced. The ZORA gauge dependence is small for almost all properties, except for the electron density very close to a heavy nucleus. The electron density very close to a heavy nucleus can be used for the interpretation of isomer shifts in Mössbauer spectroscopy.

Recommendations:

¹ P.H.T. Philipsen, E. van Lenthe, J.G. Snijders and E.J. Baerends, *Relativistic calculations on the adsorption of CO on the (111) surfaces of Ni, Pd, and Pt within the zeroth-order regular approximation*, *Physical Review B* 56, 13556 (1997) (<https://doi.org/10.1103/PhysRevB.56.13556>)

```

Relativity
  Level Scalar
  Formalism ZORA
  Potential MAPA
End

```

or

```

Relativity
  Level Spin-Orbit
  Formalism ZORA
  Potential MAPA
End

```

4.3.1 Pauli

Specification of the Pauli formalism means that the first-order relativistic corrections (the Pauli Hamiltonian) will be used^{2,3,4,5,6,7,8,9,10,11}. In a *scalar* relativistic run ADF employs the single point-group symmetry and only the so-called *scalar* relativistic corrections, Darwin and mass-velocity. The treatment is not strictly first-order, but is *quasi*-relativistic, in the sense that the first-order scalar relativistic Pauli Hamiltonian is diagonalized in the space of the non-relativistic solutions, i.e. in the non-relativistic basis set.

The quasi-relativistic approach improves results considerably over a first-order treatment. There are, however, theoretical deficiencies due to the singular behavior of the Pauli Hamiltonian at the nucleus. This would become manifest in a complete basis set, but results are reasonable with the normally employed basis sets. However, this aspect implies that it is not recommended to apply this approach with an all-electron basis set for the heavy atoms, and for very heavy elements even a frozen core basis set often fails to give acceptable results. The problems with the quasi-relativistic approach of the Pauli Hamiltonian are discussed, for example, in Ref.¹².

² J.G. Snijders and E.J. Baerends, *A perturbation theory approach to relativistic calculations. I. Atoms*, Molecular Physics 36, 1789 (1978) (<https://doi.org/10.1080/00268977800102771>)

³ J.G. Snijders, E.J. Baerends and P. Ros, *A perturbation theory approach to relativistic calculations. II. Molecules*, Molecular Physics 38, 1909 (1979) (<https://doi.org/10.1080/00268977900102941>)

⁴ T. Ziegler, J.G. Snijders and E.J. Baerends, *Relativistic effects on bonding*, Journal of Chemical Physics 74, 1271 (1981) (<https://doi.org/10.1063/1.441187>)

⁵ R.L. DeKock, E.J. Baerends, P.M. Boerrigter and J.G. Snijders, *On the nature of the first excited states of the uranyl ion*, Chemical Physics Letters 105, 308 (1984) ([https://doi.org/10.1016/0009-2614\(84\)85036-8](https://doi.org/10.1016/0009-2614(84)85036-8))

⁶ R.L. DeKock, E.J. Baerends, P.M. Boerrigter and R. Hengelmolen, *Electronic structure and bonding of Hg(CH₃)₂, Hg(CN)₂, Hg(CH₃)₂(CN), Hg(CCCCH₃)₂, and Au(PMe)₃(CH₃)*, Journal of the American Chemical Society 106, 3387 (1984) (<https://doi.org/10.1021/ja00324a001>)

⁷ P.M. Boerrigter, *Spectroscopy and bonding of heavy element compounds*, 1987, Vrije Universiteit.

⁸ P.M. Boerrigter, M.A. Buijse and J.G. Snijders, *Spin-Orbit interaction in the excited states of the dihalogen ions F₂⁺, Cl₂⁺ and Br₂⁺*, Chemical Physics 111, 47 (1987) ([https://doi.org/10.1016/0301-0104\(87\)87007-6](https://doi.org/10.1016/0301-0104(87)87007-6))

⁹ P.M. Boerrigter, E.J. Baerends and J.G. Snijders, *A relativistic LCAO Hartree-Fock-Slater investigation of the electronic structure of the actinocenes M(COT)₂, M=Th, Pa, U, Np and Pu*, Chemical Physics 122, 357 (1988) ([https://doi.org/10.1016/0301-0104\(88\)80018-1](https://doi.org/10.1016/0301-0104(88)80018-1))

¹⁰ T. Ziegler, V. Tschinke, E.J. Baerends, J.G. Snijders and W. Ravenek, *Calculation of bond energies in compounds of heavy elements by a quasi-relativistic approach*, Journal of Physical Chemistry 93, 3050 (1989) (<https://doi.org/10.1021/j100345a036>)

¹¹ J. Li, G. Schreckenbach and T. Ziegler, *A Reassessment of the First Metal-Carbonyl Dissociation Energy in M(CO)₄ (M = Ni, Pd, Pt), M(CO)₅ (M = Fe, Ru, Os), and M(CO)₆ (M = Cr, Mo, W) by a Quasirelativistic Density Functional Method*, Journal of the American Chemical Society 117, 486 (1995) (<https://doi.org/10.1021/ja00106a056>)

¹² E. van Lenthe, A.E. Ehlers and E.J. Baerends, *Geometry optimization in the Zero Order Regular Approximation for relativistic effects*, Journal of Chemical Physics 110, 8943 (1999) (<https://doi.org/10.1063/1.478813>)

4.3.2 ZORA

The ZORA approach gives generally better results than the Pauli formalism. For all-electron calculations, and in fact also for calculations on very heavy elements (actinides), the Pauli method is absolutely unreliable. Therefore the ZORA method is the recommended approach for relativistic calculations with ADF.

ZORA refers to the Zero-Order Regular Approximation^{Page 109, 1217181920}. This formalism requires special basis sets, primarily to include much steeper core-like functions; applying the ZORA method with other, non-adapted basis sets, gives unreliable results. The ZORA basis sets can be found in subdirectories under the \$AMSHOME/atomicdata/ADF/ZORA directory.

The ZORA formalism can also be used in geometry optimizations. However, there is a slight mismatch between the energy expression and the potential in the ZORA approach, which has the effect that the geometry where the gradients are zero does not exactly coincide with the point of lowest energy. The differences are very small, but not completely negligible, on the order of 0.0001 angstrom.

4.3.3 X2C and RA-X2C

X2C stands for an exact transformation of the 4-component Dirac equation to 2 components²¹²². RA-X2C also stands for an exact transformation of the 4-component Dirac equation to 2 components, in this case using a regular approach to calculate the transformation matrix. In practice, however, approximations are often made, and this is also true for the implementation in ADF. In the X2C and RA-X2C method implemented in ADF, first the 4-component Dirac equation for a model potential (MAPA) of the molecule is calculated for the given ADF basis set, using the modified Dirac equation by Dyall¹³ for X2C, or using the regular approach¹⁴ to the modified Dirac equation for RA-X2C.

With the method used in ADF, in the basis set limit X2C and RA-X2C should lead to the same results for the model potential (MAPA). However, since in practice always a finite basis set is used, even for the model potential the results for X2C and RA-X2C will differ. Next the (electronic) 4-component Dirac solutions are transformed exactly to 2 components¹⁵. The transformation used is also used to calculate an effective one-electron 2-component kinetic energy operator in a basis set representation. This kinetic energy matrix is then assumed to be constant in further ADF SCF calculation on the molecule. The full Hamiltonian is approximated using the electron density in the 2-component picture, the so-called Foldy-Wouthuysen picture.

In a similar way, a spin-free (scalar relativistic) form of X2C and RA-X2C is calculated. The spin-free form of X2C and RA-X2C will be different even in the basis set limit, see Ref.¹⁶.

X2C and RA-X2C in ADF can be used in single-point calculations only. An all-electron basis set is needed. For bond energies, polarizabilities, and TD-DFT excitation energies the Foldy-Wouthuysen picture will be used. For the calculation

¹⁷ E. van Lenthe, E.J. Baerends and J.G. Snijders, *Relativistic regular two-component Hamiltonians*, *Journal of Chemical Physics* 99, 4597 (1993) (<https://doi.org/10.1063/1.466059>)

¹⁸ E. van Lenthe, E.J. Baerends and J.G. Snijders, *Relativistic total energy using regular approximations*, *Journal of Chemical Physics* 101, 9783 (1994) (<https://doi.org/10.1063/1.467943>)

¹⁹ E. van Lenthe, J.G. Snijders and E.J. Baerends, *The zero-order regular approximation for relativistic effects: The effect of spin-orbit coupling in closed shell molecules*, *Journal of Chemical Physics* 105, 6505 (1996) (<https://doi.org/10.1063/1.472460>)

²⁰ E. van Lenthe, R. van Leeuwen, E.J. Baerends and J.G. Snijders, *Relativistic regular two-component Hamiltonians*, *International Journal of Quantum Chemistry* 57, 281 (1996) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1996\)57:3%3C281::AID-QUA2%3E3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-461X(1996)57:3%3C281::AID-QUA2%3E3.0.CO;2-U))

²¹ K.G. Dyall, *Interfacing relativistic and nonrelativistic methods. I. Normalized elimination of the small component in the modified Dirac equation*, *Journal of Chemical Physics* 106, 9618 (1997) (<https://doi.org/10.1063/1.473860>)

²² W. Kutzelnigg and W. Liu, *Quasirelativistic theory equivalent to fully relativistic theory*, *Journal of Chemical Physics* 123, 241102 (2005) (<https://doi.org/10.1063/1.2137315>)

¹³ K.G. Dyall, *An exact separation of the spin-free and spin-dependent terms of the Dirac-Coulomb-Breit Hamiltonian*, *Journal of Chemical Physics* 100, 2118 (1994) (<https://doi.org/10.1063/1.466508>)

¹⁴ A.J. Sadlej and J.G. Snijders, *Spin separation in the regular Hamiltonian approach to solutions of the Dirac equation*, *Chemical Physics Letters* 229, 435 (1994) ([https://doi.org/10.1016/0009-2614\(94\)01067-6](https://doi.org/10.1016/0009-2614(94)01067-6))

¹⁵ E. van Lenthe, E.J. Baerends, and J.G. Snijders, *Construction of the Foldy-Wouthuysen transformation and solution of the Dirac equation using large components only*, *Journal of Chemical Physics* 105, 2373 (1996) (<https://doi.org/10.1063/1.472104>)

¹⁶ L. Visscher and E. van Lenthe, *On the distinction between scalar and spin-orbit relativistic effects*, *Chemical Physics Letters* 306, 357 (1999) ([https://doi.org/10.1016/S0009-2614\(99\)00458-3](https://doi.org/10.1016/S0009-2614(99)00458-3))

of the EFG, ESR g-value, and ESR A-tensor, the Dirac picture will be used. X2C and RA-X2C are not implemented for frozen cores, optimization of nuclear coordinates, frequencies, or NMR properties.

4.3.4 Spin-Orbit coupling

The Spin-Orbit option uses double-group symmetry. The symmetry-adapted orbitals are labeled by the quantum number J rather than L and any references in input to subspecies, such as a specification of occupation numbers, must refer to the double group labels.

Create runs must *not* use the Spin-Orbit formalism. The SFO analysis of Molecular Orbitals for a Spin-Orbit calculation is only implemented in the case of a scalar relativistic fragment file, which is the whole molecule.

In a Spin-Orbit run each level can allocate 2 electrons (times the dimension of the irreducible representation) as in a normal restricted calculation. However, contrary to the normal case these two electrons are not directly associated with spin- α and spin- β , but rather with the more general Kramers' symmetry. Using the unrestricted feature in order to assign different numbers of electrons to alpha and beta spin respectively cannot be applied as such. However, one can use the unrestricted option in combination with the collinear or non-collinear approximation. In that case one should use symmetry NOSYM, and each level can allocate 1 electron.

Partial ZORA

Expert option. The partial ZORA method is an analysis method to suppress spin-orbit coupling locally, such that one can analyze the effect of spin-orbit coupling into atomic contributions, see Ref.²³.

Intended for use with atomic fragments. In spin-orbit (SO) coupled ZORA calculations, the keyword can be used to suppress the SO interaction locally at selected atomic fragment types (internal ordering). There is a matching setup in the NMR program without the need for additional input. For example, if in the ADF input the following keyword is given:

```
PartialZora atom 2 4
```

this will disable SO effects at atomic fragment types 2 and 4 (internal ordering of atomic fragments). This is achieved via a modification of the atomic potentials that are used to assemble the ZORA SO integrals, as explained in the publication cited above. When used for NMR calculations, for example, this can be used to suppress spin-orbit 'heavy atom' effects on light atom NMR shielding (HALA) for purposes of analysis.

4.4 Solvents and other environments

The solvation methods SCRF (Self-Consistent Reaction Field) and VSCRF (Vertical Excitation SCRF) are no longer supported in ADF 2024. They are available in older versions; see the ADF 2023 manual on [SCRF](https://www.scm.com/doc.2023/ADF/Input/SCRF.html) (https://www.scm.com/doc.2023/ADF/Input/SCRF.html) and [VSCRF](https://www.scm.com/doc.2023/ADF/Input/VSCRF.html) (https://www.scm.com/doc.2023/ADF/Input/VSCRF.html).

²³ J. Autschbach, K. Sutter, L.A. Truflandier, E. Brendler, J. Wagler, *Atomic Contributions from Spin-Orbit Coupling to ²⁹Si NMR Chemical Shifts in Metallasilatrane Complexes*, *Chemistry - A European Journal* 18, 12533 (2012) (https://doi.org/10.1002/chem.201200746)

4.4.1 COSMO: Conductor-like Screening Model

You can study chemistry in solution, as contrasted to the gas phase, with the implementation in ADF¹ of the Conductor-like Screening Model (COSMO) of solvation^{2,3,4}. The energy derivatives can also be calculated, so geometry optimization, harmonic frequencies, et cetera are available within this model.

The COSMO model is a dielectric model in which the solute molecule is embedded in a molecule-shaped cavity surrounded by a dielectric medium with given dielectric constant ϵ . Energy-related terms are computed for a conductor first, then scaled by the function

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + x} \quad (2.1.1)$$

The empirical scaling factor x is specified in the input data block for the SOLVATION key. The block key SOLVATION turns the solvation calculation on. In most cases default values are available for the involved parameters. In order to construct the cavity, atomic cavity radii are used. The default COSMO atomic cavity radii used in ADF are the Van der Waals radii from the MM3 method by Allinger (Ref.⁵) divided by 1.2.

It is also possible to include a linear parametrization of non-electrostatic terms as a function of surface area. To include such a term, specify it in the input data block for the SOLVATION key. The default is to include only the part of this term that is proportional to the surface area (default CAV0=0.0, CAV1=0.0067639):

$$E_{\text{non-elst}} = f(\epsilon)(CAV0 + CAV1 \times \text{area}) \quad (2.1.2)$$

If a calculation was done on a fragment, then the wave function obtained would be optimal for the fragment in solution, but not optimal for gas phase. The energies with the gas phase Hamiltonian would be higher, and the apparent solvation contribution to bonding would also be higher. The net point is that normally the COSMO procedure reports the energy of Esolv(AB), but to get the solvation energy, you need to subtract E(AB, solv) from E(AB, gas) because the wave function changes (unless you are doing it post-SCF). For this you need to have the same reference fragments in each case A(g) and B(g).

Because of precision issues in ADF2016 the default surface has been changed to Delley, instead of Esurf.

```
SOLVATION
{SURF Surface {NOKEEP}}
{SOLV {Name=solvent} {Eps=78.4} {Del=1.4} {Rad=1.4}
  {Neql=1.9} {Emp=0.0} {Cav0=0.0} {Cav1=0.0067639} }
{DIV {Ndiv=3} {NFdiv=1} {Min=0.5} {OFAC=0.8}
  {leb1=23} {leb2=29} {rleb=1.5} }
{NOASS}
{RADII
  name1=value1
  name2=value2
  ...
End }
{CHARGED {Method=meth} {Conv=1e-8} {Omega=1.0} {Iter=1000}
  {Corr} {LoCosmo LoCosmoDist}}
{C-MAT How {SCF} tol=1e-10 }
```

(continues on next page)

¹ C.C. Pye and T. Ziegler, *An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package*, Theoretical Chemistry Accounts 101, 396 (1999) (<https://doi.org/10.1007/s002140050457>)

² A. Klamt and G. Schürmann, *COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient*, Journal of the Chemical Society: Perkin Transactions 2, 799 (1993) (<https://doi.org/10.1039/P29930000799>)

³ A. Klamt, *Conductor-like Screening Model for real solvents: A new approach to the quantitative calculation of solvation phenomena*, Journal of Physical Chemistry 99, 2224 (1995) (<https://doi.org/10.1021/j100007a062>)

⁴ A. Klamt and V. Jones, *Treatment of the outlying charge in continuum solvation models*, Journal of Chemical Physics 105, 9972 (1996) (<https://doi.org/10.1063/1.472829>)

⁵ N.L. Allinger, X. Zhou, J. Bergsma, *Molecular mechanics parameters*, Journal of Molecular Structure: THEOCHEM 312, 69 (1994) ([https://doi.org/10.1016/S0166-1280\(09\)80008-0](https://doi.org/10.1016/S0166-1280(09)80008-0))

(continued from previous page)

```
{DISC {SC=0.01} {LEG=4} {TOL=0.1} }
{SCF {When} {How}}
{NOCSMRSP}
{LPRT}
End
```

Presence of the SOLVATION key block triggers the solvent calculation and does not require additional data. With subkeys you can customize various aspects of the model, for instance to specify the type of solute. None of the subkeys is obligatory. Follows a description of the subkeys.

SURF Surface {NOKEEP}

Defines the type of cavity to be used. Surface can be one of the following: Wsurf, Asurf, Esurf, Klamt, or Delley. **Default: Delley**. The Wsurf, Asurf, and Esurf surfaces are constructed with the GEPOL93 algorithm⁶.

Wsurf

Wsurf triggers the Van der Waals surface (VdW), which consists of the union of all atomic spheres. Not recommended.

Asurf

Asurf gives the Solvent-Accessible-Surface (SAS). This is similar to VdW but consists of the path traced by the center of a spherical solvent molecule rolling about the VdW surface or, equivalently, a VdW surface created by atomic spheres to which the solvent radius has been added. These two surface types contain cusps at the intersection of spheres. Not recommended.

Esurf

Esurf gives the Solvent-Excluding-Surface (SES), which consists of the path traced by the *surface* of a spherical solvent molecule rolling about the VdW surface. Primarily, this consists of the VdW surface but in the regions where the spheres would intersect, the concave part of the solvent sphere replaces the cusp.

Klamt

The fourth surface option is Klamt as described in [Page 112, 2](#). It excludes the cusp regions also. Note that this surface might give an incomplete COSMO surface in case of more complicated molecules. Not recommended.

Delley

The fifth surface (default surface) is the so-called Delley surface, see also Ref.⁷. This Delley type of cavity construction is recommended for COSMO calculations whose results are used as input for COSMO-RS calculations; see the corresponding [manual for COSMO-RS](#). This Delley surface is the default COSMO surface in ADF.

NOKEEP

The optional parameter NOKEEP controls surface creation during calculation of frequencies by numerical differentiation. By default, the surface is constructed only once at the central geometry and is used for the rest of the calculation. If the NOKEEP is specified then ADF will construct a new surface at each displaced geometry.

DIV

The actual construction of the surface involves a few technical parameters controlled with the subkey DIV.

Ndiv, NFdiv

Ndiv controls how fine the spheres that in fact describe the surface are partitioned in small surface triangles, each containing one point charge to represent the polarization of the cavity surface. Default division level for triangles Ndiv=3. Default final division level for triangles NFdiv=1 ($\text{NFdiv} \leq \text{Ndiv}$). Not used in the Delley surface.

⁶ J.L. Pascual-ahuir, E. Silla and I. Tuñón, *GEPOL: An improved description of molecular surfaces. III. A new algorithm for the computation of a solvent-excluding surface*, *Journal of Computational Chemistry* 15, 1127 (1994) (<https://doi.org/10.1002/jcc.540151009>)

⁷ B. Delley, *The conductor-like screening model for polymers and surfaces*, *Molecular Simulation* 32, 117 (2006) (<https://doi.org/10.1080/08927020600589684>)

Min

Min specifies the size, in Angstrom, of the smallest sphere that may be constructed by the SES surface. For VdW and SAS surfaces it has no meaning. Default Min=0.5. Not used in the Delley surface.

Ofac

Ofac is a maximum allowed overlap of new created spheres, in the construction procedure. Default Ofac=0.8. Not used in the Delley surface.

leb1, leb2, rleb

Only used in the Delley surface. For the Delley type of construction one needs to set the variables leb1 (default value 23), leb2 (default value 29), and rleb (default value 1.5 Angstrom) to set the number of surface points. If the cavity radius of an atom is lower than rleb use leb1, otherwise use leb2. These values can be changed: using a higher value for leb1 and leb2 gives more surface points (maximal value leb1, leb2 is 29). A value of 23 means 194 surface points in case of a single atom, and 29 means 302 surface points in case of a single atom. Typically one could use leb1 for the surface point of H, and leb2 for the surface points of other elements.

NOASS

By default all new spheres that are created in the surface-construction are assigned to atoms, for the purpose of gradient computations (geometry optimization). Specifying the noass subkey turns this off. It has no argument.

SOLV

Solvent details.

Eps, Rad

Eps specifies the dielectric constant (the default relates to water). In ADF an infinite value for Eps is chosen if Eps is specified to be lower than 1.0. Rad specifies the radius of the (rigid sphere) solvent molecules, in Angstrom. Instead of specifying Eps and Rad one can specify a solvent name or formula after 'name='. The following table lists names and formulas that are recognized with the corresponding values for Eps and Rad. The Rad in this table is calculated from the density, the molar mass, and a spherical approximation for the solvent. The names and formulas are case-insensitive.

Name	Formula	Eps	Rad
AceticAcid	CH ₃ COOH	6.19	2.83
Acetone	CH ₃ COCH ₃	20.7	3.08
Acetonitrile	CH ₃ CN	37.5	2.76
Ammonia	NH ₃	16.9	2.24
Aniline	C ₆ H ₅ NH ₂	6.8	3.31
Benzene	C ₆ H ₆	2.3	3.28
BenzylAlcohol	C ₆ H ₅ CH ₂ OH	13.1	3.45
Bromoform	CHBr ₃	4.3	3.26
Butanol	C ₄ H ₉ OH	17.5	3.31
isoButanol	(CH ₃) ₂ CHCH ₂ OH	17.9	3.33
tertButanol	(CH ₃) ₃ COH	12.4	3.35
CarbonDisulfide	CS ₂	2.6	2.88
CarbonTetrachloride	CCl ₄	2.2	3.37
Chloroform	CHCl ₃	4.8	3.17
Cyclohexane	C ₆ H ₁₂	2	3.5
Cyclohexanone	C ₆ H ₁₀ O	15	3.46
Dichlorobenzene	C ₆ H ₄ Cl ₂	9.8	3.54
DiethylEther	(CH ₃ CH ₂) ₂ O	4.34	3.46
Dioxane	C ₄ H ₈ O ₂	2.2	3.24
DMFA	(CH ₃) ₂ NCHO	37	3.13
DMSO	(CH ₃) ₂ SO	46.7	3.04
Ethanol	CH ₃ CH ₂ OH	24.55	2.85

continues on next page

Table 4.1 – continued from previous page

EthylAcetate	CH ₃ COOCH ₂ CH ₃	6.02	3.39
Dichloroethane	ClCH ₂ CH ₂ Cl	10.66	3.15
EthyleneGlycol	HOCH ₂ CH ₂ OH	37.7	2.81
Formamide	HCONH ₂	109.5	2.51
FormicAcid	HCOOH	58.5	2.47
Glycerol	C ₃ H ₈ O ₃	42.5	3.07
HexamethylPhosphoramide	C ₆ H ₁₈ N ₃ OP	43.3	4.1
Hexane	C ₆ H ₁₄	1.88	3.74
Hydrazine	N ₂ H ₄	51.7	2.33
Methanol	CH ₃ OH	32.6	2.53
MethylEthylKetone	CH ₃ CH ₂ COCH ₃	18.5	3.3
Dichloromethane	CH ₂ Cl ₂	8.9	2.94
Methylformamide	HCONHCH ₃	182.4	2.86
Methylpyrrolidinone	C ₅ H ₉ NO	33	3.36
Nitrobenzene	C ₆ H ₅ NO ₂	34.8	3.44
Nitrogen	N ₂	1.45	2.36
Nitromethane	CH ₃ NO ₂	35.87	2.77
PhosphorylChloride	POCl ₃	13.9	3.33
IsoPropanol	(CH ₃) ₂ CHOH	19.9	3.12
Pyridine	C ₅ H ₅ N	12.4	3.18
Sulfolane	C ₄ H ₈ SO ₂	43.3	3.35
Tetrahydrofuran	C ₄ H ₈ O	7.58	3.18
Toluene	C ₆ H ₅ CH ₃	2.38	3.48
Triethylamine	(CH ₃ CH ₂) ₃ N	2.44	3.81
TrifluoroaceticAcid	CF ₃ COOH	8.55	3.12
Water	H ₂ O	78.39	1.93

Del

Del is the value of Klamt's delta_sol parameter, only relevant in case of Klamt surface.

Neql

If Neql = ϵ_{NEQL} is included a non-equilibrium solvation is used, i.e. that the dielectric constant ϵ_{NEQL} used in RESPONSE is different from the ground state dielectric constant ϵ . Only relevant in case of TDDFT calculations. Default $\epsilon_{\text{NEQL}} = \epsilon$. The reason for using two different dielectric constants is that the electronic transition can be so fast that only the electronic component of the solvent dielectric can respond, i.e., one should use the optical part of the dielectric constant. This is typically referred to as non-equilibrium solvation. The optical dielectric constant can be obtained from the (frequency dependent) refractive index n of the solvent as: $\epsilon_{\text{NEQL}} = n^2$.

Emp

Emp addresses the empirical scaling factor x in the formula 2.1.1 above.

Cav0, Cav1

Other options specify a linear parametrization of non-electrostatic terms as a function of surface area, see the formula 2.1.2 above. Possible values for CAV0 and CAV1 are CAV0 = 1.321 and CAV1 = 0.0067639, see Ref.⁸). In ADF2010 the default values for CAV0 and CAV1 are CAV0 = 0.0 and CAV1 = 0.0. However, starting from ADF2012 the default values for CAV0 and CAV1 are CAV0 = 0.0 and CAV1 = 0.0067639. If CAV0 is not zero, Esolv(AB) is not the same as Esolv(A) + Esolv(B) if A and B are far apart. This is the reason why CAV0 is set to zero, by default. By default CAV1 is not set to zero, thus by default there is a solvation energy term that does depend on the size of the cavity (surface area).

COSMO Radii

⁸ T.N. Truong and E.V. Stefanovich, *A new method for incorporating solvent effect into the classical, ab initio molecular orbital and density functional theory frameworks for arbitrary shape cavity*, *Chemical Physics Letters* 240, 253 (1995) ([https://doi.org/10.1016/0009-2614\(95\)00541-B](https://doi.org/10.1016/0009-2614(95)00541-B))

In order to construct the surface you have to specify the atomic ('Van der Waals') radii. There are three ways of doing this. In the first method you append 'adf.R=value' to the atomic coordinates record, in the ATOMS key block. This would look like, for instance:

```
C 1 2 3 CC CCO CCOH adf.f=C.dz adf.R=2.0
```

It assigns a radius of 2.0 to the Carbon atom. In the second method you apply the same format, but specify a symbol (identifier) rather than a value:

```
C 1 2 3 CC CCO CCOH adf.f=C.dz adf.R=C-sp3
```

The identifiers must be defined in the (optional) RADII subkey block in the Solvation data block (see next). In the third method, you don't modify the Atoms block at all. In this case, the RADII subkey must be used and the 'identifiers' in it must be exactly the atom type names in the Atoms block.

RADII

This subkey is block type. Its data block (if the subkey is used) must terminate with a record End. In the Radii data block you give a list of identifiers and values:

```
SOLVATION
...
Radii
  name1=value1
  name2=value2
  ...
End
...
```

The values are the radii of the atomic spheres, in the same units of length as used in the Atoms block (Angstrom or bohr). The names specify to which atoms these values apply. As discussed for the Solv subkey this depends on the Atoms block. If in the specification of atomic coordinates you have used the 'adf.R=' construct to assign radii, with identifiers rather than values for the R-value, these identifiers must be defined in the Radii sub block. If no 'adf.R=' construct was applied in the Atoms block, you must use the atom type names as they occurred in the Atoms data block. Referring to the example given in the Solv subkey discussion, you might have:

```
Radii
  C-sp3=2.0
  ...
End
```

A simple atom type reference might look like:

```
Radii
  C=2.0
  ...
End
```

When no radius is specified a default value is used. The default value for an atom is the corresponding Van der Waals radius from the MM3 method by Allinger (Ref.⁹Page 112, 5) divided by 1.2, see Ref.⁹.

Another popular choice are the so-called Klamt atomic cavity radii (Ref.¹⁰), which are optimized for a few elements:

⁹ M. Swart, E. Rösler, F.M. Bickelhaupt, *Proton Affinities in Water of Maingroup-Element Hydrides - Effects of Hydration and Methyl Substitution*, *European Journal of Inorganic Chemistry* 2007 3646 (2007) (<https://doi.org/10.1002/ejic.200700228>)

¹⁰ A. Klamt, V. Jonas, T. Bürger and J.C. Lohrenz, *Refinement and Parametrization of COSMO-RS*. *J. Phys. Chem. A* 102, 5074 (1998) (<https://doi.org/10.1021/jp980017s>)

```

Radii
  H  1.30
  C  2.00
  N  1.83
  O  1.72
  F  1.72
  Si 2.48
  P  2.13
  S  2.16
  Cl 2.05
  Br 2.16
  I  2.32
End

```

**CHARGED {Method=meth} {Conv=1e-8} {Omega=1.0} {Iter=1000} {Corr} {LoCosmo
LoCosmoDist}**

This addresses the determination of the (point) charges that model the cavity surface polarization. In COSMO calculations you compute the surface point charges q by solving the equation $A*q*=-f$, where f is the molecular potential at the location of the surface charges q and A is the self-interaction matrix of the charges. The number of charges can be substantial and the matrix A hence very large. A direct method, i.e. inversion of A , may be very cumbersome or even impossible due to memory limitations, in which case you have to resort to an iterative method. Meth specifies the equation-solving algorithm. Meth=INVER requests direct inversion. Meth=GAUS calls for the Gauss-Seidel iterative method. Meth=Jacobi activates another standard iterative procedure. The latter two methods require a positive-definite matrix (which may fail to be the case in an actual calculation) and can be used with a relaxation technique, controlled by the relaxation parameter OMEGA (1.0=no relaxation). Meth=CONJ (default) uses the preconditioned biconjugate gradient method. This is guaranteed to converge and does not require huge amounts of memory. CONV and ITER are the convergence criterion and the maximum number of iterations for the iterative methods. Some of the molecular electronic charge distribution may be located outside the cavity. This affects the assumptions underlying the COSMO equations. LOCOSMO can only be used in combination with FDE.

Specifying the CORR option to the CHARGED subkey constrains the computed solvent surface charges to add up to the negative of the molecular charge. In ADF2016 this outlying charge correction is also done during the SCF. Note that before ADF2016 it was only a post-SCF correction on the COSMO charges. In ADF2018 a bug that was introduced in ADF2016 in case of this outlying charge correction was fixed for the energy (typically a small effect).

C-MATRIX

How: For the potential f we need the Coulomb interaction between the charges q and the molecular electronic density (and nuclei). Three methods are available, specified by the first option to the C-Matrix subkey.

- EXACT: compute the straightforward Coulomb potential due to the charge q in each point of the molecular numerical integration grid and integrate against the electronic charge density. This is, in principle, exact but may have inaccuracies when the numerical integration points are very close to the positions of a charge q . To remedy this, the point charges q can be 'smeared out' and represented by a disc, see the next subkey DISC.
- FIT: same as EXACT, but the q -potentials are now integrated not against the exact electronic charge density, but against the (much cheaper-to-compute) fitted density. The same DISC considerations apply.
- POT: evaluate the molecular potential at the position of the charge q and multiply against the q -strength. Since the molecular Coulomb potential is computed from the fit density, any difference in results between the FIT and the POT approach should be attributed to the DISC issue. POT is the default, because it is faster, and is only inadequate if the fit density is very inaccurate, which would be a problem anyway.

SCF: If you specify this option, the computation of the Coulomb interaction matrix (between electrons and surface charges) is carried out during the SCF procedure, but this turns out to hamper the SCF convergence behavior. Therefore: not recommended. *If* you use it, the program will switch to one of the other 3 methods, as given by

the 'How' option, as soon as the SCF convergence error drops below TOL: (applies only to the SCF option, which is not recommended).

DISC

Applies only when the C-matrix method is EXACT or FIT. Note, however, that the default for the C-matrix method is POT, in which case the DISC subkey has no meaning. The DISC key lets the program replace the point charges q by a solid uniformly charged spherical surface disc whenever the numerical integration accuracy requires so, i.e. for those charges that are close to numerical integration points. Options: SC defines a shrinking factor, by which the actual disc radius used is reduced from its 'normal' value: an inscribed disc in the triangular surface partitions that define the distribution of surface charges, see the subkey DIV. LEG gives the polynomial expansion order of the disc potentials. The Legendre expansion converges rapidly and the default should be adequate.

TOL is a tolerance parameter to control the accuracy of the disc potential evaluations.

SCF

In COSMO calculations you can include the surface charges in the Fock operator self-consistently, i.e. by recomputing the charges q at every SCF cycle and include them in the equations, or in a perturbational manner, i.e. post-SCF. This is controlled with the first option. The When option must be either VAR or PERT, for variational and perturbational, respectively. Default is VAR. The second (HOW) option applies only to the WHEN=VAR case and may affect the speed of SCF convergence. The COSMO calculation implies a considerable increase in CPU time! Values for HOW:

- ALL: This includes it in all SCF cycles (except for the first SCF cycle, which is gas-phase)
- LAST: This lets the program first converge the SCF completely without any solvent effects. Thereafter, the COSMO is turned on, hopefully converging in fewer cycles now, to compensate for the 'double' SCF effort.
- TOL=0.1 (or another value) is an in-between approach: converge the gas-phase SCF until the SCF error is below TOL, then turn on COSMO.

NOCSEMRSP

Relevant only in combination with the time-dependent DFT (TDDFT) applications: the EXCITATIONS, the RESPONSE, or the AORESPONSE key. If this subkey NOCSEMRSP is included the induced electronic charges which are present in the TDDFT calculations, will not influence the COSMO surface charges. No dielectric constant in the response might be closer to the optical dielectric constant than using the full dielectric constant, see also sub-argument NEQL of the subkey SOLV of the key SOLVATION. By default, in absence of this subkey NOCSEMRSP, the induced electronic will influence the COSMO surface charges. If one does geometry optimization of the excited state this makes sense, since then the solvent dielectric has time to fully respond.

LPRT

This is a debug switch and triggers a lot more output related to the cavity construction etc.

Warning

Numerical frequencies calculated with COSMO should be checked for stability with respect to the `NumericalDifferentiation%NuclearStepSize` in the AMS part of the input, the numerical differentiation step size. The problem is that the COSMO surface changes slightly when a nucleus is moved from its equilibrium position. The change is usually small but in some cases it may result in creation or annihilation of surface points, which will lead to discontinuities in the potential energy surface and may result in inaccurate frequencies.

Thus, when calculating vibrational frequencies numerically with COSMO, one should try decreasing the `NumericalDifferentiation%NuclearStepSize` value in the AMS part of the input, until no changes in frequencies are observed. However, the value should not be too small because then the total numerical noise may become too large compared to the generated forces. A general recommendation would be to try to decrease NuclearStepSize by a factor of 2 at a time. Of course, this procedure may be very expensive for a large molecule. If this the case, one could use the `NormalModes%ReScanModes` or `NormalModes%ReScanFreqRange` in the AMS part of the input, in order to recalculate frequencies along a normal mode. It should be noted that generally frequencies that have a small force constant are more sensitive to the numerical noise.

4.4.2 SM12: Solvation Model 12

Continuum solvation can be done with the Minnesota Solvation Model 12 (SM12)¹. Details on the implementation of SM12 in ADF can be found in Ref.².

The SM12 model in ADF can use *CM5* (page 338), *CHELPG* (page 338), or *RESP* (page 338) charges. The calculation of SM12 analytical gradients with CHELPG or RESP charges is implemented (ADF2026), which allows one to do geometry optimizations, for example. The calculation of SM12 analytical gradients with CM5 charges is not implemented.

The energetics of solvation is calculated using:

$$\Delta G_S^{\otimes} = \Delta E_E + G_P + G_{CDS} + \Delta G_N + \Delta G_{conc}^{\otimes}$$

where the symbol $\otimes$ denotes an arbitrary choice of standard states, ΔE_E is the change in the solute's internal electronic energy in transferring from the gas phase to the liquid phase at the same geometry, G_P is the polarization free energy of the solute-solvent system when the solute is inserted, G_{CDS} is the component of the free energy that is nominally associated with cavitation, dispersion, and solvent structure, ΔG_N is the change in ΔG_S^0 due to a change in nuclear coordinates, and $\Delta G_{conc}^{\otimes}$ accounts for the difference in concentrations, if any, in the gas-phase standard state and the solution-phase one. In case of 1 M concentration in both solution and gas, then $\Delta G_S^{\otimes} = 0$ kcal/mol, which yields ΔG_S^* . If the same geometry is used in solution and gas phase calculation, then ΔG_N is zero.

SM12 makes use of the Generalized Born approximation to calculate the bulk electrostatic contribution. This is comprised of several terms that are together known as the ENP (Electronic, Nuclear, and Polarization) term G_P . The SM12 model in ADF can use *CM5 charges* (page 338)³ or charges which are derived from the electrostatic potential (ESP), namely *CHELPG or RESP* (page 338). CM5 is a class 4 charge model, making use of both empirical and density related terms. It is comprised of Hirshfeld charges⁴, a simple bond order calculation, atomic distances, and atom-specific parameters^{Page 119, 3}. The ESP charges are calculated in ADF using atom-centered Lebedev grids, which is different from the way they are calculated in Ref.¹. The covalent radii utilized are based on the atomic covalent radius from the Handbook of Chemistry and Physics⁵. The Coulomb integral is described with the use of an approximation from Still et al.⁶. Several parameters go into describing this, which include: interatomic distance, an empirical Born constant, and the Born area, which is calculated with the Analytical Surface Area (ASA) algorithm⁷. The Born area is calculated using Legendre-Gauss quadrature from the atomic radii to a sphere that encapsulates the entire molecule.

The ASA algorithm is also used to calculate the solvent accessible surface area (SASA), which is computed within the CDS (Cavitation, Dispersion, Solvation) term of SM12. The CDS term depends on three terms:

- SASA (ASA Algorithm)
- Atomic surface tension
- Macroscopic surface tension

Atomic surface tension is based on atom-atom distances and the solvent. Macroscopic surface tension is solvent-specific. The SM12 implementation in ADF reports energies in an atom-specific way. You can attribute exact CDS and polarization energies to each atom in your solute. The parameters for SM12 are derived to explicitly incorporate organic elements (N,

¹ A.V. Marenich, C.J. Cramer, and D.G. Truhlar, *Generalized Born Solvation Model SM12*, *Journal of Chemical Theory and Computation* 9, 609 (2013) (<https://doi.org/10.1021/ct300900e>)

² C.A. Peebles and G. Schreckenbach, *Implementation of the SM12 Solvation Model into ADF and Comparison with COSMO*, *Journal of Chemical Theory and Computation* 12, 4033 (2016) (<https://doi.org/10.1021/acs.jctc.6b00410>)

³ A.V. Marenich, S.V. Jerome, C.J. Cramer, D.G. Truhlar, *Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases*, *Journal of Chemical Theory and Computation* 8, 527 (2012) (<https://doi.org/10.1021/ct200866d>)

⁴ F.L. Hirshfeld, *Bonded-atom fragments for describing molecular charge densities*, *Theoretica Chimica Acta* 44, 129 (1977) (<https://doi.org/10.1007/BF00549096>)

⁵ M. Mantina, R. Valero, C.J. Cramer, D.G. Truhlar, in *CRC Handbook of Chemistry and Physics*, 91st ed. (2010-2011), ISBN13 9781439820773, W.M. Haynes, Ed., CRC Press: Boca Raton, FL, 2010.

⁶ W.C. Still, A. Tempczyk, R.C. Hawley, and T. Hendrickson, *Semianalytical treatment of solvation for molecular mechanics and dynamics*, *Journal of the American Chemical Society* 112, 6127 (1990) (<https://doi.org/10.1021/ja00172a038>)

⁷ D.A. Liotard, G.D. Hawkins, G.C. Lynch, C.J. Cramer, and D.G. Truhlar, *Improved Methods for Semiempirical Solvation Models*, *Journal of Computational Chemistry* 16, 422 (1995) (<https://doi.org/10.1002/jcc.540160405>)

C, O, F, Si, P, S, Cl, Br, I), with less emphasis on non-organics. Also, while most solvents have a generic atomic surface tension reliance for atoms, water has its own explicit set of parameters to better describe it.

```
SOLVATION SM12
{SM12SolvationPotential <CM5|CHELPG|RESP>}
{SOLV NAME=solvent}
{CUST {NAME=solvent}}
{REF 1.33}
{ACID 0.82}
{BASE 0.35}
{TENS 103.62}
{EPS 78.36}
{ARO 0.0}
{HALO 0.0}
{RADSOLV 0.4}
{CHGAL 2.474}
{BORNC 3.70}
{PRINTSM12}
{SM12printSCRF}
{SM12espgridorder 19}
{SM12espgridspacing 0.5}
End
```

Presence of the SOLVATION SM12 block key triggers the solvent calculation and does not require additional data. Curly brackets are not part of the key. If no other keywords are present the default is Water. If SM12 gradients are wanted one needs to specify CHELPG or RESP for the SM12SolvationPotential keyword as these are not implemented in case of CM5. With subkeys you can customize various aspects of the model, for instance to specify the type of solute. None of the subkeys is obligatory. Follows a description of the subkeys

SM12SolvationPotential <CM5|CHELPG|RESP>

Which partial charges to use in SM12. Default CM5. CHELPG or RESP is needed for analytical gradients.

SOLV NAME=solvent

Defines which solvent to be used. Each solvent has parameters set for each of the variables defined below. All of which can be found in the SM12 ref.¹. Any variable can be changed with the inclusion of its key. *solvent* can be one of the following:

• ACETICACID	• CARBONTETRACHLORIDE
• ACETONITRILE	• CHLOROBENZENE
• ACETOPHENONE	• CHLOROFORM
• ANILINE	• CHLOROHEXANE
• ANISOLE	• M-CRESOL
• BENZENE	• CYCLOHEXANE
• BENZONITRILE	• CYCLOHEXANONE
• BENZYLALCOHOL	• DECALIN
• BROMOBENZENE	• DECANE
• BROMOETHANE	• DECANOL
• BROMOFORM	• 1-2-DIBROMOETHANE
• BROMOOCTANE	• DIBUTYLETHER
• N-BUTANOL	• O-DICHLOROBENZENE
• SEC-BUTANOL	• 1-2-DICHLOROETHANE
• BUTANONE	• DIETHYLETHER
• BUTYLACETATE	• DIISOPROPYLETHER
• N-BUTYLBENZENE	• N-N-DIMETHYLACETAMIDE
• SEC-BUTYLBENZENE	• N-N-DIMETHYLFORMAMIDE
• T-BUTYLBENZENE	• 2-6-DIMETHYLPYRIDINE
• CARBONDISULFIDE	• DIMETHYLSULFOXIDE

- DODECANE
- ETHANOL
- ETHOXYBENZENE
- ETHYLACETATE
- ETHYLBENZENE
- FLUOROBENZENE
- 1-FLUORO-N-OCTANE
- HEPTANE
- HEPTANOL
- HEXADECANE
- HEXADECYL IODIDE
- HEXANE
- HEXANOL
- IODOBENZENE
- ISOBUTANOL
- ISOOCTANE
- ISOPROPANOL
- ISOPROPYLBENZENE
- P-ISOPROPYLTOLUENE
- MESITYLENE
- METHANOL
- METHOXYETHANOL
- METHYLENECHLORIDE
- N-METHYLFORMAMIDE
- 2-METHYLPYRIDINE
- 4-METHYL-2-PENTANONE
- NITROBENZENE
- NITROETHANE
- NITROMETHANE
- O-NITROTOLUENE
- NONANE
- NONANOL
- OCTANE
- OCTANOL
- PENTADECANE
- PENTANE
- PENTANOL
- PERFLUOROBENZENE
- PHENYLETHER
- PROPANOL
- PYRIDINE
- TETRACHLOROETHENE
- TETRAHYDROFURAN
- TETRAHYDROTHIOPHENEDIOXIDE
- TETRALIN
- TOLUENE
- TRIBUTYLPHOSPHATE
- TRIETHYLAMINE
- 1-2-4-TRIMETHYLBENZENE
- UNDECANE
- WATER
- XYLENE
- 1-2-DIBROMOETHANE_WATER
- 1-2-DICHLOROETHANE_WATER
- BENZENE_WATER
- CARBONTETRACHLORIDE_WATER
- CHLOROBENZENE_WATER
- CHLOROFORM_WATER
- CYCLOHEXANE_WATER
- DIBUTYLETHER_WATER
- DIETHYLETHER_WATER
- ETHYLACETATE_WATER
- HEPTANE_WATER
- HEXANE_WATER
- NITROBENZENE_WATER
- OCTANOL_WATER

CUST {NAME=solvent}

A solvent with user specified parameters can be used. A user-specified name of the solvent `solvent` can be provided, but should not match one of the solvent names listed above. Any unspecified parameters will be set to zero, with the exception of the dielectric constant, which will be set to the dielectric constant of water.

REF

Index of refraction at 293K (n).

ACID

Abrahams hydrogen bond acidity (α).

BASE

Abrahams hydrogen bond basicity (β).

TENS

Macroscopic surface tension of the solvent at the air interface ($\text{cal mol}^{-1} \text{ \AA}^{-2}$)(γ).

EPS

Dielectric constant. If not specified it will be set to the default of water. (ϵ).

ARO

Square root of the fraction of non-hydrogen atoms in the solvent molecule that are aromatic carbon atoms (carbon

aromaticity) (ϕ).

HALO

Square of the fraction of non-hydrogen atoms in the solvent molecule that are halogens (electronegative halogenicity)(ψ).

RADSOLV

Solvent radius, this is added to the van der Waals radius used for the cavity calculation.

CHGAL

CM5 alpha parameter for Pauling bond order.

BORNC

Empirical Born constant, see Ref. [Page 119, 1](#).

PRINTSM12

Print more information on the SM12 calculation: CDS atom terms, ENP charges.

SM12printSCRF

Print more information on the SCRF (self-consistent reaction field) during the SM12 calculation.

SM12espgridorder

ESP Lebedev Grid order for SM12 CHELPG and RESP. Accepted values are 19 (default), 23, 29, 31, and 41.

SM12espgridspacing

ESP Lebedev Grid spacing for SM12 CHELPG and RESP in Angstrom. Reasonable choices are 0.1, 0.2, 0.3, or 0.5 (default) Angstrom.

4.4.3 Quild

The QUILD (Quantum-regions Interconnected by Local Description) program has been developed to enable calculations with multilevel approaches, in which different computational treatments are used for different regions of the system under study; see the separate [Quild manual](https://www.scm.com/doc.2024/Quild/index.html) (<https://www.scm.com/doc.2024/Quild/index.html>).

4.4.4 Hybrid Engine (QM/MM, QM/QM')

The Hybrid engine is meant for mechanical or electrostatic embedding and QM/MM (QM/QM') calculations that combine multiple engines. Some of the functionality of QUILD can be achieved using the Hybrid engine. See the separate [Hybrid Engine manual](#).

4.4.5 DIM/QM: Discrete Interaction Model/Quantum Mechanics

The Discrete Interaction Model/Quantum Mechanics (DIM/QM) method facilitates calculating the optical properties of molecules under the influence of a discrete solvent or a metal nanoparticle; see, for example, Ref.¹. DIM/QM relies on one of three descriptions of the system: Discrete Reaction Field (DRF), where the atoms interact via induced dipoles and static charges, Capacitance Polarizability Interaction Model (CPIM), where the atoms interact via induced dipoles and induced charges, and Polarizability Interaction Model (PIM), where the atoms interact via induced dipoles only. DRF is best for solvents, CPIM is best for small metal nanoparticles, and PIM is best for large metal nanoparticles.

The DRF module is now part of DIM/QM, so DRF is a submodule of DIM/QM.

To perform a DIM/QM calculation, two block keys are required. The first is the DIMQM block, which activates the DIM/QM module. The parameters for each DIM atom must also be given, and they can be given with either the DIMPAR block, which is most convenient for metal nanoparticles, or with the EXTERNALS block, which is designed for DRF.

¹ J.L. Payton, S.M. Morton, Justin E. Moore, and Lasse Jensen, *A discrete interaction model/quantum mechanical method for simulating surface-enhanced Raman spectroscopy*, *Journal of Chemical Physics* 136, 214103 (2012) (<https://doi.org/10.1063/1.4722755>)

In ADF2019, the bond energies calculated with DIM/QM in ADF have been corrected.

DRF

The Discrete Solvent Reaction Field (DRF) model is a hybrid quantum mechanical and molecular mechanics (QM/MM) model for studying solvation effects on (time-dependent) molecular properties such as dipole moments, excitation energies, and (hyper)polarizabilities⁷⁸⁹¹⁰¹¹. The classical solvent molecules are represented using distributed atomic charges and polarizabilities.

With the ADF-GUI it is simple to set up a DRF calculation. Another possibility is to use and/or modify a Python script that is explained in the example *DIMQM_DRF_plams* (page 595). Both the ADF-GUI and the DRF Python script have default settings that can be easily modified if this is required. In the simplest case, the user just needs to provide the QM and DRF regions. By default, the atomic charges used (in the ADF-GUI or the DRF Python script) for the DRF are computed with the LDA functional, DZP basis set, and normal numerical quality. Also by default, atomic polarizabilities (computed with the Thole model) are taken from an internal database including H, C, N, O, F, S, Cl, Br, and I atoms². If one does not use the ADF-GUI or the DRF Python script, the user has to specify this by hand.

Within the Discrete Solvent Reaction Field model, the QM/MM operator is

$$H_{\text{QM/MM}} = \sum_i v_{\text{DRF}}(r_i, \omega) = \sum_i V^{\text{el}}(r_i) + V^{\text{pol}}(r_i, \omega)$$

where the first term, v^{el} , is the electrostatic operator and describes the Coulombic interaction between the QM system and the permanent charge distribution of the solvent molecules. The second term, v^{pol} , is the polarization operator and describes the many-body polarization of the solvent molecules, i.e. the change in the charge distribution of the solvent molecules due to interaction with the QM part and other solvent molecules. The charge distribution of the solvent is represented by atomic point charges and the many-body polarization by induced atomic dipoles at the solvent molecules. The induced atomic dipole at site s is found by solving a set of linear equations

$$\mu_{s,\alpha}^{\text{ind}}(\omega) = \alpha_{s,\alpha\beta} \left(F_{s,\beta}^{\text{init}}(\omega) + \sum_{t \neq s} T_{st,\beta\gamma}^{(2)} \mu_{t,\gamma}^{\text{ind}}(\omega) \right)$$

where $\alpha_{s,\alpha\beta}$ is a component of the atomic polarizability tensor at site s . The screened dipole interaction tensor is given by

$$T_{st,\beta\gamma}^{(2)} = 3f_{st}^T R_{st,\alpha} R_{st,\beta} / R_{st}^5 - f_{st}^E \delta_{\alpha\beta} / R_{st}^3$$

where the damping functions f_{st}^T and f_{st}^E have been introduced, see also^{Page 123, 2}. A smeared-out point charge model³ is used for short-range damping of the QM/MM operator

$$1/R_{st} \rightarrow 1/S_{st} = \text{erf}(R_{st})/R_{st}$$

The scaled distance, S_{st} , then replaces the normal distance, R_{st} , in the QM/MM operator.

⁷ L. Jensen, P.T. van Duijnen and J.G. Snijders, *A discrete solvent reaction field model within density functional theory*, *Journal of Chemical Physics* 118, 514 (2003) (<https://doi.org/10.1063/1.1527010>)

⁸ L. Jensen, P.T. van Duijnen and J.G. Snijders, *A discrete solvent reaction field model for calculating molecular linear response properties in solution*, *Journal of Chemical Physics* 119, 3800 (2003) (<https://doi.org/10.1063/1.1590643>)

⁹ L. Jensen, P.T. van Duijnen and J.G. Snijders, *A discrete solvent reaction field model for calculating frequency-dependent hyperpolarizabilities of molecules in solution*, *Journal of Chemical Physics* 119, 12998 (2003) (<https://doi.org/10.1063/1.1627760>)

¹⁰ L. Jensen, M. Swart and P.T. van Duijnen, *Microscopic and macroscopic polarization within a combined quantum mechanics and molecular mechanics model*, *Journal of Chemical Physics* 122, 34103 (2005) (<https://doi.org/10.1063/1.1831271>)

¹¹ L. Jensen, *Modelling of optical response properties: Application to nanostructures*, (<https://downloads.scm.com/Doc/jensen.pdf>) PhD thesis, Rijksuniversiteit Groningen, 2004.

² P.T. van Duijnen and M. Swart, *Molecular and Atomic Polarizabilities: Thole's Model Revisited*, *Journal of Physical Chemistry A* 102, 2399 (1998) (<https://doi.org/10.1021/jp980221f>)

³ L. Jensen, P.-O. Astrand, A. Osted, J. Kongsted and K.V. Mikkelsen, *Polarizability of molecular clusters as calculated by a dipole interaction model*, *Journal of Chemical Physics* 116, 4001 (2002) (<https://doi.org/10.1063/1.1433747>)

In order to perform a DRF calculation, two types of parameters (model atomic charges and atomic polarizabilities) for each type of atom in the MM part are required. The point charges should represent at least the permanent molecular dipole moment, and the distributed atomic polarizabilities the full molecular polarizability tensor. The atomic charges can be straightforwardly obtained using, e.g., Multipole Derived Charges (MDC) (see [section on MDC](#) (page 338)), and the distributed polarizabilities by adopting standard parameters or refitting them to match the calculated polarizability tensor^{2Page 123, 3}. This allows for a simple procedure to obtain the solvent model parameters which subsequently can be used in the DRF calculation.

DRF gradients can be calculated by using the DRF2 keyword in the DIMQM block. This is an expert option and should be used with great caution. The DRF2 keyword uses DRF but with Gaussian screening like that of the PIM method. It also allows for input of parameters by atom type like the PIM method. The user must specify a radius and charge for the atom type, as shown below.

```
DIMPAR
O
  rad=0.9028
  char=-0.6690
  STATIC
SUBEND
H
  rad=0.2479
  char=0.3345
  STATIC
SUBEND
Ag
  rad=1.445
  char=0.0000
SUBEND
END
```

Here, the STATIC keyword is used to tell DIM/QM to ignore the frequency-dependent response for those atom types.

Surface-enhanced response properties

In addition to the calculation of solvation effects on response properties, DIM/QM can also be used for simulating non-linear optical properties of molecules near metal surfaces of a nanoparticle. A TDDFT description of the molecule is coupled to an electrodynamical treatment of the nanoparticle, including electrostatics and polarization of the atoms. In this way DIM/QM can be used to study surface-enhanced Raman scattering (SERS)^{Page 122, 1}, surface-enhanced Raman optical activity (SEROA)⁴, and plasmon-enhanced photochemistry.

Starting from ADF2018, the Polarizability Interaction Model (PIM) can be used to calculate damped first hyperpolarizabilities β and damped second hyperpolarizabilities γ . Different types of β -tensors can be calculated, such as STATIC, OPTICALR, EOPE, and SHG. This allows for simulation of surface-enhanced hyper-Raman scattering (SEHRS)⁵. All the (sub)keywords for regular damped β , such as BETA and QUADRATIC, can also be used. Also different types of γ -tensors can be calculated, such as STATIC, EFIOR, OKE, IDRI, EFISHG, THG and TPA. This allows for simulation of plasmon-enhanced two-photon absorption (PETPA). Except CUBIC, all the other (sub)keywords for regular damped γ can also be used.

⁴ D.V. Chulhai and L. Jensen, *Simulating Surface-Enhanced Raman Optical Activity Using Atomistic Electrodynamics-Quantum Mechanical Models*, *Journal of Physical Chemistry A* 118, 9069 (2014) (<https://doi.org/10.1021/jp502107f>)

⁵ Z. Hu, D.V. Chulhai, and L. Jensen, *Simulating Surface-Enhanced Hyper-Raman Scattering Using Atomistic Electrodynamics-Quantum Mechanical Models*, *Journal of Chemical Theory and Computation* 12, 5968 (2016) (<https://doi.org/10.1021/acs.jctc.6b00940>)

Input options

```

DIMQM
  <DRF|PIM|CPIM>
  NOPOL
  NOCHAR
  NOCROSS
  DDA
  FULLGRID
  LOCALFIELD <Resp|All|Static>
  NOIMAGE
  EFIELD x y z
  SCREEN <ERF|EXP|ESP|GAU|NONE> {length}
  :: FREQUENCY-DEPENDENT PARAMETERS
  FREQUENCY
  OM_H value
  OM_C value
  OM_O value
  OM_N value
  :: CONTROL OVER SOLVER
  ALGORITHM <BEST|DIRECT|BRUTE|SINGLE|MULTI>
  TOLERANCE tol
  NITER iterations
  VOLUME vol_in_nm^3
  MULTIPLIER aterm bterm cterm
  GRID <COARSE|MEDIUM|FINE>
  :: GRADIENT OPTIONS
  FORCEFIELD
  CHEMBOND qmindex dimindex
  COORDDEPEND
  CHEMISORPTION
  COORDPAR atomtype e0 e1 r0 r1 CNmax Rmax Rmin
  CHEMPAR atomtype e0 e1 r0 r1 cutoff
  PROJECTIONMATRIXPOINTS <ALL|CUTOFF radius|OFF>
  :: OUTPUT CONTROL
  PRINTATOMICDIPOLES
  PRINTLJPAR
  DEBUG
  LOCALDIM
  LOCALDIRECT
  DIMBUFFER
  QMBUFFER
  CUTOFFDIST
END

```

<DRF|CPIM|PIM>

DIM/QM relies on one of three descriptions of the system: Discrete Reaction Field (DRF), where the atoms interact via induced dipoles and static charges, Capacitance Polarizability Interaction Model (CPIM), where the atoms interact via induced dipoles and induced charges, and Polarizability Interaction Model (PIM), where the atoms interact via induced dipoles only. DRF is best for solvents, CPIM is best for small metal nanoparticles, and PIM is best for large metal nanoparticles. One and only one of these three keys must be included in every DIM/QM calculation. However, in ADF2019, there is also the expert DRF2 possibility, which allows for DRF gradients but should be used cautiously.

NOPOL

The NOPOL key turns off the polarization terms, and thus all induced dipoles are zero. This key is only valid for DRF or CPIM calculations.

NOCHAR

The NOCHAR key turns off the charge terms, and thus all induced or static charges are zero. This key is only valid for DRF or CPIM calculations.

NOCROSS

The NOCROSS key turns off the charge-dipole interactions. This key is only valid for CPIM calculations.

DDA

By default, the dipole-dipole, charge-dipole, and charge-charge interactions are screened to take into account that atoms are not point charges. The DDA key will turn off this screening so that the results can be compared directly to the discrete dipole approximation (DDA).

FULLGRID

This is used in conjunction with the frozen density approximation.

LOCALFIELD <Resp|All|Static>

Default is All, when no option is specified. When the molecule interacts with a (for example) metal nanoparticle, there are two types of interactions: the image field and the local field. The image field is caused by the dipoles induced into the nanoparticle by the molecule's electron density. This is always taken into account in a DIM/QM calculation. The local field arises by direct interactions of the nanoparticle with an external field. Addition of the LOCALFIELD key causes the DIM/QM calculation to include this effect, but by default this is not included in a DIM/QM calculation. In ADF2016, the correct behavior with local fields for the electric dipole-dipole, electric dipole-quadrupole, and electric dipole-magnetic dipole response tensors in the velocity gauge is implemented. This allows for correct calculation of surface-enhanced Raman optical activity (SEROA) (Ref.⁴) and plasmonic circular dichroism (Ref.⁶).

The default option should be used in most situations as other options are expert options. In an effort to speed up calculation times, one can request to just calculate the local fields during the response section of the calculation by using the Resp keyword after local fields. All will calculate the local field for both ground state calculations and the response calculations, while static will calculate the local field during the ground state only.

NOIMAGE

Expert option. By default, the image field is always included in a DIM/QM calculation. With this keyword one can turn it off.

EFIELD x y z

The EFIELD key is used to include an external static electric field in the vector x y z. Internally, the static charges used in a DRF calculation use AMS's System%ElectrostaticEmbedding, and therefore the use of the AMS System%ElectrostaticEmbedding is not allowed in combination with the DIMQM block. This key is included so the user may include an external static electric field.

SCREEN <ERF|EXP|ESP|GAU|NONE> {length}

The SCREEN key indicates what functional form is used to screen the interactions between each DIM atom and the QM density. The choices are ERF (error function), EXP (exponential), ESP (error function for potential operator only), GAU (Gaussian), or NONE. For CPIM and PIM the default is GAU; for DRF, the default is ESP. In all cases, the default screening length is 1.0, but this may be changed with the optional length parameter.

FREQUENCY

The FREQUENCY key turns on frequency-dependent parameters.

OM_[HCON] value

The OM_H, OM_C, OM_O, and OM_N keys provide the resonance frequency (in atomic units) for the elements H, C, O and N, respectively. These keys are only for use with DRF and only when the older EXTERNALS block is used.

ALGORITHM <BEST|DIRECT|BRUTE|SINGLE|MULTI>

DIM/QM can choose between several solver algorithms. The DIRECT method solves the linear system of equations

⁶ D.V. Chulhai and L. Jensen, *Plasmonic Circular Dichroism of 310- and α -Helix Using a Discrete Interaction Model/Quantum Mechanics Method*, Journal of Physical Chemistry A 119, 5218 (2015) (<https://doi.org/10.1021/jp5099188>)

directly with a LAPACK routine; this should be considered the most robust method, but scales poorly with the number of atoms ($O(N^3)$ where N is the number of atoms in the system). The other three methods use an iterative technique, The BRUTE method (brute force) takes into account all atoms in the matrix-vector multiply step, and scales as $O(N^2)$. The SINGLE method uses the single-level cell-multipole-method (CMM), wherein dipoles that are spatially similar are collected into a multipole moment which effectively reduces the system size. This also scales as $O(N^2)$ but with a lower prefactor than BRUTE. The MULTI method uses the multi-level cell-multipole-method, which uses larger and large multipole the farther apart the dipoles are. This is the fastest method and scales as $O(N \log N)$.

Due to technical limitations, CPIM can only use DIRECT. Further, depending on the system size DIRECT or SINGLE may be more efficient than MULTI. To simplify choosing the solving algorithm, there is a BEST option that chooses the best algorithm for the particular system. BEST is the default option for algorithm.

TOLERANCE tol

The TOLERANCE key allows the user to specify a tolerance for the iterative solver. By default the tolerance is based on ADF's INTEGRATION key. This has no effect with the DIRECT solver.

NITER iterations

The NITER key allows the user to specify the maximum number of iterations for the iterative solver. By default this is $\text{MAX}(N/100, 200)$ where N is the number of DIM atoms.

VOLUME vol_in_nm3

The VOLUME key is used to specify the DIM system volume. The volume is used to determine how to partition the system for the cell multipole method (ALGORITHM options SINGLE or MULTI), and is also used to determine the scattering efficiencies for frequency-dependent polarizability calculations. The volume does not need to be supplied; if it is missing, it will be calculated based on each atom's radius and the MULTIPLIER key.

MULTIPLIER aterm bterm cterm

An efficient way to get a approximation for the volume of the system is to sum the volume of each atom in the system, modified to account for the space between the atoms. This is done by modifying the atomic radius by a formula that takes into account the number of DIM atoms so that the effective radius changes with surface-to-bulk ratio. This formula is given by

$$r_{\text{eff}} = -ar/N^b + c$$

where r is the atomic radius, r_{eff} is the effective radius, N is the number of atoms, and the a , b , and c terms are the three parameters defined by the MULTIPLIER key. If the MULTIPLIER key is missing, the default values are 0.7, 0.5, and 1.13, respectively.

GRID <COARSE|MEDIUM|FINE>

In the cell multipole method (ALGORITHM options SINGLE or MULTI), a certain number of the closest atom interactions must be calculated explicitly. The GRID key controls how many atoms must be calculated this way, with COARSE being the least and FINE being the most. COARSE will be the fastest to calculate but may be numerically unstable. FINE is slowest to calculate but is the most stable. If the GRID key is missing, the default is MEDIUM.

FORCEFIELD

The FORCEFIELD key indicates that the DIM/QM calculation will include the DIM/QM force field. Currently the only maintained potential is the Lennard-Jones 12-6 potential (see Ref. ^{Page 122, 1}). This key is required to perform a DIM/QM geometry optimization and vibrational frequencies. By default, the DIM/QM force field is not included into the calculation. DRF gradients are not implemented.

Currently, DIM/QM geometry optimizations must be done in Cartesian coordinates which is specified in the GEOMETRY block. The user should be aware that ADF's default convergence criterion for a geometry optimization are relatively low, thus it is strongly suggested for a DIM/QM calculation to set the numerical integration quality (BeckeGrid) to good and change the convergence criterion of the max gradient to $1E-4$. It is not possible to do geometry optimization with DRF.

COORDDEPEND

The COORDDEPEND key indicates that the DIM/QM force field will be coordination dependent. This only affects the Lennard-Jones parameters for DIM atoms (see Ref.^{Page 122, 1}). By default, the DIM/QM force field is not coordination dependent.

CHEMISORPTION

The CHEMISORPTION key will include chemisorption corrections for all atoms that have chemisorption parameters within a given cutoff radius. By default, the DIM/QM force field does not include chemisorption corrections.

COORDPAR *atomtype* *e0* *e1* *r0* *r1* *CNmax* *Rmax* *Rmin*

The COORDPAR key allows the user to add additional coordination dependent parameter for a selected element type. *atomtype* specifies the element type (i.e., Ag for silver) for the given parameter set. *e0*, *e1*, *r0*, and *r1* are the coordination dependent Lennard-Jones parameters; see Ref.^{Page 122, 1}) for more details. The coordination numbers of the DIM atoms are computed as an effective coordination number. This scheme requires a maximum and minimum cutoff distances, *Rmax* and *Rmin* respectively, and a maximum coordination number, *CNmax*. All parameters need to be in atomic units.

CHEMPAR *atomtype* *e0* *e1* *r0* *r1* CUTOFF

The CHEMPAR key allows the user to add additional chemisorption dependent parameter for a selected element type. *atomtype* specifies the element type (i.e., N for nitrogen) for the given parameter set. *e0*, *e1*, *r0*, and *r1* are the coordination dependent Lennard-Jones parameters; see Ref.^{Page 122, 1}) for more details. The code determines if there is a chemical bond by a cutoff distance parameter, CUTOFF. If the QM-DIM bond is within the cutoff, the code uses the chemisorption parameter; otherwise, the code uses the standard parameter set. All parameters need to be in atomic units.

CHEMBOND *qmindex* *dimindex*

The CHEMBOND key indicates that there will a chemisorption correction used for the bond between the specified QM and DIM atoms. The user may repeat the CHEMBOND key up to 50 times to specify up to 50 different chemical bonds for the force field. The *qmindex* is an integer based on the order of atoms in the ATOMS block; i.e. the fifth QM atom in the ATOMS block would have *qmindex* = 5. The *dimindex* is the same but corresponds to the DIM atom involved in the bond. This key should only be used when the CHEMISORPTION key is also specified. When using CHEMBOND, the cutoff distance parameter for chemisorption correction parameter key will be ignored. It is suggested to use CHEMBOND if the user is generating a potential energy surface with a chemisorbed QM system.

PROJECTIONMATRIXPOINTS <ALL|CUTOFF *radius*|OFF>

The PROJECTIONMATRIXPOINTS key specifies what DIM atoms to include for the projection matrix when removing rigid motions out of the gradient. The methods available are ALL, CUTOFF, or OFF. The ALL option causes PROJECTIONMATRIXPOINTS to include all DIM atoms. OFF will turn off the removal of rigid motions. CUTOFF includes any DIM atom points within a cutoff radius from the center of mass of the QM system to the DIM atom points and requires a cutoff radius to be given in Angstrom. This key only applies to a geometry optimization. If the PROJECTIONMATRIXPOINTS key is not given, the option CUTOFF with a cutoff radius of 25.4 Angstrom is assumed.

PRINTATOMICDIPOLES

The PRINTATOMICDIPOLES key causes all the induced dipole moments of each DIM atom to be printed at the conclusion of each SCF cycle and each RESPONSE or AORESPONSE polarizability calculation. Because DIM/QM is typically used with many thousands of atoms, this can result in a large output file, but they may be useful for debugging purposes or to calculate electric fields. By default these are not printed.

PRINTLJP

The PRINTLJP key specifies that all Lennard-Jones parameters used for the calculation will be printed in the output file. The QM atoms' Lennard-Jones parameters are also printed with the DEBUG key.

DEBUG

The DEBUG key will print out extra information in the process of the calculation.

LocalDIM

LocalDIM performs the calculation fully for a specified CutOffDist (in Bohr) but ignores the image dipoles from

atoms outside of this distance. This option should converge to the full simulation and the distance should be chosen wisely. Must have LocalDirect keyword as well.

LocalDirect

Tells LocalDIM calculation to use the direct solver for the DIM dipoles. This solver is generally much faster than the other solvers available when the system is small. Currently, LocalDIM only works with the intention of using this faster solver, so this option must be used with LocalDIM

DIMBUFFER

Default value = 0.85. This keyword tells DIM how to decide for DRF2 calculations which atoms are in the same molecular grouping. This grouping decides if the charges polarize other atomic dipoles. For example, the charge for atoms in the same molecule will not polarize each other but they will polarize atomic dipoles in other molecules. This value should be adjusted based on the XYZ you supply and checked in the output file to ensure proper grouping behavior.

QMBUFFER

Default value = 0.85. This keyword tells DIM how to decide if the QM atoms are “bonded” to one another to determine the force field parameters needed calculations requiring DIM/QM gradient terms. As with the DIM-BUFFER keyword, this value should be adjusted for each system and checked in the output file to ensure proper behavior.

CutOffDist

Distance in Bohr that determines if the image dipoles of a DIM atom is included in a LocalDIM calculation. Any DIM atom that is inside the supplied distance from any QM atom will be fully included in the calculation.

DRF atomic parameters

The EXTERNALS block key controls the input data for the MM atoms. The EXTERNALS block is designed for DRF calculations. For each MM atom the following data are required:

```
EXTERNALS
  atm num grp-nam grp-num, char, x, y, x, pol
  ...
GROUP
{...}
end
```

atm

Type of atom, i.e., H, O, ...

num

number of atoms (optional)

grp-nam

Name of the group to which the atom belongs

grp-num

Number of the group to which the atom belong

char

atomic charge (in atomic units)

x

x-coordinate

y

y-coordinate

z

z-coordinate

pol

atomic polarizability (in atomic units)

GROUP

Indicates the end of group

The separation of molecules into GROUP's are important. Since in the many-body polarization operator only inter-molecular interactions, i.e. only interaction between sites which do not belong to the same group, are included. Therefore, it is important that the combined string (grp-nam + grp-num) is unique for each GROUP.

An example of a EXTERNALS block for two water molecules:

```
EXTERNALS
O 4 water 2, -0.6690, -11.380487, -11.810553, -4.515226, 9.3005
H 5 water 2, 0.3345, -13.104751, -11.837669, -3.969549, 0.0690
H 6 water 2, 0.3345, -10.510898, -12.853311, -3.320199, 0.0690
GROUP
O 7 water 3, -0.6690, -1.116350, 9.119186, -3.230948, 9.3005
H 8 water 3, 0.3345, -2.822714, 9.717033, -3.180632, 0.0690
H 9 water 3, 0.3345, -0.123788, 10.538199, -2.708607, 0.0690
GROUP
{...}
end
```

DIM atomic parameters

In this block, the parameters for the DIM atoms are defined.

```
DIMPAR
Element
RAD val
POL val
CAP val
CHAR val
OM val
OM1 val
OM2 val
GM1 val
GM2 val
SIZE val
BOUND val
STATIC
EXP /path/to/experimental/dielectric/file
DRUDE plasma damping {EV}
FERMI val
<LRTZ|LRTZ1> osc res damp {EV}
LRTZ2 osc pls res damp {EV}
LRTZ3 pls res damp {EV}
SUBEND
XYZ
{/absolute/path/to/coordinates.xyz}
{natoms
elem x.xxx y.yyy z.zzz
elem x.xxx y.yyy z.zzz
```

(continues on next page)

(continued from previous page)

```

    elem x.xxx y.yyy z.zzz
    ...}
SUBEND
LCLFLD /absolute/path/to/localfields.txt
{freq1 freq2 freq3 ..
  .....
}
GROUP groupname
  natoms
    elem x.xxx y.yyy z.zzz {pol=pol} {cap=cap} {char=char} {...}
    elem x.xxx y.yyy z.zzz {pol=pol} {cap=cap} {char=char} {...}
    elem x.xxx y.yyy z.zzz {pol=pol} {cap=cap} {char=char} {...}
    ...
  SUBEND
END

```

Element

Within the DIMPAR block, you will need a sub-block that defines the parameters for each element that is in your DIM system. You will need to replace 'Element' with the element you are assigning parameters to, as in:

```

Ag
...
SUBEND

```

if you are assigning parameters to Ag. Note that the first letter **MUST** be capitalized and the second **MUST** be lowercase.

RAD val

RAD specifies the atomic radius in the unit defined by the input file. RAD is required for all PIM calculations, all calculations with ALGORITHM options SINGLE or DIRECT, and all frequency-dependent calculations where the AOESPONSE LIFETIME key is given.

POL val

POL specifies the polarizability parameter (in a.u.) used in DRF or CPIM.

CAP val

CAP specifies the capacitance parameter (in a.u.) used in CPIM.

CHAR val

CHAR specifies the atomic charge (in a.u) used in DRF.

OM val

OM specifies the resonance frequency (in a.u) used in DRF. This replaces the OM_[HCON] key in the DIMQM block.

OM1 val

OM1 specifies the ω_1 parameter (in a.u) used in CPIM.

OM2 val

OM2 specifies the ω_2 parameter (in a.u) used in CPIM.

GM1 val

GM1 specifies the γ_1 parameter (in a.u) used in CPIM.

GM2 val

GM2 specifies the γ_2 parameter (in a.u) used in CPIM.

SIZE val

SIZE specifies the size-dependent parameter used in CPIM.

STATIC

Calculate the response properties for this atom type as static during a frequency dependent calculation.

EXP /absolute/path/to/experimental/dielectric/file

In PIM, the atomic polarizabilities are calculated from the dielectric constant. If you have access to the experimental dielectric constant, this may be supplied directly to DIM/QM. The values will be splined, so it is not necessary to ensure that each frequency at which you are calculating be in the file. DIM/QM expects the file to be formatted with the wavelength (in nm) in the first column, the real part of the dielectric in the second column, and the imaginary part of the dielectric in the third column. All other columns that may exist will be ignored, as well as lines beginning with the hash (#) symbol.

BOUND val

A Drude function is typically written as

$$\epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

with the second term being the Drude function, and the first term accounting for bound electrons. For a conductor with no bound electrons, $\epsilon_{\infty} = 1$ which is the default value for BOUND. To account for bound electrons you may set BOUND to a value greater than 1. This key only affects PIM.

DRUDE plasma damping {EV}

The formula for a Drude function is

$$\epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

where ϵ_{∞} represents the bound electrons (as discussed for BOUND), ω_p (plasma) is the plasma frequency, and γ (damping) is the damping parameter (decay rate). Optionally, EV may be added to specify the values be read in units of electron volts, otherwise they are read in units of a.u. This key only affects PIM.

FERMI val

The FERMI key is used to specify a Fermi velocity (in m/s) so that the Drude function may be size-corrected using a modified Drude function:

$$\epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i(\gamma + v_{\text{fermi}}/R_{\text{eff}}))}$$

where $+v_{\text{fermi}}$ is the Fermi velocity and R_{eff} is the effective nanoparticle radius. This can also be used in conjunction with EXP and DRUDE to size-correct experimental dielectric parameters. This key only affects PIM:

```
<LRTZ|LRTZ1> osc res damp {EV}
LRTZ2 osc pls res damp {EV}
LRTZ3 pls res damp {EV}
```

There are three forms of the Lorentzian function seen in the literature:

$$\sum_n \frac{f_n \Omega_{0,n}^2}{\Omega_{0,n}^2 - \omega^2 - i\Gamma_n \omega}$$

$$\sum_n \frac{f_n \omega_p^2}{\Omega_{0,n}^2 - \omega^2 - i\Gamma_n \omega}$$

$$\sum_n \frac{\Omega_{p,n}^2}{\Omega_{0,n}^2 - \omega^2 - i\Gamma_n \omega}$$

where $\Omega_{0,n}$ (res) is a bound electron resonance frequency, f_n (osc) is a bound electron oscillator strength, Γ_n (damp) is a bound electron excited state decay rate (or damping parameter), ω_p (pls) is the free electron

plasma frequency, and $\Omega_{p,n}$ (pls) is the bound electron plasma frequency. You may choose the Lorentzian for against which your parameters were parametrized. The top form is LRTZ1, the middle is LRTZ2, and the bottom is LRTZ3. Because LRTZ1 is the most common, it is also aliased as LRTZ. Optionally, EV may be added to specify the values be read in units of electron volts, otherwise they are read in units of a.u. This key only affects PIM. You may give any of the form of the LRTZ key up to 50 times supply up to 50 Lorentzian functions to make a Drude-Lorentz function.

XYZ

The XYZ sub-block is where the DIM atom coordinates are given. Two methods of supplying coordinates are allowed.

In-File Coordinates

As an example of how to supply coordinates in-file, imagine you wish to calculate a Au dimer system on the Z-axis. You might define your coordinates as:

```
XYZ
2
Au 0.0 0.0 0.0
Au 0.0 0.0 3.0
SUBEND
```

The first line gives the number of atoms to follow. Every line after that contains the element in the first column (first letter MUST be capitalized, second MUST be lowercase), then the x-component, then the y-component, then the z-component. You may not number the atoms.

External File Coordinates

When the DIM system size becomes large, it is often more convenient to keep the DIM coordinates in a separate file. The XYZ block would then look like:

```
XYZ
/absolute/path/to/coordinates.xyz
SUBEND
```

Note that you MUST include the absolute path to your file and the file name must end with `.xyz`.

The `.xyz` file is set up identically to the in-file table, except that there is a comment line between the number of atoms and the first atom. The `.xyz` file for our dimer system would be:

```
2
A gold dimer (this line will be ignored)
Au 0.0 0.0 0.0
Au 0.0 0.0 3.0
```

LCLFLD /absolute/path/to/localfields.txt

Text file of the local field induced dipoles that can be read in to reduce calculation time. The file must be in the following format:

```
freq1 freq2 freq3 ...
1
X
Atom1R-DipoleX      Atom1R-DipoleY      Atom1R-DipoleZ
Atom1I-DipoleX      Atom1I-DipoleY      Atom1I-DipoleZ
Atom2R-DipoleX      Atom2R-DipoleY      Atom2R-DipoleZ
Atom2I-DipoleX      Atom2I-DipoleY      Atom2I-DipoleZ
...
Y
Atom1R-DipoleX      Atom1R-DipoleY      Atom1R-DipoleZ
Atom1I-DipoleX      Atom1I-DipoleY      Atom1I-DipoleZ
```

(continues on next page)

(continued from previous page)

```
Atom2R-DipoleX   Atom2R-DipoleY   Atom2R-DipoleZ
Atom2I-DipoleX   Atom2I-DipoleY   Atom2I-DipoleZ
...
```

Here freq1 freq2 freq3 ... are the frequencies that are being used in the response calculation and 1 tells the program that the following dipoles are to be used with the first frequency. X and Y tell the program that these are the induced dipoles from perturbations in the X and Y Cartesian direction respectively.

GROUP groupname

The GROUP sub-block is where the DIM atom coordinates and parameters are given. Combines the XYZ subblock and Element subblock. A (unique) groupname is required (maximum 10 characters).

Example for a water molecule:

```
GROUP water1
3
O  0.00000  0.00000  0.59372  pol=5.7494  char=-0.6690
H  0.00000  0.76544 -0.00836  pol=2.7927  char=0.3345
H  0.00000 -0.76544 -0.00836  pol=2.7927  char=0.3345
SUBEND
```

The first line gives the number of atoms to follow. Every line after that contains the element in the first column (first letter MUST be capitalized, second MUST be lowercase), then the x-component, then the y-component, then the z-component. You may not number the atoms. At the end of the line for each element you can specify the DIM/QM parameters, as in the format in the example. The DIM/QM parameters can be 'POL', 'CAP', 'CHAR', 'OM1', 'OM2', 'GM1', 'GM2', 'SIZE', 'RAD', 'SPILLOUT', 'BOUND', 'DRUDE', 'FERMI', 'LRTZ', or 'EXP'.

4.4.6 QM/FQ: Quantum Mechanics/Fluctuating Charges (and Fluctuating Dipoles)

The Quantum Mechanics/Fluctuating Charges (QM/FQ) and QM/FQ and Fluctuating Dipoles (QM/FQF μ) methods are multiscale models designed to describe the properties of a chemical system perturbed by the presence of its molecular environment, where the latter is described using a polarizable classical force field; see for example Refs.¹²³⁴⁵. The QM/FQ model has been applied to the calculation of spectroscopic properties of molecules in aqueous solution and different solvents (see⁶), whereas QM/FQF μ has only been applied to aqueous solutions. The method has also been coupled with the GW many-body-perturbation-theory method¹¹. In QM/FQ each atom of the environment (e.g. a solvation shell) is endowed with a fluctuating charge (FQ) which can vary in response to the electrostatic potential generated by the solute, whereas in QM/FQF μ an additional source of polarization (an induced dipole moment) is placed on each atom. The FQ and FQF μ charges can be constrained such that each molecule within the environment remains electrically neutral. The

¹ T. Giovannini, F. Egidi, C. Cappelli, *Molecular spectroscopy of aqueous solutions: a theoretical perspective*, *Chemical Society Reviews*, 49, 5664 (2020) (<https://doi.org/10.1039/C9CS00464E>)

² C. Cappelli, *Integrated QM/polarizable MM/continuum approaches to model chiroptical properties of strongly interacting solute-solvent systems*, *International Journal of Quantum Chemistry*, 116, 1532 (2016) (<https://doi.org/10.1002/qua.25199>)

³ T. Giovannini, F. Egidi, C. Cappelli, *Theory and algorithms for chiroptical properties and spectroscopies of aqueous systems*, *Physical Chemical Chemistry Physics*, 22, 22864 (2020) (<https://doi.org/10.1039/D0CP04027D>)

⁴ T. Giovannini, A. Puglisi, M. Ambrosetti, C. Cappelli, *Polarizable QM/MM approach with fluctuating charges and fluctuating dipoles: the QM/FQF μ model*, *Journal of Chemical Theory and Computation*, 15, 2233-2245 (2019) (<https://doi.org/10.1021/acs.jctc.8b01149>)

⁵ T. Giovannini, R. R. Riso, M. Ambrosetti, A. Puglisi, C. Cappelli, *Electronic transitions for a fully polarizable QM/MM approach based on fluctuating charges and fluctuating dipoles: linear and corrected linear response regimes*, *The Journal of Chemical Physics*, 151, 174104 (2019) (<https://doi.org/10.1063/1.5121396>)

⁶ M. Ambrosetti, S. Skoko, T. Giovannini, C. Cappelli, *Quantum Mechanics/Fluctuating Charge Protocol to Compute Solvatochromic Shifts*, *Journal of Chemical Theory and Computation* (2021) (<https://doi.org/10.1021/acs.jctc.1c00763>)

¹¹

G. Nottoli, P. Lafiosca, F.E.Q. Rodríguez, F. Egidi, A. Förster, C. Cappelli, *GW Approximation Coupled with Classical Fluctuating Charges and Dipoles*, *Journal of Chemical Theory and Computation* 22 (2026) 371-384 (<https://doi.org/10.1021/acs.jctc.5c01722>)

energy functional of the FQ and FQFμ systems can be written as:

$$F(q, \lambda) = \sum_{\alpha, i} q_{\alpha, i} \chi_{\alpha, i} + 1/2 \sum_{i\alpha j\beta} q_{\alpha, i} T_{\alpha i, \beta j}^{qq} q_{\beta, j} + \sum_{\alpha} \lambda_{\alpha} \left(\sum_i q_{\alpha, i} - Q_{\alpha} \right)$$

$$F(q, \mu, \lambda) = \frac{1}{2} \sum_{i\alpha j\beta} q_{i\alpha} T_{i\alpha, j\beta}^{qq} q_{j\beta} + \frac{1}{2} \sum_{ij} \mu_{i\alpha}^{\dagger} T_{i\alpha, j\beta}^{\mu\mu} \mu_{j\beta} + \sum_{ij} q_{i\alpha} T_{i\alpha, j\beta}^{q\mu} \mu_{j\beta}^{\dagger} + \sum_{i\alpha} q_{i\alpha} \chi_{i\alpha} + \sum_{\alpha} \lambda_{\alpha} \left[\sum_i q_{\alpha i} - Q_{\alpha} \right]$$

where $q_{\alpha, i}$ and $\mu_{\alpha, i}$ are the i -th FQ charge and the i -th dipole belonging to the α -th molecule, $\chi_{\alpha, i}$ is the electronegativity of each atom, λ_{α} is the Lagrange multiplier associated with the α -th molecule, whose purpose is to fix the total charge to be Q_{α} . The matrix $T_{\alpha i, \beta j}^{qq}$ describes the interaction kernel between the charges: while the diagonal elements are related to the self-interaction through the chemical hardnesses *et al*, the off-diagonal elements may be specified through different formulations. The $T_{i\alpha, j\beta}^{q\mu}$ and $T_{i\alpha, j\beta}^{\mu\mu}$ matrices describe the interaction kernel between charges and dipoles and between the dipoles, respectively. The electric variables (the FQ charges and the dipoles) can be obtained by minimizing the energy functional with respect to the charges, the dipoles and the Lagrange multipliers, which leads to the following set of linear equations:

$$\left(\begin{array}{cc|c} \mathbf{T}^{qq} & \mathbf{1}_{\lambda} & \mathbf{T}^{q\mu} \\ \hline \mathbf{1}_{\lambda}^{\dagger} & \mathbf{0} & \mathbf{0} \\ \hline -\mathbf{T}^{q\mu\dagger} & \mathbf{0} & \mathbf{T}^{\mu\mu} \end{array} \right) \begin{pmatrix} \mathbf{q} \\ \lambda \\ \mu \end{pmatrix} = \begin{pmatrix} -\chi \\ \mathbf{Q} \\ \mathbf{0} \end{pmatrix} \Rightarrow \mathbf{DQ}_{\lambda} = -\mathbf{C}_Q$$

where $\mathbf{1}_{\lambda}$ is a rectangular matrix which accounts for the Lagrangians, $\mathbf{C}_Q$ is a vector containing atomic electronegativities and total charge constraints. $\mathbf{Q}_{\lambda}$ is a vector containing charges, dipoles and Lagrange multipliers.

The coupling of the FQ/FQFμ models with a QM Hamiltonian can be done by introducing the QM/FQ(Fμ) interaction operator as

$$H_{\text{QM/FQ}} = \sum_i^N q_i V[\rho](r_i), H_{\text{QM/FQF}\mu} = \sum_i^N q_i V[\rho](r_i) - \sum_i^N \mu_i E[\rho](r_i),$$

where N is the number of atoms, q_i and μ_i are the i -th FQ charge and dipole located at position r_i , respectively. $V[\rho](r_i)$ and $E[\rho](r_i)$ are the electric potential and field generated by the QM system at the same point. The introduction of the QM/FQ interaction leads to a modified set of linear equations for the FQ charges, i.e.

$$DQ_{\lambda} = -C_Q - R[\rho]$$

where R is an array collecting the electric potential and field generated by the QM electrons and nuclei at the position of each atom. The FQ charges (and dipoles) are thus determined self-consistently along with the ground-state density. Since the charges (and dipoles) depend on the QM density, explicit terms also appear within response equations that are solved to simulate spectroscopic and excited-state properties of the QM system.

Starting from AMS2021.103 a screening is included for the interaction between MM atoms and the QM density, to avoid unstable results in case numerical integration points are accidentally close to MM atoms. The screened $1/r_{ij}$ has the form:

$$\begin{aligned} \text{ERF:} &= \frac{\text{erf}(ar_{ij})}{r_{ij}} \\ \text{EXP:} &= \frac{(1 - \exp(-ar_{ij}))^2}{r_{ij}} \\ \text{GAUS:} &= \frac{\text{erf}(r_{ij}/a)}{r_{ij}} \end{aligned}$$

where a can be changed with the QMSCREENFACTOR keyword.

Gradients and geometry optimization

Starting from AMS2025 the QM/FQ(F μ) model can be used when calculating gradients and geometry optimizations. QM/FQ(F μ) is a “focused model” developed to reproduce the properties of the central QM system under the perturbation of the environment, and not the property of the entire system (QM + environment). In keeping with this philosophy, whenever geometries or gradients are calculated, the atoms in the environment are kept frozen in place and the gradients are only evaluated for the QM atoms. While in their simplest form these are purely electrostatic models, when evaluating gradients it is crucial to include non-electrostatic contributions, particularly repulsion forces that keep the QM atoms from approaching the MM atoms. This can be done through the `NonEle` keyword (see below). At present, only ground-state gradients are implemented.

Coupling with FDE

Starting from AMS2022 the coupling between *Frozen Density Embedding (FDE)* (page 144) and FQ is implemented (see Ref.⁷). When a FDE calculation is set up, the FQ(F μ) environment atoms respond to both layers of the FDE embedding.

In the case of an excited-state calculation performed with the Time-Dependent DFT method (TDDFT), the atoms belonging to the frozen density layer do not normally respond dynamically to the external field. This can create an imbalance because both the non-frozen QM layer and the fluctuating charge (and dipole) layer both do. A very cost-effective way to include the response of the frozen-density layer into the calculation is to use the FQ(F μ) model to estimate it (see Ref. ^{Page 136, 7} for more details) provided the parameters defining the molecular entities in the frozen layer are available.

This can be accomplished by simply including the `FDERESP` keyword in the input (see below).

Input options

The scheme below presents all keywords that can be used in a QM/FQ(F μ) calculation. Further down below you can find a detailed explanation of how to specify the coordinates of the FQ(F μ) atoms.

```
QM FQ
  AtomType
    Alpha float
    Area float
    Charge float
    Chi float
    Dfermi float
    Efermi float
    Eta float
    R0 float
    Sfermi float
    Sigma0 float
    Symbol string
    Tau float
    wQFMuFile string
  End
  Coords # Non-standard block. See details.
  ...
End
FDERESP Yes/No
Forcefield [FQ | FQFMU | wFQ | wFQ_RQ | wQFMu | wQFMu_RQRMU]
Frozen Yes/No
```

(continues on next page)

⁷ F.Egidi, S. Angelico, P. Lafiosca, T. Giovannini, C. Cappelli, *A polarizable three-layer frozen density embedding/molecular mechanics approach*, The Journal of Chemical Physics, 154, 164107 (2021) (<https://doi.org/10.1063/5.0045574>)

(continued from previous page)

```

Kernel [OHNO | COUL | GAUS]
LifeFrequency float
LifeState integer
MolCharge float
NonEle [LJ | None]
QMSCREEN [ERF | EXP | GAUS | NONE]
QMSCREENFACTOR float
ReadDynamicMatrix string
End

```

QMFQ**Type**

Block

Description

Block input key for QM/(w)FQ(FMu).

AtomType**Type**

Block

Recurring

True

Description

Definition of atomic types in MM environment

Alpha**Type**

Float

Description

Polarizability of FQFMU atom

Area**Type**

Float

Description

Effective charge-transfer area time between same-type wFQ atoms

Charge**Type**

Float

Description

MM fixed charge (non-polarizable only)

Chi**Type**

Float

Description

Electronegativity of FQ atom

Dfermi

Type

Float

Description

wFQ d parameter for Fermi damping

Efermi**Type**

Float

Description

Fermi Energy of wFQ carbon-based structure

Eta**Type**

Float

Description

Chemical Hardness of FQ atom

R0**Type**

Float

Description

wFQ R0 parameter for Fermi damping

Sfermi**Type**

Float

Description

wFQ s parameter for Fermi damping

Sigma0**Type**

Float

Description

Static conductivity time of wFQ atom

Symbol**Type**

String

Description

Symbol associated with atom type

Tau**Type**

Float

Description

Scattering time of wFQ atom

wFQMuFile**Type**

String

Description

The absolute path to the wFQFMu interband polarizability file

Coords**Type**

Non-standard block

Description

Coordinates and fragment information (FQ only)

FDERESP**Type**

Bool

Default value

No

Description

In response calculations (TD), the polarization contribution of the FDE part is introduced at the FQ level [See F. Egidi et al. J. Chem. Phys. 2021, 154, 164107].

Forcefield**Type**

Multiple Choice

Default value

FQ

Options

[FQ, FQFMU, wFQ, wFQ_RQ, wFQFmu, wFQFmu_RQRMU]

Description

Version of the FQ family of polarizable forcefields

Frozen**Type**

Bool

Default value

No

Description

Expert option. Do not introduce polarization effect in response calculations.

Kernel**Type**

Multiple Choice

Default value

OHNO

Options

[OHNO, COUL, GAUS]

Description

Expert option. KERNEL can be used to choose the functional form of the charge-charge interaction kernel between MM atoms. Recommended is to use the default OHNO. The COUL screening is the standard Coulomb interaction $1/r$. The OHNO choice introduce the Ohno

functional (see [K. Ohno, Theoret. Chim. Acta 2, 219 (1964)]), which depends on a parameter n that is set equal to 2. Finally, the GAUS screening models each FQ charge by means of a spherical Gaussian-type distribution, and the interaction kernel is obtained accordingly. For QM/FQFMU only GAUS SCREEN is implemented.

LifeFrequency**Type**

Float

Default value

0.0

Description

Input frequency for calculating TDDFT/wFQ(Fmu) lifetimes

LifeState**Type**

Integer

Default value

0

Description

Target excited state for state-specific TDDFT/wFQ(Fmu) lifetimes

MolCharge**Type**

Float

Default value

0.0

Description

Total charge of each fragment (FQ only)

NonEle**Type**

Multiple Choice

Default value

LJ

Options

[LJ, None]

Description

Whether to include non-electrostatic contributions to the energy. Default is the Lennard-Jones (LJ) model.

QMSCREEN**Type**

Multiple Choice

Default value

GAUS

Options

[ERF, EXP, GAUS, NONE]

Description

Expert option. QMSCREEN can be used to choose the functional form of the charge-charge interaction kernel between MM atoms and the QM density. The screening types available are ERF (error function), EXP (exponential), GAUS (Gaussian), or NONE. The default is GAUS.

QMSCREENFACTOR**Type**

Float

Default value

0.2

Description

Expert option. Sets the QM/MM interaction kernel screening length. Recommended is to use the default value 0.2 with the GAUS QM/MM screening function.

ReadDynamicMatrix**Type**

String

Description

The absolute path to the decomposed wFQ(FMu) matrix file

The FQ(F μ) region is specified within the Coords block, using the following scheme.

```
Coords
  elem1 x.xxx y.yyy z.zzz N
  elem2 x.xxx y.yyy z.zzz N
  elem3 x.xxx y.yyy z.zzz N
  ...
End
```

You will need to replace 'elem#' with the element you are assigning parameters to, and after the coordinates you need to include a number N assigning the element to a specific molecule. The latter number is important because the total charge of each environment molecule is constrained to be a specific value (0 by default), which can be specified with the MolCharge keyword if nonzero (see above scheme). For instance, the following block specifies two water molecules, where the oxygen and hydrogen atoms have been given the names OW and HW respectively:

```
Coords
  OW -0.9957202 0.0160415 1.2422556 1
  HW -1.4542703 -0.5669741 1.8472817 1
  HW -0.9377950 -0.4817912 0.4267562 1
  OW -0.2432343 -1.0198566 -1.1953808 2
  HW 0.4367536 -0.3759433 -0.9973297 2
  HW -0.5031835 -0.8251492 -2.0957959 2
End
```

Parameters must have been assigned for the atom types OW and HW in the respective AtomType blocks.

In case of water, it is recommended to use the optimized FQ parameters Chi and Eta for O and H in water proposed in Ref.⁹

```
AtomType
  Symbol O
  Chi 0.189194
```

(continues on next page)

⁹ T. Giovannini, P. Lafiosca, B. Chandramouli, V. Barone, C. Cappelli, *Effective yet reliable computation of hyperfine coupling constants in solution by a QM/MM approach: Interplay between electrostatics and non-electrostatic effects*, *Journal of Chemical Physics* 150 (2019) 124102 (<https://doi.org/10.1063/1.5080810>)

(continued from previous page)

```
Eta 0.523700
End
AtomType
  Symbol H
  Chi 0.012767
  Eta 0.537512
End
```

Alternatively, in case of water as solvent, one could use the parameters proposed in Ref.¹⁰

```
AtomType
  Symbol O
  Chi 0.116859
  Eta 0.584852
End
AtomType
  Symbol H
  Chi 0.000001
  Eta 0.625010
End
```

For other solvents, it is recommended to use the parameters reported in Ref.^{Page 134, 6}.

For QM/FQF_μ calculations for water as solvent, the parameters reported in Ref.^{Page 134, 4} can be used

```
AtomType
  Symbol O
  Chi 0.290840
  Eta 0.562510
  Alpha 2.218790
End
AtomType
  Symbol H
  Chi 0.167570
  Eta 0.609320
  Alpha 1.190640
End
```

¹⁰ S.W. Rick, S.J. Stuart, B.J. Berne, *Dynamical fluctuating charge force fields: Application to liquid water*, *Journal of Chemical Physics* 101 (1994) 6141 (<https://doi.org/10.1063/1.468398>)

4.4.7 QM/ ω FQ: Quantum Mechanics/Frequency-Dependent Fluctuating Charges (and Fluctuating Dipoles)

The Quantum Mechanics/Frequency-Dependent Fluctuating Charges (QM/ ω FQ) and Frequency-Dependent Charges and Fluctuating Dipoles (QM/ ω FQF μ) methods are multiscale models designed to describe the properties of a chemical system perturbed by a plasmonic substrate, where the latter is described with the polarizable ω FQ or ω FQF μ models.^{1,2,3,4,5,6} The QM/ ω FQ(F μ) model has been applied, among others, to Surface-Enhanced Raman Scattering^{Page 143, 2} and Surface-Enhanced Fluorescence⁷. In these models, each atom is endowed with complex, frequency-dependent electric variables: fluctuating charges in ω FQ, and fluctuating charges and dipoles in ω FQF μ . Charge transfer between atoms is governed by a classical Drude-like conduction mechanism, while short-range quantum tunneling effects are effectively accounted for through a distance-dependent damping function. The response is evaluated at a given frequency ω of the external perturbation.

These methods can be used, for example, to study the spectra of an organic molecule adsorbed on a metal nanoparticle. The electromagnetic field probing the spectroscopic response can resonate with the nanoparticle and originate surface plasmons that greatly enhance the response of the adsorbed molecule. As in the standard QM/FQ model used for solvation, in QM/ ω FQ the target molecule is described quantum-mechanically (typically using DFT) while the substrate is described classically.

The ω FQ charges, and the ω FQF μ charges and dipoles of the atoms in the substrate are obtained by solving the following complex linear systems.^{1,2,3}

$$[\bar{\mathbf{K}}\mathbf{T}^{qq} - z_q(\omega)\mathbf{I}_N] \mathbf{q}(\omega) = -\bar{\mathbf{K}}\mathbf{V}(\omega)$$

$$\left[\begin{pmatrix} \bar{\mathbf{K}} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_{3N} \end{pmatrix} \begin{pmatrix} \mathbf{T}^{qq} & \mathbf{T}^{q\mu} \\ \mathbf{T}^{\mu q} & \mathbf{T}^{\mu\mu} \end{pmatrix} - \begin{pmatrix} z_q(\omega)\mathbf{I}_N & \mathbf{0} \\ \mathbf{0} & z_\mu(\omega)\mathbf{I}_{3N} \end{pmatrix} \right] \begin{pmatrix} \mathbf{q}(\omega) \\ \boldsymbol{\mu}(\omega) \end{pmatrix} = \begin{pmatrix} \bar{\mathbf{K}} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_{3N} \end{pmatrix} \begin{pmatrix} -\mathbf{V}(\omega) \\ \mathbf{E}(\omega) \end{pmatrix}$$

where $\mathbf{q}(\omega)$ and $\boldsymbol{\mu}(\omega)$ are the vectors of complex, frequency-dependent fluctuating charges and dipoles, respectively, and ω is the frequency of the external perturbation. $\mathbf{V}(\omega)$ and $\mathbf{E}(\omega)$ denote the potential and electric field, respectively, originating from the perturbed molecular density.

The matrices $\mathbf{T}^{qq}$, $\mathbf{T}^{q\mu}$, and $\mathbf{T}^{\mu\mu}$ describe charge–charge, charge–dipole, and dipole–dipole interactions, respectively. Moreover, the matrix $\bar{\mathbf{K}}$ encodes atomistic charge transport and is constructed from a Drude-like conduction model including short-range tunneling corrections. The quantities $z_q(\omega)$ and $z_\mu(\omega)$ introduce the frequency dependence of the intraband and interband electronic response.

The coupling of the ω FQ/ ω FQF μ models with a QM Hamiltonian can be done by introducing the QM/ ω FQ(F μ) interaction operator as

$$H_{\text{QM}/\omega\text{FQ}} = \sum_i^N q_i(\omega)V[\rho](r_i), H_{\text{QM}/\omega\text{FQF}\mu} = \sum_i^N q_i(\omega)V[\rho](r_i) - \sum_i^N \mu_i(\omega)E[\rho](r_i),$$

where N is the number of atoms, q_i and μ_i are the i -th ω FQF μ charge and dipole located at position r_i , respectively. $V[\rho](r_i)$ and $E[\rho](r_i)$ are the electric potential and field generated by the QM system on the same point.

¹ T.Giovannini et al. *Do We Really Need Quantum Mechanics to Describe Plasmonic Properties of Metal Nanostructures?* ACS Photonics 9 (2022) 3025 (<https://doi.org/10.1021/acsp Photonics.2c00761>)

² P.Lafiosca et al. *QM/Classical Modeling of Surface Enhanced Raman Scattering Based on Atomistic Electromagnetic Models* JCTC 19 (2023) 3616 (<https://doi.org/10.1021/acs.jctc.3c00177>)

³ S.Sodomaco et al. *Computational Insights into the Adsorption of Ligands on Gold Nanosurfaces* JPC A 127 (2023) 10282 (<https://doi.org/10.1021/acs.jpca.3c05560>)

⁴ T. Giovannini, A. Puglisi, M. Ambrosetti, C. Cappelli, *Polarizable QM/MM approach with fluctuating charges and fluctuating dipoles: the QM/ ω FQF μ model*, Journal of Chemical Theory and Computation, 15, 2233–2245 (2019) (<https://doi.org/10.1021/acs.jctc.8b01149>)

⁵ L. Nicoli et al. *Atomistic Multiscale Modeling of Colloidal Plasmonic Nanoparticles* ACS Phys. Chem. Au 4 (2024) 669 (<https://doi.org/10.1021/acspchemau.4c00052>)

⁶ S.Sodomaco et al. *Atomistic QM/Classical Modeling of Surface-Enhanced Infrared Absorption* JPC C 130 (2026) 1919 (<https://doi.org/10.1021/acs.jpcc.5c07549>)

⁷ P.Grobas Illobre et al. *Multiscale modeling of surface enhanced fluorescence* Nanoscale Adv. 6 (2024) 3410 (<https://doi.org/10.1039/D4NA00080C>)

Since the charges (and dipoles) depend on the QM density, explicit terms also appear within response equations that are solved to simulate spectroscopic and excited-state properties of the QM system. Note that this is also true in the standard QM/FQ method for solvation, but the difference here is that the interaction terms also carry an imaginary part and are frequency-dependent.

A screening is included for the interaction between MM atoms and the QM density to avoid unstable results if numerical integration points are accidentally close to MM atoms. The screened $1/r_{ij}$ has the form:

$$\begin{aligned}\text{ERF} &= \frac{\text{erf}(ar_{ij})}{r_{ij}} \\ \text{EXP} &= \frac{(1 - \exp(-ar_{ij}))^2}{r_{ij}} \\ \text{GAUS} &= \frac{\text{erf}(r_{ij}/a)}{r_{ij}}\end{aligned}$$

where a can be changed with the QMSCREENFACTOR keyword.

Input options

The input scheme for a QM/ ω FQ(Fu) calculation is identical to that for a regular *QM/FQ calculation* (page 134) and is explained in the corresponding manual page.

The number of parameters that should be specified is greater. For this reason we provide *several examples* (page 656) that show how to build a sample input and that already contain parameters for the most common substrates.

4.4.8 FDE: Frozen Density Embedding

The Frozen-Density-Embedding (FDE) option invokes calculation of the effective embedding potential introduced by Wesolowski and Warshel¹ in order to take into account the effect of the environment on the electronic structure of an embedded system. The embedding potential (Eq. 3 in Ref.⁵) depends explicitly on electron densities corresponding to the embedded subsystem (e.g. a solvated molecule) and its environment (e.g. solvent). For a detailed review, see Ref.³. The ADF implementation of the method is described in detail in Ref.²⁴.

A time-dependent linear-response generalization of this embedding scheme was derived in Ref.⁶. Its implementation in an approximate form, which assumes a localized response of the embedded system only (uncoupled FDE), is described in the supplementary material to Ref.⁷. For possible drawbacks and pitfalls in connection with this approximation, see Refs. [Page 144, 289](#).

¹ T.A. Wesolowski and A. Warshel, *Frozen Density Functional Approach for ab-initio Calculations of Solvated Molecules*, *Journal of Physical Chemistry* 97, 8050 (1993) (<https://doi.org/10.1021/j100132a040>)

⁵ T.A. Wesolowski and J. Weber, *Kohn-Sham equations with constrained electron density: an iterative evaluation of the ground-state electron density of interacting molecules*, *Chemical Physics Letters* 248, 71 (1996) ([https://doi.org/10.1016/0009-2614\(95\)01281-8](https://doi.org/10.1016/0009-2614(95)01281-8))

³ T.A. Wesolowski, in: *Computational Chemistry: Reviews of Current Trends - Vol. 10*, World Scientific, 2006.

² J. Neugebauer, C.R. Jacob, T.A. Wesolowski and E.J. Baerends, *An Explicit Quantum Chemical Method for Modeling Large Solvation Shells Applied to Aminocoumarin C15I*, *Journal of Physical Chemistry A* 109, 7805 (2005) (<https://doi.org/10.1021/jp0528764>)

⁴ C.R. Jacob, J. Neugebauer and L. Visscher, *A flexible implementation of frozen-density embedding for use in multilevel simulations*, *Journal of Computational Chemistry* 29, 1011 (2008) (<https://doi.org/10.1002/jcc.20861>)

⁶ M.E. Casida and T.A. Wesolowski, *Generalization of the Kohn-Sham equations with constrained electron density formalism and its time-dependent response theory formulation*, *International Journal of Quantum Chemistry* 96, 577 (2004) (<https://doi.org/10.1002/qua.10744>)

⁷ T.A. Wesolowski, *Hydrogen-Bonding-Induced Shifts of the Excitation Energies in Nucleic Acid Bases: An Interplay between Electrostatic and Electron Density Overlap Effects*, *Journal of the American Chemical Society* 126, 11444 (2004) (<https://doi.org/10.1021/ja048846g>)

⁸ C.R. Jacob, J. Neugebauer, L. Jensen and L. Visscher, *Comparison of frozen-density embedding and discrete reaction field solvent models for molecular properties*, *Physical Chemistry Chemical Physics* 8, 2349 (2006) (<https://doi.org/10.1039/B601997H>)

⁹ J. Neugebauer and E.J. Baerends, *Exploring the Ability of Frozen-Density Embedding to Model Induced Circular Dichroism*, *Journal of Physical Chemistry A* 110, 8786 (2006) (<https://doi.org/10.1021/jp0622280>)

The theory of coupled excited states for subsystems is described in Refs.^{35,34}, and extended for general response properties in Ref.¹⁰. This theory (subsystem TDDFT, coupled FDE) allows you to treat the mutual response of several subsystems, including the ones that are considered the environment.

A generalization of the FDE scheme to the calculation of NMR shieldings has been given in Ref.¹¹, where also the approximations involved and possible problems are discussed.

With the exception of interaction energies, the current implementation in ADF only allows the calculation of molecular properties that depend only on the electron density and of response properties using TDDFT. For an application to the calculation of several molecular properties in solution and a comparison to the DRF model also available in ADF, see Ref.⁸. For further applications of the ADF implementation, see Ref.¹² (weakly interacting complexes), Refs.^{Page 144, 2Page 144, 83738} (solvent effects), and Refs.^{39,40} (other environment effects).

To invoke a frozen-density embedding calculation, three additional specifications in the input are required. First and second, one or more frozen fragments have to be included both in the FRAGMENTS and FDEFRAGMENTS block, and third, the block key FDE has to be included. Note that block key FDEFRAGMENTS has been introduced in AMS2025. For previous versions, see older documentation. In the simplest case, this input should look like this:

```
FRAGMENTS
...
FragType FragFile
...
END
FDEFRAGMENTS
...
FragType type=FDE
...
END
FDE
  PW91K
End
```

In the FDEFRAGMENTS block, for any fragment you can specify the option type=FDE to indicate that the density of this fragment is kept frozen. This density is imported from the file FragFile. The frozen fragments have to be included in addition to the usual, non-frozen fragments. The atoms of the frozen fragments have to be included in the ATOMS block. As with normal fragments, the fragment found in the file will be rotated and translated to its position specified in the ATOMS block. For more details on specifying fragments, see the section ‘fragment files’. In the FDE input block, the recommended PW91k (also known as GGA97) approximant is used for the non-additive kinetic energy (the default is the local density approximant). A recommended alternative is NDS. For all other options the defaults will be used.

Please note that throughout the FDE part of the documentation, the word “approximant” is used instead of the more usual

³⁵ J. Neugebauer, *Couplings between electronic transitions in a subsystem formulation of time-dependent density functional theory*, *Journal of Chemical Physics* **126**, 134116 (2007) (<https://doi.org/10.1063/1.2713754>).

³⁴ J. Neugebauer, *Photophysical Properties of Natural Light-Harvesting Complexes Studied by Subsystem Density Functional Theory*, *Journal of Physical Chemistry B* **112**, 2207 (2008) (<https://doi.org/10.1021/jp709956k>).

¹⁰ J. Neugebauer, *On the calculation of general response properties in subsystem density functional theory*, *Journal of Chemical Physics* **131**, 084104 (2009) (<https://doi.org/10.1063/1.3212883>).

¹¹ C.R. Jacob and L. Visscher, *Calculation of nuclear magnetic resonance shieldings using frozen-density embedding*, *Journal of Chemical Physics* **125**, 194104 (2006) (<https://doi.org/10.1063/1.2370947>).

¹² C.R. Jacob, T.A. Wesolowski and L. Visscher, *Orbital-free embedding applied to the calculation of induced dipole moments in CO₂... X (X=He, Ne, Ar, Kr, Xe, Hg) van der Waals complexes*, *Journal of Chemical Physics* **123**, 174104 (2005) (<https://doi.org/10.1063/1.2107567>).

³⁷ J. Neugebauer, M.J. Louwerse, E.J. Baerends and T.A. Wesolowski, *The merits of the frozen-density embedding scheme to model solvatochromic shifts*, *Journal of Chemical Physics* **122**, 94115 (2005) (<https://doi.org/10.1063/1.1858411>).

³⁸ J. Neugebauer, M.J. Louwerse, P. Belanzoni, T.A. Wesolowski and E.J. Baerends, *Modeling solvent effects on electron-spin-resonance hyperfine couplings by frozen-density embedding*, *Journal of Chemical Physics* **123**, 114101 (2005) (<https://doi.org/10.1063/1.2033749>).

³⁹ M. Zbiri, M. Atanasov, C. Daul, J.-M. Garcia Lastra and T.A. Wesolowski, *Application of the density functional theory derived orbital-free embedding potential to calculate the splitting energies of lanthanide cations in chloroelpasolite crystals*, *Chemical Physics Letters* **397**, 441 (2004) (<https://doi.org/10.1016/j.cplett.2004.09.010>).

⁴⁰ M. Zbiri, C.A. Daul and T.A. Wesolowski, *Effect of the f-Orbital Delocalization on the Ligand-Field Splitting Energies in Lanthanide-Containing Elpasolites*, *Journal of Chemical Theory and Computation* **2**, 1106 (2006) (<https://doi.org/10.1021/ct060035a>).

“functional” to emphasize that the exact functional is not known, also in the case of the kinetic energy functional. In the literature one may encounter both words used interchangeably.

By including more than one frozen fragment, it is possible to use a frozen fragment that is a superposition of the densities of isolated molecules (this was possible in the previous version of ADF using the DENSPPREP option). For a discussion and tests of the use of such approximate environment densities, see Ref. [Page 144, 2](#).

There is no restriction on the use of symmetry in FDE calculations, and usually the correct symmetry will be detected automatically. However, in the preparation of frozen fragments that will be rotated and/or translated in the FDE calculation, one has to include the keyword NOSYMFIT for technical reasons.

In the current implementation, only the electron density of the embedded (non-frozen) system is calculated. Therefore, with the exception of interaction energies, only properties that depend directly on the electron density (e.g. dipole moments) are available. In particular, the calculation of energy gradients is not implemented yet. All quantities given in the output refer (unless explicitly specified otherwise) to the non-frozen system only.

To employ the extension of FDE to the calculation of NMR shieldings, the file TAPE10 has to be used in the FDE calculation (by including the option SAVE TAPE10), and subsequently the NMR shielding has to be calculated using the program NMR. The TDDFT extension of the FDE formalism allows the calculation of electronic excitation energies and polarizabilities. This extension is automatically activated if FDE is used in combination with the EXCITATIONS or the RESPONSE key. To allow the mutual response of several subsystems, see the section on *subsystem TDDFT* (page 153).

Fragment-specific FDE options

For each frozen fragment, several additional options can be applied. To do this, the fragment specification is used as a subblock key by appending an & sign. The subblock is terminated with SubEnd. This subblock key looks, in the most general form, as follows:

```
FRAGMENTS
...
  FragType FragFile
...
END
FDEFRAGMENTS
...
  FragType type=FDE &
    {FDEOPTIONS [USEBASIS] [RELAX or FREEZEANDTHAW] [OPTIMIZE]}
    {FDEENSTYPE [SCF | SCFexact | SCFfitted]}
    {RELAXCYCLES n or FREEZEANDTHAWCYCLES n}
    {XC [LDA | GGA ggapotx ggapotc | MODEL SAOP]}
  SubEnd
...
END
```

FDEOPTIONS

FDEOPTIONS USEBASIS

If the USEBASIS option is specified, the basis functions of this frozen fragment will be included in the calculation of the embedded subsystem. This allows you to expand the density of the embedded subsystem using not only atom-centered basis sets localized in the embedded subsystem but also the ones in the environment; see Ref. ¹³. In large-scale simulations using the embedding potential, this option is recommended to be used in the preparation stage to investigate the basis set dependence of the results (chapter 5.3 in Ref. [Page 144, 3](#)). This option is also an indispensable element in the procedure introduced in Ref. ¹³ to test approximants to the kinetic-energy component of the embedding potential introduced by Wesolowski and Warshel.

¹³ T.A. Wesolowski and J. Weber, *Kohn-Sham equations with constrained electron density: The effect of various kinetic energy functional parametrizations on the ground-state molecular properties*, *International Journal of Quantum Chemistry* 61, 303 (1997) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1997\)61:2%3C303::AID-QUA13%3E3.0.CO;2-C](https://doi.org/10.1002/(SICI)1097-461X(1997)61:2%3C303::AID-QUA13%3E3.0.CO;2-C))

FDEOPTIONS RELAX or FREEZEANDTHAW

If the RELAX option (or equivalent FREEZEANDTHAW option) is specified, the density of this frozen fragment will be relaxed in freeze-and-thaw cycles^{Page 144, 5}, i.e., the embedded subsystem is frozen, while this fragment is thawed. This is repeated, until convergence is reached or until the maximum number of iterations has been performed. By relaxing frozen fragments, it is possible to improve a given approximate environment density by including the polarization of the environment due to the embedded system. This option is recommended to be used in the preparation stage of a large-scale numerical simulation. The freeze-and-thaw calculations lead to a pair of electron densities (embedded system and environment) that minimizes the total energy. As a consequence, the electron density of the environment derived from the freeze-and-thaw calculations can be used as a reference to verify the adequacy of the assumed electron density for the environment in a large-scale simulation. Due to technical restrictions, freeze-and-thaw is not possible if an open-shell (unrestricted) fragment is present.

FDEOPTIONS USEBASIS RELAX or FDEOPTIONS USEBASIS FREEZEANDTHAW

It is further possible to combine USEBASIS and RELAX or FREEZEANDTHAW. In this case, the basis functions of the non-frozen fragment will be included when the density of the fragment is relaxed. This allows fully relaxed calculations with supermolecular expansion of the electron density of each subsystem. This option is used to test approximants to the kinetic-energy component of the embedding potential introduced by Wesolowski and Warshel by means of the procedure introduced in Ref.^{Page 146, 13}.

FDEDENSTYPE

The FDEDENSTYPE option can be used to specify which density is read from the fragment file. The possible options are:

FDEDENSTYPE SCF (or FDEDENSTYPE SCFexact)

The exact density (not calculated using the fit functions) is used. This is the default.

FDEDENSTYPE SCFfitted

The fitted density is used. This is less accurate but can be significantly faster.

RELAXCYCLES n or FREEZEANDTHAWCYCLES n

This gives the maximum number of freeze-and-thaw cycles that are performed for this fragment. If the maximum number given in the FDE block is smaller, or if convergence is reached earlier, then fewer cycles are performed. For historical reasons, two equivalent keywords are available.

XC

The XC option can be used to select the exchange-correlation potential that is used for this fragment when it is relaxed. By default, the same potential as for the non-frozen system is used, but in some cases it might be preferable to use another approximation for certain fragments. An example is given in Ref.^{Page 145, 12}.

XC LDA

This option selects LDA as exchange-correlation potential for relaxing this fragment.

XC GGA ggapotx ggapotc

This selects a GGA potential for relaxing this fragment. The GGA potential is specified by giving the name of the exchange potential, followed by the name of the correlation potential. The available potentials are listed in the documentation for the XC key.

XC MODEL SAOP

This selects the model potential SAOP for relaxing this fragment.

Kinetic energy approximants

The approximants to the kinetic energy dependent component of the embedding potential are described here.

```
FDE
{approximants to the kinetic energy dependent
  component of the embedding potential}
{CJCORR [rho_cutoff]}
{GGAPOTXFD exchange approximant}
{GGAPOTCFD correlation approximant}
End
```

approximants to the kinetic energy dependent component of the embedding potential

Several approximants to the kinetic-energy-dependent component of the effective potential given in Eq. (21) of ref.^{Page 144, 1} are available. None of them is applicable if the embedded system is covalently bound to its environment. The user is recommended to look at the numerical value of the TSNAD(LDA) parameter which is given in the units of energy and can be considered as a measure of the overlap. The following rule of thumb should be applied: if this parameter is smaller than the estimated interaction energy between the embedded subsystem and the environment, then the available approximants are most probably adequate. If it exceeds this limit, the results can be less reliable. Printing TSNAD(LDA) is not done by default, as it can be quite time-consuming. Its printing is switched on by including “EXTPRINTENERGY”, and “PRINTRHO2”, and “FULLGRID” in the FDE input block. If no kinetic energy approximant is specified, by default the local-density approximation (Thomas-Fermi approximant) is used. For an assessment of approximants for weakly overlapping pairs of densities see Refs.^{Page 146, 13161517}. Based on these studies, the use of PW91k (= GGA97) is recommended.

APPROXIMANTS TO BE USED IN NORMAL APPLICATIONS

THOMASFERMI (default)

Local-density-approximation form of $vt[\rho_A, \rho_B]$ ²⁰ derived from Thomas-Fermi expression for $Ts[\rho]$ ¹⁸¹⁹.

GGA97 (or PW91K)

Generalized-gradient-approximation form of $vt[\rho_A, \rho_B]$ ¹⁶ derived from the Lembarki-Chermette²¹ approximant to $Ts[\rho]$. This approximant is currently the recommended one based on the numerical analysis of its accuracy¹⁵¹⁶ and the fact that the used enhancement factor disappears at large reduced density gradients, i.e. where the second-order gradient-expansion approximation fails^{Page 146, 1317}.

NDSD

Similarly to GGA97, the NDSD approximant is constructed by taking into account the asymptotic behavior of the functional $vt[\rho_A, \rho_B]$ at small density gradients. In the construction of NDSD, the exact property of $vt[\rho_A, \rho_B]$ at $\rho_A \rightarrow 0$ and for $\int \rho_B = 2$ given in Eq. A6 of Ref.²² is also taken into account. The analysis of the accuracy of this potential²² shows that NDSD is of the same or superior quality as GGA97.

¹⁶ T.A. Wesolowski, H. Chermette and J. Weber, *Accuracy of Approximate Kinetic Energy Functionals in the Model of Kohn-Sham Equations with Constrained Electron Density: the FH... NCH complex as a Test Case*, *Journal of Chemical Physics* 105, 9182 (1996) (<https://doi.org/10.1063/1.472823>)

¹⁵ T.A. Wesolowski, *Density functional theory with approximate kinetic energy functionals applied to hydrogen bonds*, *Journal of Chemical Physics* 106, 8516 (1997) (<https://doi.org/10.1063/1.473907>)

¹⁷ Y.A. Bernard, M. Dulak, J.W. Kaminski and T.A. Wesolowski, *The energy-differences based exact criterion for testing approximations to the functional for the kinetic energy of non-interacting electrons*, *Journal of Physics A* 41, 55302 (2008) (<https://doi.org/10.1088/1751-8113/41/5/055302>)

²⁰ P. Cortona, *Self-consistently determined properties of solids without band-structure calculations*, *Physical Review B* 44, 8454 (1991) (<https://doi.org/10.1103/PhysRevB.44.8454>)

¹⁸ L.H. Thomas, *The calculation of atomic fields*, *Mathematical Proceedings of the Cambridge Philosophical Society* 23, 542 (1927) (<https://doi.org/10.1017/S0305004100011683>)

¹⁹ E. Fermi, *Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente*, *Zeitschrift für Physik* 48, 73 (1928) (<https://doi.org/10.1007/BF01351576>)

²¹ A. Lembarki and H. Chermette, *Obtaining a gradient-corrected kinetic-energy functional from the Perdew-Wang exchange functional*, *Physical Review A* 50, 5328 (1994) (<https://doi.org/10.1103/PhysRevA.50.5328>)

²² J.M. Garcia Lastra, J.W. Kaminski and T.A. Wesolowski, *Orbital-free effective embedding potential at nuclear cusps*, *Journal of Chemical Physics* 129, 074107 (2008) (<https://doi.org/10.1063/1.2969814>)

NDSD is, therefore, recommended as the successor of GGA97 to be used anywhere where the quality of the results depends directly on the accuracy of the potential $v_t[\rho_A, \rho_B]$, i.e., for obtaining electronic-structure-dependent properties. The analytical form of the corresponding approximant to the functional $T_s^{\text{nad}}[\rho_A, \rho_B]$ exists (Eq. 23 in Ref.²²). It is not possible, however, to obtain the analytical form of the corresponding parent functional for the kinetic energy $T_s[\rho]$. To reflect this and the fact that, similarly to the GGA approximants to $v_t[\rho_A, \rho_B]$, the numerical values of only first- and second derivatives of density are needed, the label NDSD (Non-Decomposable Second Derivatives) is used.

OBSOLETE APPROXIMANTS (can be used but GGA97 leads usually to a better embedding potential see refs. ^{Page 146, 13} ^{Page 148, 16})

LLP91

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ^{Page 146, 13} derived from Lee-Lee-Parr²³ approximant to $T_s[\rho]$.

PW86k

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ^{Page 146, 13} derived from the Fuentealba-Reyes approximant to $T_s[\rho]$ ²⁴.

THAKKAR92

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ^{Page 148, 16} derived from the Thakkar approximant to $T_s[\rho]$ ²⁵.

APPROXIMANTS WHICH MIGHT BE USEFUL ONLY FOR THEORY DEVELOPMENT

The accuracy of **some** of these approximants was investigated in detail ^{Page 148, 16} ^{Page 146, 13} ^{Page 148, 15} ^{Page 148, 17}. Each of them was shown to lead to a qualitatively incorrect embedding potential. They shouldn't be used in practical applications.

COULOMB

Neglecting completely $v_t[\rho_A, \rho_B]$ ($v_t[\rho_A, \rho_B]$ equals zero) together with the exchange-correlation component of the embedding potential introduced by Wesolowski and Warshel.

TF9W

The approximant to $v_t[\rho_A, \rho_B]$ ^{Page 144, 1} derived from the second-order gradient expansion²⁴ for $T_s[\rho]$.

WEIZ

The approximant to $v_t[\rho_A, \rho_B]$ ^{Page 148, 17} derived from the von Weizsäcker approximant to $T_s[\rho]$ ^{Page 144, 6}.

OL91A

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ^{Page 146, 13} derived from the first Ou-Yang and Levy approximant to $T_s[\rho]$ ²⁶.

OL91B

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ^{Page 148, 16} derived from the second Ou-Yang and Levy approximant to $T_s[\rho]$ ²⁶.

E00

Generalized-gradient-approximation form of $v_t[\rho_A, \rho_B]$ ²⁷ derived from a kinetic energy functional by Ernzerhof²⁸ which represents the gradient expansion approximation up to the fourth order.

²³ H. Lee, C. Lee and R.G. Parr, *Conjoint gradient correction to the Hartree-Fock kinetic- and exchange-energy density functionals*, *Physical Review A* 44, 768 (1991) (<https://doi.org/10.1103/PhysRevA.44.768>)

²⁴ D.A. Kirzhnits, *Soviet Physics JETP-USSR* 5, 64 (1957)

²⁵ A.J. Thakkar, *Comparison of kinetic-energy density functionals*, *Physical Review A* 46, 6920 (1992) (<https://doi.org/10.1103/PhysRevA.46.6920>)

²⁶ H. Ou-Yang and M. Levy, *Approximate noninteracting kinetic energy functionals from a nonuniform scaling requirement*, *International Journal of Quantum Chemistry* 40, 379 (1991) (<https://doi.org/10.1002/qua.560400309>)

²⁷ A.W. Götz, S.M. Beyhan and L. Visscher, *Performance of Kinetic Energy Functionals for Interaction Energies in a Subsystem Formulation of Density Functional Theory*, *Journal of Chemical Theory and Computation* 5, 3161 (2009) (<https://doi.org/10.1021/ct9001784>)

²⁸ M. Ernzerhof, *The role of the kinetic energy density in approximations to the exchange energy*, *Journal of Molecular Structure: THEOCHEM* 501-502, 59 (2000) ([https://doi.org/10.1016/S0166-1280\(99\)00414-5](https://doi.org/10.1016/S0166-1280(99)00414-5))

P92

Generalized-gradient-approximation form of $vt[\rho_A, \rho_B]$ ²⁷ derived from a kinetic energy functional by Perdew²⁹ which represents the gradient expansion approximation up to the sixth order.

LONG DISTANCE CORRECTIONS TO THE EFFECTIVE POTENTIAL**CJCORR**

Option to switch on a long-distance correction. By default this option is not used. As was shown in Ref.³⁰, with the available approximate kinetic-energy approximants, the embedding potential has the wrong form in the limit of a large separation of the subsystems. In particular, it was shown that this can have serious consequences in the case of “supermolecular expansion of electron density of each subsystem” calculations (USEBASIS option). In Ref.³⁰, a correction is proposed that enforces the correct long-distance limit. (See also this reference for limitations of this correction.)

CJCORR [rho_cutoff]

This option switches on the long-distance correction. This option has to be used in combination with one of the above kinetic-energy approximants. By default, a density cut-off of 0.1 is employed.

NONADDITIVE EXCHANGE-CORRELATION APPROXIMANT**GGAPOTXFDGGAPOTCFD**

Option to specify the non-additive exchange-correlation approximant. By default, in the construction of the effective embedding potential the exchange-correlation approximant that was specified in the XC block is used. It is possible to specify a different approximant with the GGAPOTXFD and GGAPOTCFD options. This is particularly useful in combination with the use of model potentials like SAOP, that can not be used in the embedding potential because of their orbital dependence. (For a discussion, see Ref.^{Page 145, 12.})

GGAPOTXFD exchange approximant

The exchange approximant is used in the construction of the embedding potential. The same exchange approximants as in the XC key are available.

GGAPOTCFD correlation approximant

The correlation approximant is used in the construction of the embedding potential. The same correlation approximants as in the XC key are available.

General FDE options

In addition to the fragment-specific options and the kinetic energy approximants, there are also a number of options available in FDE calculations that will be described in the following.

```
FDE
{FULLGRID}
{RELAXCYCLES n or FREEZEANDTHAWCYCLES n}
{RELAXPOSTSCF or FREEZEANDTHAWPOSTSCF}
{EXTPRINTENERGY}
{PRINTRHO2}
{ENERGY}
{SDFTEENERGY}
{DIPOLE}
End
```

FULLGRID

By default, FULLGRID is not used, and in FDE calculations the integration grid is generated as described in Ref.^{Page 144, 2} by including only atoms of the frozen subsystem that are close to the embedded subsystem in the

²⁹ J.P. Perdew, *Generalized gradient approximation for the fermion kinetic energy as a functional of the density*, *Physics Letters A* 165, 79 (1992) ([https://doi.org/10.1016/0375-9601\(92\)91058-Y](https://doi.org/10.1016/0375-9601(92)91058-Y))

³⁰ C.R. Jacob, S.M., Beyhan and L. Visscher, *Exact functional derivative of the nonadditive kinetic-energy bifunctional in the long-distance limit*, *Journal of Chemical Physics* 126, 234116 (2007) (<https://doi.org/10.1063/1.2743013>)

generation of the integration grid. The distance cutoff used is chosen automatically, based on the extent of the basis functions of the embedded subsystem. (It can also be chosen manually, see the option `qpnear` in the `INTEGRATION` key.) This scheme results in an efficient and accurate integration grid. However, it is possible that the default integration scheme is not accurate enough. This can be the case for weakly interacting systems and when the distance between the frozen and the embedded system is large. It is therefore recommended to check the quality of the default integration grid by comparing to results obtained using the full supermolecular grid (`FULLGRID` option).

If the subkey `FULLGRID` is included, all atoms of the frozen system are included in the generation of the integration grid. This results in the same grid that would be used in a supermolecular calculation of the combined frozen and embedded system. The integration grid generated by this option might be much larger than the default grid. This option should be used to check the quality of the default integration grid.

RELAXCYCLES *n* or FREEZEANDTHAWCYCLES *n*

Specifies the maximum number *n* of freeze-and-thaw iterations^{Page 144, 5} that are performed (for frozen fragments with the `RELAX` option). If a smaller number of iterations is specified as a fragment-specific option, for this fragment this smaller number is used. Furthermore, if convergence is reached earlier, no more iterations will be performed.

RELAXPOSTSCF or FREEZEANDTHAWPOSTSCF

If this option is included, several post-SCF properties will be calculated after each freeze-and-thaw cycle [Ref.^{Page 144, 5}]. These are otherwise only calculated in the last cycle.

EXTPRINTENERGYPRINTRHO2

If the options `EXTPRINTENERGY` and `PRINTRHO2` are included (both are needed and should be listed on separate lines), several additional quantities will be printed, including `TSNAD(LDA)`. In order to obtain meaningful numbers, also the `FULLGRID` keyword (see above) has to be used.

ENERGY

Option to switch on the calculation of the FDE energy as the sum of the energy $E[\rho_A]$ of the active, embedded system and the interaction energy $E_{\text{int}}[\rho_A, \rho_B]$ of the embedded system with the frozen environment. This relies on the calculation of the total energy for the embedded system and all caveats and restrictions for total energy evaluations apply (see keyword *TOTALENERGY* (page 294)). All energy contributions are evaluated on the grid of the active subsystem. Some contributions to the interaction energy $E_{\text{int}}[\rho_A, \rho_B]$ require an accurate integration grid in the region of the environment. Thus, in pure embedding calculations (without fragment-specific option `RELAX`), an accurate calculation of the FDE energy requires a full supermolecular integration grid (`FULLGRID` option). Details on the implementation and the performance of kinetic energy functionals for interaction energies are documented in Ref.^{Page 149, 27}

The calculation of the full, variationally minimized subsystem DFT energy, that is, the sum of the energy of two subsystems $E[\rho_A]$ and $E[\rho_B]$ and their interaction energy $E_{\text{int}}[\rho_A, \rho_B]$ in the framework of FDE, is invoked if then the fragment densities are relaxed in freeze-and-thaw cycles (option `RELAXCYCLES` and fragment-specific FDE option `RELAX`). In this case the supermolecular integration grid is not required. Instead, in each step of the freeze-and-thaw cycle, the critical energy terms are taken from the previous freeze-and-thaw step of the presently frozen fragment. The convergence of the energy contributions with the number of freeze-and-thaw iterations should be carefully monitored. Due to conceptual problems for the evaluation of the non-additive kinetic energy contribution, only two subsystems, that is, one frozen fragment, is supported for FDE energy calculations with freeze-and-thaw.

SDFTENERGY

This is a generalization of the original `ENERGY` implementation that allows for the evaluation of the FDE/sDFT total energy. Usage of a supermolecular integration grid is recommended (`FULLGRID` option), because of the non-additive kinetic and XC contributions. `EXTPRINTENERGY` can be combined with this option to print the subsystem DFT energy after each freeze-and-thaw cycle. For pure embedding calculations, the `SDFTENERGY` implementation reads the total energy from each frozen fragment's `adf.rkf` (TAPE21) file. The total energy of frozen fragments is not (re-)evaluated during FDE calculations. It is therefore mandatory to add the *TOTALENERGY* (page 294) keyword to the preparatory isolated fragment calculations.

DIPOLE

The dipole of the supersystem is calculated as the sum of analytically integrated fragment dipole moments. Note that the dipole moment becomes origin dependent for charged (sub-)fragments. The current implementation does NOT take care of this.

Frozen Density Embedding with External Orthogonality

An implementation of External Orthogonality (EO) into the FDE framework in ADF can be found in Ref.³¹. In this method in the fragment calculation one needs to specify ghost atoms at the positions of the atoms in all the other fragments. Thus each fragment is calculated in the supermolecular basis.

```
AOMat2File
IgnoreOverlap
FDE
  EXTERNALORTHO {factor}
  ...
END
```

EXTERNALORTHO

Used to specify the use of external orthogonality (EO) in the FDE block, with an optional factor (default factor is 1e6). Note that the overlap region is defined by ghost atoms, and the general keyword IGNOREOVERLAP is necessary. Additionally, the general keyword AOMAT2FILE is required to save some important fragment AO matrices to adf.rkf for use in an EO calculation. It is recommended that one uses the STOFIT keyword for the STOFIT density fitting method.

FDE and (localized) COSMO

COSMO solvation can be included in combination with FDE. This means that a COSMO cavity will be created that holds both the active and frozen fragments.

For very large systems the solution of the COSMO equations can become the bottleneck of the calculation. A local COSMO variant, which exploits the subsystem nature of the underlying electronic description, is implemented in ADF, see Ref.³². This method, called LoCOSMO, is an approximation to regular COSMO for fragment-based electronic structure methods. If a given fragment is active (i.e. only its own density changes over the SCF cycles), the surface charges outside a given radius around this fragment will be kept fixed in magnitude (excluded from the COSMO optimization). However, no interactions are ignored by adding a corresponding constant term to the COSMO solution vector.

```
SOLVATION
..
  CHARGED LoCosmo LoCosmoDist
END
```

LoCosmo LoCosmoDist

If LoCosmo is included the local COSMO will be used in the calculation. LoCosmoDist is a cutoff radius (Angstrom), which must be specified by the user, if LoCOSMO is included. All surface charges within this radius from any atom of the active fragment are included in the active charge space. A sensible value for LoCosmoDist is 5.0 Angstrom.

To be really useful, Freeze-and-Thaw cycles should be carried out with LoCOSMO. After each fragment calculation, the KF file LOCSURCH is written to disk. If present, this file will be automatically read in during the next (LoCOSMO) fragment calculation. This means that if the internal FT cycles are used by specifying RELAXCYCLES, the code creates

³¹ D.V. Chulhai and L. Jensen, *Frozen Density Embedding with External Orthogonality in Delocalized Covalent Systems*, *Journal of Chemical Theory and Computation* 11, 3080 (2015) (<https://doi.org/10.1021/acs.jctc.5b00293>).

³² A. Goetz, and J. Neugebauer, *A Local Variant of the Conductor-Like Screening Model for Fragment-Based Electronic-Structure Method*, *Journal of Chemical Theory and Computation* 11, 5277 (2015) (<https://doi.org/10.1021/acs.jctc.5b00832>).

and reads in the file in a fully automatic fashion. LOCSURCH is neither created nor read during a regular COSMO calculation.

In case one calculates excitation energies with the EXCITATIONS block key, and LoCOSMO is specified, only the solvent response due to surface charges within the specified cutoff radius will be taken into account, see also Ref.³³. It should be noted that in a regular (uncoupled) FDE TDDFT calculation, the response due to the frozen density is neglected.

FDE and QM/FQ(F μ)

FDE can also be combined with the QM/FQ(F μ) (page 134) method which can be used to embed a quantum system in a polarizable classical environment. The fluctuating classical layer can be included in all stages of an FDE calculation, i.e. when performing the separate calculations for the two isolated fragments as well as the full FDE system. There is also the possibility of using the QM/FQ(F μ) method to account for the mutual response of the subsystems by endowing the frozen layer's atoms with fluctuating charges (and dipoles), provided a suitable parametrization is available. See the QM/FQ(F μ) (page 134) manual page for more details.

Subsystem TDDFT, coupled FDE

The linear-response subsystem TDDFT code implements the theory of coupled excited states for subsystems as described in Refs.^{Page 145, 35}^{Page 145, 34}. This theory is based on the FDE extension to excited states^{Page 144, 6}, which is implemented in ADF in a local response approximation, i.e., neglecting the dynamic response of the environment^{Page 144, 7}.

The subsystem TDDFT code allows to treat the mutual response of several subsystems, including the ones that are considered environment. A more typical situation would be a system composed of several equivalent chromophores treated as individual subsystems. In this case, the local response approximation leads to uncoupled excited states of the subsystems (hence the acronym FDEu is employed often), while the subsystem TDDFT code couples the monomer excitations to obtain the excited states of the total system (often denoted as coupled frozen density embedding, FDEc). This can be related to excitonic couplings between the monomers^{Page 145, 34}.

The current implementation is restricted to NOSYM calculations and Singlet-Singlet excitations without frozen core approximation. It makes use of the ALDA kernel (including a Thomas-Fermi part for the contribution arising from the non-additive kinetic energy) for consistency with the uncoupled FDE implementation for excited states. Some features have not or not extensively been tested and should be used with great care, e.g., linear dependencies in the basis set. Details on the calculation of transition moments, oscillator and rotational strengths are described in Ref.^{Page 145, 10}.

Subsystem TDDFT (FDEc) calculations can be invoked with the SUBEXCI key.

SUBEXCI input

FDEc calculations on coupled excited states first require that an uncoupled FDE-TDDFT calculation has been performed for every subsystem that should be included in the coupled calculation, and that the corresponding adf.rkf files, in which the considered subsystems are "active", have been saved (see the separate FDE input description). This means that it is not possible to use the information on frozen/inactive fragments from a adf.rkf file of a previous uncoupled FDE calculation, which contains all subsystems.

Although it is technically possible to use adf.rkf files from non-FDE calculations on the separate subsystems, this would lead to results that are inconsistent with the subsystem TDDFT methodology from Ref.^{Page 145, 35}. In any case, a previous TDDFT calculation for each subsystem that should be included in the coupling procedure is necessary. If that is not the case, the subsystem will still be considered in the calculation of the total electron density (needed in the setup of the exchange-correlation kernel), but will not be included in the coupling procedure.

The first subsystem should always be one of the coupled subsystems. The input will then look like the corresponding input for an uncoupled FDE-TDDFT calculation, but in addition should contain the following block:

³³ A. Goez, and J. Neugebauer, *Including protein density relaxation effects in first-principles embedding calculations of cofactor excitation energies*, *Molecular Physics* 115, 526 (2016) (<https://doi.org/10.1080/00268976.2016.1199823>)

```

SUBEXCI
{LOWEST nlowest}
{OPTSTATES list_of_optstates}
{CTHRES coupling_threshold}
{SFTHRES solutionfactor_threshold}
{COUPLBLOCK}
{TDA}
{CICOUPL}
END

```

LOWEST nlowest

The selection of the excited states to be coupled consists of two steps. First, a number of reference states are selected. As a default, the nlowest (default: 10) lowest excited states present on the fragment file for the first subsystem are considered.

OPTSTATES list_of_optstates

If the keyword OPTSTATES is given, only those excited states of the first subsystem are considered as reference states that are given in the list_of_optstates (numbers of states separated by blanks).

CTHRES coupling_threshold

Second, all excitations of all subsystems (present on the fragment adf.rkf files) with an excitation energy that differs by less than coupling_threshold (to be given in units of eV; default: 30 eV) from one of the reference states are selected to be included in the coupling. Note that additional excited states of system 1 may be included here.

COUPLBLOCK

If COUPLBLOCK is specified in the input, all couplings between all of these local excited states are included. Otherwise (default), the coupling_threshold is also applied to select pairs of states for which couplings are calculated. I.e., couplings are not calculated if the two particular states to be coupled differ in energy by more than coupling_threshold.

SFTHRES solutionfactor_threshold

To reduce the computational effort, it is possible to ignore the effect of orbital pairs with coefficients less than solutionfactor_threshold in the solution factors (TDDFT eigenvectors) of the underlying uncoupled calculation in the construction of the exact trial densities during the calculation of the coupling matrix elements. These orbital pair contributions are not ignored in the subsequent calculation of transition moments, oscillator, and rotational strengths. The default value of 0.00001 typically leads to a precision of the coupled excitation energies of about 0.0001 eV.

TDA

TDA specifies the use of the Tamm-Dancoff-Approximation (*Tamm-Dancoff approximation* (page 181)) in the underlying uncoupled FDE-TDDFT calculations (Ref.³⁶). Contrary to the full SUBEXCI-TDDFT variant, SUBEXCI-TDA allows for the usage of hybrid functionals in the underlying uncoupled FDE-TDDFT calculations.

CICOUPL

Within the Tamm-Dancoff Approximation, the couplings between localized excited states on different subsystems correspond directly to so-called exciton couplings (see Ref.^{Page 154, 36}). The CICOUPL keyword, in conjunction with TDA, prints these exciton couplings. It is also possible to use CICOUPL with full FDEc-TDDFT. In that case, the excitonic couplings between monomers are reconstructed from an effective 2x2 CIS-like eigenvalue problem, as e.g. done in Ref.^{Page 145, 34}.

In addition, the input file may contain either an EXCITATIONS block or the keyword DIFFUSE. Both options lead to a slight adaption of the integration grid. Apart from this, the EXCITATIONS block will be ignored.

The key ALLOW PARTIALSUPERFRAGS is currently necessary to be able to use subsystem information for only one subsystem from a adf.rkf file of a previous FDE calculation:

³⁶ C. König, N. Schlüter, J. Neugebauer, *Direct Determination of Exciton Couplings from Subsystem TDDFT within the Tamm-Dancoff Approximation*, *Journal of Chemical Physics* 138, 034104 (2013) (<https://doi.org/10.1063/1.4774117>)

ALLOW PARTIALSUPERFRAGS

Restrictions and pitfalls

In the current implementation, only the electron density of the embedded system is calculated. Therefore, with the exception of interaction energies, only properties that depend directly on the electron density (e.g., dipole moments) are available. In addition, the TDDFT extension allows the calculation of electronic excitation energies and polarizabilities, and NMR shieldings can be calculated.

Warning: EVERYTHING ELSE IS NOT YET IMPLEMENTED. THE RESULTS OBTAINED FOR OTHER PROPERTIES MIGHT BE MEANINGLESS.

Kinetic energy approximant: Although the effective embedding potential is derived from first principles using universal density approximants, the ADF implementation relies on approximations. Currently, two implemented approximations are recommended^{Page 148, 15}: PW91k (also known as GGA97) which uses electron densities and the corresponding gradients to express the non-additive kinetic energy component of the embedding potential, or TF (Thomas-Fermi LDA approximant), which does not use gradients at all. Either approximation is applicable only in cases where the overlap between electron densities of the corresponding interactions is small. Note: so far, no approximation has been developed for the strong-overlap case - two subsystem linked by covalent bonds for instance.

4.4.9 3D-RISM: 3D Reference Interaction Site Model

Introduction

The three-dimensional reference interaction site model (3D-RISM) provides the solvent structure in the form of a 3D site distribution function, $g_{\gamma}^{UV}(r)$, for each solvent site, γ .

It enables, at modest computational cost, the calculation of thermodynamics, electronic properties and molecular solvation structure of a solute molecule in a given molecular liquid or mixture. Using 3D-RISM, one can study chemical reactions, including reaction coordinates and transition state searches, with the molecular solvation described from first principles based on a molecular-mechanics type description of the solvent. The method yields all of the features available by using other solvation approaches.

The 3D-RISM implementation has been revised and supplemented (AMS2022) by a new option that uses the fitted electron density in the interaction between solvent and solute directly. Without the use of point charges, numerical stability has been improved. Using this option, 3D-RISM can now be used for structure optimization, (numerical) frequencies, vertical excitation energies and magnetic properties. The code has also been parallelized. Details can be found in Ref.¹. Starting from AMS2022, new point-charge-based options are available to be used in combination with structure optimization, numerical frequencies and vertical excitation energies.

Details on the original implementation of 3D-RISM-KH in ADF can be found in Ref.², with applications in Ref.³. The

¹ M. Reimann and M. Kaupp, *Evaluation of an Efficient 3D-RISM-SCF Implementation as a Tool for Computational Spectroscopy in Solution*, *Journal of Physical Chemistry A* 124, 7439 (2020) (<https://dx.doi.org/10.1021/acs.jpca.0c06322>)

² S. Gusarov, T. Ziegler and A. Kovalenko, *Self-Consistent Combination of the Three-Dimensional RISM Theory of Molecular Solvation with Analytical Gradients and the Amsterdam Density Functional Package*, *Journal of Physical Chemistry A* 110, 6083 (2006) ([https://doi.org/10.1021/jp05\[ref11\]_4t](https://doi.org/10.1021/jp05[ref11]_4t))

³ D. Casanova, S. Gusarov, A. Kovalenko and T. Ziegler, *Evaluation of the SCF Combination of KS-DFT and 3D-RISM-KH; Solvation Effect on Conformational Equilibria, Tautomerization Energies, and Activation Barriers*, *Journal of Chemical Theory and Computation* 3, 458 (2007) (<https://doi.org/10.1021/ct6001785>)

theory of 3D-RISM-KH in combination with DFT can be found in Refs.⁴⁵⁶⁷. A combination of 3D-RISM-KH with FDE (frozen-density embedding) can be found in Ref.⁸.

Similar to explicit solvent simulations, 3D-RISM properly accounts for chemical peculiarities of both solute and solvent molecules, such as hydrogen bonding and hydrophobic forces, by yielding the 3D site density distributions of the solvent. Moreover, it readily provides, via analytical expressions, all of the solvation thermodynamics, including the solvation free energy potential, partial molar volume, and compressibility. Starting from AMS2023, enthalpic and entropic decomposition of the solvation free energy can be obtained approximately using analytic expressions (which are exact for CHRGVL=MM or pure Lennard-Jones fluids), also including the macroscopic dependence of the dielectric constant on temperature and solvent density.⁹ The expression for the solvation free energy (and its derivatives) in terms of integrals of the correlation functions follows from a particular approximation for the so-called closure relation used to complete the integral equation for the direct and total correlation functions.

Solvation free energy

The solvation free energy can be calculated as:

$$\begin{aligned} \text{Solvation Free Energy} = & \\ & [(\text{Total Bonding Energy}) + (\text{Internal Energy}) \\ & - T * (\text{Entropy}) + (\text{Excess Chemical Potential})]_{\text{3D-RISM}} \\ & - [(\text{Total Bonding Energy}) + (\text{Internal Energy}) - T * (\text{Entropy})]_{\text{Gas-Phase}} \end{aligned}$$

If one assumes that the internal energy and the vibrational and rotational entropy of the solute molecule is the same in solution and in gas phase, then this simplifies to:

$$\begin{aligned} \text{Solvation Free Energy} = & \\ & [(\text{Total Bonding Energy}) + (\text{Excess Chemical Potential})]_{\text{3D-RISM}} \\ & - [(\text{Total Bonding Energy})]_{\text{Gas-Phase}} \end{aligned}$$

However, a formally accurate calculation should include the difference between the thermal corrections from frequency calculations produced by ADF in the SCF calculation with 3D-RISM solvation and in gas phase.

Input

When performing 3D-RISM simulations, each atom in the **ATOMS** block in the AMS part of the input must have two Lennard-Jones parameters specified, `adf.SigU` and `adf.EpsU`, for example:

```
System
  ATOMS
    C      0.00      0.00      0.00      adf.SigU=3.50      adf.EpsU=0.066      adf.ChgU=-0.
  ↪ 4000
    . . .
  END
End
```

⁴ A. Kovalenko and F. Hirata, *Potentials of mean force of simple ions in ambient aqueous solution. II. Solvation structure from the three-dimensional reference-interaction site model approach, and comparison with simulations*, *Journal of Chemical Physics* 112, 10403 (2000) (<https://doi.org/10.1063/1.481677>)

⁵ A. Kovalenko and F. Hirata, *Self-consistent description of a metal-water interface by the Kohn-Sham density functional theory and the three-dimensional reference-interaction site model*, *Journal of Chemical Physics* 110, 10095 (1999) (<https://doi.org/10.1063/1.478883>)

⁶ A. Kovalenko and F. Hirata, *Potentials of mean force of simple ions in ambient aqueous solution. I. Three-dimensional reference-interaction site model approach*, *Journal of Chemical Physics* 112, 10391 (2000) (<https://doi.org/10.1063/1.481676>)

⁷ A. Kovalenko, *Three-dimensional RISM theory for molecular liquids and solid-liquid interfaces*, In *Molecular Theory of Solvation*; Hirata, Fumio, Ed.; Understanding Chemical Reactivity (series); Mezey, Paul G., Series Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; Vol. 24, pp 169-275.

⁸ J.W. Kaminski, S. Gusarov, A. Kovalenko and T.A. Wesolowski, *Modeling solvatochromic shifts using the orbital-free embedding potential at statistically mechanically averaged solvent density*, *Journal of Physical Chemistry A* 114, 6082 (2010) (<https://doi.org/10.1021/jp100158h>)

⁹ M. Reimann and M. Kaupp *Reaction Entropies in Solution from Analytical Three-Dimensional Reference Interaction Site Model Derivatives with Application to Redox and Spin-Crossover Processes*, *Journal of Physical Chemistry A* 126, 3708 (2022) (<https://pubs.acs.org/doi/10.1021/acs.jpca.2c02317>)

They can be obtained from a Lennard-Jones force-field parameter set. Atom-centered point charges `adf.ChgU` can optionally be set as well but will only be used in combination with `CHRGVL=MM` (see below).

All other 3D-RISM-related input keys are contained in a **RISM** input block. Below, only the mandatory keywords are shown. Optional keywords are described in the next section.

```
RISM title
RISM1D
  FLUIDPARAM temper=298. DielConst=78.497 UTotDens=1/A3 0.03333
SUBEND
SOLVENT ArbitrarySolventName
  UNITS uWeight=g/mol ULJsize=A ULJenergy=kcal/mol Ucoord=A Udens=1/A3
  PARAMETERS Weight=weight nAtoms=NSiteTypes
    N1      Z_alpha1      Sigma_alpha1      Eps_alpha1      X1_1 Y1_1 Z1_1
                                                X1_2 Y1_2 Z1_2
                                                ...  ...  ...
    N2      Z_alpha2      Sigma_alpha2      Eps_alpha2      X2_1 Y2_1 Z2_1
                                                X2_2 Y2_2 Z2_2
                                                ...  ...  ...
    ...
  DENSPE=density
SUBEND
SOLUTE ArbitrarySoluteName
  BOXSIZE  sizeX  sizeY  sizeZ
  BOXGRID  npX    npY    npZ
SUBEND
END
```

The **RISM1D** sub-block contains general parameters for the preceding 1D-RISM calculation of the solvent(s) to create the bulk susceptibility function. Even though all technical RISM1D sub-keys have reasonable defaults, the **FLUIDPARAM** sub-key will most likely require attention because its default values for density and dielectric constant are only applicable if the solvent is water. Thus, you may need to change these values when modeling a different solvent. Note that even when using all default values from the RISM1D sub-block the sub-block itself must be specified, even if empty. See below for a complete description of the RISM1D sub-block.

The **SOLVENT** sub-block can be repeated for each component if the solvent is a mixture. Each **SOLVENT** sub-block contains parameters for one solvent. First, each solvent has a name, which is specified on the **SOLVENT** keyword's line and is arbitrary. The first line in the **SOLVENT** sub-block must contain the **UNITS** key. Usually, only the **Udens** part should be changed. Then follow the actual solvent parameters. In principle, each solvent consists of multiple atoms and functional groups (so-called sites). For example, in 3D-RISM terms, methanol consists of 3 sites: CH₃, O, and H. Each such site has a set of three parameters, shared between all sites of the same type, and the coordinates. These parameters follow the **PARAMETERS** keyword. The line with the **PARAMETERS** keyword itself must specify the molecular weight of the solvent and the number of site types that follow. The first line for each site type contains, in this order: number of equivalent sites of this type, z_α (the point charge assigned), σ_α , ϵ_α (the Lennard-Jones parameters assigned), three coordinates for the first site of this type. If there is more than one site of this type then the coordinates for the second and other sites follow on subsequent lines. The **SOLVENT** sub-block is concluded by the specific density of this solvent, by default, in molecules per cubic Angstrom. This number should be equal to the total density for mono-component solvents. Using **Udens=MOL**, the specific density needs to be given in molar fractions, and should therefore be one for mono-component solvents.

For example, the **SOLVENT** block for water would typically look as:

```
SOLVENT water
  UNITS      uWeight=g/mol  ULJsize=A  ULJenergy=kcal/mol  Ucoord=A  Udens=1/A3
  PARAMETERS Weight=18.015  nAtoms=2
    1      -0.8476   3.166   0.1554      0.000000   0.00000   -0.064605
    2       0.4238   1.000   0.0560     -0.816495   0.00000   0.512747
```

(continues on next page)

(continued from previous page)

```

                                0.816495  0.00000  0.512747
DENSPE=0.03333
SUBEND

```

The **SOLUTE** sub-block specifies 3D-RISM parameters for your molecule. The **BOXSIZE** and **BOXGRID** sub-keys specify dimensions of the simulation box, in Angstrom, and the number of points of grid in each direction. The box should at least be twice as large as the molecule and the **BOXGRID** values must be even numbers. Due to the 3D-FFT routines, the largest prime factor of the **BOXGRID** values should be 7 for optimal performance. The size/np ratio defines the grid spacing in each direction and this should not be larger than 0.5 Angstrom for energy calculations and not larger than 0.35 Angstrom for structure optimizations. When the **BOXSIZE** and **BOXGRID** keywords are not specified, the grid is calculated based on the **GRIDSTEP** and **BOXEXTENT** values; see below. The number of grid points along the Cartesian coordinate i will then be determined as $N_i = (range(i) + 2 * BOXEXTENT) / GRIDSTEP + 1$, where $range(i)$ is the span of Cartesian coordinate i of the solute molecule. The number of grid points may be increased to be a product of prime numbers not larger than 7.

The **optional** 3D-RISM keys for the **RISM1D** and **SOLUTE** sub-blocks are listed below together with their defaults.

```

! optional RISM1D subkeys with their default values:
RISM1D Theory=RISM Closure=KH NOSPEEDUP
  FLUIDPARAM temper=298. DielConst=78.497 UTotDens=1/A3 0.03333
  OUTPUT PrintLev=5 File=solvent
  GRID   Nr=8192  dR=0.025 MaxRout=100.0 MaxKout=0.0
  MDIIS  N=20 Step=0.5 Tolerance=1.e-12
  ELSTAT LRsmear=1.0 Adbcor=0.5
  ITER   Ksave=-1 Kshow=1 Max=10000
  DODEPS alpha=-1.0 kappa=-1.0 dedtp=-1.0 dedpt=-1.0
  Restart1D=restartfile
SUBEND

```

RISM1D

Theory - Version of 1D-RISM used: RISM - extended RISM, DRISM - dielectrically consistent RISM (should be used for solvents with a static dipole moment).

Closure - Closure for the 1D problem: KH - Kovalenko-Hirata, HNC - hypernetted chain, PSEn - partial series expansion of HNC up to order n (n=1 is identical to KH), PY - Perkus-Yevik, KGK - Kobryn-Gusarov-Kovalenko.

NOSPEEDUP - Switch off the automatic adjustment of the MDIIS step width.

FLUIDPARAM

Temper - temperature.

DielConst - dielectric constant (only used when theory=DRISM).

UTotDens - units for total density: G/CM3, KG/M3, 1/A3 are valid units followed by the density value.

OUTPUT

PrintLev - print level.

File - common base name for output files.

OutList - which information will be written to additional output files (no additional information will be written by default): G - distribution function, C - direct correlation function, H - total correlation function, U - interaction function, X - ".xv" file (only required up to ADF2019), T - thermodynamics, D - density and temperature derivatives of all correlation functions (automatically set when DERIV option is chosen in the SOLUTE block).

GRID

Nr - the size of the 1D-RISM grid, must be a power of 2 (max. value: 16384).

dR - mesh size in Angstrom.

MaxRout - plot range in direct space.

MaxKOut - plot range in reciprocal space.

MDIIS

N - number of vectors in the DIIS space.

Step - step size.

Tolerance - convergence criterion.

ELSTAT

LRsmear - smearing parameters for Coulomb potential.

Abdcor - switching parameter for dielectric correction (only used if theory=DRISM).

ITER

Ksave - save the current solution every Ksave steps (0 - do not save).

Kshow - print convergence progress every Kshow steps.

Max - maximum number of iterations.

DODEPS

If this block is set, the temperature and density dependence of the dielectric constant is included in the calculation of temperature and density derivatives (OutList=D).

Alpha - isobaric thermal expansion coefficient of the solvent (in 1/K, not set by default!).

Kappa - isothermal compressibility of the solvent (in 1/Pa, not set by default!).

dedtp - temperature derivative of the dielectric constant at constant pressure (in 1/K, not set by default!).

dedpt - pressure derivative of the dielectric constant at constant temperature (in 1/Pa, not set by default!).

Restart1D - use the given restart file (of the RISMDATA type) to restart the 1D-RISM calculation.

```
SOLUTE ArbitrarySoluteName
  outlist=M closure=KH xvvfile=solvent.xvv outfile=rism3d
  Nis=10 DELOZ=0.5 TOLOZ=2.0e-6
  Ksave=-1 Kshow=1 Maxste=10000
  Output=4
  CHRGLVL=ZLM
  GRIDSTEP=0.33
  BOXEXTENT=12.0
SUBEND
```

Outlist - output requested: M - detailed output for the excess chemical potential, F - some corrections (GF, PC+, UC, ...) to the excess chemical potential, G - distribution function, C - direct correlation function, H - total correlation function.

Closure - closure for the 3D problem: KH - Kovalenko-Hirata, HNC - hypernetted chain approximations, PSEn - partial series expansion of HNC up to order n (n=1,2,...; n=1 is identical to KH), KGK - Kobryn-Gusarov-Kovalenko.

RBC - Use the current closure in combination with the repulsive bridge correction (incompatible with analytical gradients).

UCA - The value of the a-parameter in the universal correction ($a \cdot V + b$, mandatory to compute the UC correction).

UCB - The value of the b-parameter in the universal correction ($a \cdot V + b$, mandatory to compute the UC correction).

Xvvfile - name of the file with the results of the 1D-RISM calculation specified in the RISM1D keyword above, with .xvv appended to it (only used up to ADF2019).

Outfile - name of the output text files.

Output - print level.

CHRGVL - which charges computed by ADF to use. This can be ZLM - use the electron density (default), CHELPG - use point charges fitted to the electron density in analogy to the CHELPG procedure, RESP - same as CHELPG but with a harmonic restraint to keep the charges small, MM - use constant point charges given in the System block, MDCq, MDCd, MDCm, or EXMDC (labeled EXACT in older versions). The MDCq, MDCd, MDCm, or EXMDC levels cannot be combined with analytical gradients.

OLDZLM - reproduce the exact ZLM results obtained with ADF2019 and ADF2020;

RESPWEIGHT - pre-factor of the harmonic restraint in the RESP-like procedure, default value: 0.05.

VDWTYPE - functional form of the van der Waals interaction requested: 12-6 (default), 9-6.

SPHINT - calculate the spherical averaged distribution function around the given atom: 1,2,... - atom in input order, 0 - center of mass.

SOLVPOS - find the most likely positions of a solvent site: 1,2,... - site in input order, 0 - all sites.

OLDPCODE - run the old version of the code (ADF2019 and older), should only be used by experts.

DERIV - compute the temperature and density derivative of the excess chemical potential analytically (only exact for CHRGVL=MM or pure Lennard-Jones fluids). When DODEPS is set in the RISM1D block, enthalpy and entropy of solvation are calculated as well.

NOSPEEDUP - switch off the automatic adjustment of the MDIIS step width.

GRIDSTEP - grid spacing, in Angstrom.

BOXEXTENT - extent of the grid, in Angstrom, beyond the space occupied by atoms in each direction.

The Nis, DELOZ, and TOLOZ have the same meaning for 3D-RISM as parameters of the MDIIS keyword of the RISM1D block. Likewise, Ksave, Kshow, and Maxste are analogous to the parameters of the ITER key in RISM1D.

Parameters for some solvents

The following, compiled set of solvent parameters is taken from the literature (see Ref.¹ and references therein for these and additional solvents).

Table 4.2: **Water Weight=18.015 nAtoms=2**

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
O	-0.8476	3.166	0.1554	0.000000	0.000000	-0.064605
H	0.4238	1.000	0.0560	0.000000	0.816495	0.512747
				0.000000	-0.816495	0.512747

Table 4.3: **Methanol Weight=32.04 nAtoms=3**

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
H	0.435	1.000	0.0560	0.000000	0.000000	0.000000
O	-0.700	3.070	0.1700	0.000000	0.000000	0.945000
CH3	0.265	3.775	0.2070	1.35136	0.000000	1.39716

Table 4.4: **Ethanol Weight=47.07 nAtoms=4**

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
H	0.435	1.000	0.0560	0.000000	0.000000	0.000000
O	-0.700	3.070	0.1700	0.000000	0.000000	0.945000
CH2	0.265	3.775	0.2070	1.356103	0.000000	1.398746
CH3	0.000	3.905	0.1750	1.342751	0.000000	2.928687

Table 4.5: Isopropanol Weight=60.10 nAtoms=4

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
H	0.435	1.000	0.0560	0.000000	0.000000	0.000000
O	-0.700	3.070	0.1700	0.000000	0.000000	0.945000
CH	0.265	3.850	0.0800	1.356103	0.000000	1.398746
CH3	0.000	3.910	0.1600	1.578230	1.268465	2.224915
				1.578230	-1.268465	2.224915

Table 4.6: Acetonitrile Weight=41.052 nAtoms=3

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
CH3	0.150	3.775	0.2070	1.458000	0.000000	0.000000
C	0.280	3.650	0.1500	0.000000	0.000000	0.000000
N	-0.430	3.200	0.1700	-1.157000	0.000000	0.000000

Table 4.7: Dimethylsulfoxide Weight=78.13 nAtoms=3

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
O	-0.459	2.930	0.2800	0.000000	0.000000	1.530000
S	0.139	3.560	0.3950	0.000000	0.000000	0.000000
CH3	0.160	3.810	0.1600	0.000000	1.716700	-0.541300
				-1.665300	-0.416800	-0.541300

Table 4.8: Acetone Weight=58.08 nAtoms=3

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
O	-0.424	2.960	0.2100	0.000000	0.000000	-1.208737
C	0.300	3.750	0.1050	0.000000	0.000000	0.013263
CH3	0.062	3.910	0.1600	0.000000	1.286301	0.798425
				0.000000	-1.286301	0.798425

Table 4.9: Dichloromethane Weight=84.93 nAtoms=3

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
C	-0.364	3.400	0.1094	0.000000	0.000000	-0.814053
H	0.218	2.293	0.0157	-0.926635	0.000000	-1.406798
				0.926635	0.000000	-1.406798
Cl	-0.036	3.564	0.2550	0.000000	-1.451416	0.177892
				0.000000	1.451416	0.177892

Table 4.10: Chloroform Weight=119.38 nAtoms=3

Atom	z_{α} / a.u.	σ_{α} / Å	ϵ_{α} / kcal/mol	X/Å	Y/Å	Z/Å
C	-0.386	3.400	0.1094	0.000000	0.000000	0.463135
H	0.266	2.115	0.0157	0.000000	0.000000	1.563010
Cl	0.040	3.564	0.2550	1.607217	-0.475149	-0.067114
				-0.392118	1.629465	-0.067114
				-1.215099	-1.154317	-0.067114

OPLS-AA Parameters for common atoms and atom groups

The table below contains possible sigma and epsilon parameters for some of the most common solvent groups collected from Ref.¹⁰¹¹¹². These parameters are kindly provided by Leonardo Costa.

Table 4.11: All atoms model

Atom	Example	$\sigma_\alpha / \text{\AA}$	$\epsilon_\alpha / \text{kcal/mol}$	Reference
C (SP3)	methane	3.73	0.294	¹⁰
C (SP3)	neopentane	3.80	0.050	¹⁰
C (SP2)	isobutene	3.75	0.105	¹⁰
C (SP)	acetonitrile	3.40	0.099	¹¹
C (arom)	benzene	3.55	0.07	¹¹
C	chloroform	4.10	0.05	¹²
H	O—H	0.7	0.046	¹¹
H	hydrocarbons	2.42	0.03	¹¹
O	water	3.166	0.1554	¹¹
O	alcohol	3.07	0.17	¹¹
O	sulfoxide	2.93	0.28	¹¹
N (SP)	acetonitrile	3.3	0.099	¹¹
S	sulfoxide	3.56	0.395	¹¹
Cl	chloroform	3.40	0.300	¹²

Table 4.12: United atom model

Atom	Example	$\sigma_\alpha / \text{\AA}$	$\epsilon_\alpha / \text{kcal/mol}$	Reference
CH (SP3)	isobutane	3.850	0.080	¹⁰
CH (SP2)	2-butene	3.800	0.115	¹⁰
CH (arom)	benzene	3.750	0.110	¹⁰
CH2 (SP3)	n-butane	3.905	0.118	¹⁰
CH2 (SP2)	1-butene	3.850	0.140	¹⁰
CH3	hydrocarbon	3.775	0.207	¹⁰
CH3	acetonitrile	3.6	0.38	¹¹
CH3	sulfoxide	3.81	0.16	¹¹
NH2	amine	3.3	0.17	¹¹

4.5 Electric Field: Homogeneous, Point Charges, Polarizability

A homogeneous external electric field and/or the field due to point charges can be included in the Fock operator. Either can be applied in both a single-point calculation or in geometry optimization. When applied in geometry optimization, it will allow the molecule to rotate with respect to point charges or the field vector but not translate. Rigid translation is explicitly disabled to avoid drifting of the molecule in the external electric field.

Homogeneous electric fields, point charges, and external dipole moments should be defined in the **System block**, which is part of the AMS driver input. [This section of the AMS driver manual](#) describes the various input options.

Symmetry

¹⁰ W.L. Jorgensen, J.D. Madura and C.J. Swenson, *Optimized intermolecular potential functions for liquid hydrocarbons*, *Journal of the American Chemical Society* 106, 6638 (1984) (<https://doi.org/10.1021/ja00334a030>)

¹¹ A.E. Kobryn and A. Kovalenko, *Molecular theory of hydrodynamic boundary conditions in nanofluidics*, *Journal of Chemical Physics* 129, 134701 (2008) (<https://doi.org/10.1063/1.2972978>)

¹² O. Acevedo and W.L. Jorgensen, *Influence of Inter- and Intramolecular Hydrogen Bonding on Kemp Decarboxylations from QM/MM Simulations*, *Journal of the American Chemical Society* 127, 8829 (2005) (<https://doi.org/10.1021/ja051793y>)

The homogeneous electric field and the point charge fields may polarize the electronic charge density. This must be accounted for in the point group symmetry. If symmetry is not specified in input and the homogeneous electric field and/or the point charges break symmetry, ADF uses symmetry NOSYM. You can specify a symmetry, but ADF will not check its correctness. An incorrect symmetry may lead to incorrect results.

Bonding energy

The bonding energy is computed as the energy of the molecule in the field minus the energy of the constituent fragments without the field. This may not always be the desired bonding energy. In the energy decomposition analysis (EDA) there is a separate term called 'Electric Field (initial)', which is the interaction energy of the electric field with the sum-of-fragment electron density and nuclei. You should subtract this term if you are interested in the energy of the molecule in the field minus the energy of the constituent fragments in the field.

Polarizability and hyperpolarizability

ADF supports a direct calculation of the (hyper)polarizability (see the section on Spectroscopic Properties). The static (hyper)polarizabilities could also be computed by applying a small homogeneous field and comparing the results with the field-free data.

STRUCTURE AND REACTIVITY

See also:

ADF-GUI tutorials: [geometry optimization](#), [vibrational frequencies](#), [spin coupling in Fe4S4](#)

Examples: [geometry optimization](#) (page 804), [reactivity](#) (page 814)

5.1 Single point calculations

A single point calculation calculates one point on the potential energy surface.

- [Single point calculations](#) section of the AMS manual.

5.2 Geometry optimization

A geometry optimization tries to find a (local) minimum on the potential energy surface, where the gradients are zero and the Hessian only has positive eigenvalues. With AMS one can do an optimization using delocalized or Cartesian coordinates. Constraints (also block constraints) and restraints are possible. An initial Hessian can be provided.

- [Geometry Optimization](#) section of the AMS manual.

5.3 Transition state search

A transition state corresponds to a saddle point on the potential energy surface, where the gradients are zero and the Hessian has one negative eigenvalue.

- [Transition state search](#) section of the AMS manual.

A reaction coordinate for transition state search can be specified.

5.4 Linear Transit, PES scan

The PES scan task in AMS allows users to scan the potential energy surface of a system along one or multiple degrees of freedom, while relaxing all other degrees of freedom. If only one coordinate is scanned, this kind of calculation is usually just called a linear transit.

- [Linear Transit, PES scan section of the AMS manual.](#)

5.5 Nudged Elastic Band (NEB)

The Nudged Elastic Band (NEB) method can be used to find a reaction path and the transition state between a reactant and a product state.

- [Nudged Elastic Band \(NEB\) section of the AMS manual.](#)

5.6 Intrinsic Reaction Coordinate (IRC)

The path of a chemical reaction can be traced from the transition state to the products and/or reactants using the IRC method.

- [Intrinsic Reaction Coordinate \(IRC\) section of the AMS manual.](#)

5.7 Excited state optimizations

ADF can calculate the nuclear gradient for a particular electronically excited state, which makes it possible to do excited state optimizations.

- [Excited state gradient section of the ADF manual](#) (page 210),
- [Excited state optimizations section of the AMS manual.](#)

5.8 Molecular dynamics

Molecular dynamics can be used to simulate the evolution of a system in time.

- [Molecular dynamics section of the AMS manual.](#)

GRADIENTS, HESSIAN, THERMODYNAMICS

6.1 Gradients

A nuclear gradient is the first derivative of the energy with respect to the nuclear coordinates. The nuclear gradients are not forces; the difference is the sign.

- [Nuclear gradients section of the AMS manual.](#)

6.2 Hessian

A Hessian is the second derivative of the energy with respect to the nuclear coordinates.

- [Hessian section of the AMS manual.](#)

One can also calculate a partial Hessian. The Hessian calculation is related to the calculation of IR frequencies; see the [IR frequencies and normal modes section of the AMS manual.](#)

6.3 PES point character

The AMS driver can quickly, and without calculating the full Hessian, characterize a PES point as a local minimum, a transition state, a higher order saddle point, or a non-stationary point.

- [PES point character section of the AMS manual.](#)

6.4 Thermodynamics, gas phase Gibbs free energy

At the end of a completed IR frequencies (normal modes) calculation, a survey is given of thermodynamic properties: entropy, internal energy, constant volume heat capacity, enthalpy and Gibbs free energy, see:

- [IR frequencies section of the AMS manual](#)
 - Thermodynamics
 - Gibbs free energy change for a gas phase reaction

SPECTROSCOPIC PROPERTIES

See also:

ADF-GUI tutorials: [excitation energies](#), [vibrational frequencies](#)

Examples: [IR spectra](#) (page 843), [excitation energies](#) (page 868), [response properties](#) (page 932), [NMR](#) (page 980), [ESR](#) (page 1001), [EFG](#) (page 1016)

7.1 Vibrational Spectroscopy

See the [Vibrational Spectroscopy](#) section of the AMS manual.

7.1.1 IR frequencies and normal modes

See the [IR frequencies and normal modes](#) section of the AMS manual.

The Hessian that is needed can be calculated numerically (for almost all XC functionals) or analytically (for a limited amount of XC functionals, mostly LDA or GGA). This can be set in the AMS part of the input.

```
$ADFBIN/ams <<eor
  NormalModes
    Hessian [Auto | Analytical | Numerical]
  End
  ...
eor
```

Analytical Hessian

The analytical second derivatives (Hessian) implementation in ADF is based on Ref.¹²³. The analytical Hessian is as accurate as the numerical Hessian for the same integration accuracy, but can be up to 3 to 5 times quicker to compute, depending on the molecule, integration grid parameters, and choice of basis set. Using the analytical Hessian AMS will calculate the vibrational frequencies and normal modes.

¹ A. Bérces, R. M. Dickson, L. Fan, H. Jacobsen, D. Swerhone and T. Ziegler, *An implementation of the coupled perturbed Kohn-Sham equations: perturbation due to nuclear displacements*, *Computer Physics Communications* 100, 247 (1997) ([https://doi.org/10.1016/S0010-4655\(96\)00120-8](https://doi.org/10.1016/S0010-4655(96)00120-8))

² H. Jacobsen, A. Bérces, D. Swerhone and T. Ziegler, *Analytic second derivatives of molecular energies: a density functional implementation*, *Computer Physics Communications* 100, 263 (1997) ([https://doi.org/10.1016/S0010-4655\(96\)00119-1](https://doi.org/10.1016/S0010-4655(96)00119-1))

³ S.K. Wolff, *Analytical second derivatives in the Amsterdam density functional package*, *International Journal of Quantum Chemistry* 104, 645 (2005) (<https://doi.org/10.1002/qua.20653>)

Warning: In previous versions ADF2006-ADF2020 contained a bug for analytical frequency calculations of spin-polarized molecules using PBEC.

Bug PBEC The bug for analytical frequency calculations of spin-polarized molecules using PBEC affects calculations with the exchange-correlation functionals PBE, OPBE, RPBE, revPBE, and S12g. This bug was introduced in ADF2006 and fixed in AMS2020.103. Analytical frequencies using LibXC were not affected. A workaround for older versions is to use numerical frequencies. For AMS2020 one should use AMS2020.103 or later. For ADF2019.3 one should use ADF2019.307.

Calculating the analytical Hessian requires the solution of the Coupled Perturbed Kohn-Sham (CPKS) equations, which is an iterative process. This part of the process is of order $3 \times \text{number of atoms}$, and is generally the main bottleneck in calculating the frequencies. The immediate result of the solution of the CPKS equations is the U1 matrix, the components of which are closely related to the derivatives of the MO coefficients. One of the adjustable parameters in the input of an analytical frequency calculation can be used to control the accuracy of the U1 matrix components.

One disadvantage in calculating the analytical Hessian is that the range of exchange-correlation functionals is limited. This is because derivative formulas have to be derived for each exchange-correlation functional in ADF, which is not a straightforward task. Here are the currently available functionals:

LDA: XONLY, VWN, STOLL, PW92

Exchange GGA: Becke88, OPTx, PBEx, rPBEx, revPBEx, S12g

Correlation GGA: LYP, Perdew86, PBEC

XC GGA shortcuts: BP86, PBE, RPBE, revPBE, BLYP, OLYP, OPBE

Any functional not mentioned above is not implemented, including PW91 and Hartree-Fock.

A note of caution: For accurate frequencies it is especially important to also have an accurately optimized geometry. During a geometry optimization the integration accuracy is set by default to “Normal”, and so the resulting frequencies will also have this level of integration accuracy while it may be desirable to have frequencies computed with a higher accuracy. One might consider using Good NumericalQuality (or BeckeGrid quality) and set the convergence criteria for the geometry optimization tighter.

```
AnalyticalFreq
  B1Size float
  B1Thresh float
  Check_CPKS_From_Iteration integer
  Debug string
  Hessian [reflect | average]
  Max_CPKS_Iterations integer
  Print string
  PrintNormalModeAnalysis Yes/No
  U1_Accuracy float
End
```

AnalyticalFreq

Type

Block

Description

Define options for analytical frequencies.

B1Size

Type

Float

Description

Sparse grid max memory size

B1Thresh**Type**

Float

Default value

1e-10

Description

MMGF_DENB1 and MMGF_GRADB1 cutoff values

Check_CPKS_From_Iteration**Type**

Integer

Default value

1

Description

Solution of the CPKS equations is an iterative process, and convergence is achieved if the difference between U1 matrix of successive iterations falls below a certain threshold. This key can be used to determine at which iteration the checking should start taking place.

Debug**Type**

String

Description

For debugging purposes. Options: fit, hessian, b1, densities, numbers, symmetry, all.

Hessian**Type**

Multiple Choice

Default value

reflect

Options

[reflect, average]

Description

Whether the final Hessian is obtained by reflecting or averaging?

Max_CPKS_Iterations**Type**

Integer

Default value

20

Description

Calculating the analytical frequencies requires the solution of the Coupled Perturbed Kohn-Sham (CPKS) equations, which is an iterative process. If convergence is not achieved (a warning will be printed in the output if this is the case) then this subkey can be used to increase the number of iterations, although convergence is not guaranteed. The user required accuracy of the U1 matrix, as well as the ADF integration accuracy, can effect the rates of convergence.

Print**Type**

String

Description

Primarily for debugging purposes. Options: eigs, u1, parts. Choosing EIGS results in the print out of the MO eigenvectors, while U1 results in the print out of the U1 matrices. Except for small molecules this will result in a lot of data being output, and so they are not recommended. Choosing PARTS results in the print out of various sub-hessians that add up to give the final analytical hessian.

PrintNormalModeAnalysis**Type**

Bool

Default value

No

Description

Request ADF to print analysis of the normal modes independently of AMS.

U1_Accuracy**Type**

Float

Default value

5.0

Description

Solution of the CPKS equations is an iterative process, and convergence is achieved if the difference between U1 matrix of successive iterations falls below a certain threshold. This subkey can be used to set the threshold. The accuracy of the U1 will be $10^{*(-x)}$. So, the higher the number the more accurate the U1 will be. While this parameter effects the accuracy of the frequencies, other factors also effect the accuracy of the frequencies, especially the ADF integration accuracy.

7.1.2 (Resonance) Raman

See the [\(Resonance\) Raman section of the AMS manual](#). As explained there, you have two methods for calculating resonance Raman. One method uses the geometrical derivatives of the frequency-dependent polarizability with a finite lifetime, and the other method uses excited-state energy gradients projected onto the ground-state normal modes.

For (resonance) Raman calculations that use the geometrical derivatives of the frequency-dependent polarizability, AORESPONSE is used by default. To use RESPONSE instead of AORESPONSE, include the RESPONSE block key in the Engine ADF part of the input:

```
Engine ADF
  Response
End
EndEngine
```

7.1.3 VROA: (Resonance) vibrational Raman optical activity

See the VROA section of the AMS manual.

7.1.4 VCD: Vibrational Circular Dichroism

In AMS2020 it became possible to calculate VCD also for open-shell systems in a spin-unrestricted calculation.

See the VCD section of the AMS manual.

7.1.5 Vibrational Polarizabilities

Following a vibrational frequency calculation, ADF will automatically print the pure vibrational polarizability⁴ of the system. The full polarizability tensor is printed in atomic units along with the isotropic average.

See the Vibrational Polarizabilities section of the AMS manual.

7.2 Time-dependent DFT

Excitation energies, frequency-dependent (hyper) polarizabilities, Van der Waals dispersion coefficients, higher multipole polarizabilities, Raman scattering intensities and depolarization ratios of closed-shell molecules are all available in ADF^{1,2} as applications of time-dependent DFT (TDDFT); see³ for a review.

New in ADF2004.01 is the calculation of circular dichroism (CD) spectra, and the calculation of the optical rotation (dispersion).

Starting from the ADF2005.01 version it is possible to calculate excitation energies for open-shell systems with TDDFT, including spin-flip excitation energies. New in ADF2005.01 is the possibility to use time-dependent current-density functional theory (TDCDFT).

New in ADF2006.01 is the possibility to calculate excitation energies for closed-shell molecules including spin-orbit coupling.

New in ADF2008.01 is the possibility to calculate lifetime effects in (dynamic) polarizabilities (AORESPONSE key).

The input description for these properties is split into three parts: (a) general advice and remarks, (b) excitation energies, and (c) frequency-dependent (hyper) polarizabilities (two alternative implementation: RESPONSE key and AORESPONSE key) and related properties.

Tip: See also the ADF Advanced TDDFT tutorial: [TDDFT Study of 3 different Dihydroxyanthraquinones](#)

4

M. J. Cohen, A. Willetts, R. D. Amos, and N. C. Handy, *Vibrational contributions to static polarizabilities and hyperpolarizabilities*, *Journal of Chemical Physics* 100, 4467 (1994) (<https://doi.org/10.1063/1.474503>)

¹ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Implementation of time-dependent density functional response equations*, *Computer Physics Communications* 118, 119 (1999) ([https://doi.org/10.1016/S0010-4655\(99\)00187-3](https://doi.org/10.1016/S0010-4655(99)00187-3))

² S.J.A. van Gisbergen, **Molecular Response Property Calculations using Time Dependent Density Functional Theory**, in **Chemistry**. 1998, (<https://downloads.scm.com/Doc/gisbergen.pdf.tar.gz>) Vrije Universiteit: Amsterdam. p. 190.

³ E.K.U. Gross, J.F. Dobson and Petersilka, in *Density Functional Theory*, R.F. Nalewajski, Editor. 1996, Springer: Heidelberg.

7.2.1 General remarks on the Response and Excitation functionality

Symmetry

As in calculations without TDDFT the symmetry is automatically detected from the input atomic coordinates and need not be specified, except in the following case: infinite symmetries cannot be handled in the current release (ATOM, C(lin), D(lin)). For such symmetries a subgroup with finite symmetry must be specified in the input. The usual orientation requirements apply. If higher multipole polarizabilities are required, it may also be necessary to use a lower subgroup (the program will stop with an error message otherwise). For verification of results one can always compare to a NOSYM calculation.

Closed-shell

The current implementation often supports only closed-shell molecules. If occupation numbers other than 0 or 2 are used, the program will detect this (but only at a later stage of the calculation) and abort. All 'RESPONSE' calculations must be spin-restricted.

Open-shell

Excitation energies can be obtained for open-shell systems in a spin-unrestricted TDDFT calculation. Spin-flip excitation energies can only be obtained in a spin-unrestricted TDDFT calculation.

Atomic coordinates in a RAMAN calculation

Atomic coordinate displacements in a RAMAN calculation must be Cartesian, not Z-matrix. Furthermore, the current implementation does not yet support constrained displacements, i.e. you must use *all* atomic coordinate displacements.

Use of diffuse functions

The properties described here may require diffuse functions to be added to the basis (and fit) sets. Poor results will be obtained if the user is unaware of this. As a general rule, diffuse functions are more important for smaller than for larger molecules, more important for hyperpolarizabilities than for normal polarizabilities, more important for high-lying excitation energies (Rydberg states) than for low-lying excitations, more important for higher multipole polarizabilities than for dipole polarizabilities. The user should know when diffuse functions are required and when they are not: the program will not check anything in this respect. For example, in a study on low-lying excitation energies of a large molecule, diffuse functions will usually have little effect, whereas a hyperpolarizability calculation on a small molecule is pointless unless diffuse functions are included. Diffuse even-tempered basis sets are included in the ET/ directory in \$AMSHOME/atomicdata/ADF for the elements H-Kr. Somewhat older basis sets can be found in the Special/Vdiff directory in \$AMSHOME/atomicdata/ADF. For other atoms, the user will have to add diffuse basis and fit functions to the existing database sets. It is not necessary to start from basis V as was done for the basis sets in Special/Vdiff. For example, for heavier elements it may be a good idea to start from the ZORA/QZ4P basis sets. It may be expected that even more extensive basis sets will come available in the future, when usage and experience increase.

Linear dependency in basis

If large diffuse basis sets are used, or if diffuse functions are used for atoms that are not far apart, the calculation may suffer from numerical problems because of (near-) linear dependencies in the basis set. The user should be aware of this danger and use the DEPENDENCY key to check and solve this.

The LINEARSCALING input keyword

For reasons of numerical robustness and safety rather strict defaults apply for the neglect of tails of basis and fit functions (see the key LINEARSCALING) in a Response or Excitation calculation. This may result in longer CPU times than needed for non-TDDFT runs, in particular for larger molecules. Possibly this precaution is not necessary, but we have not yet tested this sufficiently to relax the tightened defaults.

Relativistic effects

The Response and Excitations options can be combined with scalar relativistic options (ZORA or Pauli). The one-electron relativistic orbitals and orbital energies are then used as input for the property calculation. Spin-orbit effects have been incorporated only in this part of the code (excitation energies). In case of a ZORA calculation, the so-called 'scaled' orbital energies are used as default.

Choice of XC potential

For properties that depend strongly on the outer region of the molecule (high-lying excitation energies, (hyper)polarizabilities), it may be important to use an XC potential with correct asymptotic behavior (approaching $-1/r$ as r tends to infinity). Finally, several asymptotically correct XC potentials have been implemented in ADF, such as the LB94 potential⁴ and the statistical average of orbital potentials SAOP^{8,6}. SAOP is recommended. Because of the correct asymptotic behavior the SAOP potential (and the LB94 potential) can describe Rydberg states correctly. The potentials based upon the so-called GRAdient regulated seamless connection of model potentials (GRAC) for the inner and the outer region^{5,7} have similar performance to SAOP, but have the disadvantage that the ionization energy of the molecule has to be used as input.

With the SAOP and GRAC functionals for the potential (as well as for LB94), the XC potential is computed from the exact charge density for reasons of stability and robustness (whereas for other functionals the (cheaper) fit density is used). This implies that computation times may be longer. Another 'side effect' is that, since there is no energy expression corresponding to these potentials, the final (bonding) energy of such calculations uses another GGA and hence the energy result is not (exactly) consistent with the SCF procedure. Note, finally, that these potentials have been found to be not suitable for geometry optimizations because they may not be sufficiently accurate in the bonding region, see the discussion of the XC input key. Applications with SAOP to (hyper)polarizabilities and excitation energies, also for Rydberg transitions, can be found in^{Page 175, 6} and with SAOP and Becke-Perdew-GRAC in^{5,7}. Applications with the old LB94 potential to response calculations can be found in refs.⁹ (polarizabilities),^{20,21,22} (hyperpolarizabilities),¹⁰ (high-lying excitation energies),¹¹ (multipole polarizabilities and dispersion coefficients).

XC kernel

In most cases the adiabatic local density approximated (ALDA) kernel is used in the TDDFT functionality. In case of calculating excitation energies with hybrid functionals the Hartree-Fock percentage times the Hartree-Fock kernel plus one minus the Hartree-Fock percentage times the ALDA kernel is used (hybrid ALDA kernel). For the LibXC range separated functionals, like CAM-B3LYP, starting from ADF2016.102 the kernel consists of range separated ALDA plus the kernel of the range separated exact exchange part. In ADF2016.101 the kernel for LibXC range separated functionals, like CAM-B3LYP, was using a 100% ALDA plus range separated exact exchange kernel (the ALDA part was not range-separated corrected).

For excitation energy calculations in some cases the full (non-ALDA) kernel can be evaluated, see the *full XC kernel*

⁴ R. van Leeuwen and E.J. Baerends, *Exchange-correlation potential with correct asymptotic behavior*, *Physical Review A* 49, 2421 (1994) (<https://doi.org/10.1103/PhysRevA.49.2421>)

⁸ O.V. Gritsenko, P.R.T. Schipper and E.J. Baerends, *Approximation of the exchange-correlation Kohn-Sham potential with a statistical average of different orbital model potentials*, *Chemical Physics Letters* 302, 199 (1999) ([https://doi.org/10.1016/S0009-2614\(99\)00128-1](https://doi.org/10.1016/S0009-2614(99)00128-1))

⁶ P.R.T. Schipper, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *Molecular calculations of excitation energies and (hyper)polarizabilities with a statistical average of orbital model exchange-correlation potentials*, *Journal of Chemical Physics* 112, 1344 (2000) (<https://doi.org/10.1063/1.480688>)

⁵ M. Grüning, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *Shape corrections to exchange-correlation Kohn-Sham potentials by gradient-regulated seamless connection of model potentials for inner and outer region*, *Journal of Chemical Physics* 114, 652 (2001) (<https://doi.org/10.1063/1.1327260>)

⁷ M. Grüning, O.V. Gritsenko, S.J.A. van Gisbergen and E.J. Baerends, *On the required shape correction to the LDA and GGA Kohn Sham potentials for molecular response calculations of (hyper)polarizabilities and excitation energies*, *Journal of Chemical Physics* 116, 9591 (2002) (<https://doi.org/10.1063/1.1476007>)

⁹ S.J.A. van Gisbergen, V.P. Osinga, O.V. Gritsenko, R. van Leeuwen, J.G. Snijders and E.J. Baerends, *Improved density functional theory results for frequency-dependent polarizabilities, by the use of an exchange-correlation potential with correct asymptotic behavior*, *Journal of Chemical Physics* 105, 3142 (1996) (<https://doi.org/10.1063/1.472182>)

²⁰ S.J.A. van Gisbergen, J.G. Snijders, and E.J. Baerends, *Time-dependent Density Functional Results for the Dynamic Hyperpolarizability of C₆₀*, *Physical Review Letters* 78, 3097 (1997) (<https://doi.org/10.1103/PhysRevLett.78.3097>)

²¹ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory*, *Journal of Chemical Physics* 109, 10644 (1998) (<https://doi.org/10.1063/1.477762>)

²² S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Accurate density functional calculations on frequency-dependent hyperpolarizabilities of small molecules*, *Journal of Chemical Physics* 109, 10657 (1998) (<https://doi.org/10.1063/1.477763>)

¹⁰ M.E. Casida, C. Jamorski, K.C. Casida and D.R. Salahub, *Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold*, *Journal of Chemical Physics* 108, 4439 (1998) (<https://doi.org/10.1063/1.475855>)

¹¹ V.P. Osinga, S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Density functional results for isotropic and anisotropic multipole polarizabilities and C₆, C₇, and C₈ Van der Waals dispersion coefficients for molecules*, *Journal of Chemical Physics* 106, 5091 (1997) (<https://doi.org/10.1063/1.473555>)

description (page 182). The Full kernel cannot be used in combination with symmetry or excited state geometry optimizations.

COSMO

The COSMO model for solvation is a cheap method to include solvation effects in the TDDFT applications, see the SOLVATION key. Note that in TDDFT calculations one may have to use two dielectric constants. The reason is that the electronic transition is so fast that only the electronic component of the solvent dielectric can respond, i.e., one should use the optical part of the dielectric constant. This is typically referred to as non-equilibrium solvation. The optical dielectric constant can be obtained from the (frequency dependent) refractive index n of the solvent as: $\epsilon_{\text{opt}} = n^2$. One can use the argument NEQL in the subkey SOLV of the key SOLVATION to set a value for the optical dielectric constant. No dielectric constant in the response might be closer to the optical dielectric constant than using the full dielectric constant. This can be achieved if one includes the subkey NOCSMRSP in the block key SOLVATION, such that the induced electronic charges do not influence the COSMO surface charges. However, if one does geometry optimization then the full dielectric constant should be used in the TDDFT simulations since the solvent dielectric now has time to fully respond. The default is that the full dielectric constant is used in the TDDFT calculations.

Accuracy check list

We strongly recommend the user to build experience with aspects that may affect the accuracy of TDDFT results. In particular we advise to ‘experiment’ with

- Varying basis sets
- Varying numericalquality
- Varying the TOLERANCE values in an Excitation calculation
- Using diffuse functions in case of small molecules
- Using the DEPENDENCY key in case of large basis sets
- Applying the ZORA relativistic corrections for molecules containing heavy nuclei
- Using an asymptotically correct XC potential such as SAOP

7.2.2 Analysis options for TDDFT (excitation energies and polarizabilities)

Several options are available to obtain more detailed results than a few bare numbers for excitation energies, oscillator strengths, transition dipole moments, and (hyper)polarizabilities. For a zero-order understanding of which occupied and virtual orbitals play an important role in the polarizability or intensity of an absorption peak,

it may be useful to know the values of the dipole matrix elements between (ground-state) occupied and virtual Kohn-Sham orbitals. If these dipole matrix elements are large for a particular occupied-virtual orbital pair, then this pair is almost certainly of great importance for the whole spectrum or polarizability. This information can be obtained by specifying somewhere in the input file (but NOT inside the RESPONSE or EXCITATIONS block keys):

PRINT DIPOLEMAT

7.2.3 Time-dependent Current DFT

The time-dependent current-density-functional (TDCDFT) implementation is built entirely upon the normal TDDFT implementation. Therefore all general remarks that are made for the TDDFT part of the program are also valid for TDCDFT. Only the polarizability and excitation energies of closed shell molecules can be calculated with TDCDFT in the present implementation.

If TDCDFT is used together with the ALDA functional (NOVK option) it will give the same results for the polarizability and excitation energies as TDDFT in a complete basis set. TDCDFT in ADF by default uses the VK functional^{12,13}, since this is the only current dependent functional that is known presently. Many aspects of the functional are still unknown and the functional should therefore be used with caution. The user is referred to the references for more information on when the VK functional gives good results and when not.

For more information on the implementation and applications of the TDCDFT and the VK functional please read the references^{23,24,25,26}. For more details on the theory and implementation in ADF see:¹⁴.

To activate TDCDFT and the VK functional one should add the following block key to the input file:

```
CURRENTRESPONSE
END
```

To calculate the polarizability the keyword Response can be used with the following options:

```
RESPONSE
  ALLCOMPONENTS
  Frequencies freq1 freq2 ... freqN
END
```

The block key EXCITATIONS can be used with all of its options.

In ADF2012 the block keyword AORESPONSE can also be used with the Vignale-Kohn functional. The current-density is generated on the fly but otherwise the computation is based on the time dependent density response.

By default the VK functional will be applied where the NCT parametrization¹⁵ is chosen for the transverse exchange-correlation kernel for the polarizability and singlet excitation energies (giving the best results for the systems studied so far). For triplet excitation energies the only available parametrization will be used¹⁶. This option is not tested much and the results are in general much worse than ALDA^{Page 177, 14}. It is therefore suggested that VK is not used to calculate triplet excitation energies.

¹² G. Vignale and W. Kohn, *Current-Dependent Exchange-Correlation Potential for Dynamical Linear Response Theory*, *Physical Review Letters* 77, 2037 (1996) (<https://doi.org/10.1103/PhysRevLett.77.2037>)

¹³ G. Vignale and W. Kohn, in *Electronic Density Functional Theory: Recent Progress and New Direction*, ISBN13: 9780306458347, J. F. Dobson, G. Vignale, and M. P. Das, Editors. 1998, Plenum: New York.

²³ M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger and J. G. Snijders, *Ultranonlocality in Time-Dependent Current-Density-Functional Theory: Application to Conjugated Polymers*, *Physical Review Letters* 88, 186401 (2002) (<https://doi.org/10.1103/PhysRevLett.88.186401>)

²⁴ M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger and J. G. Snijders, *Application of time-dependent current-density-functional theory to nonlocal exchange-correlation effects in polymers*, *Journal of Chemical Physics* 118, 1044 (2003) (<https://doi.org/10.1063/1.1529679>)

²⁵ M. van Faassen and P. L. de Boeij, *Excitation energies for a benchmark set of molecules obtained within time-dependent current-density functional theory using the Vignale-Kohn functional*, *Journal of Chemical Physics* 120, 8353 (2004) (<https://doi.org/10.1063/1.1697372>)

²⁶ M. van Faassen and P. L. de Boeij, *Excitation energies of Π -conjugated oligomers within time-dependent current-density-functional theory*, *Journal of Chemical Physics* 121, 10707 (2004) (<https://doi.org/10.1063/1.1810137>)

¹⁴ M. van Faassen, *Time-Dependent Current-Density-Functional Theory for Molecules*, (<https://downloads.scm.com/Doc/faassen.pdf>) PhD thesis, Rijksuniversiteit Groningen, 2004.

¹⁵ R. Nifosi, S. Conti and M. P. Tosi, *Dynamic exchange-correlation potentials for the electron gas in dimensionality $D=3$ and $D=2$* , *Physical Review B* 58: p. 12758 (1998) (<https://doi.org/10.1103/PhysRevB.58.12758>)

¹⁶ Z.X. Qian and G. Vignale, *Dynamical exchange-correlation potentials for the electron liquid in the spin channel*, *Physical Review B* 68, 195113 (2003) (<https://doi.org/10.1103/PhysRevB.68.195113>)

In the output the polarizability tensor (in case of an ALLCOMPONENTS calculation) has a different shape, the results are printed in the more intuitive order x, y, z, instead of y, z, x that the TDDFT implementation uses.

The following subkeys are available within the datablock of CURRENTRESPONSE

```
CURRENTRESPONSE
  QIANVIGNALE
  NOVK
END
```

QIANVIGNALE

The QV parametrization¹⁶ will be used for the transverse exchange-correlation kernel instead of NCT.

NOVK

TDCDFT will be applied with the ALDA functional instead of the VK functional. In a complete basis this will give the same results as a TDDFT calculation.

Magnetic properties within TDCDFT

It is now possible to calculate several magnetic properties via TDCDFT, among which magnetizabilities, rotational g-tensors, NMR shielding constants, specific rotations and circular dichroism. This alternative method is based on the diamagnetic-current sum rule, which consists of rewriting the diamagnetic current in terms of the response functions. This is the magnetic analogue of the conductivity sum rule, which is invalid when an external magnetic field is applied.

Details on the method can be found in these references:^{17,18}. Further details regarding the implementation can be found in the following PhD thesis as well:¹⁹.

In order to obtain these properties, the following subkeys can be used:

```
CURRENTRESPONSE
  MAGNET
  GTENSOR
  NMRSHIELDING
  CDSPEC
  DAMPING Damping
END
```

Depending on which property is calculated, the program chooses a reference point for the external vector potential (see references). For the magnetizability, the center of electronic charges is chosen, while for the rotational g-tensor, the center of nuclear charges is picked up. This choice has no influence in the static case, and has no influence neither for the specific rotations nor for the circular dichroism. It actually only affects the dynamical magnetizabilities (the rotational g-tensor being always computed at zero frequency). Below is a brief description of each subkey and how to use them.

MAGNET

The (static or dynamical) magnetizability tensor.

GTENSOR

The rotational g-tensor, calculated directly from the magnetizability.

NMRSHIELDING

The NMR shielding tensor. Care should be taken when using this keyword, though, as it was observed that the results failed to match experimental and other theoretical studies when using standard basis sets except for the lightest elements. Only when using very large basis sets should the results be trusted.

¹⁷ N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, *Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from the Current Density*, *Physical Review Letters* 114, 066404 (2015) (<https://doi.org/10.1103/PhysRevLett.114.066404>)

¹⁸ N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, *Gauge-Invariant Formulation of Circular Dichroism*, *Journal of Chemical Theory and Computation* 12, 3278 (2016) (<https://doi.org/10.1021/acs.jctc.6b00068>)

¹⁹ N. Raimbault, *Gauge-invariant magnetic properties from the current* (<https://tel.archives-ouvertes.fr/tel-01235055>), PhD thesis, Université Paul Sabatier, LCPQ, Toulouse, 2015

CDSPEC

Calculates both the specific rotation and the circular dichroism. This keyword should be used in combination with DAMPING if one wants to simulate CD spectra. The output spectrum will exhibit relatively sharp peaks. Linear-interpolating the results with a third-tier program is then necessary. This is done on purpose, so that the final spectrum could be broadened easily (only the absolute amplitudes of the peaks will be affected by this broadening).

DAMPING Damping

Adds a (fixed) damping factor to the response function. This allows one to avoid divergences that may arise from the response function when close to resonance, hence helping the self-consistent cycle converge. The value for Damping should be given in eV. A value of 0.1 eV seems to be reasonable.

7.3 Excitation energies: UV/Vis, X-ray, CD, MCD

Ultraviolet-visible (UV/Vis) spectroscopy studies electronic excitations of valence electrons, whereas X-ray spectroscopy studies electronic excitations of core electrons. Excitation energies and oscillator strengths are all available in ADF as applications of time-dependent DFT (TD-DFT). Excitation energies can be calculated for closed-shell as well as for open-shell molecules. It is also possible to include spin-orbit coupling and to calculate core excitations (X-ray absorption spectra). Circular dichroism (CD) is the differential absorption of left- and right-handed circularly polarized light. Starting from AMS2023 it is also possible to calculate excitation energies and oscillator strengths using the GW-Bethe-Salpeter equation (GW-BSE) formalism.

Tip: See also the ADF Advanced TD-DFT tutorial: [TDDFT Study of 3 different Dihydroxyanthraquinones](#)

7.3.1 Excitation energies, UV/Vis spectra

You can perform a calculation of singlet-singlet and singlet-triplet excitation energies of a closed-shell molecule by supplying in the input file the block key EXCITATIONS. See the next sections for settings of technical parameters, the calculation of excitation energies for open shell molecules, inclusion of spin-orbit coupling, and the calculation of CD spectra.

```
EXCITATIONS
  EXACT
    {IRREP1 N1}
    {IRREP2 N2}
  END
  DAVIDSON
    {IRREP3 N3}
    {IRREP4 N4}
  END
  ALLOWED
  ONLYSING
  ONLYTRIP
  LOWEST nlowest
End
```

Several options can be addressed with subkeys in the data block. This functionality is based on TD-DFT and consequently has a different theoretical foundation than the SCF techniques described elsewhere in this User's Guide. Two possible ways are available to solve the eigenvalue equation from which the excitation energies and oscillator strengths are obtained, of which the iterative Davidson procedure is the default. In this case, the program needs to know how many excitation energies are needed per irrep, what accuracy is required, and what type of excitation energies are required (singlet-singlet or singlet-triplet). Suitable defaults have been defined for all of these. Each of these points is discussed below.

Exact diagonalization vs. iterative Davidson procedure

The most straightforward procedure is a direct diagonalization of the matrix from which the excitation energies and oscillator strengths are obtained. Since the matrix may become very large, this option is possible only for very small molecules. It can be activated by specifying the block EXACT as one of the subkeys in the Excitations data block. The default is the iterative Davidson method. A few of the lowest excitation energies and oscillator strengths are then found within an error tolerance. An advantage of the EXACT option is that additional information is produced, such as the Cauchy coefficients that determine the average dipole polarizability. The EXACT option cannot be used in unrestricted calculations.

Singlet versus triplet

By default, the singlet-singlet and singlet-triplet excitation energies are both calculated. The singlets are handled first, then the corresponding triplet excitation energies. One can skip one of these two parts of the calculation by specifying either ONLYSING or ONLYTRIP as a subkey in the data block.

In case of a calculation including spin-orbit coupling one cannot separate the singlet-singlet and singlet-triplet excitations. The subkeys ONLYSING and ONLYTRIP are misused in this case to do a spin-restricted calculation, or a spin-polarized calculation, respectively. One should in fact only use the results of the spin-polarized calculation.

Dipole-allowed versus general excitations.

If you are interested in the optical absorption spectrum, you may not want to compute singlet-triplet excitation energies, nor singlet-singlet excitation energies which, by symmetry, have zero oscillator strengths. This subkey should not be used in case of spin-orbit coupling. The subkey ALLOWED tells ADF to treat only those irreducible representations for which the oscillator strengths will be nonzero. Of course, the oscillator strengths may still be negligibly small. The ALLOWED subkey automatically implies ONLYSING. The simplest, fastest, and recommended way to obtain information about the ten lowest dipole-allowed excitation energies would be:

```
EXCITATIONS
  ALLOWED
  LOWEST 10
END
```

Which excitation energies and how many?

The user can specify how many excitation energies per irrep should be calculated. If no pertaining input is available the program determines these numbers from the smallest differences between occupied and virtual Kohn-Sham orbital energies. By default it looks at the 10 lowest orbital energy differences. This number can be modified, by specifying inside the Excitation block key, for example:

```
LOWEST 30
```

One should be aware that this procedure does not guarantee that the lowest 10 (or 30) excitation energies will actually be found, since the orbital energy difference approximation to the excitation energy is rather crude. However, if the program decides on the basis of this procedure to calculate 4 excitation energies in a certain irreducible representation, these 4 excitation energies are certainly the lowest in that particular irrep.

The user has more control when the number of excitations per irrep is explicitly specified within the EXCITATIONS block key by the Davidson subkey:

```
DAVIDSON
  E'' 5
  T1.u 2
END
```

The DAVIDSON sub block may contain any number of records and must end with a record END. In the subkey data block a list of irreps, followed by the number of requested excitation energies is specified. Note that the irrep name may not be identical to the usual ADF name. For example E'' is called EEE in ADF. The Excitation code will skip an irrep if the label is not recognized. For multidimensional irreps, only the first column is treated, because the other would produce identical output. This implies that the oscillator strengths for E-irreps have to be multiplied by

2 and the oscillator strengths for T-irreps by 3. The ALLOWED subkey should not be used if irreps are specified with the Davidson block subkey, however, the subkey ONLYSING (or ONLYTRIP) can be used in this case.

The EXACT sub-block, mentioned already above, can also be used to treat only a few irreps instead of all. The number of excitation energies does not have to be specified then.

Some early applications of the Excitation feature in ADF can be found in Refs.^{45,46,47,48,49,50}.

In case of closed-shell molecules the unrelaxed excited state electric dipole moment is calculated, see Ref.⁶⁰. In case of a TDDFT-gradients calculation also the relaxed excited state electric dipole moment is calculated. For the definition of unrelaxed and relaxed excited state density, see Ref.⁵⁹.

Tamm-Dancoff approximation

Excitation energies can be calculated using the Tamm-Dancoff approximation (TDA)¹ if one includes, besides the EXCITATIONS block key, the key TDA:

```
TDA
```

GW-Bethe-Salpeter equation (GW-BSE)

Starting from AMS2023 it is possible to calculate excitation energies using the GW-BSE method instead of TD-DFT. The implementation in ADF is described in Ref.⁶¹. Currently, the BSE kernel is compatible with all options inside the XC block and also with the TDA and spin-orbit coupling. As GW-BSE uses the results of a GW calculation, GW-BSE should also not be used in combination with solvent models, like COSMO, or other environments. A GW-BSE calculation is performed by including the BSE key in the EXCITATIONS block,

```
EXCITATIONS
...
BSE
END
```

In a GW-Bethe-Salpeter Equation calculation a GW calculation is performed to calculate single-particle energies and the screened electron-electron interaction which are then used to calculate optical excitation energies. In a hybrid-DFT calculation, KS-DFT single-particle energies and the unscreened electron-electron interaction are used instead to calculate optical excitation energies.

⁴⁵ S.J.A. van Gisbergen, F. Kootstra, P.R.T. Schipper, O.V. Gritsenko, J.G. Snijders and E.J. Baerends, *Density-functional-theory response-property calculations with accurate exchange-correlation potentials*, *Physical Review A* 57, 2556 (1998) (<https://doi.org/10.1103/PhysRevA.57.2556>)

⁴⁶ S.J.A. van Gisbergen, A. Rosa, G. Ricciardi and E.J. Baerends, *Time-dependent density functional calculations on the electronic absorption spectrum of free base porphyrin*, *Journal of Chemical Physics* 111, 2499 (1999) (<https://doi.org/10.1063/1.479617>)

⁴⁷ A. Rosa, G. Ricciardi, E.J. Baerends and S.J.A. van Gisbergen, *The Optical Spectra of NiP, Nipz, NiTBP, and NiPc. Electronic effects of meso-tetraaza substitution and tetrabenzoannulation*, *Journal of Physical Chemistry A* 105, 3311 (2001) (<https://doi.org/10.1021/jp003508x>)

⁴⁸ G. Ricciardi, A. Rosa and E.J. Baerends, *Ground and Excited States of Zinc Phthalocyanine studied by Density Functional Methods*, *Journal of Physical Chemistry A* 105, 5242 (2001) (<https://doi.org/10.1021/jp0042361>)

⁴⁹ S.J.A. van Gisbergen, J.A. Groeneveld, A. Rosa, J.G. Snijders and E.J. Baerends, *Excitation energies for transition metal compounds from time-dependent density functional theory. Applications to MnO₄⁻, Ni(CO)₄ and Mn²⁺(CO)₁₀*, *Journal of Physical Chemistry A* 103, 6835 (1999) (<https://doi.org/10.1021/jp991060y>)

⁵⁰ A. Rosa, E.J. Baerends, S.J.A. van Gisbergen, E. van Lenthe, J.A. Groeneveld and J. G. Snijders, *Article Electronic Spectra of M(CO)₆ (M = Cr, Mo, W) Revisited by a Relativistic TDDFT Approach*, *Journal of the American Chemical Society* 121, 10356 (1999) (<https://doi.org/10.1021/ja990747t>)

⁶⁰ P. Grobas-Illobre, M. Marsili, S. Corni, M. Stener, D. Toffoli, and E. Coccia, *Journal of Chemical Theory and Computation* 17, 6314 (2021) (<https://doi.org/10.1021/acs.jctc.1c00211>)

⁵⁹ F. Furche, R. Ahlrichs, *Adiabatic time-dependent density functional methods for excited state properties*, *Journal of Chemical Physics* 117, 7433 (20002) (<https://doi.org/10.1063/1.1508368>)

¹ S. Hirata and M. Head-Gordon, *Time-dependent density functional theory within the Tamm-Dancoff approximation*, *Chemical Physics Letters* 314, 291 (1999) ([https://doi.org/10.1016/S0009-2614\(99\)01149-5](https://doi.org/10.1016/S0009-2614(99)01149-5))

⁶¹ Arno Förster, Lucas Visscher, *Quasiparticle Self-Consistent GW-Bethe-Salpeter equation calculations for large chromophoric systems*, *Journal of Chemical Theory and Computation* 18 (11) 6779–6793 (2022) (<https://doi.org/10.1021/acs.jctc.2c00531>)

By default the G_0W_0 variant of the GW approximation is used in a BSE calculation. This can be changed in the GW block, see the [GW description](#) (page 255). Almost all options in the GW block are compatible with a BSE calculation. For open-shell systems, partially self-consistent GW options are currently not supported.

The recommended numerical settings for a GW-BSE calculation are the same as for a GW calculation, see the [MBPT description](#) (page 384). ADF uses `Dependency bas=5e-3` and `RIHartreeFock DependencyThreshold=5e-3` in case of (any variant of) GW and GW-BSE. This can be overwritten but it is not recommended to do so. In case of convergence problems and/or variational collapse it is recommended to switch on the [MODIFYEXCITATION](#) (page 190) key and restrict the particle-hole basis in which the BSE is solved to particle-hole pairs with energy differences below for instance 2 Hartree.

For instance, one could do the following:

```
EXCITATIONS
...
BSE
END

MODIFYEXCITATION
  UseOccVirtRange 0.0 2.0
END

GW
...
END

MBPT
...
END
```

Full XC kernel

With XCFUN the full (non-ALDA) kernel can be evaluated, see the [XCFUN description](#) (page 97). To use the non-ALDA kernel the keyword FULLKERNEL should be put in the EXCITATIONS block. FULLKERNEL can be used with GGAs (including hybrids and RS functionals) but not meta-GGAs or meta-hybrids. For some of the LibXC functionals (mostly GGA's and hybrids) it is also possible to use the Full (non-ALDA) kernel. FULLKERNEL cannot be used in combination with excited state geometry optimizations or other response properties. If symmetry is used, recommended is to check that SYMMETRY NOSYM gives the same results.

```
XC
...
XCFUN
End
EXCITATIONS
...
FullKernel
END
```

```
XC
  LibXC ...
End
EXCITATIONS
...
  FullKernel
END
```

Singlet-triplet excitations are now also possible with FULLKERNEL.

Plasmons in Molecules

In Ref.² a scaling approach was used to identify plasmons in molecules. To identify plasmons in general molecules, they proposed to analyze the excitations by scaling the electron-electron interaction in the response calculation. While single-particle excitations are only slightly affected by this scaling, plasmonic excitations are sensitive to variations in the scaling parameter λ . More specifically, their squared excitation energies should increase linearly with the scaling parameter λ . Scaling of Coulomb, XC, and HF parts of the response kernel in TD-DFT, can be performed using the subkeywords SCALECOUL, SCALEXC, SCALEHF in the EXCITATIONS block.

```
EXCITATIONS
  SCALECOUL scalecoul
  SCALEXC   scalexc
  SCALEHF   scalehf
END
```

SCALECOUL scalecoul

Scaling of Coulomb kernel with scale parameter scalecoul.

SCALEXC scalexc

Scaling of the XC-kernel (excluding a possible HF-part) with scale parameter scalexc.

SCALEHF scalehf

Scaling of the HF part of the kernel with scale parameter scalehf.

Transition dipole moments between excited states

In Ref.^{Page 181, 60} transition dipole moments (electric dipole approximation) between different excited states are calculated. In ADF these transition dipole moments between different calculated excited states can be calculated if the subkey ESESTD is included. Spin-orbit coupling can also be included. Only implemented for closed shell molecules.

```
EXCITATIONS
  ESESTD
END
```

ESESTD

Compute transition dipole moments between excited states.

Accuracy and other technical parameters

For details regarding the (near linear scaling and parallelized) implementation, please check Refs.³⁴.

A summary of technical parameters with their defaults is:

```
EXCITATIONS
  VECTORS 40
  TOLERANCE 1e-6
  ORTHONORMALITY 1e-8
  ITERATIONS 200
```

(continues on next page)

² S. Bernadotte, F. Evers, and C.R. Jacob, *Plasmons in Molecules*, *Journal of Physical Chemistry C* 117, 1863 (2013) (<https://doi.org/10.1021/jp3113073>)

³ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Implementation of time-dependent density functional response equations*, *Computer Physics Communications* 118, 119 (1999) ([https://doi.org/10.1016/S0010-4655\(99\)00187-3](https://doi.org/10.1016/S0010-4655(99)00187-3))

⁴ S.J.A. van Gisbergen, C. Fonseca Guerra and E.J. Baerends, *Towards excitation energies and (hyper)polarizability calculations of large molecules. Application of parallelization and linear scaling techniques to time-dependent density functional response theory*, *Journal of Computational Chemistry* 21, 1511 (2000) ([https://doi.org/10.1002/1096-987X\(200012\)21:16%3C1511::AID-JCC8%3E3.0.CO;2-C/abstract](https://doi.org/10.1002/1096-987X(200012)21:16%3C1511::AID-JCC8%3E3.0.CO;2-C/abstract))

(continued from previous page)

```
KFWRITE 3
END
```

VECTORS *vectors*

The maximum number of trial vectors in the Davidson algorithm for which space is allocated. If this number is small less memory will be needed, but the trial vector space is smaller and has to be collapsed more often, at the expense of CPU time. The default is usually adequate.

TOLERANCE *tolerance*

Specifies the error tolerance in *the square* of the excitation energies in Hartree units. The default is probably acceptable but we recommend that you verify the results against a stricter default (e.g. 1e-8) for at least a few cases. In case of a BSE calculation, the default is 1e-5.

ORTHONORMALITY *orthonormality*

The Davidson algorithm orthonormalizes its trial vectors. Increasing the default orthonormality criterion increases the CPU time somewhat, but is another useful check on the reliability of the results.

ITERATIONS *iterations*

The maximum number of attempts within which the Davidson algorithm has to converge. The default appears to be adequate in most cases.

KFWRITE *kfwrite*

If kfwrite is 0 then do not write contributions, transition densities, and restart vectors to adf.rkf, since this can lead to a huge adf.rkf, especially if many excitations are calculated. Default value kfwrite is 3, which means that contributions, transition densities, and restart vectors are written to adf.rkf.

7.3.2 Excitation energies for open-shell systems

Excitation energies can be obtained for open-shell systems in a spin-unrestricted TDDFT calculation⁵. To perform an open-shell TD-DFT calculation (unrestricted TDDFT) one just needs to do an unrestricted SCF calculation and use the EXCITATIONS keyword. For ROKS TDA-DFT¹⁰⁶² in addition one needs to include the subkey ROSCF of the key SCF and the key TDA (Tamm-Dancoff approximation). Presently the excitation energies can only be found with Davidson's procedure. In case of spin-orbit coupling, see the section on *spin-orbit coupled excitation energies open shell molecule* (page 194).

The printed symmetry in the output in TDDFT calculations is actually the symmetry of transition density. For closed-shell systems, the symmetry of the excited state is the same as the symmetry of the transition density, while for open-shell systems, the symmetry of the excited states is the direct product between the symmetry of the transition density and the ground state symmetry. Note that the ground state symmetry of an open shell molecule is not necessarily A1.

For degenerate representations such as the 2-dimensional E-representations or the 3-dimensional T-representations, the occupation should be either fully occupied or zero. For example, for an orbital in an E-representation the α and β occupation number should be either 2 or 0. The α occupation number can of course be different from the β occupation number.

⁵ F. Wang and T. Ziegler, *Excitation energies of some d1 systems calculated using time-dependent density functional theory: an implementation of open-shell TDDFT theory for doublet-doublet excitations*, Molecular Physics 102, 2585 (2004) (<https://doi.org/10.1080/0026897042000275080>)

¹⁰ C.S. Chibueze and L. Visscher, *Restricted open-shell time-dependent density functional theory with perturbative spin-orbit coupling*, Journal of Chemical Physics 161, 094112 (2024) (<https://doi.org/10.1063/5.0226870>)

⁶² C.S. Chibueze and L. Visscher, *Spin-adapted spin-flip-down time-dependent density functional theory*, Journal of Chemical Physics 163, 094111 (2025) (<https://doi.org/10.1063/5.0275059>)

Unrestricted TDDFT

In case of unrestricted TDDFT the spin of the excited state is not well defined. As for the spin-state in unrestricted TDDFT, the general rule is that if the excited state mainly results from transitions from the singly occupied orbitals to virtual orbitals or from fully occupied orbitals to the singly occupied orbitals, the spin state of the excited state should roughly be the same as that of the ground state. However, if the excited state mainly comes from transitions from fully occupied orbitals to virtual orbitals, the spin state of the excited state are usually a mixture since TDDFT can only deal with single excitations within adiabatic approximation for the XC kernel⁷. Sometimes we just suppose the spin state of this kind of excited states to be the same as that of ground state^{Page 184, 5}. In the MO $\rightarrow$ MO transitions part for the excitations of the output file, the spin of each molecular orbitals are also specified to help assign the spin state of the excited states. The transitions are always from α spin-orbital to α spin-orbital or from β spin-orbital to β spin-orbital.

Excited state gradients can be calculated.

Unrestricted TDDFT: spin-flip excitations

Spin-flip excitation energies⁸⁹ can only be calculated with Tamm-Dancoff approximation (TDA)^{Page 181, 1} and Davidson's method. This unrestricted TDDFT method can not be used in case of spin-orbit coupling. Excited state gradients can be calculated.

To calculate spin-flip excitation energies, one must specify two keys SFTDDFT and TDA:

```
SFTDDFT
TDA
Unrestricted
SpinPolarization spinpolarization
EXCITATIONS
  {...}
End
```

For open-shell molecules, spin-flip transition can result in transition to the ground state with a different S_z value, while the symmetry of the transition density is A1. The excitation energy of this transition should be zero and this can be used to test the reliability of spin-flip TDDFT.

The symmetry of the excited states can be determined in the same way as that in spin-unrestricted TDDFT calculations. As for the spin state, similar to that in the spin-unrestricted TDDFT calculations, some states may be more or less pure spin states, others may just be mixtures. The users can interpret the excited state through the transitions that contribute to this state. Note that the transitions are always from α spin-orbital to β spin-orbital in spin-flip calculations, or from β spin-orbital to α spin-orbital.

⁷ Z. Rinkevicius, I. Tunell, P. Salek, O. Vahtras and H. Agren, *Restricted density functional theory of linear time-dependent properties in open-shell molecules*, *Journal of Chemical Physics* 119, 34 (2003) (<https://doi.org/10.1063/1.1577329>)

⁸ F. Wang and T. Ziegler, *Time-dependent density functional theory based on a noncollinear formulation of the exchange-correlation potential*, *Journal of Chemical Physics* 121, 12191 (2004) (<https://doi.org/10.1063/1.1821494>)

⁹ F. Wang and T. Ziegler, *The performance of time-dependent density functional theory based on a noncollinear exchange-correlation potential in the calculations of excitation energies*, *Journal of Chemical Physics* 122, 74109 (2005) (<https://doi.org/10.1063/1.1844299>)

ROKS TDA-DFT

In case of ROKS-TDA-DFT^{Page 184, 10Page 184, 62} the spin of the excited state is well defined. The default is that the spin of the excited state is the same as that of the ground state (SS, $S_{excited} = S_{groundstate}$). In spin-flip up ROKS TDA-DFT calculations the spin of the excitation is 1 higher than the spin of the ground state (SU, $S_{excited} = S_{groundstate} + 1$). In spin-flip down ROKS TDA-DFT calculations (implemented in ADF2026) the spin of the excitation is 1 lower than the spin of the ground state (SD, $S_{excited} = S_{groundstate} - 1$). In this case the spin of the ground state should be at least 1. This ROKS TDA-DFT method can be used in case of spin-orbit coupling if one includes spin-orbit coupling perturbatively, see *spin-orbit coupled excitation energies open shell molecule* (page 194).

Excited state gradients can not be calculated with ROKS-TDA-DFT.

The ROKS method implemented in ADF needs integer occupation numbers, and a positive spin polarization, see *ROKS for high-spin open shell molecules* (page 61). It requires the subkey ROSCF of the key SCF (and the keyword UNRESTRICTED, and the key SPINPOLARIZATION), and the the key TDA (Tamm-Dancoff approximation), thus add:

```
TDA
Scf
  ROSCF
  End
End
Unrestricted
SpinPolarization spinpolarization
EXCITATIONS
  {...}
End
```

One can do spin-conserved (same-spin, SS), spin-flip up (SU), or spin flip down (SD) ROKS TDA-DFT calculations, or do combinations of them. One can specify the corresponding types with SSType, SUType, and SDType. If spin flip down (SD) is included one should use an Abelian point-group symmetry (symmetry NOSYM can always be used).

Remark: with the subkey Excitations%Lowest one can specify the number of wanted excited states. For example if one calculates SS-SU and 2 numbers are provided the first number is the wanted number of excited states with same spin (SS) and the second number the wanted number of excited states with higher spin (SU).

```
Excitations
  RoksTddftType
    Calculate [SD | SS | SU | SD-SS | SS-SU | SD-SS-SU]
    SDType [SD-TDA | SD-CIS | QSD-TDA]
    SSType [R-TDA | S-TDA | X-TDA]
    SUType [SF-TDA]
  End
End
```

Excitations

RoksTddftType

Type

Block

Description

Excitation energies from RoksTddft: UV/Vis

Calculate

Type

Multiple Choice

Default value

SS

Options

[SD, SS, SU, SD-SS, SS-SU, SD-SS-SU]

GUI name

RoksTddft Calculate

Description

Specifies the types of RoksTddft methods to target several target spins: spin-down (SD), same-spin (SS), and/or spin-up (SU).

SDType**Type**

Multiple Choice

Default value

QSD-TDA

Options

[SD-TDA, SD-CIS, QSD-TDA]

GUI name

RoksTddft SD-Type

Description

Specifies the flavor to be used in the case of spin-down (SD) RoksTddft

SSType**Type**

Multiple Choice

Default value

S-TDA

Options

[R-TDA, S-TDA, X-TDA]

GUI name

RoksTddft SS-Type

Description

Specifies the flavor to be used in the case of same-spin (SS) RoksTddft

SUType**Type**

Multiple Choice

Default value

SF-TDA

Options

[SF-TDA]

GUI name

RoksTddft SU-Type

Description

Specifies the flavor to be used in the case of spin-up (SU) RoksTddft

ROKS TDA-DFT: spin-conserved excitations

In spin-conserved ROKS-TDA-DFT calculations (same spin, SS) the spin of the excitation is 1 higher than the spin of the ground state. For example if the ground state is a doublet, then the excited states in spin-flip ROKS TDA-DFT will be quartet states. There are several flavors (SSType) of spin-conserved ROKS TDA-DFT^{Page 184, 1030}, namely R-TDA^{Page 185, 7}, S-TDA³⁴, and X-TDA³⁵. R-TDA is the original restricted open-shell TD-DFT method within the TDA by Rinkevicius and co-workers. S-TDA stands for spin-adapted TD-DFT within TDA in which also triplet coupled closed-to-virtual single excitation are incorporated. S-TDA is the default method in ADF. When one applies RPA corrections to the frequency-independent kernel in S-TDA, one obtains the X-TDA method. Li and Liu have shown that X-TDA is just as good as S-TDA but due to simplicity, X-TDA may be more efficient. Note that for X-TDA the calculation of HF exchange integrals is needed, thus for LDA and GGA functionals one needs to include the key HARTREEFOCK.

ROKS TDA-DFT: spin-flip up excitations

In spin-flip up ROKS TDA-DFT (SFU-TDA) calculations the spin of the excitation is 1 higher than the spin of the ground state. For example if the ground state is a doublet, then the excited states in spin-flip up ROKS TDA-DFT will be quartet states. Excited state gradients can not be calculated with ROKS-TDA-DFT. One flavor (SUType) of spin-flip up ROKS TDA-DFT is implemented, namely SF-TDA^{Page 184, 10}.

ROKS TDA-DFT: spin-flip down excitations

In spin-flip down ROKS TDA-DFT (SFD-TDA) calculations the spin of the excitation is 1 lower than the spin of the ground state. For example if the ground state is a triplet, then the excited states in spin-flip down ROKS TDA-DFT will be singlet states. Excited state gradients can not be calculated with ROKS-TDA-DFT. There are several flavors (SDType) of spin-flip down ROKS TDA-DFT, namely SD-TDA, SD-CIS, and QSD-TDA, all described in Ref.^{Page 184, 62}. Two fully spin-adapted ROKS-SFD-TDA methods were described in this paper that either stem from configuration interaction with single excitations (SD-CIS, in the paper called SF-CIS) or from the equation-of-motion ansatz (SD-TDA, or in the paper called SF-TDA). It was shown in the paper that the spin-adaptation in SF-CIS (SD-CIS) and SF-TDA (SD-TDA) gives rise to artificial double counting of correlation effects by incorporating double excitations. When discarding this double counting, one ends up with an excited state that is partly spin-adapted (only in the open-to-open configurations). In the paper this method was called quasi-spin-adapted SF-TDA (QSD-TDA, or in the paper called Q-SF-TDA) and was shown in the paper to be a stable and efficient method that performs similarly to spin-unrestricted SFD-TD-DFT.

Spin-flip excitations: ALDA kernel

In spin-flip unrestricted TDDFT and spin-flip ROKS-TDA, the XC kernel can be calculated directly from the XC potential. To use the LDA potential for the XC kernel, which roughly corresponds to the ALDA in ordinary TDDFT, one must specify the key

FORCEALDA

anywhere in the input file. Only calculations using the LDA potential in the SCF are fully tested. Using other GGA potentials in the SCF and using the FORCEALDA key at the same time may introduce unreasonable results, while using LB94 or SAOP potential in the SCF without the FORCEALDA key may give unstable results. Unstable results have been reported for the PW91 functional. In AMS2025 the stability of the results without using the FORCEALDA key have been improved by using for small spin-polarization densities the same as if the FORCEALDA key was used.

³⁰ Z. Li, W. Liu, *Spin-adapted open-shell random phase approximation and time-dependent density functional theory. I. Theory.*, *Journal of Chemical Physics* 133, 064106 (2010) (<https://doi.org/10.1063/1.3463799>)

³⁴ Z. Li, W. Liu, Y. Zhang, B. Suo, *Spin-adapted open-shell time-dependent density functional theory. II. Theory and pilot application.*, *Journal of Chemical Physics* 134, 134101 (2010) (<https://doi.org/10.1063/1.3573374>)

³⁵ Z. Li, W. Liu, *Spin-adapted open-shell time-dependent density functional theory. III. An even better and simpler formulation.*, *Journal of Chemical Physics* 135, 194106 (2010) (<https://doi.org/10.1063/1.3660688>)

7.3.3 Select (core) excitation energies, X-ray absorption

Two methods can be used to reduce the computational costs of, for example, core excitation energies, or some other high lying excitation energy. In the state selective method scheme a guess vector for the orbital transition has to be provided. An overlap criterion is used to follow the wanted eigenvector. In this scheme the one-electron excited state configuration space remains complete, see Ref.¹². In the second scheme, the range of excitations that are calculated is modified, which means that the one-electron excited state configuration space is reduced to the interesting part, see Ref.¹¹. The calculated excited states are more accurate with the state selective method if convergence is reached, however, the second scheme is more robust, and it is easier to find convergence.

These selection methods can, for example, also be used in case one calculates excitation energies as Kohn-Sham orbital energy differences, see subkey *SINGLEORBTRANS* (page 192) of the key EXCITATIONS.

For X-ray spectra it can be important to include quadrupole intensities.

State selective optimization excitation energies

The state selective method (key SELECTEXCITATION) can be used to reduce the computational costs of, for example, core excitation energies. In this scheme a guess vector for the orbital transition has to be provided. It should be used in combination with the Davidson method to calculate excitation energies. An overlap criterion is used to follow the wanted eigenvector. This method for state selective optimization of excitation energies is based on the method by Kovyshin and Neugebauer, see Ref.^{Page 189, 12}. This key can also be used in case of spin-orbit coupling. The use of the key SELECTEXCITATION is similar as the use of the key MODIFYEXCITATION. However, the key SELECTEXCITATION can not be used in combination with the key MODIFYEXCITATION. In the state selective method (key SELECTEXCITATION) the one-electron excited state configuration space remains complete, whereas it is reduced in case the scheme with the MODIFYEXCITATION key.

The starting guess vector(s) for the excitation energies can be selected, for example by selecting 1 occupied orbital and 1 virtual orbital.

```
SELECTEXCITATION
  OscStrength oscstrength
  UseOccVirtRange elowoccvirt ehighoccvirt
  UseOccVirtNumbers nrlowoccvirt nrhighoccvirt
  UseOccRange elowocc ehighocc
  UseVirtRange elowvirt ehighvirt
  UseOccupied
    irrep orbitalnumbers
    irrep orbitalnumbers
    ...
  SubEnd
  UseVirtual
    irrep orbitalnumbers
    irrep orbitalnumbers
    ...
  SubEnd
  UseScaledZORA
end
```

OscStrength oscstrength

Use only pairs of an occupied and virtual orbital as guess vectors, for which the oscillator strength of the single-orbital transition is larger than oscstrength.

¹² A. Kovyshin, J. Neugebauer, *State-selective optimization of local excited electronic states in extended systems*, *Journal of Chemical Physics* 133, 174114 (2010) (<https://doi.org/10.1063/1.3488230>)

¹¹ M. Stener, G. Fronzoni and M. de Simone, *Time dependent density functional theory of core electrons excitations*, *Chemical Physics Letters* 373, 115 (2003) ([https://doi.org/10.1016/S0009-2614\(03\)00543-8](https://doi.org/10.1016/S0009-2614(03)00543-8))

UseOccVirtRange elowoccvirt ehighoccvirt

Use only pairs of an occupied and virtual orbital as guess vectors, for which the orbital energy difference is between elowoccvirt and ehighoccvirt (in hartree). If one is interested in the lowest excitation energies, use for elowoccvirt a value smaller than the HOMO-LUMO gap, and for ehighoccvirt a value larger than the energy range one is interested in.

UseOccVirtNumbers nrLOWoccvirt nrHIGHoccvirt

Use only pairs of an occupied and virtual orbital as guess vectors, for which in the sorted list of the orbital energy differences, the number of the single-orbital transition is between nrLOWoccvirt and nrHIGHoccvirt.

UseOccRange elowocc ehighocc

Use only occupied orbitals in the guess vectors which have orbital energies between elowocc and ehighocc (in hartree).

UseVirtRange elowvirt ehighvirt

Use only virtual orbitals in the guess vectors which have orbital energies between elowvirt and ehighvirt (in hartree).

UseOccupied

Use only the occupied orbitals in the guess vectors which are specified.

UseVirtual

Use only the virtual orbitals in the guess vectors which are specified.

irrep

The name of one of the irreducible representations (not a subspecies) of the point group of the system. See the Appendix for the irrep names as they are used in ADF.

orbitalnumbers

A series of one or more numbers: include all numbers of the orbitals in the guess vectors that are to be used. In an unrestricted calculation the same numbers are used for the spin- α orbitals and the spin- β orbitals.

Modify range of excitation energies

The key MODIFYEXCITATION can be used to reduce the computational costs of, for example, core excitation energies. This key can also be used in case of spin-orbit coupling. The use of the key MODIFYEXCITATION is similar as the use of the key SELECTEXCITATION. However, the key MODIFYEXCITATION can not be used in combination with the key SELECTEXCITATION. In the state selective method (key SELECTEXCITATION) the one-electron excited state configuration space remains complete, whereas it is (effectively) reduced in case the scheme with the MODIFYEXCITATION key.

One possibility is to allow only selected occupied orbitals and or selected virtual orbitals in the TDDFT calculations. In this scheme the complete one-electron excited state configuration space is reduced to the subspace where only the core electrons are excited, see Stener et al.¹¹. In the actual implementation this is done by artificially changing the orbital energies of the uninteresting occupied orbitals to a large negative value (default -1d6 Hartree), and by by artificially changing the orbital energies of the uninteresting virtual orbitals to a large positive value (default 1d6).

In ADF2010 an extra possibility is added with the subkey UseOccVirtRange, which restricts the space of excitation energies, by allowing only pairs of occupied and virtual orbitals, for which the difference in orbital energy is between a certain range.

```
MODIFYEXCITATION
  OscStrength oscstrength
  UseOccVirtRange elowoccvirt ehighoccvirt
  UseOccVirtNumbers nrLOWoccvirt nrHIGHoccvirt
  UseOccRange elowocc ehighocc
  UseVirtRange elowvirt ehighvirt
  UseOccupied
  irrep orbitalnumbers
```

(continues on next page)

(continued from previous page)

```

    irrep orbitalnumbers
    ...
SubEnd
UseVirtual
    irrep orbitalnumbers
    irrep orbitalnumbers
    ...
SubEnd
SetOccEnergy esetocc
SetLargeEnergy epsbig
UseScaledZORA
end

```

OscStrength oscstrength

Use only pairs of an occupied and virtual orbital as guess vectors, for which the oscillator strength of the single-orbital transition is larger than oscstrength.

UseOccVirtRange elowoccvirt ehighoccvirt

Use only pairs of an occupied and virtual orbital, for which the orbital energy difference is between elowoccvirt and ehighoccvirt (in hartree).

UseOccVirtNumbers nrlowoccvirt nrhighoccvirt

Use only pairs of an occupied and virtual orbital as guess vectors, for which in the sorted list of the orbital energy differences, the number of the single-orbital transition is between nrlowoccvirt and nrhighoccvirt.

UseOccRange elowocc ehighocc

Use only occupied orbitals which have orbital energies between elowocc and ehighocc (in Hartree).

UseVirtRange elowvirt ehighvirt

Use only virtual orbitals which have orbital energies between elowvirt and ehighvirt (in Hartree).

UseOccupied

Use only the occupied orbitals which are specified.

UseVirtual

Use only the virtual orbitals which are specified.

irrep

The name of one of the irreducible representations (not a subspecies) of the point group of the system. See the Appendix for the irrep names as they are used in ADF.

orbitalnumbers

A series of one or more numbers: include all numbers of the orbitals that are to be used. In an unrestricted calculation the same numbers are used for the spin- α orbitals and the spin- β orbitals.

SetOccEnergy esetocc

All occupied orbitals that have to be used will change their orbital energy to esetocc. In practice only useful if one has selected one occupied orbital energy, and one want to change this to another value. Default: the orbital energies of the occupied orbitals that are used are not changed.

SetLargeEnergy epsbig

The orbital energies of the uninteresting occupied orbitals are changed to -epsbig Hartree, and the orbital energies of the uninteresting virtual orbitals are changed to epsbig Hartree (Default: epsbig = 1d6 Hartree).

UseScaledZORA

Use everywhere the scaled ZORA orbital energies instead of the ZORA orbital energies in the TDDFT equations. This can improve deep core excitation energies. Only valid if ZORA is used. Default: use the unscaled ZORA orbital energies.

Excitations as orbital energy differences

Instead of the relative expensive TDDFT calculation of excitation energies, sometimes just calculating Kohn-Sham orbital energy differences may already be useful. The subkeyword SINGLEORBTRANS in the block key EXCITATIONS, will calculate excitation energies as Kohn-Sham orbital energy differences. The subkeyword SINGLEORBTRANS in the block key EXCITATIONS replaces the obsolete key KSSPECTRUM. For a given excitation from an occupied orbital to a virtual orbital the oscillator strength is calculated from the the dipole transition moment between this occupied orbital and this virtual orbital. This method is best suited if LDA or a GGA is used in the SCF.

Especially useful for core excitation energy calculations. If SINGLEORBTRANS is used, it is possible to use fractional occupation numbers in the SCF, like is used in the DFT transition state (DFT-TS) scheme, see, for example, Ref.¹⁵. Note: for fractional occupation numbers, typically an orbital is treated in the excitation calculation as if it is fully occupied if the occupation number is 1.5 or more, and it is treated as if it is fully unoccupied if the occupation number is 0.5 or less. In the transition state procedure for core excitations half an electron is moved from an initial core orbital to final virtual orbital and the SCF KS eigenvalue difference is taken as excitation energy. This is the original Slater formulation and is justified doing a Taylor expansion of total energy with respect to occupation numbers, it can be shown that errors arise from third order terms which are small. This, however, is not very practical: to converge SCF by putting half an electron in virtual orbitals is very hard, usually it works only for the lowest virtuals. In order to avoid this problem one neglects the half an electron in virtual, this scheme (only half an electron removed from occupied orbital) is called Transition Potential (TP) and is widely employed in XAS from K-edges.

```
EXCITATIONS
  SingleOrbTrans
END
```

SingleOrbTrans

keyword to use only orbital energy differences

The value for the subkeyword KFWRITE in the EXCITATIONS block key is set by default to 0 in case of SINGLE-ORBTRANS. If kfwrite is 0 then do not write contributions, transition densities, and restart vectors to adf.rkf, since this can lead to a huge adf.rkf, especially if many excitations are calculated.

Quadrupole intensities in X-ray spectroscopy

For electronic excitations in the ultraviolet and visible range of the electromagnetic spectrum, the intensities are usually calculated within the dipole approximation, which assumes that the oscillating electric field is constant over the length scale of the transition. For the short wavelengths used in hard X-ray spectroscopy, the dipole approximation may not be adequate. In particular, for metal K-edge X-ray absorption spectroscopy (XAS), it becomes necessary to include higher-order contributions. An origin-independent calculation of quadrupole intensities in XAS was implemented in ADF by Bernadotte et al., see Ref.¹⁶. These quadrupole intensities may also be important for the calculation of X-ray emission spectroscopy, see [section on XES](#) (page 193). Can not be used in combination with spin-orbit coupling.

Usage

```
EXCITATIONS
  . . .
  XAS
  { ALLXASMOMENTS }
  { ALLXASQUADRUPOLE }
END
```

¹⁵ R. De Francesco, M. Stener, and G. Fronzoni, *Theoretical Study of Near-Edge X-ray Absorption Fine Structure Spectra of Metal Phthalocyanines at C and N K-Edges*, *Journal of Physical Chemistry A*, 116 2285 (2012) (<https://doi.org/10.1021/jp2109913>)

¹⁶ S. Bernadotte, A.J. Atkins, Ch.R. Jacob, *Origin-independent calculation of quadrupole intensities in X-ray spectroscopy*, *Journal of Chemical Physics* 137, 204106 (2012) (<https://doi.org/10.1063/1.4766359>)

XAS

Use XAS within the EXCITATIONS block to initiate the calculation of the higher order multipole moment integrals and the calculation of the quadrupole oscillator strengths. This will only print the total oscillator strength and the excitation energy.

ALLXASMOMENTS

Use ALLXASMOMENTS within the EXCITATIONS block in combination with the XAS keyword. This will print out all the individual transition moments used within the calculation of the total oscillator strength.

ALLXASQUADRUPOLE

Use ALLXASQUADRUPOLE within the EXCITATIONS block in combination with the XAS keyword. This will print out the individual oscillator strength components to the total oscillator strength.

The *MODIFYEXCITATION* (page 190) or *SELECTEXCITATION* (page 189) keyword could be used to select a core orbital.

7.3.4 XES: X-ray emission spectroscopy

For the calculation of XES (X-ray emission spectroscopy) spectra the approach of Ref.¹⁷ is implemented in the ADF program by Atkins et. al., see Ref.¹⁸. This is a frozen orbital, one-electron Δ DFT approach which uses orbital energy differences between occupied orbitals to model the X-ray emission energies. Even though it is the simplest possible approximation for the calculation of XES spectra, it has been shown to work well for V2C-XES (valence-to-core X-ray emission spectroscopy) spectra of transition metal complexes.

The XES keyword initiates the calculation of X-ray emission energies to a core orbital. In addition to dipole oscillator strengths this keyword also triggers the calculation of the higher order moment integrals and the calculation of the quadrupole oscillator strengths. By default it calculates the emission to the first orbital in the first symmetry, often the deepest core orbital, and only prints the total oscillator strength and the excitation energy. Can not be used in combination with spin-orbit coupling.

```
XES
  {COREHOLE irrep number}
  {ALLXESMOMENTS}
  {ALLXESQUADRUPOLE}
END
```

COREHOLE irrep number

This allows the selection of the acceptor orbital for the calculation of the emission oscillator strengths. For example 'COREHOLE A1 2' calculates oscillator strengths to the orbital 2 in irrep A1.

ALLXESMOMENTS

Use ALLXESMOMENTS within the XES block. This will print out all the individual transition moments used within the calculation of the total oscillator strength.

ALLXESQUADRUPOLE

Use ALLXESQUADRUPOLE within the XES block. This will print out the individual oscillator strength components to the total oscillator strength.

¹⁷ N. Lee, T. Petrenko, U. Bergmann, F. Neese, and S. DeBeer, *Probing Valence Orbital Composition with Iron K β X-ray Emission Spectroscopy*, Journal of the American Chemical Society 132, 9715 (2010) (<https://doi.org/10.1021/ja101281e>)

¹⁸ A.J. Atkins, M. Bauer, and Ch.R. Jacob, *The chemical sensitivity of X-ray spectroscopy: high energy resolution XANES versus X-ray emission spectroscopy of substituted ferrocenes*, Physical Chemistry Chemical Physics 15, 8095 (2013) (<https://doi.org/10.1039/C3CP50999K>)

7.3.5 Excitation energies and Spin-Orbit coupling

Spin-orbit coupling can be included in the TDDFT calculation of excitation energies. Two methods can be used in ADF. The first one includes spin-orbit coupling as a perturbation to a scalar relativistic calculation of excitation energies, in which spin-orbit coupling matrix elements (SOCMEs) between excited states are calculated. The second one includes spin-orbit coupling self-consistently in the ground state calculation. If spin-orbit coupling is large, the second one is more accurate for closed shell ground states, but is also more time-consuming. For open shell ground states the perturbative ROKS-TDA-SOC method is to be preferred over the highly approximate method which includes spin-orbit coupling self-consistently.

The results of these spin-orbit coupled TDDFT calculations include the calculation of the zero field splitting (ZFS) of triplet excited states in case of a closed shell ground state and the calculation of radiative rate constants, which could be used to calculate radiative phosphorescence lifetimes.

Perturbative inclusion of spin-orbit coupling

```
SOPERT
  {NCALC ncalc}
  {ESHIFT eshift}
  {GSCorr Yes/No}
End
Relativity
  Level Scalar
  Formalism ZORA
End
EXCITATIONS
END
```

The perturbative method, which is described in Ref.¹⁹, is an approximate time-dependent density-functional theory (TDDFT) formalism to deal with the influence of spin-orbit coupling effect on the excitation energies for closed-shell systems. In this formalism scalar relativistic TDDFT calculations are first performed to determine the lowest single-group excited states and the spin-orbit coupling operator is applied to these single-group excited states to obtain the excitation energies with spin-orbit coupling effects included. The computational effort of the present method is much smaller than that of the two-component TDDFT formalism. The compositions of the double-group excited states in terms of single-group singlet and triplet excited states are obtained automatically from the calculations. In Ref.^{Page 194, 19} it was shown that the calculated excitation energies based on the present formalism affords reasonable excitation energies for transitions not involving 5p and 6p orbitals. For transitions involving 5p orbitals, one can still obtain acceptable results for excitations with a small truncation error, while the formalism will fail for transitions involving 6p orbitals, especially 6p1/2 spinors. In AMS2025 a bug has been fixed such that one can use symmetry C(2H).

Although this method is not completely correctly implemented for (meta-)hybrids or Hartree-Fock, it still gives reasonable excitation energies, and can thus be useful also in that case.

NCALC=ncalc

Number of spin-orbit coupled excitation energies to be calculated. Default (and maximum) value: 4 times the number of scalar relativistic singlet-singlet excitations.

ESHIFT=eshift

The actually calculated eigenvalues are calculated up to the maximum singlet-singlet or singlet-triplet scalar relativistic excitation energy plus eshift (in Hartree). Default value: 0.2 Hartree.

GSCORR Yes/No

The singlet ground state is included, which means that spin-orbit coupling can also have some effect on energy of

¹⁹ F. Wang and T. Ziegler, *A simplified relativistic time-dependent density-functional theory formalism for the calculations of excitation energies including spin-orbit coupling effect*, *Journal of Chemical Physics* 123, 154102 (2005) (<https://doi.org/10.1063/1.2061187>)

the ground state. The spin-orbit matrix in this case is on basis of the ground state and the singlet and triplet excited states. Default Yes.

Some extra information about the spin-orbit matrix is written to the output if one includes

```
SOPERT
  {NCALC ncalc}
  {ESHIFT eshift}
  {GSCorr Yes/No}
End
PRINT SOMATRIX
```

If one includes PRINT SOMATRIX the spin-orbit matrix (in Hartree) on basis of singlet and triplet excited states will be printed. Note that a triplet has three sublevels. The numbering of the basis of singlets and triplets is given above the spin-orbit matrix. The spin-orbit matrix has a real and imaginary part. On the diagonal the singlet or triplet energies is added. This spin-orbit matrix is the one that is diagonalized to get the spin-orbit coupled excitation energies. For example, for the effect of spin-orbit coupling between T1 and S1 one finds 3 complex values, between the 3 sublevels of T1 and the one level of S1. For a magnitude one could take the square root of the (real part squared + imaginary part squared).

Starting from ADF2018 these spin-orbit coupling matrix elements (SOCMEs) are printed in an easier format in the output. The SOCME that is printed is calculated as a root mean square: square root of (the sum of squares of spin-orbit coupling matrix elements of all sublevels of the uncoupled states).

ROKS-TDA-SOC

The perturbative method ROKS-TDA-SOC method described in Refs.^{Page 184, 1063}, is an approximate time-dependent density-functional theory (TDDFT) formalism to deal with the influence of spin-orbit coupling effect on the excitation energies for open-shell systems. In ROKS-TDA-SOC spin-orbit coupling (SOC) is included perturbatively on top of a restricted open-shell Kohn–Sham (ROKS) time-dependent density functional theory, in which the Tamm–Dancoff approximation (TDA) is used. Thus scalar relativistic excited states are calculated with TDA-DFT, after which the Hamiltonian that includes SOC is diagonalized in the basis of these states.

The ROKS method implemented in ADF needs integer occupation numbers, and a positive spin polarization, see [ROKS for high-spin open shell molecules](#) (page 61). It requires the subkey ROSCF of the key SCF (and the keyword UNRESTRICTED, and the key SPINPOLARIZATION), and the the key TDA (Tamm–Dancoff approximation). In order to perform ROKS-TDA-SOC calculations in addition one needs to include the block keyword SOPERT. Symmetry NOSYM should be used. One needs to specify (with Exctations%RoksTddftType%Calculate) which scalar relativistic ROKS-TDA excitations to include: those with the same spin as the ground state (SS, $S_{excited} = S_{groundstate}$), those with a spin 1 higher than the ground state (SU, $S_{excited} = S_{groundstate} + 1$), and/or those those with a spin 1 lower than the ground state (SD, $S_{excited} = S_{groundstate} - 1$). The possibility to include spin-flip down (SD) excitations in ROKS-TDA-SOC, see Ref.⁶³, is implemented in ADF2026.

```
UnRestricted
SpinPolarization spinpolarization
Symmetry NOSYM
Scf
  ROSCF
  End
End
TDA
SOPERT
End
Relativity
```

(continues on next page)

⁶³ C.S. Chibueze and L. Visscher, *Restricted open-shell time-dependent density functional theory with perturbative spin-orbit coupling: Inclusion of spin-flip-down states*, Journal of Chemical Physics 164, 024101 (2026) (<https://doi.org/10.1063/5.0305111>)

(continued from previous page)

```

Level Scalar
End
EXCITATIONS
  RoksTddftType
    Calculate [SD | SS | SU | SD-SS | SS-SU | SD-SS-SU]
  End
End
END

```

Remark: with the subkey `Excitations%Lowest` one can specify the number of wanted excited states. For example if one calculates SD-SS-SU and 3 numbers are provided the first number is the wanted number of excited states with lower spin (SD), the second number the wanted number of excited states with same spin (SS), and the third number the wanted number of excited states with lower spin (SU). For open shell excitations typically the excited states with higher spin than the ground state are higher in energy than those of the excited states with the same spin as the ground state, and excited states with lower spin than the ground state may be lowest.

Self-consistent spin-orbit coupling

```

Relativity
  Level Spin-Orbit
  Formalism ZORA
End
EXCITATIONS
  {ALSORESTRICTED}
END

```

Starting from the ADF2006.01 version in ADF the relativistic TDDFT formalism, including spin-orbit coupling, is implemented for closed-shell molecules with full use of double-group symmetry²⁰. This relativistic time-dependent density-functional theory (TDDFT) is based on the two-component zeroth-order regular approximation (ZORA) and a non-collinear exchange-correlation (XC) functional. This two-component TDDFT formalism has the correct non-relativistic limit and affords the correct threefold degeneracy of triplet excitations. In AMS2025 a bug has been fixed such that one can use symmetry C(2H).

Starting from AMS2023 spin-orbit coupling can be included in the calculation of CD spectra³², see [section on CD spectra](#) (page 205).

In case of a calculation including spin-orbit coupling one can not separate the singlet-singlet and singlet-triplet excitations. By default the spin-polarized excitation energies are calculated (the noncollinear scheme is used for the spin-dependent exchange-correlation kernel). The subkeys `ALSORESTRICTED` can be used to include also excitation energies in which a spin-restricted exchange-correlation kernel is used. One should in fact only use the results of the spin-polarized calculation, which is based on the noncollinear exchange-correlation (XC) functional. For the same reason, the `ALLOWED` subkey should not be used if spin-orbit coupling is included.

To perform a spin-orbit coupled TDDFT calculation one just needs to do a spin-orbit coupled SCF calculation and use the `EXCITATIONS` keyword. The molecule needs to be closed shell, and should be calculated spin-restricted. Thus do not use the `UNRESTRICTED`, `COLLINEAR`, or `NONCOLLINEAR` keyword. See, however, also next section.

The contribution to the double group excited states in terms of singlet and triplet single group excited states can be estimated through the inner product of the transition density matrix obtained from two-component and scalar relativistic

²⁰ F. Wang, T. Ziegler, E. van Lenthe, S.J.A. van Gisbergen and E.J. Baerends, *The calculation of excitation energies based on the relativistic two-component zeroth-order regular approximation and time-dependent density-functional with full use of symmetry*, *Journal of Chemical Physics* 122, 204103 (2005) (<https://doi.org/10.1063/1.1899143>)

³² H.D. Ludowieg, M. Srebro-Hooper, J. Crassous, J. Autschbach, *Optical Activity of Spin-Forbidden Electronic Transitions in Metal Complexes from Time-Dependent Density Functional Theory with Spin-Orbit Coupling*, *ChemistryOpen* 2022, 11, e202200020 (<https://doi.org/10.1002/open.202200020>)

TDDFT calculations to better understand the double group excited states²¹. In order to get this analysis one needs to perform a scalar relativistic TDDFT calculation of excitation energies on the closed shell molecule first, and use the resulting `adf.rkf` as a fragment in the spin-orbit coupled TDDFT calculation of excitation energies, including the keyword `STCONTRIB` (Singlet and Triplet CONTRIButions):

```
STCONTRIB
```

This `STCONTRIB` analysis is not performed for (meta-)hybrids, unless one uses the Tamm-Dancoff approximation (TDA) approximation, but then it may also fail. If one wants a similar analysis for (meta-)hybrids one may consider to the perturbative inclusion of spin-orbit coupling in the calculation of excitation energies.

Note that if hybrids are used, the dependency key is automatically set, and this may effectively reduce the number of excitations, which may give problems in the `STCONTRIB` analysis. A workaround for these problems is to first calculate the scalar relativistic fragment without the `EXCITATIONS` keyword. Use the `adf.rkf` of this calculation as fragment in a scalar relativistic calculation with the `EXCITATIONS` keyword. Use the `adf.rkf` of the second calculation as fragment in the spin-orbit coupled calculation, including the `STCONTRIB` keyword.

Highly approximate spin-orbit coupled excitation energies open shell molecule

Excitation energies can be obtained for open-shell systems in a spin-unrestricted TDDFT calculation including spin-orbit coupling. This approximate method uses a single determinant for the open shell ground state. The Tamm-Dancoff approximation (TDA) is needed and symmetry `NOSYM` should be used. Best is to use the noncollinear approximation. For analysis it is advised to calculate the molecule also with the scalar relativistic spin-restricted method and use it as fragment in the spin-orbit coupled calculation. This will make it easier to identify the excitations.

```
Unrestricted
Symmetry NOSYM
Relativity
  Level Spin-Orbit
  Formalism ZORA
  SpinOrbitMagnetization NONCOLLINEAR
End
TDA
Excitations
End
```

Note that this approximate method for open shell molecules is not able to show the subtle effects of spin-orbit coupling. Some of the reasons are the approximate nature of the XC functionals for open shell molecules, the single determinant that is used for the open shell ground state, and that only single excitations are included in the excitation. If one does not include spin-orbit coupling the spin-unrestricted TDDFT approach introduces spin-contamination such that the result does not represent transitions between pure spin states. Inclusion of spin-orbit coupling will not simplify this. However, if spin-orbit coupling is large, then this method may help to identify excitations.

Note that the approximations made in this approximate method are much worse than for spin-orbit coupled TDDFT for closed shell systems. In that case one can get a reasonable description of the subtle effects of spin-orbit coupling, for example, for the zero-field splitting of a triplet excited state.

²¹ F. Wang and T. Ziegler, *Theoretical study of the electronic spectra of square-planar platinum (II) complexes based on the two-component relativistic time-dependent density-functional theory*, *Journal of Chemical Physics* 123, 194102 (2005) (<https://doi.org/10.1063/1.2104427>)

7.3.6 CV(n)-DFT: Constricted Variational DFT

In the constricted nth order variational density functional method (CV(n)-DFT)^{22,623} the occupied excited state orbitals are allowed to relax in response to the change of both the Coulomb and exchange-correlation potential in going from the ground state to the excited state. This theory is not time-dependent nor is it based on response theory. It is instead variational in nature and has been termed constricted variational DFT or CV(n)-DFT.

Due to bugs in older versions it is important to use ADF2016.105 or later. In ADF2017 the relaxation density is a bit differently calculated than in ADF2016, which will slightly modify the results compared to ADF2016. In ADF2017 singlet-triplet excitations are added²⁴ There have been different working equations implemented in different modified versions of ADF. In ADF2016 and ADF2017 all CV-DFT excitation energies are calculated consistently, this is why some energies may differ from previously published values.

CV(n)-DFT requires an all electron basis set.

The CVNDFT block key regulates the execution of the CV(n)-DFT code, which calculates the singlet or triplet electronic excitations for the closed shell molecules. Note that one has to choose either singlet-singlet excitations (subkey ONLYSING in EXCITATIONS) or singlet-triplet excitations (subkey ONLYTRIP in EXCITATIONS), in case of CV(n)-DFT, one can not calculate them both in one run. The parameter n in (n) describes the order of this theory. There are two limiting cases implemented in the CV(n)-DFT code: $n=2$ and $n=\infty$. Since CV(n)-DFT coincides in the second order with TDDFT, CV(n)-DFT code is designed as an extension of the EXCITATIONS module. Therefore, the EXCITATIONS block has to be present in the input file together with CVNDFT. CVNDFT takes all the information about the number of excitations and their symmetry from the EXCITATIONS block. Moreover, the TDDFT transition density vectors are used as an initial guess for the CV(∞)-DFT calculations.

There are a few approximations within the CV(∞)-DFT approach, therefore there are a few corresponding sub-blocks in the CVNDFT block. In the simplest case the TDDFT transition density U-vector is substituted into the infinite order CV(∞)-DFT excitation energy. This approximation corresponds to the CV_DFT sub-block, so the input fragment would look like this:

```
CVNDFT
  CV_DFT &
  SUBEND
END
EXCITATIONS
  ONLYSING|ONLYTRIP
  ...
END
```

In general, the U-vector has to be optimized with respect to the infinite order CV(∞)-DFT excitation energy. It is accomplished iteratively in the SCF-CV(∞)-DFT method²⁵, which is invoked when the SCF_CV_DFT sub-block is present. Therefore, there are input parameters that control the SCF procedure, i.e. the total number of iterations and tolerance. The corresponding input fragment would look like this:

```
CVNDFT
  ITERATION iter
  TOLERANCE tol
```

(continues on next page)

²² J. Cullen, M. Krykunov, and T. Ziegler, *The formulation of a self-consistent constricted variational density functional theory for the description of excited states*, *Chemical Physics* 391, 11 (2011) (<https://doi.org/10.1016/j.chemphys.2011.05.021>)

⁶ M. Krykunov and T. Ziegler, *Self-consistent Formulation of Constricted Variational Density Functional Theory with Orbital Relaxation. Implementation and Applications*, *Journal of Chemical Theory and Computation* 9, 2761 (2013) (<https://doi.org/10.1021/ct300891k>)

²³ T. Ziegler, M. Krykunov, I. Seidu, Y.C. Park, *Constricted Variational Density Functional Theory Approach to the Description of Excited States*, *Density Functional Methods for Excited States: Topics in Current Chemistry* 368, 61 (2016) (https://doi.org/10.1007/128_2014_611)

²⁴ Y.C. Park, F. Senn, M. Krykunov, and T. Ziegler, *Self-Consistent Constricted Variational Theory RSCF-CV(∞)-DFT and Its Restrictions To Obtain a Numerically Stable Δ SCF-DFT-like Method: Theory and Calculations for Triplet States*, *Journal of Chemical Theory and Computation* 12, 5438 (2016) (<https://doi.org/10.1021/acs.jctc.6b00333>)

²⁵ T. Ziegler, M. Krykunov, J. Cullen, *The implementation of a self-consistent constricted variational density functional theory for the description of excited states*, *Journal of Chemical Physics* 136, 124107 (2012) (<https://doi.org/10.1063/1.3696967>)

(continued from previous page)

```

SCF_CV_DFT &
  DAMPING mix
SUBEND
END
EXCITATIONS
  ONLYSING|ONLYTRIP
  ...
END

```

iter

iter is the maximum number of iterations. Default 50.

tol

tol is the convergence criterion, i.e. the SCF-CV(∞)-DFT procedure stops when the given accuracy is achieved. Default 1e-4.

mix

mix is the relative weight of the new U-vector that is added to the one from the previous iteration (default value is mix=0.2).

Another feature of CV(∞)-DFT is a possibility to optimize (or relax) the molecular orbitals for the particular excitation. This is accomplished in the R-CV(∞)-DFT method, see for an application Ref.²⁶. In the last case, the transition U-vector is frozen, while the orbitals are relaxed. For example, the input fragment which employs the U-vector from TDDFT would look like this:

```

CVNDFT
  ITERATION iter
  TOLERANCE tol
  R_CV_DFT &
    RELAXALPHA start_a_iter
    RELAXBETA  start_b_iter
    DAMPORBRELAX mix_relax
  SUBEND
END
EXCITATIONS
  ONLYSING|ONLYTRIP
  ...
END

```

start_a_iter

start_a_iter is the SCF cycle number at which the relaxation of α orbitals starts. Default value 1.

start_b_iter

start_b_iter is the SCF cycle number at which the relaxation of β orbitals starts. Default value 1.

Since there is no optimization of the U-vector in R-CV(∞)-DFT, the relaxation of orbitals (either α or β or both) should be turned on at the very first iteration.

mix_relax

The mix_relax parameter defines the relative weight of the new relaxation vector that is added to the one from the previous iteration (the default value is mix_relax=0.2).

Note that all tree methods can be used in the input file. The corresponding input fragment would look like this:

²⁶ F. Senn, M. Krykunov, *Excited State Studies of Polyacenes Using the All-Order Constricted Variational Density Functional Theory with Orbital Relaxation*, *Journal of Physical Chemistry A* 119, 10575 (2015) (<https://doi.org/10.1021/acs.jpca.5b07075>)

```

CVNDFT
  ITERATION iter
  TOLERANCE tol
  CV_DFT &
  SUBEND
  SCF_CV_DFT &
    DAMPING mix
  SUBEND
  R_CV_DFT &
    RELAXALPHA start_a_iter
    RELAXBETA  start_b_iter
    DAMPORBRELAX mix_relax
  SUBEND
END
EXCITATIONS
  ONLYSING|ONLYTRIP
  ...
END

```

In this case the U-vector will be optimized with respect to the infinite order CV(∞)-DFT excitation energy by the SCF-CV(∞)-DFT code and then supplied to the R-CV(∞)-DFT code.

CVNDFT prints in the output the excitation energies as well as the maximum value of the lambda parameter λ . This number corresponds to the largest singular value of the singular value decomposition of the U matrix/vector (i.e. the U-vector can be considered as a matrix with *nvir* rows and *nocc* columns, where *nvir* is the number of virtual orbitals and *nocc* is the number of occupied orbitals). If this number is close to $\pi/2$ (i.e. $\lambda_{max} \approx 1.57$), then the corresponding electronic excitation can be approximated by a single natural transition orbital (NTO) to another single NTO transition. This type of transitions are obtained in Δ SCF. Therefore, this information can be used, for example, to compare the CV(∞)-DFT results to the Δ SCF excitation energies.

7.3.7 HDA, TD-DFT+TB, TDDFT-aas, sTDDFT

There are several approximations that can be made to speed up the TD-DFT excitation calculations that will be discussed here: *HDA* (page 200), *TD-DFT+TB*, *TDA-DFT+TB* (page 201), *TDDFT-aas* (page 202), *sTDA* (page 203), and *sTDDFT* (page 203). An alternative to these approximations is *PolTDDFT* (page 222), which is discussed in a different part of the ADF manual.

HDA: Hybrid Diagonal Approximation

This method is only relevant if a (meta-)hybrid is used in the SCF. The hybrid diagonal approximation (HDA)⁵⁸ is based on utilizing the hybrid exchange only for the diagonal terms in the response equations to calculate excitations. This allows one to limit the computational cost of the TD-DFT simulation while keeping basically the same accuracy as in the full TD-DFT scheme using hybrid xc-functionals. It is furthermore not necessary to correct all the diagonal terms with hybrid exchange. A cutoff parameter can be chosen in the input in order to reduce the number of diagonal terms that have to be calculated, which can speed up the HDA calculations.

```

EXCITATIONS
  HDA
  HDA_CutOff hda_cutoff
End

```

⁵⁸ M. Medves, L. Sementa, D. Toffoli, G. Fronzoni, A. Fortunelli, *An efficient hybrid scheme for time dependent density functional theory*, *Journal of Chemical Physics* 152, 184104 (2020) (<https://doi.org/10.1063/5.0005954>)

HDA

Activate the hybrid diagonal approximation (HDA).

hda_cutoff

Cutoff on difference in energy between virtual and occupied orbitals `eps_virt-eps_occ`, in order to reduce the number of diagonal terms that are corrected. Default is a huge value, which means that all diagonal terms are corrected.

This method can not be used in excited state geometry optimizations. For spin-orbit coupled HDA excitations one needs to use symmetry NOSYM:

```
relativity
  level spin-orbit
end
Symmetry NOSYM
EXCITATIONS
  HDA
  HDA_CutOff hda_cutoff
End
```

TD-DFT+TB, TDA-DFT+TB

The basic idea of TD-DFT+TB²⁷ is to use the molecular orbitals from a DFT ground state calculation as input to an excited state calculation with TD-DFTB coupling matrices. TB means tight binding. In ADF2023 TDA-DFT+TB is implemented, which is similar as TD-DFT+TB, but now using TDA. Starting from ADF2023 one can also use TD-DFT+TB and TDA-DFT+TB for open shell molecules. If many excitations are required, this method will speed up the calculation drastically in comparison to the standard time needed for TDDFT calculations of excitation energies. This method is best suited if a (meta-)GGA or LDA is used in the SCF. Since ADF2023 the TD-DFT+TB method can be used in *excited state geometry optimizations* (page 210) in case of closed-shell singlet-singlet and closed shell singlet-triplet excitations, see Ref.¹³.

For TD-DFT+TB use

```
SYMMETRY NOSYM
EXCITATIONS
  TD-DFTB
END
```

For TDA-DFT+TB use

```
SYMMETRY NOSYM
EXCITATIONS
  TDA-DFTB
END
```

One can use this, for example, in combination with the *MODIFYEXCITATION* key (page 190) to use only single-orbital transitions that have a minimal oscillator strength:

```
SYMMETRY NOSYM
EXCITATIONS
  TD-DFTB
  ONLYSING
```

(continues on next page)

²⁷ R. Rüger, E. van Lenthe, T. Heine, L. Visscher, *Tight-Binding Approximations to Time-Dependent Density Functional Theory - a fast approach for the calculation of electronically excited states*, *Journal of Chemical Physics* 144, 184103 (2016) (<https://doi.org/10.1063/1.4948647>)

¹³ S. Havenridge, R. Rüger, C.M. Aikens, *Analytical excited state gradients for time-dependent density functional theory plus tight binding (TDDFT + TB)* *The Journal of Chemical Physics* 158, 224103 (2023) (<https://doi.org/10.1063/5.0142240>)

(continued from previous page)

```
END
MODIFYEXCITATION
  OscStrength 0.001
End
```

In TD-DFT+TB reducing the space of single-orbital transitions with the key MODIFYEXCITATION will reduce the memory needed in ADF. Starting from ADF2016.102 for TD-DFT+TB only the lowest (in energy) 100000 single orbital transitions are included by default. One can override this by using a different value for the subkey UseOccVirtNumbers of the key MODIFYEXCITATION.

```
MODIFYEXCITATION
  UseOccVirtNumbers 1 100000
END
```

The value for the subkeyword KFWRITE in the EXCITATIONS block key is set by default to 0 in case of TD-DFT+TB. If kfwrite is 0 then do not write contributions, transition densities, and restart vectors to adf.rkf, since this can lead to a huge adf.rkf, especially if many excitations are calculated.

TDDFT-aas

TDDFT-aas¹⁴ (TDDFT-approximate auxiliary s function) resembles the TDDFT-as method and the TDDFT+TB method: when solving the K coupling integrals in the excited state, an approximation is made instead of calculating the exact two-electron integrals. TDDFT-aas utilizes the γ_{AB} function from the TDDFT-as method to calculate the coupling matrix K:

$$K_{ia,jb} = \sum_{AB} q_{ia,A} \gamma_{AB} q_{jb,B}$$

$$\gamma(R_{AB}) = \frac{\text{erf}\left(R_{AB} \sqrt{\alpha/2}\right)}{R_{AB}}$$

In ADF TDDFT-aas can be calculated for singlet excited states only, symmetry NOSYM is required. This method is best suited if a (meta-)GGA or LDA is used in the SCF. The TDDFT-aas method can be used in *excited state geometry optimizations* (page 210) in case of closed-shell singlet-singlet excitations, see Ref. ^{Page 202, 14}.

For TDDFT-aas use

```
SYMMETRY NOSYM
EXCITATIONS
  ONLYSING
  AAS
  {AASALPHA aasalpha}
END
```

aasalpha

alpha value for the TDDFT-aas method. Default alpha=0.2.

¹⁴ Y. Wang, S. Havenridge, C.M. Aikens, *Implementation of energy and gradient for the TDDFT-approximate auxiliary function (aas) method*, *Journal of Chemical Physics* 161, 024101 (2024) (<https://doi.org/10.1063/5.0213587>)

sTDA, sTDDFT

The simplified Tamm-Dancoff approach (sTDA)²⁸ and simplified time-dependent DFT approach (sTDDFT)²⁹ by Grimme et al. are implemented in ADF. In these approaches the time-dependent DFT equations are simplified by the evaluation of the two-electron integrals as short-range damped Coulomb interactions between (transition) charge density monopoles and a truncation of the single excitation expansion space. These methods are best suited if a (meta-)hybrid or a range-separated-hybrid is used in the SCF. These methods will speed up the calculation drastically in comparison to the standard time needed for TDA or TDDFT calculations of excitation energies for hybrids. Starting from ADF2023 one can use sTDA and sTDDFT for open shell molecules. These methods can not be used in excited state geometry optimizations.

An example application of sTDDFT is given in the [TDDFT advanced tutorial](#)

For sTDA use:

```
SYMMETRY NOSYM
EXCITATIONS
  sTDA
END
```

For sTDDFT use:

```
SYMMETRY NOSYM
EXCITATIONS
  sTDDFT
END
```

For global hybrids ADF will use the parameters α and β that depend on the amount of exact exchange a_x as:

$$\alpha = \alpha_1 + \alpha_2 a_x$$

$$\beta = \beta_1 + \beta_2 a_x$$

where $\alpha_1 = 1.42$, $\alpha_2 = 0.48$, $\beta_1 = 0.2$, $\beta_2 = 1.83$ are used in ADF. These values are fitted parameters by Grimme^{Page 203, 28}. For range-separated hybrids one should set the parameters α , β and a_x in the input of ADF with the keyword MODIFYEXCITATION. See Ref.³¹ for parameters that are used by Risthaus et al. for a few range-separated functionals. However the α and β parameters are mixed up in Ref.³¹. Thus use:

Functional	a_x	α	β
CAM-B3LYP	0.38	0.90	1.86
WB97	0.61	4.41	8.00
WB97X	0.56	4.58	8.00

For example, for CAM-B3LYP use

```
MODIFYEXCITATION
  GrimmeAlpha 0.9
  GrimmeBeta 1.86
  GrimmeAex 0.38
END
```

²⁸ S. Grimme, *A simplified Tamm-Dancoff density functional approach for the electronic excitation spectra of very large molecules*, *Journal of Chemical Physics* **138**, 244104 (2013) (<https://doi.org/10.1063/1.4811331>)

²⁹ C. Bannwarth and S. Grimme, *A simplified time-dependent density functional theory approach for electronic ultraviolet and circular dichroism spectra of very large molecules*, *Computational and Theoretical Chemistry* **1040-1041**, 45 (2014) (<https://doi.org/10.1016/j.comptc.2014.02.023>)

³¹ T. Risthaus, A. Hansen, and S. Grimme, *Excited states using the simplified Tamm-Dancoff-Approach for range-separated hybrid density functionals: development and application*, *Physical Chemistry Chemical Physics* **16**, 14408 (2014) (<https://doi.org/10.1039/C3CP54517B>)

If one uses the keyword MODIFYEXCITATION one may also set more parameters that are used in the sTDA and sTDDFT approach.

```
MODIFYEXCITATION
  GrimmeAlpha Alpha
  GrimmeBeta Beta
  GrimmeAex Aex
  GrimmeDEmax DEmax
  GrimmeTPmin TPmin
  GrimmePertC|NoGrimmePertC
END
```

GrimmeAlpha Alpha

To set the α parameters, should be used with GrimmeBeta and GrimmeAex.

GrimmeBeta Beta

To set the β parameters, should be used with GrimmeAlpha and GrimmeAex.

GrimmeAex Aex

To set a_x that is used in the sTDA or sTDDFT part of the calculation, should be used with GrimmeAlpha and GrimmeBeta.

GrimmeDEmax DEmax

Single orbital transitions that have an orbital energy difference less than DEmax (in Hartree) are included. Default value DEmax = 0.4 Hartree. See also the meaning of E_{max} in Grimme²⁸.

GrimmeTPmin TPmin

Single orbital transitions that would have a cumulative perturbative energy contribution larger than TPmin is included. Default value TPmin = 10^{-4} . See also the meaning of t_p in Grimme^{Page 203, 28}.

GrimmePertC|NoGrimmePertC

In case of GrimmePertC, which is the default, if the cumulative perturbative energy contribution for a single orbital transition is smaller TPmin, this contribution is used to modify the diagonal value of a matrix that is used in the sTDA or the sTDDFT method. If NoGrimmePertC is included such contributions are neglected. See Grimme^{Page 203, 28} for more details on the truncation of the single excitation space.

Starting from ADF2016.102 for sTDA or sTDDFT only the lowest (in energy) 10000 single orbital transitions are included by default. One can override this by using a different value for the subkey UseOccVirtNumbers of the key MODIFYEXCITATION.

```
MODIFYEXCITATION
  UseOccVirtNumbers 1 10000
END
```

The value for the subkeyword KFWRITE in the EXCITATIONS block key is set by default to 0 in case of sTDA or sTDDFT. If kfwrite is 0 then do not write contributions, transition densities, and restart vectors to adf.rkf, since this can lead to a huge adf.rkf, especially if many excitations are calculated.

7.3.8 CD spectra

Circular dichroism (CD) is the differential absorption of left- and right-handed circularly polarized light. Starting from ADF2010 Hartree-Fock and hybrids can also be used to calculate CD spectra.

Starting from AMS2023 spin-orbit coupling can be included in the calculation of CD spectra, see Ref.^{Page 196, 32}, which allows one, for example, to calculate circularly polarized luminescence (CPL) for spin-forbidden transitions such as T1-S0 emission, and spin-forbidden electronic circular dichroism. These are spin-forbidden if one would not include spin-orbit coupling. Phosphorescence dissymmetry factors are calculated.

```
EXCITATIONS
CDSPECTRUM
ANALYTICAL
VELOCITY
End
```

CDSPECTRUM

If the subkey *CDSPECTRUM* is included in the key *EXCITATIONS* the rotatory strengths for the calculated excitations are calculated, in order to simulate Circular Dichroism (CD) spectra³⁶³⁷. Interesting for chiral molecules.

Velocity

If the subkey *VELOCITY* is included ADF calculates the dipole-velocity representation of the oscillator strength. If applicable (use of subkey *CDSPECTRUM*) the dipole-velocity representation of the rotatory strength is calculated. Default the dipole-length representation of the oscillator strength and rotatory strength is calculated. Remark: in case of (range separated) (meta-) hybrids and TDA the dipole-length and velocity representation of the oscillator strength are not the same (not even in the basis set limit), see Ref.³³.

7.3.9 MCD

MCD or magnetic circular dichroism is the differential absorption of left and right circularly polarized light in the presence of a magnetic field. MCD intensity is usually described in terms of different contributions called A, B and C terms, see Refs.³⁸³⁹. A further parameter D is often discussed in MCD studies. D is proportional to the intensity of an absorption band and is closely related to the oscillator strength. A and B terms for closed and open-shell molecules and C terms of open-shell molecules induced by spin-orbit coupling can be calculated. Starting from ADF2010 C terms related to spatially degenerate states, i.e. breaking of degeneracies can be calculated. The A term is only calculated in case the molecule has symmetry and then only for excited states that belong to multi-dimensional irreps.

For MCD calculations for molecules that have C(2) or D(2) symmetry use *SYMMETRY NOSYM*.

Input options

```
EXCITATIONS
MCD {options}
ONLYSINGLET
{SELECT transition number}
{DTENSOR {Dxx Dxy Dyy Dxz Dyx|D E/D}}
End
```

(continues on next page)

³⁶ J. Autschbach and T. Ziegler, *Calculating molecular electric and magnetic properties from time-dependent density functional response theory*, *Journal of Chemical Physics* 116, 891 (2002) (<https://doi.org/10.1063/1.1420401>)

³⁷ J. Autschbach, T. Ziegler, S.J.A. van Gisbergen and E.J. Baerends, *Chiroptical properties from time-dependent density functional theory. I. Circular dichroism spectra of organic molecules*, *Journal of Chemical Physics* 116, 6930 (2002) (<https://doi.org/10.1063/1.1436466>)

³³ R.A. Harris, *Oscillator Strengths and Rotational Strengths in Hartree-Fock Theory*, *Journal of Chemical Physics* 50, 3947 (1969) (<https://doi.org/10.1063/1.1671653>)

³⁸ S.B. Piepho and P. N. Schatz, *Group Theory in Spectroscopy With Application to Magnetic Circular Dichroism*, (Wiley, New York, 1983).

³⁹ W.R. Mason, *A Practical Guide to Magnetic Circular Dichroism Spectroscopy*, (Wiley, New Jersey, 2007).

(continued from previous page)

```

ALLPOINTS
{Relativity
  Level Scalar
  Formalism ZORA
End}
{SOMCD}
{ZFS}

```

MCD

If the subkey MCD is included in the key EXCITATIONS the MCD parameters of some or all of the excitations considered in the TDDFT procedure are calculated⁵¹⁵²⁵³⁴¹. This subkey should not be used with spin-orbit coupling (but, see below). Several other keywords could be important.

ALLPOINTS: required for an MCD calculation.

ONLYSINGLET: this keyword should be used in combination with a MCD calculation.

RELATIVITY: Scalar Relativistic ZORA: required for a calculation of temperature-dependent C terms. In this case the keyword SOMCD must also be added as a key by itself, and the calculation must be unrestricted. If only A and B terms are calculated then ZORA is not needed but can be included if desired.

ZFS: If the ZFS keyword and MCD with SOMCD are also included then the influence of the calculated zero-field splitting (ZFS) on the temperature-dependent MCD is evaluated. The MCD in the presence of ZFS is described as anisotropic in the output because the Zeeman splitting becomes orientation dependent in the presence of ZFS.

In ADF2010 the temperature-dependent MCD due to the breaking of degeneracies of excited states by spin-orbit coupling can be calculated. Although all temperature-dependent MCD is typically called “C terms”, the parameters associated with the MCD are labeled “CE” to distinguish them from the MCD due to mixing between states caused by spin-orbit coupling that is labeled “C”. The CE terms have a derivative shape like A terms. They have the same temperature-dependence as normal C terms. If they are present, CE terms are calculated automatically along with C terms if the keyword SOMCD is included in the input.

MCD {options}

Options include NMCDTERM, NMIX, DCUTOFF, MCDOUT, CGOUT, NANAL, NANAL2, FULLOMEGA, NOAB, NODIRECT, NOCG, CONVCG, ITERCG, ITER2CG, BMIN, BMAX, TMIN, TMAX and NTEMP.

NMCDTERM=nmcdterm

Number of excitations for which MCD parameters are to be calculated. The nmcdterm lowest energy excitations are treated. The default is the number of transitions considered in the TDDFT calculation.

NMIX=nmix

Number of transitions allowed to mix in a SOS calculation. Default is the number of transitions considered in the TDDFT calculation.

DCUTOFF=dcutoff

MCD parameters will only be calculated for transitions with sufficient intensity. Each Cartesian component of each transition is considered separately. If the dipole strength D of that component is below dcutoff then the MCD is not calculated. The default is 1.0e-6.

⁵¹ M. Seth and T. Ziegler, *Formulation of magnetically perturbed time-dependent density functional theory*, *Journal of Chemical Physics* 127, 134108 (2007) (<https://doi.org/10.1063/1.2772849>)

⁵² M. Seth, M. Krykunov, T. Ziegler, J. Autschbach and A. Banerjee, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism: Calculation of B terms*, *Journal of Chemical Physics* 128, 144105 (2008) (<https://doi.org/10.1063/1.2901967>)

⁵³ M. Seth, M. Krykunov, T. Ziegler and J. Autschbach, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism. II. Calculation of A terms*, *Journal of Chemical Physics* 128, 234102 (2008) (<https://doi.org/10.1063/1.2933550>)

⁴¹ M. Seth, T. Ziegler and J. Autschbach, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism. III. Temperature-dependent magnetic circular dichroism induced by spin-orbit coupling*, *Journal of Chemical Physics* 129, 104105 (2008) (<https://doi.org/10.1063/1.2976568>)

MCDOUT=mcdout

Number that determines the amount of output to be printed about the MCD calculation. Higher means more output. Possible values are 0, (orientationally averaged and Cartesian components of MCD parameters only) 1 (as for 0 but with the addition of a short analysis) or 2 (as for 1 but with the addition of a lengthy analysis). Theoretical analyses of MCD parameters are presented in several places including Refs. ³⁸Page 205, ³⁹Page 206, ⁵²Page 206, ⁵³Page 206, ⁴¹. The default for MCDOUT is 0.

CGOUT=cgout

The perturbed transition densities used to evaluate the B and C term parameters can be obtained through an iterative conjugate-gradient procedure. Convergence information of the conjugate-gradient algorithm is printed every cgout iterations. Default is 10.

NANAL=nanal, NANAL2=nanal2

If MCDOUT is set to 2, a detailed analysis of the B and/or C term parameters in terms of which states mix and how much MCD each mixing causes, is presented. The parameters NANAL and NANAL2 determine how many contributions are included in the analyses. Defaults are 10 for NANAL and 5 for NANAL2.

FULLOMEGA

A standard TDDFT calculation involves the solution of an eigenvalue equation to obtain the excitation energies and transition densities of interest. ADF can solve this eigenvalue equation two ways: through diagonalization of the full Omega matrix or through the Davidson procedure where Omega is never explicitly constructed. Construction of the complete Omega matrix is generally only feasible for smaller problems. The matrix Omega appears again in the equations solved to obtain MCD. Here again Omega can be built or only the products of Omega with a vector can be used as is the case in the Davidson procedure. The default is to not construct Omega. If the keyword FULLOMEGA is included then Omega is constructed. Note that the choice of FULLOMEGA is completely independent of whether EXACT or DAVIDSON is chosen in the earlier TDDFT calculation.

NOAB

If this keyword is included then A and B terms are not calculated. NOAB only makes sense if SOMCD is included in the input otherwise no MCD will be calculated at all.

NODIRECT

The perturbed transition density needed to evaluate B and C term parameters is obtained through the solution of a large system of equations. This system of equations is solved in two ways: through a sum-over-states (SOS) type approach where the solution is expanded in a known set of transition densities or through the direct solution of the system of equations by the conjugate gradient procedure. The SOS method is much faster but also less accurate, particularly for larger systems. By default MCD parameters are evaluated through both approaches. If the NODIRECT keyword is included then only the SOS calculation is performed.

NOCG

The conjugate gradient procedure is first used in combination with a preconditioner that generally speeds up convergence significantly. If no solution is found in a reasonable number of iterations then the procedure is restarted without the preconditioner. If the NOCG keyword is included then the preconditioner is never used.

CONVCG

Convergence criterion for the CG iterative methods. The default value of 0.01 is probably good enough for most applications. This choice seems to produce B and C terms that are converged to 3 significant figures. Except for small systems, it is not recommended that CONVCG be set to a much smaller number as this will probably cause a large number of convergence failures.

ITERCG=itercg

Number of iterations before failure in the first (preconditioned) CG solver. This solver either succeeds quickly or not at all so the default value is 30.

ITER2CG=iterc2g

Number of iterations before failure in the B or C term parameter calculation of the unconditioned CG solver.

This solver is often slow so the default value is 200.

BMIN=bmin, BMAX=bmax, NBFIELD=nbfield, TMIN=tmin, TMAX=tmax, NTEMP=ntemp

Temperature dependent MCD intensity often varies nonlinearly with T and B when T is small and/or B is large. It may therefore be of interest to evaluate the MCD intensity over a range of temperatures and/or magnetic fields. This can be achieved through the use of the BMIN, BMAX, NBFIELD, TMIN, TMAX and NTEMP keywords. The MIN and MAX keywords give the maximum values of B or T. NBFIELD and NTEMP indicate how many values are to be considered. Note that magnetic fields are assumed to be given in Tesla and temperatures in Kelvin. For example, BMIN=1, BMAX=5, NBFIELD=5 means that fields of 1,2,3,4 and 5 T will be considered. Defaults are BMIN=BMAX=1, TMIN=TMAX=5 and NBFIELD=NTEMP=1.

SELECT nselect1 nselect2 nselect3...

Rather than selecting the first nmcdterm transitions for consideration individual transitions can be selected through the SELECT keyword. The transitions of interest are listed after the SELECT keyword. Note that the numbering follows that given in the summary table at the end of the TDDFT calculation. To consider a degenerate transition only the first component need be included. Note that it makes no sense to use both the SELECT and NMCDTERM keywords together.

DTENSOR Dxx Dxy Dyy Dxz Dyx DTENSOR D E/D

As noted earlier, if the ZFS keyword is included with MCD and SOMCD then the influence of zero-field splitting on temperature-dependent MCD will be evaluated. As an alternative to the ZFS keyword the D-tensor parameters can be entered directly through the DTENSOR keyword in the EXCITATIONS block. Two input formats are possible. Five real numbers Dxx Dxy Dyy Dxz Dyx can be entered. These five numbers are sufficient to define the traceless tensor D. Alternatively, the two parameters D and E/D can be entered. In this case the coordinate system chosen to define the molecular geometry must be the principle axis system of the D-tensor. D, Dxx, Dxy, Dyy, Dxz and Dyx should be given in wavenumbers (cm⁻¹).

Notes

If an MCD calculation is run, the transition densities obtained in the TDDFT calculation are saved to adf.rkf. For large molecules this can result in a very large adf.rkf file.

An MCD calculation relies on the excitation energies and, in particular, the transition densities that result from the preceding TDDFT calculation. If the results of the TDDFT calculation are poor then it is likely that the results of the MCD calculation will be poor. It therefore should be kept in mind that most TDDFT calculations will make use of the Davidson method for finding the eigenvalues and eigenvectors of the TDDFT equation. The Davidson approach involves some approximations that can lead to some variation in results with the applied parameters. The most important example of this is the fact that the results vary depending on how many eigenvalue/eigenvector pairs are calculated, ie how many transitions are selected through the LOWEST keyword. The variation is small for the eigenvalues (excitation energies) but can be significant for the eigenvectors (transition densities). A variation in the transition densities leads to variation in the transition dipoles which can significantly impact calculated MCD parameters. The moral of this story is that when calculating MCD parameters it is best to choose one value of LOWEST and stick with it.

The most time-consuming part of an MCD calculation is the solution of the system of equations through the conjugate-gradient solver. The solver can fail so be aware of warnings concerning convergence in the output. A few hints to improve convergence are: a) choose a value of LOWEST that is at least double the number of transitions for which you desire MCD parameters. This helps to improve the SOS calculation which provides an initial guess for the conjugate gradient solver. The solver is sensitive to the initial guess so changing LOWEST by a small amount may help (or hinder) convergence significantly. Keep the previous note in mind when playing with LOWEST however. b) The preconditioned conjugate gradient solver is usually fast but does not converge monotonically to the correct answer. The unpreconditioned solver is much slower but tends to converge monotonically. If the preconditioned solver fails but leaves a fairly well converged result for the unpreconditioned solver the latter usually converges quickly. If the preconditioned solver does not leave a fairly well converged result it may be worth changing the number of iterations it uses since a few iterations earlier or later may provide a much better converged answer. c) The SELECT keyword can be used to work on the remaining transitions for which converged results have not been obtained.

All MCD parameters are presented in au. To convert A and C terms to the alternative unit D² (Debye squared) the value in au should be multiplied by 6.46044. To convert the B term to the alternative unit of D²/cm⁻¹ the value in au should

be multiplied by 2.94359e-05.

The A, B and C terms are defined through the equation suggested by Stephens (equation 1 in^{Page 206, 41} and also see refs.^{Page 205, 38}^{Page 205, 39}⁴⁰). This equation assumes that MCD intensity varies linearly with applied magnetic field and that the temperature-dependent component varies linearly with temperature as 1/T. For the most part, these assumptions are reasonable. An exception is that the temperature-dependent part varies from linearity when T is very small. To allow for this situation a temperature and magnetic field dependent multiplicative constant ($\chi(B,T)$) is evaluated whenever temperature-dependent MCD parameters are considered. This constant includes all magnetic field and temperature dependence of the temperature-dependent MCD. Thus $\chi(B,T)*C$ can be used in place of $B*C/kT$ in equation 1 of^{Page 206, 41} when MCD spectra are to be simulated. Note that, since the g-factor for all states is here approximated by 2.0, χ applies to all transitions.

7.3.10 Analysis

By default the ADF output will show the excitation energies, oscillator strengths from ground state to excited state, and transition dipole moments from ground state to excited state. Also an analysis in terms of single orbital transitions (occupied to virtual) is given, and their contributions to the transition dipole moment. For analysis reasons one might be interested in pure single orbital transition. Such information can be obtained in case one calculates excitation energies as Kohn-Sham orbital energy differences, see subkey *SINGLEORBTTRANS* (page 192) of the key EXCITATIONS.

NTO: Natural Transition Orbitals

Natural Transition Orbitals⁴² come from a transformation of the transition density matrix. They are the closest you can get to visualizing an excitation as a one-electron excitation from 1 orbital to another. They give insight in the localization of excitations. Calculation of Natural Transition Orbitals (NTO's) will be performed if the subkey NTO is included in the key EXCITATIONS.

```
EXCITATIONS
...
  NTO
End
```

For (meta-)hybrids and range-separated functionals NTO's will be calculated only if one uses the Tamm-Dancoff approximation (TDA).

NTOs can be visualized in AMSSpectra as shown in the [GUI tutorial](#).

SFO analysis

In ADF2018 an SFO analysis of the excitation is implemented. This includes an analysis of the transition dipole moment. Especially useful in a fragment calculation, where one only has a few fragments. Not implemented for spin-orbit coupled excitations.

```
EXCITATIONS
...
  SFOANALYSIS
  N_SFO NMAXPRINTED
End
```

SFOANALYSIS

If SFOANALYSIS is included a the SFO analysis of the excitation will be calculated.

⁴⁰ A. Bérces and T. Ziegler, *The harmonic force field of benzene. A local density functional study*, *Journal of Chemical Physics* 98, 4793 (1993) (<https://doi.org/10.1063/1.464983>)

⁴² R.L. Martin, *Natural transition orbitals*, *Journal of Chemical Physics* 118, 4775 (2003) (<https://doi.org/10.1063/1.1558471>)

N_SFO NMAXPRINTED

NMAXPRINTED is the maximum number of printed contributions. Default value for NMAXPRINTED is 40.

The SFO - SFO dipole matrix elements can be printed in the output with:

```
PRINT DIPOLEMAT
```

Charge-transfer descriptors

Two methods for calculating charge-transfer descriptors are implemented (also working for spin-orbit coupled excitations).

The first method is the charge-transfer diagnostic overlap quantity LAMBDA, developed by Peach, Tozer, et al.⁴³ and a hole-electron distance R_HE, see Guido, Adamo, et al.⁴⁴.

The second method is the charge transfer descriptor CT, hole-electron distance R_HE, and some other descriptors, developed by Plasser, Lischka, et al.^{54,55,56,57}. For this method a fragment calculation is required. Using a similar method a charge transfer descriptor CT_AT was defined that uses an atomic distance criterion, which will also be calculated in case of atomic fragments.

```
EXCITATIONS
...
DESCRIPTORS
{Descriptors_CT_AT_Rab Rab}
END
```

DESCRIPTORS

If DESCRIPTORS is included the charge transfer descriptors are calculated.

Descriptors_CT_AT_Rab Rab

Rab is the atomic distance criterion used for the calculation of CT_AT (in Angstrom). Default value for Rab is 2 Angstrom.

ROSE or FOCDFT localized orbitals

The localized orbitals that *ROSE* (page 300) calculates or *FOCDFT* (page 78) calculates can be used in time-dependent DFT calculations using ADF, see section on *exciton transfer integrals with ROSE* (page 278) or *FOCDFT* (page 278). These methods are especially useful if one wants to analyze the local excitation (LE) or charge transfer (CT) character of an excitation, and allows one to study diabatic states that are pure local excitations or pure charge transfer excitations and calculate possible electronic couplings between them.

⁴³ M.J.G. Peach, P. Benfield, T. Helgaker, and D.J. Tozer, *Excitation energies in density functional theory: An evaluation and a diagnostic test*, *Journal of Chemical Physics* 128, 044118 (2008) (<https://doi.org/10.1063/1.2831900>)

⁴⁴ C.A. Guido, P. Cortona, B. Mennucci, and C. Adamo, *On the Metric of Charge Transfer Molecular Excitations: A Simple Chemical Descriptor*, *Journal of Chemical Theory and Computation* 9, 3118 (2013) (<https://doi.org/10.1021/ct400337e>)

⁵⁴ F. Plasser, and H. Lischka, *Analysis of Excitonic and Charge Transfer Interactions from Quantum Chemical Calculations*, *Journal of Chemical Theory and Computation* 8, 2777 (2012) (<https://doi.org/10.1021/ct300307c>)

⁵⁵ F. Plasser, M. Wormit, and A. Dreuw, *New tools for the systematic analysis and visualization of electronic excitations. I. Formalism*, *Journal of Chemical Physics* 141, 024106 (2008) (<https://doi.org/10.1063/1.4885819>)

⁵⁶ F. Plasser, S.A. B  ppler, Wormit, and A. Dreuw, *New tools for the systematic analysis and visualization of electronic excitations. II. Applications*, *Journal of Chemical Physics* 141, 024107 (2008) (<https://doi.org/10.1063/1.4885820>)

⁵⁷ S.A. Mewes, J.-M. Mewes, A. Dreuw, and F. Plasser, *Excitons in poly(para phenylene vinylene): a quantum-chemical perspective based on high-level ab initio calculations*, *Physical Chemistry Chemical Physics* 18, 2548 (2016) (<https://doi.org/10.1039/c5cp07077e>).

7.4 Excited state (geometry) optimizations

See also:

- Tutorial [UV/Vis spectrum of ethene](#)

It is possible to do excited state geometry optimizations, see Ref.¹. Gradients for closed-shell singlet-singlet, closed-shell singlet-triplet, conventional open-shell and spin-flip open-shell TDDFT calculations can be evaluated.

Excited state gradients can also be calculated for the approximate [TD-DFT+TB](#) (page 201) method. In ADF2023 closed-shell singlet-singlet and closed-shell singlet-triplet TD-DFT+TB excited state gradients were implemented, see Ref.². In ADF2026 open-shell and spin-flip open-shell TD-DFT+TB excited state gradients were implemented, see Ref.³. TD-DFT+TB should only be used for LDA and (meta-)GGAs. In ADF2025 the [TDDFT-aas](#) (page 202) method can be used in excited state geometry optimizations in case of closed-shell singlet-singlet excitations, see Ref.⁴.

With the keyword `EXCITEDGO` the gradients of the TDDFT excitation energy can be calculated. The [EXCITATIONS](#) (page 179) block must also be included in the input. The excitation energy gradients will only be calculated if the ground state gradients are calculated.

The gradients of the excitation energy are combined with the ground state gradients to give the gradients of the excited state. These gradients can be used in much the same way as ground state gradients are used. The type of calculation is chosen in the same way as for a ground state calculation. Examples of possible run types are:

- Geometry optimization
- Transition state search
- Frequency analysis with numerical second derivatives: (analytical second derivatives are not possible).

In general, an option that applies to a ground state geometry optimization will also apply to an excited state geometry optimization. A TDDFT geometry optimization will proceed in very much the same way as a ground state geometry optimization. The major difference will be that a TDDFT calculation will take place after the SCF and before the ground state gradients are evaluated. TDDFT gradients are calculated after the ground state gradients.

Gradients for closed-shell singlet-singlet, closed shell singlet-triplet, conventional open shell and spin-flip open-shell TDDFT calculations can be evaluated. The `FORCEALDA` option and `TDA` options should be used with spin-flip calculations.

Not all functionals can be used in combination with TDDFT gradients. The following should work:

LDA: `VWN`, `XALPHA`

GGA: Any allowed combination of the `Perdew86`, `LYP` and `PBEc` correlation functionals and the `Becke88`, `revPBE`, `RPBE`, `PBE` and `OPTx` exchange functionals.

Hybrid: `B1LYP`, `B3LYP`, `B3LYP*`, `BHANDHLYP`, `BHANDH`, `O3LYP`, `X3LYP`, `B1PW91`, `MPW1PW`, `PBE0`, `OPBE0`.

Most LibXC GGA and hybrid functionals.

RS Hybrid with `XCFUN`: `CAMY-B3LYP` and more (starting from ADF2018).

QM/MM TDDFT gradients can be calculated.

COSMO TDDFT gradients can be calculated (starting from ADF2018).

Scalar relativistic effects can be included with the `ZORA` or mass-velocity-Darwin Hamiltonians.

¹ M. Seth, G. Mazur, and T. Ziegler, *Time-dependent density functional theory gradients in the Amsterdam density functional package: geometry optimizations of spin-flip excitations*, *Theoretical Chemistry Accounts* 129, 331 (2011) (<https://doi.org/10.1007/s00214-010-0819-2>)

² S. Havenridge, R. Rüger, C.M. Aikens, *Analytical excited state gradients for time-dependent density functional theory plus tight binding (TDDFT + TB)* *The Journal of Chemical Physics* 158, 224103 (2023) (<https://doi.org/10.1063/5.0142240>).

³ D.S.N.D. Samarasinghe and C.M. Aikens, manuscript in preparation

⁴ Y. Wang, S. Havenridge, C.M. Aikens, *Implementation of energy and gradient for the TDDFT-approximate auxiliary function (aas) method*, *Journal of Chemical Physics* 161, 024101 (2024) (<https://doi.org/10.1063/5.0213587>)

At this time, gradients involving frozen cores and spin-orbit TDDFT cannot be calculated.

TDDFT gradients can take advantage of symmetry but if the point group of interest includes degenerate irreducible representations then all grid points are needed in integration (equivalent to the ALLPOINTS keyword). This situation is detected automatically. This use of the full grid may make it more efficient to use a point group with only one-dimensional irreducible representations where only the symmetry-unique slice is utilized. For TD-DFT+TB gradients symmetry NOSYM is required.

Degenerate excitations can be optimized. However, since in reality such degeneracies will be split by a Jahn-Teller distortion it is recommended that the symmetry of the chosen point group be lowered so that the transition of interest is no longer labeled by a degenerate representation. A Jahn-Teller distortion will not occur when the degeneracy cannot be broken by nuclear motion, e.g. for a diatomic molecule.

The EXCITEDGO block key has the following form:

```
EXCITEDGO
{STATE Irreplab nstate}
{SINGLET/TRIPLET}
{OUTPUT n}
{CPKS EPS=err PRECONITER=precon NOPRECONITER=noprecon ITEROUT=iter}
{EIGENFOLLOW}
END
```

STATE Irreplab nstate

Choose the excitation for which the gradient is to be evaluated.

Irreplab

Irreplab is the label from the TDDFT calculation. NOTE: the TDDFT module uses a different notation for some representation names, for example, A' is used instead of AA, A'' (A two apostrophes) instead of AAA, A1' instead of AA1, A2'' instead of AAA2. The excitations output gives the irrep levels that one should use here.

nstate

This value indicates that the nstate-th transition of symmetry Irreplab is to be evaluated. Default is the first fully symmetric transition.

Note that in a numerical FREQUENCIES calculation symmetry is turned off except to reduce the number of points calculated so irrespective of the specified point group Irreplab is A in this case. Care should be taken to ensure that nstate is correct in a frequencies calculation as this number can change when the point group is changed.

SINGLET/TRIPLET

SINGLET: A singlet-singlet excitation is considered. The default. TRIPLET: A singlet-triplet excitation is considered.

OUTPUT n

The amount of output printed. A higher value requests more detailed output. Default: n=0

CPKS EPS=err PRECONITER=precon NOPRECONITER=noprecon ITEROUT=iter

Some control parameters for the CPKS(Z-vector) part of the TDDFT gradients calculation.

EPS=err

err is a real number that gives the convergence requirement of the CPKS. Default is 0.0001

PRECONITER=precon

precon is the maximum number of iterations allowed for the preconditioned solver. Default = 30.

NOPRECONITER=noprecon

noprecon is the maximum number of iterations allowed for the unpreconditioned solver. Default=200.

ITEROUT=iter

Details of the CPKS calculation are printed every iter iterations. Default is 5.

EIGENFOLLOW This key tries to follow the eigenvector in excited state geometry optimizations. In the initial implementation the target state of an excited state geometry optimization was indicated by a number and a symmetry, e.g. A2g 3 or the 3rd state of A2g symmetry. This approach becomes problematic when states cross and the state you are interested in become the 4th A2g state for example. An eigenvector-following option has been added that attempts to alleviate this problem. This option is off by default. If the subkeyword EIGENFOLLOW is included, the state of interest in the first iteration is the same as before. In the second and subsequent iterations the state for which gradients are determined is decided on the basis of the overlap between the transition density of the transition from the previous iteration and the transition densities available in the current iteration. The same symmetry is maintained. Note that this method is not foolproof. It assumes that the transition density changes only because the contributions from the various occupied-virtual orbital pairs change but that the orbitals remain unchanged. This is not necessarily the case. Secondly, the sign of the transition density components is not taken into account.

At each iteration of a TDDFT-gradients calculation the (relaxed) excited state electric dipole moment is also calculated.

7.4.1 Nuclear gradients only

In some cases one only needs the nuclear gradients of one or more excited state in a single-point calculation. This can be calculated by requesting the gradients in the AMS driver part of the input with the EXCITEDGO keyword.

```
Task SinglePoint

Properties
  Gradients Yes
End

...
...

Engine ADF
  ...
  ...

  EXCITEDGO
    AllGradients
    SING_GRADS
      {IRREP1 integer_list}
      {IRREP2 integer_list}
    End
    TRIP_GRADS
      {IRREP3 integer_list}
      {IRREP4 integer_list}
    End
  End
EndEngine
```

AllGradients

calculate the nuclear gradient for all excitations that are calculated.

SING_GRADS

Calculate the nuclear gradient for the singlet-singlet excitations that are specified. The excitation numbers per irrep should be specified.

TRIP_GRADS

Calculate the nuclear gradient for the singlet-triplet excitations that are specified. The excitation numbers per irrep should be specified.

7.5 Vibrationally resolved electronic spectra

See the [Vibrationally resolved electronic spectra](#) section of the AMS manual.

7.5.1 AH-FC: Adiabatic Hessian Franck-Condon

See the [AH-FC](#) section of the AMS manual.

7.5.2 VG-FC: Vertical Gradient Franck-Condon

See the [VG-FC](#) section of the AMS manual.

7.6 (Hyper-)Polarizabilities, ORD, magnetizabilities, Verdet constants

A (frequency-dependent) electric field induces a dipole moment in a molecule, which is proportional to the (frequency-dependent) molecular polarizability. Van der Waals dispersion coefficients describe the long-range dispersion interaction between two molecules. Optical rotation or optical activity (ORD) is the rotation of linearly polarized light as it travels through certain materials. A (frequency-dependent) magnetic field induces a magnetic moment in a molecule, which is proportional to the (frequency-dependent) molecular magnetizability. The Faraday effect describes the rotation of plane-polarized light due to a magnetic field, which is proportional to the intensity of the component of the magnetic field in the direction of the beam of light. The Verdet constant describes the strength of the Faraday effect for a particular molecule. All these properties are available in ADF as applications of time-dependent DFT (TDDFT).

Two keys can be used for calculating these properties:

- RESPONSE
- AORESPONSE

The RESPONSE key has many unique features compared to the AORESPONSE key, like the use of symmetry during the calculation. The AORESPONSE key also has many unique features compared to the RESPONSE key, namely lifetime effects (polarizabilities at resonance), the calculation of (dynamic) magnetizabilities, Verdet constants, the Faraday B terms, and an alternative way to calculate (resonance) Raman scattering factors. Both RESPONSE and AORESPONSE can calculate polarizabilities in case of spin-orbit coupling.

7.6.1 RESPONSE: (Hyper-)Polarizabilities, ORD

RESPONSE: Polarizabilities

The calculation of frequency-dependent (hyper)polarizabilities and related properties (Raman, ORD) is activated with the block key RESPONSE.

```
RESPONSE
END
```

In this example only the *zz* component of the dipole polarizability tensor is calculated, at zero frequency. The orientation of the molecule is therefore crucial. Be aware that the program may modify the orientation of the molecule if the input coordinates do not agree with the symmetry conventions in ADF. (This calculation could equivalently be done through a finite field method.)

See also the alternative implementation with the AORESPONSE key that offers some unique features like magnetizability and lifetime options.

The impact of various approximations on the quality of computed polarizabilities has been studied in, for instance, Refs.¹²³. If you are new to this application area, we strongly recommend that you study a few general references first, in particular when you consider hyperpolarizability calculations. These have many pitfalls, technically (which basis sets to use, application of the DEPENDENCY key) and theoretically (how do theoretical tensor components relate to experimental quantities, different conventions used). Please take a good look both at ADF-specific references³¹³²⁶⁴ and at general references related to this subject: Refs.⁵³³³⁴, the entire issues of Chem. Rev. 94, the ACS Symposium Series #628, and further references in the ADF-specific references.

```
RESPONSE
ALLCOMPONENTS
Frequencies freq1 freq2 ... freqN [unit]
ALLTENSOR
Quadrupole
Octupole
Traceless
END
```

Entire tensor or only one component

You specify the ALLCOMPONENTS subkey to get the entire polarizability tensor, instead of just the zz component.

Frequencies

List of frequencies at which the polarizability is to be calculated. Default unit eV. A range of frequencies with equidistant points can be specified with the boundaries (inclusive) as well as the number of desired subintervals separated by colons. For example, 1.0:1.5:5 is equivalent to 1.0 1.1 1.2 1.3 1.4 1.5.

Higher multipole polarizabilities

Instead of just calculating the dipole-dipole polarizability, one may address the dipole-quadrupole, quadrupole-quadrupole, dipole-octupole, quadrupole-octupole, and octupole-octupole polarizability tensors. These can all be calculated in a single run, using the subkey ALLTENSOR. If only quadrupole-quadrupole or octupole-octupole tensors are needed, the subkey quadrupole or octupole should be used.

Traceless

If the subkey TRACELESS is included, this ensures the calculation of tensors using the traceless form of the quadrupole operator.

¹ S.J.A. van Gisbergen, V.P. Osinga, O.V. Gritsenko, R. van Leeuwen, J.G. Snijders and E.J. Baerends, *Improved density functional theory results for frequency-dependent polarizabilities, by the use of an exchange-correlation potential with correct asymptotic behavior*, *Journal of Chemical Physics* 105, 3142 (1996) (<https://doi.org/10.1063/1.472182>)

² S.J.A. van Gisbergen, F. Kootstra, P.R.T. Schipper, O.V. Gritsenko, J.G. Snijders and E.J. Baerends, *Density-functional-theory response-property calculations with accurate exchange-correlation potentials*, *Physical Review A* 57, 2556 (1998) (<https://doi.org/10.1103/PhysRevA.57.2556>)

³ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *A Density Functional Theory study of frequency-dependent polarizabilities and van der Waals dispersion coefficients for polyatomic molecules*, *Journal of Chemical Physics* 103, 9347 (1995) (<https://doi.org/10.1063/1.469994>)

³¹ S.J.A. van Gisbergen, J.G. Snijders, and E.J. Baerends, *Time-dependent Density Functional Results for the Dynamic Hyperpolarizability of C₆₀*, *Physical Review Letters* 78, 3097 (1997) (<https://doi.org/10.1103/PhysRevLett.78.3097>)

³² S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory*, *Journal of Chemical Physics* 109, 10644 (1998) (<https://doi.org/10.1063/1.477762>)

⁶ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Accurate density functional calculations on frequency-dependent hyperpolarizabilities of small molecules*, *Journal of Chemical Physics* 109, 10657 (1998) (<https://doi.org/10.1063/1.477763>)

⁴ B. Champagne, E.A. Perpète, S.J.A. van Gisbergen, E.J. Baerends, J.G. Snijders, C. Soubra-Ghaoui, K.A. Robins and B.Kirtman, *Assessment of conventional density functional schemes for computing the polarizabilities and hyperpolarizabilities of conjugated oligomers: An ab initio investigation of polyacetylene chains*, *Journal of Chemical Physics* 109, 10489 (1998) (<https://doi.org/10.1063/1.477731>) Erratum: *Journal of Chemical Physics* 111, 6652 (1999) (<https://doi.org/10.1063/1.479106>)

⁵ A. Willets, J.E. Rice, D.M. Burland and D.P. Shelton, *Problems in comparison of experimental and theoretical hyperpolarizabilities*, *Journal of Chemical Physics* 97, 7590 (1992) (<https://doi.org/10.1063/1.463479>)

³³ D.M. Bishop, *Aspects of Non-Linear-Optical Calculations*, *Advances in Quantum Chemistry* 25, 3 (1994) ([https://doi.org/10.1016/S0065-3276\(08\)60017-9](https://doi.org/10.1016/S0065-3276(08)60017-9))

³⁴ D.P. Shelton and J.E. Rice, *Measurements and calculations of the hyperpolarizabilities of atoms and small molecules in the gas phase*, *Chemical Reviews* 94, 3 (1994) (<https://doi.org/10.1021/cr00025a001>)

RESPONSE: Accuracy and convergence

```

RESPONSE
  erralf 1e-6
  erabsx 1e-6
  errtmx 1e-6
  ncycmx 30
END

```

erralf, erabsx, errtmx

The subkeys erralf, erabsx, errtmx determine the convergence criteria for a polarizability calculation. The strict defaults are shown. It is rarely necessary to change the defaults, as these are rather strict but do not lead to many iterations.

ncycmx

The maximum number of attempts within which the algorithm has to converge. The default appears to be adequate in most cases.

RESPONSE: Hyperpolarizabilities

Hyperpolarizabilities

```

RESPONSE
  HYPERPOL LaserFreq
END

```

The first hyperpolarizability tensor β is calculated (in atomic units in the ‘theoretician’s convention’, i.e. convention T=AB in Ref.^{Page 215, 5}) if the subkey HYPERPOL is present with a specification of the laser frequency (in Hartree units). If also the subkey ALLCOMPONENTS is specified, all components of the hyperpolarizability tensor will be obtained.

As mentioned earlier, by default only the static dipole hyperpolarizability tensor is computed. If you are interested in the frequency-dependent hyperpolarizability, the input could look like:

```

RESPONSE
  ALLCOMPONENTS
  HYPERPOL 0.01
  DYNAHYP
END

```

The subkey DYNAHYP must be added and the main frequency ω must be specified in Hartrees after the subkey HYPERPOL. In the output, all nonzero components of the tensors governing the static first hyperpolarizability, second harmonic generation, electro-optic Pockels effect, and optical rectification are printed.

Note: Second hyperpolarizabilities are currently not available analytically in case of RESPONSE. Some can, however, be obtained by calculating the first hyperpolarizability in a finite field.

The effect of using different DFT functionals (LDA, LB94, BLYP) on hyperpolarizabilities in small molecules has been investigated in^{Page 215, 6}.

RESPONSE: Optical rotation dispersion (ORD)

```

RESPONSE
  OPTICALROTATION
END

```

OPTICALROTATION

With the subkey OPTICALROTATION, the (frequency-dependent) optical rotation⁷⁸ will be calculated. For correct calculations one should calculate the entire tensor (see also the subkey ALLCOMPONENTS), which is done automatically.

An alternative implementation uses the AORESPONSE key, in which lifetime effects can be included.

7.6.2 AORESPONSE: Lifetime effects, (Hyper-)polarizabilities, ORD, magnetizabilities, Verdet constants

The AORESPONSE key offers some unique features compared to the RESPONSE key, namely lifetime effects (polarizabilities at resonance), the calculation of (dynamic) magnetizabilities, Verdet constants, the Faraday B terms, and an alternative way to calculate (resonance) Raman scattering factors. Note that the RESPONSE key also has many unique features, such as the use of symmetry during the calculation.

AORESPONSE: Polarizabilities

If the block key AORESPONSE is used, the polarizability is calculated by default.

```

AORESPONSE
  Frequencies freq1 freq2 ... freqN
  LIFETIME width
END

```

Frequencies

List of frequencies at which the time-dependent properties are to be calculated. Default unit eV. A range of frequencies with equidistant points can be specified with the boundaries (inclusive) as well as the number of desired subintervals separated by colons. For example, 1.0:1.5:5 is equivalent to 1.0 1.1 1.2 1.3 1.4 1.5.

LIFETIME width

Specify the resonance peak width (damping) in Hartree units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule; however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. A value of 0.004 Hartree was used in Ref.⁹.

The spin-orbit ZORA polarizability code (Ref.¹¹) is automatically selected if the AORESPONSE keyword is given in a spin-orbit-coupled calculation. In this case a spin-restricted calculation is required, but, unlike the rest of AORESPONSE, it also works with SYMMETRY NOSYM. Spin-polarization terms in the XC response kernel are neglected. In Ref.^{Page 217, 11} the imaginary polarizability dispersion curves (spin-restricted) match well the broadened spin-orbit

⁷ J. Autschbach and T. Ziegler, *Calculating molecular electric and magnetic properties from time-dependent density functional response theory*, *Journal of Chemical Physics* 116, 891 (2002) (<https://doi.org/10.1063/1.1420401>)

⁸ J. Autschbach, S. Patchkovskii, T. Ziegler, S.J.A. van Gisbergen and E.J. Baerends, *Chiroptical properties from time-dependent density functional theory. II. Optical rotations of small to medium sized organic molecules*, *Journal of Chemical Physics* 117, 581 (2002) (<https://doi.org/10.1063/1.1477925>)

⁹ L. Jensen, L. Zhao, J. Autschbach and G.C. Schatz, *Theory and method for calculating resonance Raman scattering from resonance polarizability derivatives*, *Journal of Chemical Physics* 123, 174110 (2005) (<https://doi.org/10.1063/1.2046670>)

¹¹ A. Devarajan, A. Gaenko, and J. Autschbach, *Two-component relativistic density functional method for computing nonsingular complex linear response of molecules based on the zeroth order regular approximation*, *Journal of Chemical Physics* 130, 194102 (2009) (<https://doi.org/10.1063/1.3123765>)

TDDFT data from Ref.¹⁰. Thus the corrections from the spin-polarization terms appear to be rather minor. No picture-change corrections were applied in the ZORA formalism. AOESPONSE with hybrids in combination with spin-orbit is not implemented.

AOESPONSE: Technical parameters and expert options

```
AOESPONSE
...
SCF          {NOCYC} {NOACCEL} {CONV=conv} {ITER=niter}
GIAO
FITAO DERIV
COMPONENTS {XX} {XY} {XZ} {YX} {YY} {YZ} {ZX} {ZY} {ZZ}
ALDA|XALPHA
ALPHA
END
```

SCF {NOCYC} {NOACCEL} {CONV=conv} {ITER=niter}

Specify CPKS parameters such as the degree of convergence and the maximum number of iterations:

NOCYC - disable self-consistency altogether

NOACCEL - disable convergence acceleration

CONV - convergence criterion for CPKS. The default value is 10^{-6} . The value is relative to the uncoupled result (i.e. to the value without self-consistency).

ITER - maximum number of CPKS iterations, 50 by default.

Specifying ITER=0 has the same effect as specifying NOCYC.

GIAO

Include the Gauge-Independent Atomic Orbitals (GIAO). This option should not be used with damping (LIFE-TIME keyword), and the VELOCITYORD option should be used instead.

FITAO DERIV

Use fitted AO derivatives. This will improve the density fitting, but can only be used in case of STO fitting. In case of ZlmFit one can improve the fitting with the ZLMFIT block key.

COMPONENTS {XX} {XY} {XZ} {YX} {YY} {YZ} {ZX} {ZY} {ZZ}

Limit the tensor components to the specified ones. Using this option may save computation time.

ALDA|XALPHA

If ALDA is specified, the VWN kernel is used. This option is the default. If ALPHA is specified, the $X\alpha$ kernel is used instead of the default VWN one. For functionals that use LYP correlation, like BLYP, always the $X\alpha$ kernel is used, even if you specified ALDA.

ALPHA

Writes perturbed density matrix to TAPE16.

¹⁰ F. Wang, T. Ziegler, E. van Lenthe, S.J.A. van Gisbergen and E.J. Baerends, *The calculation of excitation energies based on the relativistic two-component zeroth-order regular approximation and time-dependent density-functional with full use of symmetry*, *Journal of Chemical Physics* 122, 204103 (2005) (<https://doi.org/10.1063/1.1899143>)

AORESPONSE: Damped First Hyperpolarizabilities

In Ref.¹² an implementation of finite lifetimes into TDDFT for the calculation of quadratic response properties in ADF is described. All β tensor components (27 in total) will be printed in the output.

```
AORESPONSE
  BETA|QUADRATIC
  Frequencies freq1 freq2
  LIFETIME width
  STATIC|OPTICALR|EOPE|SHG
END
```

BETA

Option to calculate the damped first hyperpolarizability (β) using quadratic response theory based on the 2n+1 rule. Two input frequencies are required for this calculation and the property $\beta(-(\omega_1 + \omega_2); \omega_1, \omega_2)$ will be the output. Note that one can choose certain values of the two frequencies to calculate different types of β , such as static case $\beta(0; 0, 0)$, optical rectification $\beta(0; \omega, -\omega)$, electro-optical Pockels effect $\beta(-\omega; \omega, 0)$, and second harmonic generation $\beta(-2\omega; \omega, \omega)$. Alternatively, these can be efficiently calculated using the (sub-)keywords STATIC, OPTICALR, EOPE, and SHG, respectively. Note that the needed input frequencies all rely on ω_1 (freq1) when using the (sub)keywords above.

QUADRATIC

This option possesses the same functionality as BETA, i.e., calculate the damped β , except not adapting the 2n+1 rule. The (sub)keywords STATIC, OPTICALR, EOPE, and SHG are also applicable here. Note that this approach facilitates the direct partitioning of the response into contributions from localized orbitals and is important for natural bond analysis.

Note: Please only use HARTREE or EV as the unit for the input frequencies. The unit option ANGSTROM does not work correctly due to the current implementation structure.

AORESPONSE: Damped Second Hyperpolarizabilities

In Ref.¹³ a general implementation for damped cubic response properties is presented using time-dependent density functional theory (TDDFT) and Slater-type orbital basis sets. To directly calculate two-photon absorption (TPA) cross sections, an implementation of a reduced damped cubic response approach is described in Ref.^{Page 219, 13}. All γ tensor components (81 in total) will be printed in the output.

```
AORESPONSE
  GAMMA|CUBIC
  Frequencies freq1 freq2 freq3
  LIFETIME width
  STATIC|EFIOR|OKE|IDRI|EFISHG|THG|TPA
END
```

GAMMA

Option to calculate the damped second hyperpolarizability (γ) using cubic response theory based on the 2n+1 rule. Three input frequencies are required for this calculation and the property $\gamma(-(\omega_1 + \omega_2 + \omega_3); \omega_1, \omega_2, \omega_3)$ will be the output. Note that one can choose certain values of the three frequencies to calculate different types of γ , such as static case $\gamma(0; 0, 0, 0)$, electric field induced optical rectification $\gamma(0; \omega, -\omega, 0)$, optical Kerr effect $\gamma(-\omega; \omega, 0, 0)$, intensity dependent refractive index $\gamma(-\omega; \omega, \omega, -\omega)$, electric field induced second harmonic generation $\gamma(-2\omega; \omega, \omega, 0)$, and third harmonic generation $\gamma(-3\omega; \omega, \omega, \omega)$. Alternatively, these can be efficiently calculated using the (sub)keywords STATIC, EFIOR, OKE, IDRI, EFISHG, and THG, respectively. The

¹² Z. Hu, J. Autschbach, and L. Jensen, *Simulation of resonance hyper-Rayleigh scattering of molecules and metal clusters using a time-dependent density functional theory approach*, *Journal of Chemical Physics* 141, 124305 (2014) (<https://doi.org/10.1063/1.4895971>)

¹³ Z. Hu, J. Autschbach, and L. Jensen, *Simulating Third-Order Nonlinear Optical Properties Using Damped Cubic Response Theory within Time-Dependent Density Functional Theory*, *Journal of Chemical Theory and Computation* 12, 1294 (2016) (<https://doi.org/10.1021/acs.jctc.5b01060>)

(sub)keyword TPA can be used to calculate the γ corresponding to the two-photon absorption process (i.e., the reduced form of $\gamma(-\omega; \omega, \omega, -\omega)$); however, it can ONLY be used with the keyword GAMMA. Note that the needed input frequencies all rely on ω_1 (freq1) when using the (sub)keywords above.

CUBIC

This option possesses the same functionality as GAMMA, i.e., calculate the damped γ , except not adapting the $2n+1$ rule. The (sub)keywords STATIC, EFIOR, OKE, IDRI, EFISHG, and THG are also applicable here. Note that this approach facilitates the direct partitioning of the response into contributions from localized orbitals and is important for natural bond analysis.

Note: Please only use HARTREE or EV as the unit for the input frequencies. The unit option ANGSTROM does not work correctly due to the current implementation structure.

AORESPONSE: ORD

```
AORESPONSE
  OPTICALROTATION
  VELOCITYORD
  Frequencies freq1 freq2 ... freqN
  LIFETIME width
END
```

OPTICALROTATION

Specify OPTICALROTATION to calculate the optical rotatory dispersion spectrum instead of polarizabilities.

VELOCITYORD

This option should be used instead of OPTICALROTATION with GIAO if the finite lifetime effects need to be taken into account (LIFETIME option).

AORESPONSE: magnetizabilities, Verdet constants, Faraday B term

```
AORESPONSE
  MAGNETICPERT
  MAGOPTROT
  FREQUENCIES freq1 freq2 ... freqN [unit]
  LIFETIME width
END
```

MAGNETICPERT

Calculate static or time-dependent magnetizability, see also Ref.¹⁴.

MAGOPTROT

Specify MAGOPTROT to calculate the Verdet constant instead of polarizability; see Ref.¹⁶ for details of the implementation. When it is specified together with the LIFETIME key, the real and imaginary parts of the damped Verdet constant will be calculated. The combination of three keys MAGOPTROT, LIFETIME and FREQUENCIES yields the magnetic optical rotatory dispersion and magnetic circular dichroism spectrum (Faraday A and B terms) calculated simultaneously in the range from freq1 to freqN. It is also possible to combine MAGOPTROT, LIFETIME and FREQUENCY. In order to obtain the Faraday B terms from the Verdet constant calculations it is necessary to perform several steps, involving a fit of the imaginary Verdet data to the MCD spectrum. You can request SCM for details on the fitting procedure. For details of the method, see Ref.¹⁵.

¹⁴ M. Krykunov and J. Autschbach, *Calculation of static and dynamic linear magnetic response in approximate time-dependent density functional theory*, *Journal of Chemical Physics* 126, 24101 (2007) (<https://doi.org/10.1063/1.2423007>)

¹⁶ M. Krykunov, A. Banerjee, T. Ziegler and J. Autschbach, *Calculation of Verdet constants with time-dependent density functional theory. Implementation and results for small molecules*, *Journal of Chemical Physics* 122, 074105 (2005) (<https://doi.org/10.1063/1.1850919>)

¹⁵ M. Krykunov, M. Seth, T. Ziegler and J. Autschbach, *Calculation of the magnetic circular dichroism B term from the imaginary part of the Verdet*

AORESPONSE: Raman

```

AORESPONSE
  RAMAN
  Frequencies freq1 [unit]
  LIFETIME width
END

```

RAMAN

Calculates the Raman scattering factors. AORESPONSE Raman only works with one frequency. If one frequency is specified the Raman scattering factors are calculated at that frequency. The Raman option is compatible with the lifetime option so that resonance Raman scattering can be calculated. For details of this method, see Ref. [Page 217, 9](#). To get Raman intensities with AORESPONSE, numerical frequencies need to be calculated using a FREQUENCIES key in the GEOMETRY input block. Nonresonance Raman intensities can also be obtained using the RESPONSE key or, alternatively, using RAMANRANGE in combination with analytically or numerically pre-calculated frequencies.

Applications of AORESPONSE

It may be useful to consult the following applications of the AORESPONSE key in ADF:

- Calculation of static and dynamic linear magnetic response in approximate time-dependent density functional theory [Page 220, 14](#)
- Calculation of CD spectra from optical rotatory dispersion, and vice versa, as complementary tools for theoretical studies of optical activity using time-dependent density functional theory¹⁷
- Calculation of origin independent optical rotation tensor components for chiral oriented systems in approximate time-dependent density functional theory¹⁸
- Time-dependent density functional calculations of optical rotatory dispersion including resonance wavelengths as a potentially useful tool for determining absolute configurations of chiral molecules¹⁹
- Calculation of optical rotation with time-periodic magnetic field-dependent basis functions in approximate time-dependent density functional theory²⁰
- A Quantum Chemical Approach to the Design of Chiral Negative Index Materials²¹
- Calculation of Verdet constants with time-dependent density functional theory. Implementation and results for small molecules [Page 220, 16](#)
- Calculations of resonance Raman [Page 217, 935](#)

constant using damped time-dependent density functional theory, *Journal of Chemical Physics* 127, 244102 (2007) (<https://doi.org/10.1063/1.2806990>)

¹⁷ M. Krykunov, M.D. Kundrat and J. Autschbach, *Calculation of CD spectra from optical rotatory dispersion, and vice versa, as complementary tools for theoretical studies of optical activity using time-dependent density functional theory*, *Journal of Chemical Physics* 125, 194110 (2006) (<https://doi.org/10.1063/1.2363372>)

¹⁸ M. Krykunov and J. Autschbach, *Calculation of origin independent optical rotation tensor components for chiral oriented systems in approximate time-dependent density functional theory*, *Journal of Chemical Physics* 125, 34102 (2006) (<https://doi.org/10.1063/1.2210474>)

¹⁹ J. Autschbach, L. Jensen, G.C. Schatz, Y.C.E. Tse and M. Krykunov, *Time-dependent density functional calculations of optical rotatory dispersion including resonance wavelengths as a potentially useful tool for determining absolute configurations of chiral molecules*, *Journal of Physical Chemistry A* 110, 2461 (2006) (<https://doi.org/10.1021/jp054847z>)

²⁰ M. Krykunov and J. Autschbach, *Calculation of optical rotation with time-periodic magnetic field-dependent basis functions in approximate time-dependent density functional theory*, *Journal of Chemical Physics* 123, 114103 (2005) (<https://doi.org/10.1063/1.2032428>)

²¹ A. Baev, M. Samoc, P.N. Prasad, M. Krykunov and J. Autschbach, *A Quantum Chemical Approach to the Design of Chiral Negative Index Materials*, *Optics Express* 15, 5730 (2007) (<https://doi.org/10.1364/OE.15.005730>)

³⁵ L. Jensen, L. Zhao, J. Autschbach and G.C. Schatz, *Resonance Raman Scattering of Rhodamine 6G as calculated using Time-Dependent Density Functional Theory*, *Journal of Physical Chemistry A* 110, 5973 (2006) (<https://doi.org/10.1021/jp0610867>)

- Calculations of surface-enhanced Raman scattering (SERS)^{36,37}
- Calculation of magnetic circular dichroism spectra from damped Verdet constants^{Page 220, 15}
- Calculation of the polarizability in case of spin-orbit coupling^{Page 217, 11}

See also:

- [advanced tutorial on plasmon-enhanced two-photon absorption](#)

7.6.3 PolTDDFT: Damped Complex Polarizabilities

A fast algorithm to solve the Time-Dependent Density Functional Theory (TDDFT) equations in the space of the density fitting auxiliary basis set has been developed and implemented²⁵. The method, named PolTDDFT, extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization. The original idea which made the present scheme very efficient consists in the simplification of the double sum over occupied-virtual pairs in the definition of the complex dynamical polarizability, allowing an easy calculation of such matrix as a linear combination of constant matrices with photon-energy-dependent coefficients. The method has been extended for the calculation of circular dichroism spectra²⁶.

In AMS2023 several analysis options were added. An analysis of the absorption and CD spectrum in terms of single orbital transitions, using the subkey ANALYSIS, is available. An analysis of the spectra per region (subkey REGIONS-FORANALYSIS), using the fragment projection analysis approach, is available; see Ref.²². If you are using the GUI or *densf* (page 342), you can visualize the induced (first-order perturbed) density (relevant for polarizability), the transition (first-order perturbed) density (relevant for absorption), and the rotator strength density (relevant for CD, see Ref.²⁹). If you are using the GUI, you can visualize the so-called transition contribution maps (TCM, see Ref.²³), individual component maps of oscillatory strength (ICM-OS, see Ref.²⁴), and individual component maps of rotatory strength (ICM-RS, see Ref.²⁹).

In case a global (meta-)hybrid is used in the SCF, the hybrid diagonal approximation (HDA)³⁸ is used. HDA is based on utilizing the hybrid exchange only for the diagonal terms in the response equations. This allows one to limit the computational cost of the TD-DFT simulation while keeping basically the same accuracy as in the full TD-DFT scheme using hybrid XC functionals. It is possible to use the density fitting auxiliary basis set to further speed up the HDA (subkey HDA_fitted); see Ref.⁴⁰. In AMS2025 within this HDA_fitted scheme, range-separated XC functionals that use XCFUN,

³⁶ L.L. Zhao, L. Jensen and G.C. Schatz, Pyridine - Ag₂₀ Cluster: A Model System for Studying Surface-Enhanced Raman Scattering, *Journal of the American Chemical Society* 128, 2911 (2006) (<https://doi.org/10.1021/ja0556326>)

³⁷ L. Jensen, L.L. Zhao and G.C. Schatz, Size-Dependence of the Enhanced Raman Scattering of Pyridine Adsorbed on Ag_n (n=2-8,20) Clusters, *Journal of Physical Chemistry C* 111, 4756 (2007) (<https://doi.org/10.1021/jp067634y>)

²⁵ O. Baseggio, G. Fronzoni, and M. Stener, A new time dependent density functional algorithm for large systems and plasmons in metal clusters, *Journal of Chemical Physics* 143, 024106 (2015) (<https://doi.org/10.1063/1.4923368>)

²⁶ O. Baseggio, D. Toffoli, G. Fronzoni, M. Stener, L. Sementa, and A. Fortunelli, Extension of the Time-Dependent Density Functional Complex Polarizability Algorithm to Circular Dichroism: Implementation and Applications to Ag₈ and Au₃₈ (SC₂H₄C₆H₅)₂₄, *Journal of Physical Chemistry C* 120, 24335 (2016) (<https://doi.org/10.1021/acs.jpcc.6b07323>)

²² L. Sementa, G. Barcaro, O. Baseggio, M. De Vetta, A. Dass, E. Aprà, M. Stener, and A. Fortunelli, Ligand-Enhanced Optical Response of Gold Nanomolecules and Its Fragment Projection Analysis: The Case of Au₃₀ (SR)₁₈, *Journal of Physical Chemistry C* 121, 10832 (2017) (<https://doi.org/10.1021/acs.jpcc.6b12029>)

²⁹ L. Chang, O. Baseggio, L. Sementa, D. Cheng, G. Fronzoni, D. Toffoli, E. Aprà, M. Stener, and A. Fortunelli, Individual Component Map of Rotatory Strength and Rotatory Strength Density Plots As Analysis Tools of Circular Dichroism Spectra of Complex Systems, *Journal of Chemical Theory and Computation* 14, 3703 (2018) (<https://doi.org/10.1021/acs.jctc.8b00250>)

²³ S. Malola, L. Lehtovaara, J. Enkovaara, and H. Häkkinen, Birth of the Localized Surface Plasmon Resonance in Monolayer-Protected Gold Nanoclusters, *ACS Nano* 7, 10263 (2013) (<https://doi.org/10.1021/nn4046634>)

²⁴ S. Theivendran, L. Chang, A. Mukherjee, L. Sementa, M. Stener, A. Fortunelli, and A. Dass, Principles of Optical Spectroscopy of Aromatic Alloy Nanomolecules: Au_{36-x}Ag_x (SPh-tBu)₂₄, *Journal of Physical Chemistry C* 122, 4524 (2018) (<https://doi.org/10.1021/acs.jpcc.8b00556>)

³⁸ M. Medves, L. Sementa, D. Toffoli, G. Fronzoni, A. Fortunelli, An efficient hybrid scheme for time dependent density functional theory, *Journal of Chemical Physics* 152, 184104 (2020) (<https://doi.org/10.1063/5.0005954>)

⁴⁰ P. D'Antoni, M. Medves, D. Toffoli, A. Fortunelli, M. Stener, L. Visscher, A Resolution of Identity Technique to Speed up TDDFT with Hybrid Functionals: Implementation and Application to the Magic Cluster Series Au_{8n+4}(SC₆H₅)_{4n+8} (n = 3–6), *Journal of Physical Chemistry A* 127, 9244 (2023) (<https://doi.org/10.1021/acs.jpca.3c05368>)

like CAMY-B3LYP, can be used with PolTDDFT⁴¹. Range-separated XC functionals that use LibXC cannot be used with PolTDDFT.

It is very important to use specially made auxiliary fit sets, which are available only for a very limited number of elements. Symmetry and frozen cores can be used. Should not be used with spin-orbit coupling. STOFIT cannot be used.

UV/Vis spectra, CD spectra

If you include the POLTDDFT keyword, the (real and imaginary part of the) diagonal of the polarizability tensor and rotatory strengths will be calculated, which can be used to calculate the photoabsorption and circular dichroism (CD) spectra.

```
POLTDDFT
  IRREP
    Irrep1
    Irrep2
    ...
  END
  KGRID eVgrid
  NGRID ngrid
  FREQRANGE eVi eVf
  NFREQ nfreq
  LIFETIME eVwidth
  CUTOFF eVcutoff
  LAMBDA lambda
  VELOCITY
  HDA_fitted
  ANALYSIS
  REGIONSFORANALYSIS region_names
END
```

IRREP

Subblock key for selecting which symmetry irreps of the excitations to calculate (all excitations by default). In the subkey data block list the symmetry irrep labels, like B1, for example.

KGRID eVgrid

Keyword KGRID is used to discretize the energy scale for calculating the complex dynamical polarizability. Only pairs of an occupied and virtual orbital are included, for which the orbital energy difference is lower than eVgrid (9 eV by default).

NGRID ngrid

NGRID is the number of points within the energy grid (180 by default).

FREQRANGE eVi eVf

Keyword FREQRANGE is used to specify the equally spaced points in the spectrum for which one would like to calculate the complex dynamical polarizability. The first point is eVi (0 eV by default) and the last one is eVf (5 eV by default).

NFREQ nfreq

The total number of points in the spectrum is nfreq (100 by default).

LIFETIME eVwidth

Specify the resonance peak width (damping) in eV units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule; however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. Default value is 0.1 eV.

⁴¹ P. D'Antoni, D. Toffoli, M. Stener, *Damped Linear Response TDDFT with Range-Separated Functionals and Density Fitting*, *Journal of Physical Chemistry A* 129, 9453 (2025) (<https://doi.org/10.1021/acs.jpca.5c03798>)

CUTOFF eVcutoff

For a given point in the spectrum, only include pairs of an occupied and virtual orbital, for which the orbital energy difference is lower than the energy of the point in the spectrum plus eVcutoff. The default value for eVcutoff is 4 eV.

LAMBDA lambda

Jacob's scaling factor²⁷ for the study of plasmonic resonances. This factor, $0 < \text{lambda} < 1$ (default lambda=1), turns on the coupling matrix K.

VELOCITY

If the subkey VELOCITY is included, ADF calculates the dipole moment in velocity gauge. By default the dipole-length representation is used.

HDA_fitted

If the subkey HDA_fitted is included, the density fitting auxiliary basis set is used to calculate HDA. HDA is only relevant if (meta-)hybrids are used.

ANALYSIS

An analysis of the absorption and CD spectrum in terms of single orbital transitions.

REGIONSFORANALYSIS region_names

Analysis per region, using the fragment projection analysis approach; see Ref.²². Will split the absorption and CD spectrum in region_i -> region_j terms. The region_names are the names of the regions that should be used.
Example: Damped complex polarizabilities with POLTDDFT: Au10 (page 966) shows how to use this option.

Reduced fit set

For PolTDDFT it is very important to use specially made auxiliary fit sets. These are available³⁹ for most elements, except lanthanides and actinides, using a large frozen core. These special basis sets can be found in the atomic database directories, with a directory name POLTDDFT, for example, the directory \$AMSHOME/atomicdata/ADF/POLTDDFT/TZP. They require relativistic ZORA to be used, since the frozen core description is relativistic ZORA. An example:

```
Basis
Type POLTDDFT/DZ
PerAtomType Symbol=Au File=POLTDDFT/TZP/Au.4f
End
```

Table 7.1: Available basis sets in PolTDDFT (May 2021)

Element	ae or fc	DZ	DZP	TZP
H-He (Z=1-2)	ae	Yes	Yes	Yes
Li-Ne (Z=3-10)	.1s	Yes	Yes	Yes
Na-Ar (Z=11-18)	.2p	Yes	Yes	Yes
K-Ca (Z=19-20)	.3p	Yes	Yes	Yes
Sc-Zn (Z=21-30)	.3p	Yes		Yes
Ga-Kr (Z=31-36)	.3d	Yes	Yes	Yes
Rb-Cd (Z=37-48)	.4p	Yes		Yes
In-Ba (Z=49-56)	.4d	Yes		Yes
Hf-Hg (Z=72-80)	.4f	Yes		Yes
Tl (Z=81)	.5p	Yes		Yes
Pb-Ra (Z=82-88)	.5d	Yes		Yes

²⁷ S. Bernadotte, F. Evers, and C.R. Jacob, *Plasmons in Molecules*, Journal of Physical Chemistry C 117, 1863 (2013) (<https://doi.org/10.1021/jp3113073>)

³⁹ M. Medves, G. Fronzoni, M. Stener, *Optimization of density fitting auxiliary Slater-type basisfunctions for time-dependent density functional theory*, Journal of Computational Chemistry 43, 1923 (2022) (<https://doi.org/10.1002/jcc.26992>)

7.6.4 Van der Waals dispersion coefficients

```
RESPONSE
  ALLCOMPONENTS
  VANDERWAALS NVanderWaals
  {ALLTENSOR}
END
```

Dispersion coefficients

Simple dispersion coefficients (the dipole-dipole interaction between two identical molecules, the C_6 coefficient) are calculated in a single ADF calculation. General dispersion coefficients are obtained with the auxiliary program DISPER, which uses two output files (files named TENSOR) of two separate ADF runs as input. See the Properties and the Examples documents. To get the dispersion coefficients one has to calculate polarizabilities at imaginary frequencies between 0 and infinity. The ADF program chooses the frequencies itself. The user must specify the number of frequencies, which in a sense defines the level of accuracy, as an argument to the subkey VanDerWaals.

NVanderWaals

One can specify the number of frequencies with NVanderWaals. Ten frequencies is reasonable. Without the key ALLTENSOR only dipole-dipole interactions are considered. If ALLTENSOR is specified, higher dispersion coefficients are also calculated. This ADF calculation generates a file with name TENSOR, which contains the results of multipole polarizabilities at imaginary frequencies. This TENSOR file must be saved. Similarly, the TENSOR file for the second monomer must be saved. The files have to be renamed to files 'tensorA' and 'tensorB' (case-sensitive), respectively. Then the program DISPER must be called in the same directory where the 'tensorA' and 'tensorB' files are located. DISPER needs no further input.

DISPER program: Dispersion Coefficients

The DISPER program was originally written by V. Osinga²⁸. The original documentation was written by S.J.A. van Gisbergen.

Van der Waals dispersion coefficients

The program DISPER computes van der Waals dispersion coefficients up to C_{10} for two arbitrary closed-shell molecules. ADF itself can already compute some C_6 and C_8 coefficients between two identical closed-shell molecules. These coefficients describe the long-range dispersion interaction between two molecules. It requires previous ADF-TDDFT calculations for the polarizability tensors at imaginary frequencies for the two interacting molecules. Each such ADF calculation produces a file TENSOR (if suitable input for ADF is given). The TENSOR files must be renamed tensorA and tensorB, respectively, and must be present as local files for DISPER. The DISPER program takes no other input and prints a list of dispersion coefficients.

A schematic example, taken from the set of sample runs, for the usage of DISPER is the following:

Step 1: run ADF for, say, the HF molecule. In the input file you specify the RESPONSE data block:

```
RESPONSE
  MaxWaals 8      ! Compute dispersion coefficients up to C8
  ALLTENSOR      ! This option must be specified in the ADF calculation for a
                  ! subsequent DISPER run
  ALLCOMPONENTS ! Must also be specified for DISPER
End
```

At the end of the run, copy the local file 'TENSOR' to a file 'tensorA'. For simplicity, we will now compute the dispersion coefficients between two HF molecules. Therefore, copy 'tensorA' to 'tensorB'.

²⁸ V.P. Osinga, S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Density functional results for isotropic and anisotropic multipole polarizabilities and C_6 , C_7 , and C_8 Van der Waals dispersion coefficients for molecules*, Journal of Chemical Physics 106, 5091 (1997) (<https://doi.org/10.1063/1.473555>)

Now run DISPER (without any other input). It will look for the local files 'tensorA' and 'tensorB' and compute corresponding dispersion coefficients to print them on standard output.

```
$AMSBIN/disper -n1 << eor
eor
```

The output might look something like this:

```
DISPER 2000.02 RunTime: Apr04-2001 14:14:13
C-COEFFICIENTS
n   LA  KA  LB  KB  L   coefficient (Y)      coefficient (P)
6   0   0   0   0   0   28.29432373         28.29432373
6   2   0   0   0   2    7.487547697         3.348533127
8   0   0   0   0   0  416.1888455         416.1888455
8   0   0   2   0   2   0.4323024202E-05     0.1933315197E-05
8   2   0   0   0   2  402.3556946         179.9389368
8   2   0   2   0   4   0.4238960180E-05
8   4   0   0   0   4  -36.67895539        -12.22631846
8   4   0   2   0   6  -0.2000286301E-05
```

The n value in the first column refers to the long-range radial interaction. The case n=6 refers to the usual dipole-dipole type interaction related to a $1/R^6$ dependence in the dispersion energy. The n=7 case relates to a dipole-quadrupole polarizability on one system and a dipole-dipole polarizability on the other (this is not symmetric). The n=8 term may contain contributions from a quadrupole-quadrupole polarizability on one system in combination with a dipole-dipole polarizability on the other as well as contributions from two dipole-quadrupole polarizabilities.

Terms which are zero by symmetry are not printed. In the example above, this is the case for all n=7 terms, because the systems (apparently) are too symmetric to have a nonzero dipole-quadrupole polarizability. The best known and most important coefficients are the isotropic ones, determining the purely radial dependence of the dispersion energy. They are characterized by the quantum numbers: 6 0 0 0 0 0 (or 8 0 0 0 0 0, etc.). Other combinations of quantum numbers refer to different types of angular dependence. The complete set determines the dispersion energy for arbitrary orientations between the two subsystems A and B.

The complete expressions are rather involved and lengthy. We refer the interested reader to the paper^{Page 225, 28}, which contains a complete description of the meaning of the various parts of the output, as well as references to the earlier literature which contain the mathematical derivations. In particular, a useful review, which was at the basis of the ADF implementation, is given in³⁰. Of particular significance is Eq. (8) of the JCP paper mentioned above, as it defines the meaning of the calculated coefficients $C_n^{L_A, K_A, L_B, K_B, L}$ as printed above.

For highly symmetric systems, a different convention is sometimes employed. It is based on Legendre polynomials (hence the 'P' in the final column) instead of on the spherical harmonics (the 'Y' in the column before the last). The 'P' coefficients are defined only for those coefficients that are nonzero in highly symmetric systems and never contain additional information with respect to the 'Y' coefficients. They are defined [Eq. (14) in the mentioned J. Chem. Phys. paper] in terms of the 'Y' coefficients by:

$$C_n^L = (-1)^L C_n^{L,0,0,0,L} / \sqrt{2L+1}$$

Because the quality of the dispersion coefficients is determined by the quality of the polarizabilities that are the input for DISPER, it is important to get good polarizabilities from ADF. For that it is important, in the case of small systems, to use an asymptotically correct XC potential (several choices are available in ADF, such as SAOP or GRAC) and a basis set containing diffuse functions. We refer to the ADF User's Guide for details.

³⁰ A. van der Avoird, P.E.S. Wormer, F. Mulder, R.M. Berns, Topics in Current Chemistry 93, 1 (1980)

7.7 Ligand Field and Density Functional Theory (LFDFT)

7.7.1 Introduction

Hans Bethe and John Hasbrouck van Vleck have introduced the Ligand Field (LF) model simultaneously in the 1930s. This theory often plays a central role for molecules containing d- and/or f-elements with open shells. It is a semi-empirical model with adjustable parameters. Twenty years later Christian Klixbüll Jorgensen and Klaus Erik Schäffer proposed the Angular Overlap Model (AOM) that is a transcription of LF theory using molecular orbitals, still using adjustable parameters. Starting from the very beginning of the twenty-first century until today, a new, non-empirical, density functional theory (DFT)-based ligand field model^{1,2} was developed, called LFDFT. LFDFT emerged through the collaboration of many European scientists during these years.

The key feature of the LFDFT approach is the explicit treatment of near-degeneracy correlation using ad hoc Configuration Interaction (CI) within the active space of Kohn-Sham (KS) orbitals with dominant p-, d- or f-character. The calculation of the CI matrices is based on a symmetry decomposition in the full rotation group and/or on a ligand field analysis of the energies of all single determinants (microstates) calculated according to density functional theory (DFT) for frozen KS orbitals corresponding to the averaged configuration, possibly with fractional occupations, of the p-, d- or f-orbitals. In the literature one can find cases where this procedure yields multiplet energies with an accuracy of a few hundred wavenumbers and fine structure splitting accurate to less than a tenth of this amount. This procedure was used to calculate different molecular properties, e.g. zero-field splitting (ZFS)³, Zeeman interaction⁴, hyperfine splitting (HFS)⁵, magnetic exchange coupling^{Page 227, 56}, and shielding constants⁷.

Strictly speaking, LF theory is nothing but the consideration of active p-, d- and/or f-electrons moving in the potential of a passive chemical environment. A rigorous formulation of a passive chemical environment could be given using a frozen density embedding (FDE) scheme. However, in practice, it turns out that the method described in Ref.⁸ using an effective Hamiltonian is more advantageous and yields more insight for experimentalists. The LFDFT model was extended to two open-shell systems⁹. This has relevance for inter-shell transitions in lanthanides, important for understanding the optical and magnetic properties of rare-earth materials. It could also be used, for example, to calculate multiplet effects in X-ray absorption spectroscopy. Theory and applications for $f \rightarrow d$ transitions can be found in Refs.^{9,10,11}.

¹ M. Atanasov, C.A. Daul, C. Rauzy, *New insights into the effects of covalency on the ligand field parameters: a DFT study*, *Chemical Physics Letters* 367, 737 (2003) ([https://doi.org/10.1016/S0009-2614\(02\)01762-1](https://doi.org/10.1016/S0009-2614(02)01762-1))

² M. Atanasov, C.A. Daul, C. Rauzy, *A DFT Based Ligand Field Theory*, *Structure & Bonding* 106, 97 (2004) (<https://doi.org/10.1007/b11308>)

³ A. Borel, C.A. Daul, L. Helm, *Hybrid ligand-field theory/quantum chemical calculation of the fine structure and ZFS in lanthanide(III) complexes*, *Chemical Physics Letters* 383, 584 (2004) (<https://doi.org/10.1016/j.cplett.2003.11.082>)

⁴ M. Atanasov, E.J. Baerends, P. Beattig, R. Bruyndockx, C. Daul, C. Rauzy, *The calculation of ESR parameters by density functional theory: the g- and A-tensors of Co(acacen)*, *Chemical Physics Letters* 399, 433 (2004) (<https://doi.org/10.1016/j.cplett.2004.10.041>)

⁵ M. Atanasov, C.A. Daul, *A DFT based ligand field model for magnetic exchange coupling in transition metal dimer complexes: (i) principles*, *Chemical Physics Letters* 379, 209 (2003) ([https://doi.org/10.1016/S0009-2614\(03\)01325-3](https://doi.org/10.1016/S0009-2614(03)01325-3))

⁶ M. Atanasov, C.A. Daul, *A DFT based ligand field model for magnetic exchange coupling in transition metal dimer complexes: (ii) application to magnetic systems with more than one unpaired electron per site*, *Chemical Physics Letters* 381, 584 (2003) (<https://doi.org/10.1016/j.cplett.2003.10.024>)

⁷ F. Senn, C.A. Daul, *Calculation of ⁵⁹Co shielding tensor σ using LF-DFT*, *Journal of Molecular Structure: THEOCHEM* 954, 105 (2010) (<https://doi.org/10.1016/j.theochem.2010.02.027>)

⁸ C. Daul, *Non-empirical Prediction of the Photophysical and Magnetic Properties of Systems with Open d- and f-Shells Based on Combined Ligand Field and Density Functional Theory (LFDFT)*, *Chimia* 68 (2014) (<https://doi.org/10.2533/chimia.2014.633>)

⁹ H. Ramanantoanina, W. Urland, F. Cimpoesu, and C. Daul, *Ligand field density functional theory calculation of the $4f^2 \rightarrow 4f^1 5d^1$ transitions in the quantum cutter $\text{Cs}_2\text{KYF}_6:\text{Pr}^{3+}$* , *Physical Chemistry Chemical Physics* 15, 13902 (2013) (<https://doi.org/10.1039/C3CP51344K>).

¹⁰ H. Ramanantoanina, W. Urland, A. Garcia-Fuente, F. Cimpoesu, and C. Daul, *Ligand field density functional theory for the prediction of future domestic lighting*, *Physical Chemistry Chemical Physics* 16, 14625 (2014) (<https://doi.org/10.1039/C3CP55521F>).

¹¹ H. Ramanantoanina, M. Sahnoun, A. Barbiero, M. Ferbinteanu, F. Cimpoesu, *Development and applications of the LFDFT: the non-empirical account of ligand field and the simulation of the $f-d$ transitions by density functional theory*, *Physical Chemistry Chemical Physics* 17, 18547 (2015) (<https://doi.org/10.1039/C5CP02349A>).

7.7.2 Input description

Average of Configuration run

From a defined atomic structure (for example, obtained from geometry optimization or a crystal .cif structure file), run a DFT calculation representing the electron configuration of the system to which the metal ion belongs. This DFT run is achieved by the Average of Configuration (AOC) calculation with fractional occupations of s, p, d, or f orbitals, i.e. for $3d^7$ electron configuration of Co^{2+} , 7 electrons are evenly distributed in the molecular orbitals having dominant cobalt character. Choosing which orbitals have to be fractionally occupied may not always be trivial, since there may be several close-lying levels with different character. This may lead to problematic SCF convergence. One should check that the final fractionally occupied molecular orbitals indeed have the expected metal character, since otherwise the subsequent LFDFT calculation will be meaningless. It is required that the metal ion is placed as the first atom in the coordinate system. Besides, the calculation implies a single-point spin-restricted SCF without symmetry constraint (C1 point group = SYMMETRY NOSYM). A scalar relativistic ZORA Hamiltonian should be used.

For a Co^{2+} d^7 electron configuration the input for ADF could be something like:

```
$AMSBIN/ams << eor

System
  Atoms
    Co 0.0 0.0 0.0
    ...
  End
End

...

Engine ADF
  ...
  IrrepOccupations
    A 56 1.4 1.4 1.4 1.4 1.4
  End
  Relativity Level=Scalar
  Symmetry NOSYM
EndEngine
eor
```

LFDFT atomic database

The LFDFT atomic database is *not* included in the ADF distribution.

The easiest way to install it is using the ADF-GUI: open AMSinput and go to the LFDFT section (**Properties → Lig- and Field DFT**). Then it will automatically be installed via AMSpackages if needed. You can also install it from the command line using `$AMSBIN/amspackages install lfdft`, or with the AMSpackages GUI `$AMSBIN/amspackages gui`.

Alternatively, you can download the LFDFT atomic database LFDFT from <https://downloads.scm.com/Downloads/lfdft/LFDFT.zip>, and save the unzipped file in a different location. If you save this LFDFT atomic database in a different location, make sure to point the environment variable `SCM_LFDFT` to this directory.

Note that at present available electron configurations for the LFDFT atomic database are:

- s^n , $n=0,\dots,2$
- p^n , $n=0,\dots,6$
- d^n , $n=0,\dots,10$

- f^n , $n=0,\dots,14$
- $p^5 d^n$, $n=0,\dots,10$
- $f^n d^l$, $n=1,\dots,13$
- $d^9 f^n$, $n=1,\dots,14$

LFDFT run

The `adf.rkf` (TAPE21) file of the average of configuration (AOC) run should be an input file for the program `lfdft`. Results of the LFDFT calculation will be put on `adf.rkf`. The input for `lfdft` is keyword oriented and is read from the standard input. Spin-orbit coupling is calculated using the ZORA equation by default. In cases where this is an underestimation, the old approximate method (a simple core potential) and/or an extra multiplication factor can be included. A finite magnetic field can be included.

```
$AMSBIN/lfdft << eor
ADFFILE adffile
NSHELL nshell
NLVAL1 nval1 lval1
{NLVAL2 nval2 lval2}
MOIND1 MO#1 MO#2 ... MO#(2*lval1+1)
{MOIND2 MO#1 MO#2 ... MO#(2*lval2+1)}
SOC soc1 {soc2}
SOCTYPE
    shell1 type1
    {shell2 type2}
End
BField bx by bz
DegeneracyThreshold threshold
eor
```

ADFFILE adffile

Path to `adf.rkf` (TAPE21) file from which `lfdft` reads data and to which `lfdft` writes data. Default TAPE21.

NSHELL nshell

`nshell` is the number of shells in the electron configuration system under consideration: for Co^{2+} in $3d^7$ electron configuration, `nshell` = 1; for Fe^{2+} in $2p^5 3d^7$, `nshell` = 2. `nshell` should be equal to 1 or 2.

NLVAL1 nval1 lval1

`nval1` and `lval1` are the main quantum numbers n and l for shell 1, in case of all-electron calculations on the metal atoms. For 5d this is '5 2'. For frozen core calculations the number n should be reduced with the number of core levels with angular momentum l that are in the core. For example for 5d, with 3d and 4d in the core, one should use '3 2'.

NLVAL2 nval2 lval2

If `nshell`=2, `nval2` and `lval2` are the main quantum numbers n and l for shell 2.

MOIND1 MO#1 MO#2 ... MO#(2*lval1+1)

`MO#1`, ... are the indices of the molecular orbitals which have the most dominant `nval1 lval1` character, for example the most dominant 3d character. They should match the fractionally occupied orbitals that are used in the AOC run for shell 1.

MOIND2 MO#1 MO#2 ... MO#(2*lval2+1)

If `nshell`=2, `MO#1`, ... are the indices of the molecular orbitals which have the most dominant `nval2 lval2` character. They should match the fractionally occupied orbitals that are used in the AOC run for shell 2.

SOC soc1 {soc2}

`soc1` indicates if spin-orbit coupling is considered (1) or not (0) for shell 1. If `nshell`=2, the same applies for `soc2`

for shell 2. soc1 and soc2 can also be real numbers, in case one wants to scale the calculated approximate spin-orbit coupling(s) by LFDFT. By default, the spin-orbit coupling is included (soc1 = 1, soc2 = 1).

```
SOCTYPE
  shell1 type1
  {shell2 type2}
End
```

type1 and type2 can be either 'zora' or 'core' and indicate whether the spin-orbit coupling for the given shell is calculated using the corresponding term in the ZORA equation (type = zora) or using the old approximation with the core potential only (type = core). The default is set to zora.

BField bx by bz

Include a finite magnetic field (Tesla). For MCD calculations include a magnetic field in the z-direction. For example, BField 0.0 0.0 1.0 is a magnetic field of 1.0 Tesla in the z-direction. By default, no magnetic field is included. The DegeneracyThreshold should be small to see the splitting of levels due to the magnetic field.

DegeneracyThreshold threshold

Energy difference threshold (eV) to determine degenerate levels.

For example, for a 3d⁷ electron configuration the input for lfdft could be

```
$AMSBIN/lfdft <<eor
ADFFile ams.results/adf.rkf
NSHELL 1
NLVAL1 3 2
MOIND1 29 30 31 32 33
SOC 1
SOCTYPE
  shell1 zora
End
eor
```

EPR (ESR) g-tensor

LFDFT can be used to calculate the EPR (ESR) g-tensor, see Ref.⁴. In the LFDFT implementation in ADF the EPR (ESR) g-tensor will be calculated only for Kramers doublet states. Results of the calculations should normally only be used for an odd number of electrons. Spin-orbit coupling should be included, but a finite magnetic field should not be included, and no other keywords are needed. One should be careful when interpreting the g-tensor if two or more Kramers doublets are close in energy. In that case, in the effective Hamiltonian used to interpret EPR (ESR) experiments an effective spin higher than S=1/2 might be used, which is not taken into account in the calculations.

LFDFT intensities

One can calculate excitation energies and oscillator strengths between two atomic multiplet states which come from different electron configurations of the same molecule with the module lfdft_tdm. Note that electronic transitions between two multiplet states which come from the same electron configuration are not dipole allowed. lfdft_tdm can calculate excitation energies and oscillator strengths (in the dipole approximation) from the calculated ground state multiplet of one electron configuration to all multiplet states that can be made for the other electron configuration. The calculated transition dipole moments and oscillator strengths are in arbitrary units. They are averaged over the degeneracy of the ground state as well as over the degeneracy of the excited state multiplet. The oscillator strength has to be multiplied with the degeneracy of the excited state multiplet.

The input for lfdft_tdm is keyword oriented and is read from the standard input.

```
$AMSBIN/lfdft_tdm << eor
STATE1 file1
STATE2 file2
eor
```

STATE1 file1

Filename file1 should be a result adf.rkf of a lfdft calculation, that contains the ground state electron configuration.

STATE2 file2

Filename file2 should be a result adf.rkf of a lfdft calculation, that contains the excited state electron configuration.

Results of the lfdft_tdm calculation will be put on file2.

For example for $\text{Pr } 4f^2 \rightarrow \text{Pr } 4f^1 5d^1$ the input could be something like:

```
$AMSBIN/lfdft_tdm <<eor
STATE1 f2.results/adf.rkf
STATE2 f1d1.results/adf.rkf
eor
```

In this case lfdft_tdm will calculate the excitations from the ground state of $\text{Pr } 4f^2$ to all multiplet states that can be made with the $\text{Pr } 4f^1 5d^1$ electron configuration.

MCD

LFDFDFT can be used to calculate magnetic circular dichroism (MCD) effect in X-ray absorption spectroscopy, see Ref.¹². By using the same methodology as for an X-ray absorption calculation, one needs two LFDFDFT calculations for two atomic multiplet states which come from different electron configurations of the same molecule. Additionally, in both calculations the same finite magnetic field in the z-direction (for example, Bfield 0 0 1) should be included. Next the module lfdft_tdm can be used to calculate besides the total intensity, also the polarized part that is perpendicular to the magnetic axis, the circular-left and circular-right part.

7.8 NMR

NMR chemical shifts and NMR spin-spin couplings can be calculated. Effects due to spin-orbit coupling can be included. All-electron basis sets can be used.

Worked out examples of chemical shift and spin-spin coupling calculations can be found in the **tutorials section**:

- Chemical shifts and nuclear spin-spin coupling constants with NBO analysis: [Analysis of NMR parameters with Localized Molecular Orbitals](#)
- Chemical shifts and nuclear spin-spin coupling constants with visualization of the spectrum in the GUI: [H-NMR spectrum with spin-spin coupling](#)

¹² H. Ramanantoanina, M. Studniarek, N. Daffé, J. Dreiser, *Non-empirical calculation of X-ray magnetic circular dichroism in lanthanide compounds*, *Chemical Communications* 55, 2988 (2019) (<https://doi.org/10.1039/C8CC09321K>).

7.8.1 NMR Chemical Shifts

NMR chemical shifts have been implemented¹²³⁴⁵ in a separate property program NMR. It requires the adf.rkf (TAPE21) result file from an ADF calculation. The NMR module can be combined with the ZORA treatment for relativistic effects and with spin-orbit effects, making it suitable for treatment of heavy elements. See also the general review on relativistic computations of NMR parameters⁶.

Two GUI tutorials on NMR chemical shift calculations are currently available:

- Chemical shifts and nuclear spin-spin coupling constants with NBO analysis: [Analysis of NMR parameters with Localized Molecular Orbitals](#)
- Chemical shifts and nuclear spin-spin coupling constants with visualization of the spectrum in the GUI: [H-NMR spectrum with spin-spin coupling](#)

The NMR chemical shift δ_i is defined as the difference of the isotropic NMR chemical shielding of a reference compound σ_{ref} minus that of the interesting compound σ_i :

$$\delta_i = \sigma_{ref} - \sigma_i$$

The NMR program calculates NMR chemical shieldings σ_i .

Important notes

adf.rkf (TAPE21) and TAPE10

NMR requires an ASCII input file and adf.rkf (TAPE21) and TAPE10 result files from an ADF calculation on the molecule to be analyzed. The ADF result files adf.rkf (TAPE21) and TAPE10 must be present with names TAPE21 and TAPE10 in the directory where you execute NMR, or alternatively you can use the keys ADFFile and TAPE10File to point to an adf.rkf file and TAPE10 file. Use the keywords SAVE TAPE10 in the ADF calculation in order to obtain a TAPE10 result file.

Recalculation of TAPE10 by NMR

Warning: the NMR property program will not always give the correct result for every SCF potential in the ADF calculation, for example the SAOP potential, or if one uses COSMO in the ADF calculation, if one lets the NMR recalculate TAPE10. This is due to the GIAO method used in this program, which requires the calculation of the SCF potential, which is not done correctly for potentials other than the standard LDA and GGA potentials. To obtain correct results, you should, in addition to the use of TAPE21, also use TAPE10 that ADF generates by using the keywords SAVE TAPE10, and use it as input for the NMR property program. On TAPE10 the SCF potential is written, which is read in by the NMR program.

Atomic calculation

NMR calculations on one atom must have symmetry NOSYM.

¹ G. Schreckenbach and T. Ziegler, *The calculation of NMR shielding tensors using GIAO's and modern density functional theory*, *Journal of Physical Chemistry* 99, 606 (1995) (<https://doi.org/10.1021/j100002a024>)

² G. Schreckenbach and T. Ziegler, *The calculation of NMR shielding tensors based on density functional theory and the frozen-core approximation*, *International Journal of Quantum Chemistry* 60, 753 (1996) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1996\)60:3%3C753::AID-QUA4%3E3.0.CO;2-W](https://doi.org/10.1002/(SICI)1097-461X(1996)60:3%3C753::AID-QUA4%3E3.0.CO;2-W))

³ G. Schreckenbach and T. Ziegler, *Calculation of NMR shielding tensors based on density functional theory and a scalar relativistic Pauli-type Hamiltonian. The application to transition metal complexes*, *International Journal of Quantum Chemistry* 61, 899 (1997) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1997\)61:6%3C899::AID-QUA3%3E3.0.CO;2-R](https://doi.org/10.1002/(SICI)1097-461X(1997)61:6%3C899::AID-QUA3%3E3.0.CO;2-R))

⁴ S.K. Wolff and T. Ziegler, *Calculation of DFT-GIAO NMR shifts with inclusion of spin-orbit coupling*, *Journal of Chemical Physics* 109, 895 (1998) (<https://doi.org/10.1063/1.476630>)

⁵ S.K. Wolff, T. Ziegler, E. van Lenthe and E.J. Baerends, *Density functional calculations of nuclear magnetic shieldings using the zeroth-order regular approximation (ZORA) for relativistic effects: ZORA nuclear magnetic resonance*, *Journal of Chemical Physics* 110, 7689 (1999) (<https://doi.org/10.1063/1.478680>)

⁶ J. Autschbach and S. Zheng, *Relativistic computations of NMR parameters from first principles: Theory and applications*, *Annual Reports on NMR Spectroscopy* 67, 1 (2009) ([https://doi.org/10.1016/S0066-4103\(09\)06701-5](https://doi.org/10.1016/S0066-4103(09)06701-5))

Spin-orbit coupling

NMR calculations on systems computed by ADF with spin-orbit relativistic effects included must have used NOSYM symmetry in the ADF calculation. NMR can also be combined with ADF ZORA calculations. The NMR program reads from adf.rkf (TAPE21) the relativistic option that is used in the ADF calculation, and will use the same relativistic option in the NMR calculations.

Kernel used in spin-orbit coupling

One can include an improved exchange-correlation kernel, as was implemented by J. Autschbach⁷, but this is not used by default; see subkey USE. This is an important option that should be seriously considered and has been advocated in Ref.^{Page 233, 7}.

Bug spin-orbit part ADF2008 - ADF2013

In ADF2008.01 a bug was introduced in the spin-orbit part of the calculated chemical shielding, which caused the calculated chemical shielding to be gauge dependent. This bug is relevant for spin-orbit coupled calculations for ADF versions ADF2008-ADF2013. In ADF2014 this bug has been fixed.

Unscaled ZORA default ADF2014

There is gauge dependence if the scaled ZORA method is used in the calculation of NMR chemical shieldings. Therefore the default method for NMR chemical shielding calculations is changed in ADF2014 to use the unscaled ZORA method.

SAOP

The use of the model SAOP potential leads to isotropic chemical shifts which are substantially improved over both LDA and GGA functionals, and of similar accuracy as results with a self-interaction-corrected functional (SIC), see⁸. SAOP is computationally expedient and routinely applicable to all systems, requiring virtually the same computational effort as LDA and GGA calculations.

NICS

The Nucleus-Independent Chemical Shift (NICS) can be calculated at any point in the molecule.

Hybrids

Starting from ADF2009.01 Hartree-Fock and the hybrid potentials can be used in combination with NMR chemical shielding calculations, see Refs.^{9,10}. Use SAVE TAPE10 in the ADF calculation. The use of frozen cores and hybrids gives gauge dependent results for the NMR chemical shieldings, therefore the NMR program will stop in this case.

Meta-GGAs and meta-hybrids

Meta-GGAs and meta-hybrids should not be used in combination with NMR chemical shielding calculations. The results are wrong due to an incorrect inclusion of GIAO terms.

Range-separated Hybrids

Starting from ADF2026.01 range-separated hybrid potentials can be used in combination with NMR chemical shielding calculations. Range-separated functionals with a meta-GGA part cannot be used.

LibXC

Starting from ADF2026.01 many of the LibXC functionals can be used in combination with NMR chemical shielding calculations. XC functionals with a meta-GGA part cannot be used.

⁷ J. Autschbach, *The role of the exchange-correlation response kernel and scaling corrections in relativistic density functional nuclear magnetic shielding calculations with the zeroth-order regular approximation*, *Molecular Physics* 111, 2544 (2013) (<https://doi.org/10.1080/00268976.2013.796415>)

⁸ J. Poater, E. van Lenthe and E.J. Baerends, *Nuclear magnetic resonance chemical shifts with the statistical average of orbital-dependent model potentials in Kohn-Sham density functional theory*, *Journal of Chemical Physics* 118, 8584 (2003) (<https://doi.org/10.1063/1.1567252>)

⁹ M. Krykunov, T. Ziegler and E. van Lenthe, *Hybrid density functional calculations of nuclear magnetic shieldings using Slater-type orbitals and the zeroth-order regular approximation*, *International Journal of Quantum Chemistry* 109, 1676 (2009) (<https://doi.org/10.1002/qua.21985>)

¹⁰ M. Krykunov, T. Ziegler and E. van Lenthe, *Implementation of a hybrid DFT method for calculating NMR shieldings using Slater-type orbitals with spin-orbital coupling included. Applications to ¹⁸⁷Os, ¹⁹⁵Pt and ¹³C in heavy metal complexes*, *Journal of Physical Chemistry A* 113, 11495 (2009) (<https://doi.org/10.1021/jp901991s>)

Input options

The input file for NMR uses the block key NMR, with several (optional) subkeys, each having a series of options. For analysis, a separate block key can be used.

```
$AMSBIN/nmr << eor
ADFFile adffile
TAPE10File tape10file
ZSOAO2007
RECALCULATETAPE10
NMR
End
Analysis
End
eor
```

ADFFile adffile

Path to adf.rkf (TAPE21) file from which nmr reads data and to which nmr writes data. Default is TAPE21.

TAPE10File tape10file

Path to TAPE10 file from which nmr reads data. Default is TAPE10.

ZSOAO2007 keyword

In the ADF2008.01 a bug was introduced in the spin-orbit part of the calculated chemical shielding, which caused the calculated chemical shielding to be gauge dependent. This bug is relevant for spin-orbit coupled calculations for ADF versions ADF2008-ADF2013. Workaround in ADF versions ADF2008-ADF2013 is to include the keyword ZSOAO2007 in the NMR part of the input, which causes a one-center approximation to be used. The bug has been fixed in ADF2014 by introducing an extra gauge-correction term for the spin-orbit coupled part. One can still get the (slightly) incorrect results in ADF2014 by using the keyword WRONGSOGAUGE, and not including ZSOAO2007.

RECALCULATETAPE10 keyword

If there is no TAPE10 present, the NMR program will stop. One can use the key RECALCULATETAPE10 such that TAPE10 will be recalculated by the NMR module. This is not recommended. Better use "SAVE TAPE10" in the ADF calculation, and use this TAPE10 as input for NMR.

NMR block key

```
NMR
  Out  OutOptions
  Calc CalcOptions
  Use  UseOptions
  U1K  U1KOptions
  Nuc  NucOptions
  Atoms AtomsOptions
  Ghosts GhostsOptions
  Analysis AnalysisOptions
End
```

Out OutOptions

The subkey Out controls printed output. Its options specify the details by their (optional) presence. The following OutOptions are recognized (Default ISO TENS):

All

Implies all the other options

ISO

Isotropic shielding constants

Tens

Shielding tensors

Eig

Eigenvectors

U1

The U1 matrix

F1

The first order change in the Fock matrix

S1

The first order change in the Overlap matrix

AOP

The paramagnetic AO matrix (= the matrix in the representation of elementary atomic basis functions)

AOD

The diamagnetic AO matrix

AOF

The Fermi-contact AO matrix

REFS

Literature references

INFO

General information

Calc CalcOptions

The subkey Calc controls what is actually calculated. The following options are available (Default ALL):

All

Implies all of the other options to this key

Para

The paramagnetic part

Dia

The diamagnetic part

FC

The Fermi-contact part in case of the Pauli Hamiltonian

SO

The Fermi-contact part in case of the ZORA Hamiltonian

Use UseOptions

The subkey Use controls some options (default none)

FXC

Improves the exchange-correlation kernel used, as was implemented by J. Autschbach⁷. Important only in case of spin-orbit coupled calculations. This may give some (small) gauge dependent results when using this. Important option that should be seriously considered and has been advocated in Ref.^{Page 233, 7}.

SCALED

Implies the scaled ZORA method, which gives (slightly) gauge dependent results, as was shown in Ref.^{Page 233, 7}. Note that for the ZORA Hamiltonian the default is the unscaled ZORA method. For chemical shifts, only compare results with the same options.

SO1C

Before ADF2008.01, in the spin-orbit term a 1-center approximation was used, which does not suffer from gauge dependence. This 1-center approximation can be used with USE SO1C.

U1K U1KOptions

The subkey U1K determines which terms are included in the calculation of the U1 matrix (first order changes in MO coefficients). Options (Default Best):

Best

The best (recommended) options for each relativistic option are included for this subkey. Implies 'None' for non-relativistic and scalar relativistic ZORA, 'SO' + 'SOFULL' for spin-orbit coupled ZORA, and 'MV' + 'Dar' for the Pauli Hamiltonian.

None

Implies none of the other options to this key.

All

Implies all the other options to this key.

MV

The mass-velocity term.

Dar

The Darwin term.

ZMAN

The Spin-Zeeman term. Can be included only in case of spin-orbit coupled Pauli Hamiltonian.

SO

ZORA spin-orbit part.

SOFULL

ZORA spin-orbit part.

Note: for chemical shifts, only compare results with the same options. If the subkey U1K is used with the option ALL in the ZORA calculation, then the scaled ZORA orbital energies are used in the making of the U1 matrix, which is not recommended. Recommended is to use 'U1K Best' in all cases, which uses plain ZORA orbital energies in the making of the U1 matrix.

NUC NucOptions

This subkey NUC specifies for which nuclei the NMR shielding is calculated. By default, all nuclei are calculated, i.e. as for omitting the subkeys ATOMS and NUC. Alternatively you may use this option by simply typing Nuc in the NMR block (without any further data); this means: for no nuclei at all. You may also type the index of the atom(s) you want to see analyzed.

Example:

```
NUC 2 1
```

The numbers refer to the internal numbering of the nuclei as it appears somewhere early in the general ADF output. This internal numbering is also the internal NMR numbering, but it is not necessarily the same as the input ordering. Use the subkey ATOMS to specify the nuclei according to this input ordering in the ADF calculation.

Note that the number of nuclei has a significant consequence for the total CPU time.

Atoms AtomsOptions

This subkey ATOMS specifies for which nuclei the NMR shielding is calculated. By default, all nuclei are calculated, i.e. as for omitting the subkeys ATOMS and NUC.

Example:

```
ATOMS 2 1
```

The numbers refer to the input ordering in the ADF calculation. Use the subkey NUC to specify the nuclei according to the internal NMR numbers of the atoms.

GHOSTS

The subkey GHOSTS is a block type subkey. The format is:

```
Ghosts
  xx1 yy1 zz1
  xx2 yy2 zz2
  ...
End
```

With this key, the user can specify ANY point(s) within the molecule at which the shielding is to be calculated (whatever the physical meaning of this shielding is). One can think of those points as neutrons within the molecule. There is a publication by P. Schleyer et al. using a similar feature (J. Am. Chem. Soc. **118**, 6317, 1996). They call it NICS, Nucleus-Independent Chemical Shift. Note that the NICS value is minus 1 times the isotropic part of the shielding tensor that is calculated at these points:

```
xx1 yy1 zz1
```

real numbers that specify the Cartesian coordinates of 'ghost' 1, etc.

The coordinates have to be specified in Angstrom. The same set of coordinates has to be specified as 'point charges with charge zero' using the subsubkey MultipolePotential in the ElectrostaticEmbedding subkey of the key System in the AMS block. This is necessary in order to allow the appropriate distribution of integration points around the ghosts.

E.g., if you want to have two 'ghosts' with the coordinates xx1 yy1 zz1 and xx2 yy2 zz2 then you **must** also have in the input the key MultipolePotential key as follows:

```
System
...
ElectrostaticEmbedding
  MultipolePotential
    Coordinates
      xx1 yy1 zz1 0.0
      xx2 yy2 zz2 0.0
    End
  End
End
End
```

(the last number is the charge at these coordinates - zero).

Eventually, this step should be programmed internally but for now the procedure outlined above works. No check is done to verify whether those 'point charges' are taken care of or not, but their omission leads to unpredictable results.

Only Cartesian coordinates are possible for ghosts, even if the atoms were originally specified using internal coordinates. This should not be a problem, though (e.g., one could start an ADF run of the molecule of interest, and get very soon the Cartesian coordinates of the atoms in the output. This run would then be aborted, and restarted with the ghosts specified as desired.) The ghosts are numbered in the output as NNUC+1, NNUC+2 ... where NNUC is the total number of nuclei in this molecule. Default: no ghosts.

Analysis AnalysisOptions

The subkey Analysis controls the MO analysis. After the word (subkey) Analysis you type an integer, which then

specifies that the first so many MOs are to be analyzed. Default: no Analysis. The value of this analysis subkey in the block key NMR is somewhat limited. The separate ANALYSIS block key can give more analysis of the NMR chemical shielding.

Analysis block key

The NMR shielding tensor can be analyzed in detail; see Refs.^{12,13}Page 232, 6. For the analysis option with the ANALYSIS block key there are some restrictions. In the ADF calculation, all-electron basis sets should have been used, and SYMMETRY NOSYM. It cannot be used in case of non-relativistic calculations. The ADF calculation should use relativistic scalar ZORA or relativistic spin-orbit ZORA. In case of scalar relativistic ZORA the keyword FAKESO should be added to the NMR input (outside of the NMR or Analysis block keys). The analysis utilizes the ZORA spin-orbit branch of the NMR code. For scalar ZORA, the NMR analysis contributions will appear in equivalent pairs for spin-orbitals even if the ADF calculation is closed-shell spin restricted. The MO numbering then also reflects this doubling of MOs. In the analysis, canonical MOs number 1 and 2 are the alpha and beta spin ADF MO 1, canonical MOs number 3 and 4 correspond to the alpha and beta spin ADF MO 2, and so on. In case of spin-orbit relativistic ZORA the keyword FAKESO should not be included. Curly brackets are not part of the key. For an NBO analysis of NMR, see the [section on NBO analysis](#) (page 311).

```
Analysis
  print threshold
  canonical
  {components}
End
{FakeSO}
```

print threshold

The print keyword selects printout of contributions relative to the total diamagnetic, paramagnetic. For example in case of 'print 0.01' only contributions greater than 1% are printed. Set to zero to print ALL contributions.

canonical

It enables an analysis of the shielding in terms of the canonical MOs.

components

The components keyword is optional and enables an analysis not only of the isotropic shielding but also of the diagonal Cartesian components of the tensor XX, YY, and ZZ. In order to analyze the principal shielding tensor components with canonical MOs you can calculate the shielding tensor first with the NMR code, rotate the molecule such that the principal axes system aligns with the Cartesian coordinate system, and then repeat the NMR calculation with the analysis features switched on.

7.8.2 Paramagnetic NMR Chemical Shifts

Knowledge of the g-tensor and hyperfine A-tensor can be used in the prediction and analysis of paramagnetic NMR shifts, see Refs.^{11,14,15}. Because of the dependence on the g-tensor, prediction of paramagnetic NMR (pNMR) shifts is not straightforward, as the dependence of the pNMR shift on excess α or β electron spin density at a nucleus is to be combined with the sign and magnitude of the isotropic g-value. Ref.¹¹ describes in detail how to calculate pNMR contact

¹² J. Autschbach, *Analyzing NMR shielding tensors calculated with two-component relativistic methods using spin-free localized molecular orbitals*, *Journal of Chemical Physics* 128, 164112 (2008) (<https://doi.org/10.1063/1.2905235>)

¹³ J. Autschbach and S. Zheng, *Analyzing Pt chemical shifts calculated from relativistic density functional theory using localized orbitals: The role of Pt 5d lone pairs*, *Magnetic Resonance in Chemistry* 46, S45 (2008) (<https://doi.org/10.1002/mrc.2289>)

¹¹ J. Autschbach, S. Patchkovskii, and B. Pritchard, *Calculation of Hyperfine Tensors and Paramagnetic NMR Shifts Using the Relativistic Zeroth-Order Regular Approximation and Density Functional Theory*, *Journal of Chemical Theory and Computation* 7, 2175 (2011) (<https://doi.org/10.1021/ct200143w>)

¹⁴ S. Moon, and S. Patchkovskii, *First-principles calculations of paramagnetic NMR shifts*, in *Calculation of NMR and EPR parameters*, ISBN13: 9783527307791, M. Kaupp, M. Bühl, V.G. Malkin, Editors, (Wiley, Weinheim, 2004).

¹⁵ P. Hrobárik, Ro. Reviakine, A.V. Arbuznikov, O.L. Malkina, V.G. Malkin, F.H. Köhler, and M. Kaupp, *Density functional calculations of NMR shielding tensors for paramagnetic systems with arbitrary spin multiplicity: Validation on 3d metallocenes*, *Journal of Chemical Physics* 126, 024107 (2007) (<https://doi.org/10.1063/1.2423003>)

chemical shifts and pNMR pseudo-contact chemical shifts, using the ADF program. In ADF2024 (part of) this procedure can be included more automatically.

Warning: Procedure to calculate paramagnetic NMR chemical shifts contains a bug in AMS2024.101 - AMS2024.106. Fixed in later releases.

For doublets (effective spin $S=1/2$), or for effective spin S higher than $1/2$ where one neglects effects due to zero-field splitting (ZFS, ESR D-tensor) the paramagnetic NMR shielding σ can be written as [Ref.¹⁶]:

$$\sigma = \sigma_{orb} - \frac{\mu_B}{g_N \mu_N} \frac{S(S+1)}{3k_B T} \mathbf{g} \cdot \mathbf{A}$$

Here σ_{orb} is the so called orbital dependent part of the NMR chemical shielding, μ_B is the Bohr magneton, μ_N is the nuclear magneton, g_N is the nuclear magnetic g-factor, k_B is the Boltzmann constant, and T is the temperature in K (Kelvin). In addition S is the effective spin, $\mathbf{g}$ is the g-tensor, and $\mathbf{A}$ is the A-tensor that are used in the effective spin Hamiltonian, which is commonly used for the interpretation of ESR experiments.

For open shell molecules in ADF the so called orbital dependent part of the NMR chemical shielding σ_{orb} can only be calculated without taken into account spin-orbit coupling.

```
# ADF calculation on the molecule

$AMSBIN/ams << eor
...
Engine ADF
  SpinPolarization value
  Unrestricted Yes
  Relativity
    Level Scalar
  End
  Basis
    Core None
  End
  Symmetry NOSYM
  SAVE TAPE10
EndEngine
eor

# Calculation of the ESR A-tensors

$AMSBIN/cpl << eor
  adffile path/to/adf.rkf
  tape10file path/to/TAPE10
  hyperfine
    atoms add_all_atoms
  END
eor
rm logfile TAPE15

# Calculation of the ESR g-tensor

$AMSBIN/nmr << eor
  adffile path/to/adf.rkf
  tape10file path/to/TAPE10
```

(continues on next page)

¹⁶ B.Martin, J. Autschbach, *Temperature dependence of contact and dipolar NMR chemical shifts in paramagnetic molecules*, *Journal of Chemical Physics* 142, 054108 (2015) (<https://doi.org/10.1063/1.4906318>)

(continued from previous page)

```
nmr
  gfactors
  out iso tens
  ulk best
  calc all
END
eor
rm logfile TAPE15

# Calculation of the orbital dependent part of the NMR chemical shielding

$AMSBIN/nmr << eor
  ADFFile path/to/adf.rkf
  TAPE10File path/to/TAPE10
  ALLINONE
  nmr
    ulk best
    calc all
    out iso tens
  end
  Temperature temperature
eor
```

Note that one can only do this at the scalar relativistic ZORA level, one needs symmetry NOSYM, one needs all electron basis sets, and one needs to include the key ALLINONE in the input for NMR. If one does not specify the temperature, a default temperature of 298.15 K is used.

See also:

Examples: *pNMR chemical shielding* (page 992)

7.8.3 NMR spin-spin coupling constants

The NMR spin-spin coupling constants¹² have been implemented in a separate program CPL. It can be combined with ZORA and spin-orbit treatment of relativistic effects to study heavy elements. The original version of this part of the User's Guide was written by Jochen Autschbach, primary author of the CPL code.

Two GUI tutorials on spin-spin coupling constant calculations are currently available:

- Chemical shifts and nuclear spin-spin coupling constants with NBO analysis: [Analysis of NMR parameters with Localized Molecular Orbitals](#)
- Chemical shifts and nuclear spin-spin coupling constants with visualization of the spectrum in the GUI: [H-NMR spectrum with spin-spin coupling](#)

¹ J. Autschbach and T. Ziegler, *Nuclear spin-spin coupling constants from regular approximate density functional calculations. I. Formalism and scalar relativistic results for heavy metal compounds*, *Journal of Chemical Physics* 113, 936 (2000) (<https://doi.org/10.1063/1.481874>)

² J. Autschbach, and T. Ziegler, *Nuclear spin-spin coupling constants from regular approximate relativistic density functional calculations. II. Spin-orbit coupling effects and anisotropies*, *Journal of Chemical Physics* 113, 9410 (2000) (<https://doi.org/10.1063/1.1321310>)

Introduction

The CPL code of the Amsterdam Density Functional program system allows the user to calculate *Nuclear Spin-spin Coupling Constants* (NSSCCs)^{Page 240, 1Page 240, 2}. NSSCCs are usually observed in NMR (Nuclear Magnetic Resonance) spectroscopy and give rise to the splitting of the signals of the NMR spectrum in multiplets. They contain a wealth of information about the geometric and electronic structure of the compound being investigated.

The calculation needs a standard adf.rkf (TAPE21) ADF output file. CPL also reads an input key and optional settings from stdin (usually from an input file). Technical parameters such as the maximum memory usage can be set here as well.

One of the key features of the program is its ability to treat heavy nuclei with the ZORA relativistic formalism. We refer the reader to the literature for details about our implementation^{Page 240, 1Page 240, 2}, and the general review on relativistic computations of NMR parameters³. Please use the information printed in the output header of the CPL program in order to provide references of this work in scientific publications.

The development of the CPL program started in 2000. CPL provides the main functionality in order to evaluate NSSCCs based on DFT, as well as a number of additional features in order to provide an analysis of the results. Several analysis features for the coupling constant have been added; see the CONTRIBUTIONS subkey. Please report bugs or suggestions to SCM at support@scm.com.

Theoretical and technical aspects

Within the non-relativistic theory of nuclear spin-spin coupling, there are four terms contributing to the NSSCC between two nuclei A and B: the paramagnetic and diamagnetic orbital terms (OP and OD, respectively), and the electron-spin dependent Fermi-contact (FC) and spin-dipole term (SD). In the literature, the OP and OD terms are often named PSO and DSO (for paramagnetic and diamagnetic spin-orbital). In the more general ZORA formulation, very similar operators are responsible for the NSSCC, therefore we use the same terminology for the individual contributions. In general, the interpretation of the results for a heavy atom system is basically equivalent to a non-relativistic situation.

In most cases, the FC term yields the most important contribution to the NSSCC. However, many exceptions are known for which one or each of the other terms can be non-negligible or even dominant. We therefore suggest that you always check, at least for a smaller but similar model system, or by using a smaller basis set, which of the four terms are negligible and which are dominant.

By default, the CPL program computes the FC coupling between the first and all other nuclei of the molecule, respectively. Other couplings or the computation of the OP, OD and SD terms can be requested by input switches (see the 'Running CPL' section of this document for details).

All contributions to the NSSCC are evaluated with the help of the numerical integration scheme implemented into ADF. In general, the computation of the OD term is computationally very cheap, since only integrals involving the electron density have to be evaluated. The next expensive term is the OP term. For this contribution, the first-order perturbed MOs have to be computed. With the available density functionals in ADF, the OP term does not cause a change in the Kohn-Sham potential, and the first-order MOs can be computed directly (i.e. without an iterative procedure). This is equivalent to the approach that has been implemented in the NMR code for ADF.

Both the FC and the SD terms induce electron spin-density to first-order as a perturbation. Equivalent to the iterative solution of the unperturbed Kohn-Sham equations, the first-order MOs depend on that first-order spin-density, which in turn depends on the first-order MOs. Therefore, in order to evaluate the FC and SD NSSCC contributions, the CPL program carries out a SCF cycle. In the scalar or non-relativistic case, the computational cost for the FC term is comparable to an ADF single point calculation with a local density functional. The evaluation of the SD term is more expensive. The current implementation utilizes the CPL spin-orbit code to compute the combined FC+SD contribution and therefore leaves some room for future speed-ups. In most cases, the SD term yields a negligible NSSCC and the much faster code for the scalar- or non-relativistic FC term can be used. However, it is very important to include the SD term in the computation if coupling anisotropies are to be evaluated.

³ J. Autschbach and S. Zheng, *Relativistic computations of NMR parameters from first principles: Theory and applications*, *Annual Reports on NMR Spectroscopy* 67, 1 (2009) ([https://doi.org/10.1016/S0066-4103\(09\)06701-5](https://doi.org/10.1016/S0066-4103(09)06701-5))

In the case where the NSSCC computation is based on spin-orbit coupled relativistic two component ZORA MOs, the SD term causes only a marginal increase in computational time as compared to the FC term alone. Generally, in this case the computational cost for the FC term is already approximately one order of magnitude higher than in the scalar or non-relativistic case, since the 3 (x, y, z) components of the spin-density with respect to 3 components of the perturbation, respectively, have to be determined self-consistently. The additional presence of the SD term only shows up in a somewhat more costly evaluation of the matrix elements of the perturbation operator. However, CPL spends most of its computational time in the SCF cycle. Therefore, in spin-orbit computations the computation of the FC+SD terms is the default. The OP term has to be evaluated self-consistently, too, in this case and is added as a perturbation in the SCF cycle upon request.

We use the terminology ‘perturbing’ and ‘responding nucleus’ within the CPL output. The ‘perturbing’ nucleus is the one for which the first-order MOs have to be computed (self-consistently), while the NSSCC is then determined by these first-order MOs and the FC, SD, and OP matrix elements of the second, ‘responding’ nucleus. For the OD term, this distinction makes no sense but is used in the output for reasons of consistency.

Experimental NSSCCs between two nuclei A and B are usually reported as $J(A,B)$ in Hertz. From a computational point of view, the so-called reduced NSSCCs $K(A,B)$ are more convenient for comparisons. CPL outputs both. The J 's are set to zero in case the nuclear magneto-gyric ratio of one of the nuclei A or B is not available at run time.

Further technical aspects and current limitations

In order to facilitate the future computation of rather large molecules, all matrix elements of the perturbation operators FC, SD, and OP are evaluated in the Slater AO basis that is specified as input in the CREATE runs of ADF. The AO matrix elements are further transformed to the basis of MOs and the calculation proceeds within the MO basis. This allows for a convenient analysis of the results in terms of contributions from individual occupied and virtual MOs. Such an analysis can be requested by input.

The matrix elements themselves as well as the first-order contributions to the potential are evaluated by numerical integration. The CPL code, which is parallelized, can use multiple processors for these steps of the computation. The accuracy setting for the numerical integration is of high importance to obtain accurate matrix elements. Furthermore, the basis set being employed needs to be flexible enough to describe the perturbation correctly. This means usually that modified basis sets have to be used in particular for heavy element calculations.

The first-order potential is currently approximated by the VWN functional. The $X:\text{math:}\alpha$ potential is available as an alternative but usually leads to less accurate results. In ADF2009.01 the first-order potential of the PBE family of GGA functionals and the hybrid PBE0 functional can be used.

Currently, only spin-restricted computations for systems with an even number of electrons are supported. Further, the calculation does not make use of symmetry and must be based on an ADF run with input SYMMETRY=NOSYM. Non-Aufbau configurations are not supported. The atom input list must not contain dummy atoms.

With the present version of CPL, the SD term and the FC/SD cross term cannot be evaluated separately. Either the sum of FC + SD + cross terms, or the FC term individually, are computed.

CPL is restartable after various time-consuming steps of the computation.

In ADF2009.01 the hybrid PBE0 functional can be used in combination with NMR spin-spin coupling calculations, see the documentation for the extra keys that are needed. However, other hybrid functionals and Hartree-Fock cannot or should not be used in combination with NMR spin-spin coupling calculations.

In ADF2009.01 the effects of a finite size of a nucleus on the spin-spin couplings can be calculated. A finite size of the nucleus can be set with the NUCLEARMODEL key in the input for the ADF calculation.

Bug fix in case more than 1 perturbing atom and DSO or PSO

In the ADF2006.01b version a bug in the CPL module is fixed that gave problems in ADF2006.01 and older versions. The problem in ADF2006.01 and older versions is: In case there is more than 1 perturbing atom and the DSO or PSO term is calculated, only the results of the spin-spin couplings for the first perturbing atom are correct, but the results of the other spin-spin couplings may be incorrect.

Input file for CPL: adf.rkf

In order to run the CPL code, you need the general ADF output file adf.rkf named TAPE21 being present in the directory where CPL is running. Alternatively, one can use the key ADFFile to point to an adf.rkf file. Most of the computation's specific settings will be taken from adf.rkf (TAPE21), such as the integration accuracy, the basis set, the density functional being employed, nuclear coordinates, and so on. *That also means that nearly all of the aspects that affect the quality of CPL's results are already determined in the input for the ADF run.* Five aspects are of particular importance here:

1. The numerical integration accuracy: the perturbation operators are large in the vicinity of the nuclei. Therefore, you have to make sure that the integration grid is fine enough in the atomic core regions.
2. The basis set: NSSCCs are sensitive chemical probes, and therefore flexible basis sets have to be employed in order to yield a valid description of the MOs that determine the NSSCCs. We have found that it is imperative to use at least a TZ2P basis set. Additional polarization functions in the valence shell may be necessary. Furthermore, the FC perturbation usually requires additional steep 1s functions (i.e. with exponents much higher than the nuclear charge) for a proper description. In the relativistic heavy element case, the use of additional steep basis functions as compared to the ZORA/TZ2P basis is mandatory. The use of steep functions is only of high importance for those nuclei, for which the NSSCC is to be evaluated. In ADF2017 specialized large all electron basis sets have been added in the directory \$AMSHOME/atomicdata/ADF/ZORA/TZ2P-J and \$AMSHOME/atomicdata/ADF/ZORA/QZ4P-J, suitable for NSSCCs, where steep basis functions have been added, which is especially important for the FC term. Previously in ADF2009.01 for a limited number of elements basis sets suitable for NSSCCs have been added to the ADF basis set directory, in the directory \$AMSHOME/atomicdata/ADF/ZORA/jcpl. These specialized basis sets are especially important for the heavy NMR nuclei. For the nuclei for which NSSCCs are to be evaluated, it is necessary to use all-electron basis sets. This is not a restriction due to the implementation, but we have found that, with the available frozen core basis sets, the flexibility of the basis in the vicinity of the nuclei is not sufficient. It is possible to use frozen core basis sets if you add enough basis functions in the core region such that the basis approaches the flexibility of at least a double-zeta all-electron basis there^{Page 240, 1}. In that sense, the savings in computational time due to usage of a frozen core basis are not as pronounced as in standard ADF computations. Unless reliable frozen-core basis sets for the NSSCC computation are available we strongly discourage the use of frozen core basis sets with the CPL program!
3. The finite size of a nucleus: typically, the isotropic J-couplings are reduced in magnitude by about 10 to 15 % for couplings between one of the heaviest NMR nuclei and a light atomic ligand, and even more so for couplings between two heavy atoms, see Ref.⁴. However, one should have really large basis sets with tight basis functions to observe this effect in calculations, see the previous point about basis sets. The TZ2P-J, QZ4P-J, and jcpl basis sets are suitable for finite nucleus calculations. A finite size of the molecule can be set in the ADF program with the key NUCLEARMODEL:

NuclearModel Gaussian

4. The density functional: the results of the CPL code depend mostly on the shape of the MOs that have been determined by ADF, and their orbital energies. Both, in turn, depend on the density functional or Kohn-Sham potential that has been chosen for the ADF run (and the basis set quality). It is difficult to give a general advice here concerning the NSSCCs. So far we have found that the use of GGAs improves the NSSCCs with respect to experiment in most cases in comparison to LDA. Different GGAs often yield very similar results. Further, in particular for those cases for which the OP term is large or even dominant, both standard LDAs and GGAs sometimes do not provide an accurate enough description of the orbitals, and deviation of the CPL results as compared to experiment can be substantial. Future developments of density functionals might be able to cure these problems. For the time being, we recommend that you base the CPL run on different choices of density functionals in the ADF run, and investigate the convergence of the result with respect to basis set and integration accuracy. Note that CPL itself uses the VWN functional by default to determine the first-order perturbed MOs. There are enough indications to believe that this is a reasonable approximation for NMR purposes. In ADF2009.01 the first-order potential of the PBE family of GGA functionals and the first-order potential of the hybrid PBE0 functional can be used. See

⁴ J. Autschbach, *Magnitude of Finite-Nucleus-Size Effects in Relativistic Density Functional Computations of Indirect NMR Nuclear Spin-Spin Coupling Constants*, *ChemPhysChem* 10, 2274 (2009) (<https://doi.org/10.1002/cphc.200900271>)

Refs.⁶⁷ for applications of such first-order potentials. However, other hybrid functionals and Hartree-Fock cannot or should not be used in combination with NMR spin-spin coupling calculations.

5. Modeling the experimental setup: computing such sensitive numbers as NMR chemical shifts and in particular NSSCCs can result in substantial deviations from experimental data. The simple reason might be that the isolated system that has been computed at zero temperature is not at all a good approximation to the system that has been studied experimentally. We⁸⁹ and other authors have found that in particular solvent effects can contribute very substantially to the NSSCC. In case you are comparing CPL results to experimental data obtained in strongly coordinating solvents we suggest that you consider solvent effects as a major influence. We have found that even weakly coordinating solvents can cause sizable effects on the NSSCCs for coordinatively unsaturated metal complexes. Other sources of errors can be the neglect of vibrational corrections to the NSSCCs (usually in the range of a few percent).

If the parameters of the underlying ADF computation are carefully chosen and the density functional is able to provide an accurate description of the molecule under investigation, it is possible to compute NSSCCs by means of DFT with very satisfactory accuracy (please note that for properties as sensitive as NSSCCs, agreement with experimental results within about 10% error can be regarded as quite good). Further, chemical trends will be correctly reproduced for a related series of molecules in most cases. However, due to the inherent approximate character of the density functionals currently available with ADF, and necessary basis set limitations, great care should be taken that the results are reliable. *CPL assumes Aufbau configurations. Please make sure that there are no empty orbitals with energies below the highest occupied MO (HOMO). In addition, the SYMMETRY NOSYM key has to be used in the ADF computation.*

Running CPL

Main input switches

With the ADF output TAPE21 present in the current working directory, the CPL code is invoked by:

```
$AMSBIN/cpl < input_file
```

where `input_file` contains the input for CPL. Best is supply also the TAPE10 of the ADF calculation in addition to TAPE21 (specify `SAVE TAPE10` in the ADF input file).

`input_file` must contain at least one block-type input key in order to start the CPL run. The input key is

```
$AMSBIN/cpl << eor
  NMRCOUPLING
  END
eor
```

This represents a minimal input file for CPL. The `NMRCOUPLING` key hosts all optional keys that are relevant for the NSSCCs themselves. In addition to the mandatory `NMRCOUPLING` key, CPL recognizes the following input switches:

```
$AMSBIN/cpl << eor
  ADFFile adffile
  TAPE10File tape10file
  ...
eor
```

⁶ J. Autschbach, *Two-component relativistic hybrid density functional computations of nuclear spin-spin coupling tensors using Slater-type basis sets and density-fitting techniques*, *Journal of Chemical Physics* 129, 094105 (2008) (<https://doi.org/10.1063/1.2969100>), Erratum: *Journal of Chemical Physics* 130, 209901 (2009) (<https://doi.org/10.1063/1.3131724>)

⁷ D.L. Bryce and J. Autschbach, *Relativistic hybrid density functional calculations of indirect nuclear spin-spin coupling tensors. Comparison with experiment for diatomic alkali metal halides*, *Canadian Journal of Chemistry* 87, 927 (2009) (<https://doi.org/10.1139/V09-040>)

⁸ J. Autschbach and T. Ziegler, *A Theoretical Investigation of the Remarkable Nuclear Spin-Spin Coupling Pattern in [(NC)₅Pt-Tl(CN)]⁻*, *Journal of the American Chemical Society* 123, 5320 (2001) (<https://doi.org/10.1021/ja003866d>)

⁹ J. Autschbach and T. Ziegler, *Solvent Effects on Heavy Atom Nuclear Spin-Spin Coupling Constants: A Theoretical Study of Hg,C and Pt,P Couplings*, *Journal of the American Chemical Society* 123, 3341 (2001) (<https://doi.org/10.1021/ja003481v>)

adffile is the path to an adf.rkf (TAPE21) file from which nmr reads data and to which nmr writes data. Default: TAPE21.
tape10file is the path to a TAPE10 file from which nmr reads data. Default: TAPE10.

```
$AMSBIN/cpl << eor
  GGA
  ...
eor
```

See the separate section for this key, which influences the first order potential that is used.

```
$AMSBIN/cpl << eor
  RESTART /full/path/to/restart_file
  ...
eor
```

Restart the computation from file restart_file (full pathname should be given). This is the TAPE13 produced during a CPL run. By default, TAPE13 is deleted after a successful completion of CPL. As with ADF restarts, you cannot use the name TAPE13 for restart_file but you have to rename it, e.g. to tape13.restart.

```
$AMSBIN/cpl << eor
  SAVE TAPE13
  ...
eor
```

Keep the restart file even after a successful completion of CPL. TAPE13 is currently the only file that is meaningful as a parameter to SAVE.

NMRCOUPLING subkeys

The available switches within a NMRCOUPLING/END block control the computation of the NSSCCs. By default, the program will evaluate the FC coupling contribution for the first nucleus being the perturbing nucleus and all remaining nuclei responding.

Please **note** that the ordering of atoms in CPL is generally different from the ADF input. The ordering of atoms is the one being stored in TAPE21 and it is grouped by fragment types. In case you are in doubt about the ordering of atoms, you can run CPL for a few seconds. It will print a list of atoms with their coordinates. The ordering is currently the same as required for the NMR program in the ADF program system. On the other hand, note that for the subkeys ATOMPert and ATOMRESP the number of the atoms refer to the input ordering in the ADF calculation. Curly brackets are not part of a key.

Available subkeys are:

```
$AMSBIN/cpl << eor
  NMRCOUPLING
    NUCLEI {npert nresp1 nresp2}
    ATOMPert {npert1 npert2 npert3}
    ATOMRESP {nresp1 nresp2 nresp3}
    GAMMA {nnuc gamma}
    DSO
    PSO
    SD
    FC
    SCF {ITERATIONS=25 | NOCYCLE | CONVERGE=1e-4 }
    XALPHA
    CONTRIBUTIONS {1E19} {LMO, SFO, LMO2, SFO2}
  END
  ...
eor
```

NUCLEI {npert nresp1 nresp2}

Use nucleus no. npert as the perturbing nucleus, and nuclei nresp1, nresp2, etc as responding nuclei. You can supply more than one NUCLEI keys, in which case CPL evaluates the first-order MOs for each perturbing nucleus that is specified and computes the NSSCCs between all specified responding nuclei. For each NUCLEI line in the input, CPL has to perform an SCF cycle. Note: for the numbers of the atoms the internal CPL numbering should be used.

ATOMPERT {npert1 npert2 npert3}

See next subkey ATOMRESP.

ATOMRESP {nresp1 nresp2 nresp3}

ATOMPERT: use nucleus no. npert1, npert2, etc. as the perturbing nuclei. ATOMRESP: use nucleus no. nresp1, nresp2, etc. as the responding nuclei. You can supply more than one ATOMPERT and (or) ATOMRESP key. CPL computes the NSSCCs for all pairs of combinations of perturbing atoms and responding atoms. For each perturbing atom CPL has to perform an SCF cycle, which is the expensive part in the calculation. Note: the numbers refer to the input ordering in the ADF calculation. Use the subkey NUCLEI to specify the nuclei according to the internal CPL numbers of the atoms.

GAMMA {nnuc gamma}

Input a non-default magneto-gyric ratio of $g = \gamma$ for nucleus no. nnuc, in units of rad/(T s). Note that one should include the typical 10^7 factor. CPL normally uses the g value of the most abundant NMR active isotope for a nucleus of a given charge by default. With the GAMMA keyword you can override this value or supply a value if CPL does not know about it. A list of g 's that is used in the computation is printed in the output. You have to provide the GAMMA key for each nucleus you want to specify.

DSO

Compute the diamagnetic orbital term for each NSSCC that is requested (not default)

PSO

Compute the paramagnetic orbital term for each NSSCC (not default)

SD

Compute the SD term for each NSSCC. This is only default for spin-orbit ADF runs. The output will contain the sum of the FC and SD contributions. *Please note that requesting this option results in a greatly increased computational cost in scalar or non-relativistic runs.* The option NOSD will turn the SD computation off in spin-orbit runs and has no effect otherwise.

FC

Compute the FC contribution to the NSSCCs. This is the default option. Please note that it is currently not possible to compute the SD term without the FC term. Consult the 'practical aspects' section for instructions how to estimate the FC/SD cross term. The option NOFC will disable both the FC and SD computation.

SCF {ITERATIONS=25 | NOCYCLE | CONVERGE=1e-4 }

Settings related to the SCF cycle that is carried out by CPL. Valid options are (with default values if applicable):

ITERATIONS 25

maximum number of iterations

NOCYCLE

perform no cycle, equivalent to ITERATIONS 0

CONVERGE 1e-4

convergence criterion, an input of e corresponds approximately to a convergence of $\log(-e)$ digits, i.e. the results will be converged to about four significant digits by default. The measurement for the convergence is based on the sum S of the magnitudes of all occupied-virtual matrix elements of the induced first-order exchange potential. Note that the actual convergence criterion being used in the computation is e times S of the first cycle, i.e. the convergence criterion is set relative to the initial value of S .

XALPHA

Use first-order Xalpha potential instead of VWN potential (default). This will usually decrease the accuracy for

couplings involving hydrogen, and does not have a large effect for couplings between heavier nuclei (not default). The key is mainly intended to ensure compatibility with our previously published results.

CONTRIBUTIONS {1e19} {LMO, SFO, LMO2, SFO2}

Print contributions from individual orbitals to the FC and OP term of the NSSCCs that are larger in magnitude than a certain threshold. The threshold refers to the reduced coupling constant K in SI units (not default). Additionally, an analysis in terms of Boys localized MOs (see User's Guide and SFOs. At present, either each key LMO, SFO, LMO2, SFO2 can be used individually, or grouped as {LMO, SFO2} or {SFO2, LMO}. If you need all analyses or different combinations, it is recommended to restart the CPL calculation from TAPE13, and to specify 0 iterations in the SCF. This way, the only additional computational cost should be the analysis itself.

The equation and an application for the analyses due to the LMO and SFO keys is described in Refs.¹⁴¹⁵. The other analysis is based on the same equation as in Ref.⁵. For an NBO analysis of the spin-spin couplings, see the [section on NBO analysis](#) (page 311).

In order for the LMO-based analyses to work, the MO → LMO transformation matrix needs to be stored on TAPE21. In the ADF input, you can achieve this with the option "STORE" to the LOCORB key, i.e.

```
LOCORB STORE
... options
END
```

GGA key

```
$AMSBIN/cpl << eor
GGA
...
eor
```

GGA

Use first-order GGA potential instead of the first-order VWN potential. Should only be used for the PBE family of GGA exchange-correlation functionals and for the hybrid functional PBE0. See Refs.^{Page 244, 6Page 244, 7} for applications of calculating spin-spin couplings with PBE0. However, other hybrid functionals and Hartree-Fock cannot or should not be used in combination with this key GGA. For consistency reasons of the first-order potential one should use the keyword USESPCODE in the ADF calculation. An example input for ADF for the hybrid PBE0 would then contain:

```
USESPCODE
XC
hybrid PBE0
End
```

¹⁴ J. Autschbach, C.D. Igna, T. Ziegler, *A theoretical investigation of the apparently irregular behavior of Pt-Pt spin-spin coupling constants* *Journal of the American Chemical Society* 125, 1028 (2003) (<https://doi.org/10.1021/ja027931q>)

¹⁵ B.L. Guennic, K. Matsumoto, J. Autschbach, *On the NMR properties of platinum thallium bonded complexes: Analysis of relativistic density functional theory results*, *Magnetic Resonance in Chemistry* 42, S99 (2004) (<https://doi.org/10.1002/mrc.1450>)

⁵ J. Khandogin, T. Ziegler, *A density functional study of nuclear magnetic resonance spin-spin coupling constants in transition metal systems*, *Spectrochimica Acta Part A* 55, 607 (1999) ([https://doi.org/10.1016/S1386-1425\(98\)00265-0](https://doi.org/10.1016/S1386-1425(98)00265-0))

Practical Aspects

Minimal input

The default settings for CPL are invoked by the simple minimal content of the input file:

```
$AMSBIN/cpl << eor
  NMRCOUPLING
  END
eor
```

This is equivalent to

```
$AMSBIN/cpl << eor
  NMRCOUPLING
  NUCLEI 1 2 3 4 5 6 7 8 ..(up to number of atoms)
  SCF CONVERGE 1e-4 ITERATIONS 25
  FC
  END
eor
```

Restarts

CPL is restartable after the computation of each the complete set of FC or FC/SD and OP matrix elements, and after their transformation to the MO basis. Further, in spin-orbit runs or in scalar- or non-relativistic computations involving the SD term, CPL is restartable after each SCF cycle. As with ADF restarts, you need to supply a proper input file for a restarted computation, and the restart file TAPE13 (which needs to be renamed). Changing the input of a calculation for a restart is not supported. In restarted runs, the program will automatically continue at the latest possible point before the execution stopped, and changing the input between restarts can cause inconsistencies that may lead to a crash.

Unless you are computing a very large molecule, the most likely need for a restart will probably occur during a computation of the FC/SD SCF cycle. We have already mentioned that this is a very time consuming part of the computation, and for this reason CPL can be restarted after each completed SCF cycle. The convergence of the results should not be affected by a restart. You can, e.g., use this in order to complete a lengthy CPL computation in case you have tight time limits in your queuing system, or after a power loss.

How to avoid the unnecessary computation of many SCF cycles

As already mentioned, once the first-order MOs with respect to the perturbation by one of the nuclear spins have been determined, the NSSCC between this and all other nuclei can be computed rather quickly. For each nucleus that participates in at least one of the coupling constants to be determined, the matrix elements of the FC, SD, and OP operators have to be evaluated once (unless the computation of the respective terms is disabled).

You can use this information in order to minimize the number of nuclei for which an SCF cycle has to be performed. This can lead to a great speedup of the computation. The final result, the NSSCC between A and B, does not depend on which nucleus has been chosen as the ‘perturbing’ one, and which as the ‘responding’ one (convergence has to be good enough, though). Suppose you want to compute the NSSCCs in the water molecule, with O being nucleus no. 1. In that case,

```
NUCLEI 1 2 3
NUCLEI 2 3
```

yields the same O-H and H-H coupling constants as the input

```
NUCLEI 2 1
NUCLEI 1 3
NUCLEI 3 2
```

but with less computational effort due to the fact that only 2 instead of 3 SCF cycles will be performed. The example chosen here is trivial, but in other cases it can be worthwhile to consider different sequences of computations.

Alternatively you can use the ATOMPert and ATOMRESP subkeys:

```
ATOMPert 1 2
ATOMRESP 2 3
```

which will calculate the spin-spin coupling of the nuclei 1-2, 1-3, and 2-3 (skips 2-2, since the nuclei are the same), which are the same O-H and H-H couplings as before.

Note: The numbers of the nuclei for the subkeys ATOMPert and ATOMRESP refer to the input ordering in the ADF calculation, whereas the numbers of the nuclei for the subkey NUCLEI refer to the internal CPL numbers of the atoms.

Computing individual terms in the coupling tensor

As we have mentioned before, the FC, OP and OD terms can be calculated individually, but not the SD term. In case the SD input option is given, the FC+SD contribution is evaluated instead. This is NOT equal to the sum of the individual FC and SD contributions since there is a cross term between these two. Due to computational simplicity and efficiency, CPL evaluates either the matrix elements for the FC operator, or the combined ones for FC+SD. The final result therefore contains either FC only, or FC, SD plus the cross terms. Only the latter, in addition to the OP and OD contributions, should be compared to experimental results. We will implement the computation of the individual SD term in a future version of CPL in order to assist the analysis of the CPL results.

Likewise, in a spin-orbit based relativistic computation, there exists a cross term between the spin-dependent FC and SD terms, and the OP term. In the scalar- or non-relativistic limit, this contribution is always zero. With the PSO option present, CPL computes the FC, SD and OP terms including all cross contributions. Even though the output suggests that the individual OP and FC+SD terms are printed, they contain additional cross terms if spin-orbit coupling is large. You can run CPL with the options

```
$AMSBIN/cpl << eor
  NMRCOUPPING
  NOFC
  NOSD
  PSO
END
...
eor
```

in order to evaluate the individual OP contribution(s). In a second run, you can then compute just the FC+SD contributions. The differences between these two CPL runs and a third one with all three terms present yields the relativistic (FC+SD)/OP cross term.

Two-bond and more-bond couplings

CPL does not discriminate between one-bond and two-bond couplings etc. in any technical sense. Even though we^{Page 240, 1Page 240, 2Page 244, 8Page 244, 9} have validated the code mostly for one-bond NSSCCs, the coupling between any pair of nuclei in the molecule can be computed. See Ref.^{Page 244, 8} for an example.

Principal axis system, the whole coupling tensor

CPL evaluates the complete 3x3 coupling tensor with respect to the Cartesian input coordinate system. Depending on the orientation of the molecule, and the local symmetry, the coupling tensor has in fact often only a small number of independent components. CPL evaluates the ‘principal components’ by the following procedure: the 3x3 matrix is transformed into the basis of the eigenvectors of its symmetric part. This diagonalizes the symmetric part of the coupling tensor. A set of eigenvectors (= ‘principal axis system’) is also printed.

Main references^{Page 240, 1Page 240, 2Page 244, 9Page 244, 8Page 243, 4Page 244, 6Page 244, 7Page 241, 3}.

See also refs. ¹⁰¹¹Page 247, 51213.

7.9 ESR/EPR

The EPR (ESR) g-tensor, hyperfine interaction (A-tensor), nuclear quadrupole interaction (Q-tensor), and zero-field splitting (ZFS, D-tensor) can be calculated. Effects due to spin-orbit coupling can be included. All-electron basis sets can be used.

7.9.1 ESR/EPR g-tensor and A-tensor

A-tensor, no spin-orbit coupling

```
$AMSBIN/ams << eor
...
Engine ADF
  ESR
  END
  SpinPolarization spinpolarization
  unrestricted Yes
  {Relativity
    level scalar
    formalism ZORA
  End}
  {NUCLEARMODEL gaussian}
  ...
EndEngine
eor
```

If spin-orbit coupling is neglected, the spin in the effective spin Hamiltonian, which is commonly used for the interpretation of ESR experiments, is the real electronic spin of the paramagnetic molecule. In the spin-unrestricted DFT calculations one then uses eigenfunctions of S_z . The A-tensor can then simply be calculated as the expectation value of the corresponding operator; see Ref.³.

The A-tensor will be calculated for all nuclei. Terms due to the spin-polarization density at the nucleus are included in the evaluation of the A-tensor. For an accurate evaluation of the spin-polarization density at the nucleus it is important to use an all-electron basis set for the nuclei that one is interested in, avoiding the frozen core approximation. For heavy elements the incorporation of a Gaussian finite nucleus model can be important. However, one should have really large basis sets with tight basis functions to observe this effect in calculations. One possibility is to use the \$AMSHOME/atomicdata/ADF/ZORA/QZ4P basis set, although even this large basis set is not large enough sometimes. The basis sets in the directories ZORA/TZ2P-J, ZORA/Z4P-J, and ZORA/jcpl are suitable for finite nucleus calculations.

In case one uses a finite nuclear model for the charge distribution, starting from ADF2013 ADF also uses a finite distribution of the nuclear magnetic dipole moment for the calculation of the A-tensor.

A-tensor, perturbative inclusion spin-orbit coupling

¹⁰ N.F. Ramsey, *Electron Coupled Interactions between Nuclear Spins in Molecules*, *Physical Review* 91, 303 (1953) (<https://doi.org/10.1103/PhysRev.91.303>)

¹¹ R.M. Dickson, T. Ziegler, *NMR Spin-Spin Coupling Constants from Density Functional Theory with Slater-Type Basis Functions*, *Journal of Physical Chemistry* 100, 5286 (1996) (<https://doi.org/10.1021/jp951930l>)

¹² D.L. Bryce, R. Wasylishen, *Indirect Nuclear Spin-Spin Coupling Tensors in Diatomic Molecules: A Comparison of Results Obtained by Experiment and First Principles Calculations*, *Journal of the American Chemical Society* 122, 3197 (2000) (<https://doi.org/10.1021/ja9942134>)

¹³ G. Schreckenbach, S.K. Wolff, T. Ziegler, *Covering the Entire Periodic Table: Relativistic Density Functional Calculations of NMR Chemical Shifts in Diamagnetic Actinide Compounds*, in *Modeling NMR chemical shifts*, ACS Symposium Series, Vol 732, J.C. Facelli, A.C. de Dios, Editors (American Chemical Society, Washington DC, 1999), Chapter 7 (<https://doi.org/10.1021/bk-1999-0732.ch007>)

³ E. van Lenthe, A. van der Avoird and P.E.S. Wormer, *Density functional calculations of molecular hyperfine interactions in the zero order regular approximation for relativistic effects*, *Journal of Chemical Physics* 108, 4783 (1998) (<https://doi.org/10.1063/1.475889>)


```

$AMSBIN/ams << eor
...
Engine ADF
  SpinPolarization spinpolarization
  unrestricted Yes
  Relativity
    Level Scalar
    Formalism ZORA
  End
  Symmetry NOSYM
  ...
EndEngine
eor

$AMSBIN/cpl << eor
adffile ams.results/adf.rkf
hyperfine
  atoms 1 2 :: calculates A-tensor for atom 1 and 2, input order
  SCF Converge=1e-7 {Iterations=25}
end
...
eor

```

The calculation of A-tensors is implemented in the CPL program as a second derivative property (spin-orbit coupling and nuclear magnetic field as perturbation) within the two-component relativistic zeroth-order regular approximation (ZORA), see Ref.⁴. This implementation allows for hybrid (only PBE0) DFT calculations, but not meta-GGAs and not meta-hybrids.

Note that the CPKS convergence in CPL has to be set tightly (1e-7 or 1e-8) to get converged PSOSO terms for the A-tensor. For hyperfine calculations the default value is 1e-7.

g-tensor, perturbative inclusion spin-orbit coupling

```

$AMSBIN/ams << eor
...
Engine ADF
  SpinPolarization spinpolarization
  unrestricted Yes
  Relativity
    level scalar
    formalism ZORA
  End
  Symmetry NOSYM
  ...
EndEngine
eor

$AMSBIN/nmr << eor
adffile ams.results/adf.rkf
nmr
  gfactors
  ulk best
  calc all
  out iso tens

```

(continues on next page)

⁴J. Autschbach, S. Patchkovskii, and B. Pritchard, *Calculation of Hyperfine Tensors and Paramagnetic NMR Shifts Using the Relativistic Zeroth-Order Regular Approximation and Density Functional Theory*, *Journal of Chemical Theory and Computation* 7, 2175 (2011) (<https://doi.org/10.1021/ct200143w>)

(continued from previous page)

```
end
end input
eor
```

The calculation of g-tensors is implemented in the NMR program as a second derivative property (spin-orbit coupling and external magnetic field as perturbation) within the two-component relativistic zeroth-order regular approximation (ZORA), see Ref.⁵. This implementation allows for hybrid (B3LYP, PBE0, etc.) DFT calculations, but not meta-GGAs and not meta-hybrids. This implementation requires the use of all-electron basis sets.

For an older implementation of this method, see Refs.¹²⁸⁹.

g-tensor and A-tensor, self-consistent spin-orbit coupling

```
$AMSBIN/ams << eor
...
Engine ADF
  ESR
  END
  unrestricted Yes
  Relativity
    Level Spin-Orbit
    Formalism ZORA
    SpinOrbitMagnetization Collinear
  End
  Symmetry NOSYM
eor
```

In a spin-orbit coupled spin-unrestricted relativistic ZORA calculation and the ESR block key, the g-tensor and the nuclear magnetic dipole hyperfine interaction (A-tensor) will be calculated, see also Refs.³¹⁰. In such a calculation degenerate perturbation theory is used with the external magnetic field or nuclear magnetic field as perturbation. The calculation must use the collinear approximation, and symmetry must be NOSYM. This implementation does allow for meta-GGA and (meta-)hybrid DFT calculations, but then GIAOs are not used. There may be more than one unpaired electron. Terms due to the spin-polarization density at the nucleus are included in the evaluation of the A-tensor. However, one cannot set the number of unpaired electrons; the 'spinpolarization' argument of the key CHARGE will be ignored.

In the spin-unrestricted self-consistent spin-orbit coupled method for the calculation of g- and A-tensors implemented in ADF it is assumed that the solutions of the Kohn-Sham equations with a global magnetization direction (collinear approximation) in a certain direction are also eigenfunctions of the effective spin (present in the effective spin Hamiltonian) in that same direction. In practice this means that three self-consistent spin-orbit coupled calculations are performed with the collinear approximation in the x-, y-, and z-direction. The results of these three calculations are combined to calculate the g- and A-tensors.

Note: in a spin-orbit coupled spin-restricted relativistic ZORA calculation and the ESR block key, ADF will also calculate and print the nuclear magnetic dipole hyperfine interaction, but the terms due to the spin-polarization density at the nucleus are absent. Furthermore, if there is more than one unpaired electron, the computed results will simply be incorrect,

⁵ J. Autschbach and B. Pritchard, *Calculation of molecular g-tensors using the zeroth-order regular approximation and density functional theory: expectation value versus linear response approaches*, *Theoretical Chemistry Accounts* 129, 453 (2011) (<https://doi.org/10.1007/s00214-010-0880-x>)

¹ G. Schreckenbach and T. Ziegler, *Calculation of the G-tensor of electron paramagnetic resonance spectroscopy using Gauge-Including Atomic Orbitals and Density Functional Theory*, *Journal of Physical Chemistry A* 101, 3388 (1997) (<https://doi.org/10.1021/jp963060t>)

² S. Patchkovskii and T. Ziegler, *Calculation of the EPR g-Tensors of High-Spin Radicals with Density Functional Theory*, *Journal of Physical Chemistry A* 105, 5490 (2001) (<https://doi.org/10.1021/jp010457a>)

⁸ S. Patchkovskii and G. Schreckenbach in *Calculation of NMR and EPR parameters*, ISBN13: 9783527307791, M. Kaupp, M. Bühl, V.G. Malkin, Editors, (Wiley, Weinheim, 2004).

⁹ S. Patchkovskii, R.S. Strong, C.J. Pickard and S. Un, *Gauge invariance of the spin-other-orbit contribution to the g-tensors of electron paramagnetic resonance*, *Journal of Chemical Physics* 122, 214101 (2005) (<https://doi.org/10.1063/1.1917840>)

¹⁰ E. van Lenthe, A. van der Avoird and P.E.S. Wormer, *Density functional calculations of molecular g-tensors in the zero order regular approximation for relativistic effects*, *Journal of Chemical Physics* 107, 2488 (1997) (<https://doi.org/10.1063/1.474590>)

without any warning from the program. On the other hand, in case of one unpaired electron and very large effects of spin-orbit coupling, the spin-restricted calculation may be of interest, since it uses Kramers' symmetry exactly.

7.9.2 ESR/EPR Q-tensor

For the calculation of the ESR Q-tensor see the key [QTENS](#) (page 254).

7.9.3 ESR/EPR Zero-field splitting (D-tensor)

With the keyword ZFS the zero-field splitting (ZFS) of the ground state can be calculated.

```
ZFS
{HARTREEFOCK}
```

Zero-field splitting is the breaking of degeneracies of the ground state that is not described by a standard non-relativistic Hamiltonian. ZFS as calculated by ADF is that exhibited by molecules whose ground state has spin $S > 1/2$ and no spatial degeneracy. This type of ZFS has two contributions, second-order spin-orbit coupling and direct electron spin-spin coupling. The calculation of ZFS with DFT is described in Ref.^{6,7,11,12}. With the keyword ZFS the spin-orbit coupling term is included. If one also wants to calculate the direct electron spin-spin term, one has to include the key HARTREEFOCK, which calculates the Coulomb and (Hartree-Fock like) exchange contributions to the direct electron spin-spin term. In the spin-orbit coupling term no Hartree-Fock like exchange contributions are included.

```
HARTREEFOCK
```

ZFS can be calculated in combination with LDA and GGAs but not hybrid or meta-GGA functionals. In order to calculate ZFS, TheRelativity -> level should be set to Scalar and Relativity -> Formalism to ZORA (these are the default values).

Just the simple keyword ZFS is needed in order to calculate zero-field splitting. Several optional additional keywords can also be included. The complete list is:

```
ZFS {PEDERSON|NEESE} {ANALYSIS|FULLANALYSIS}
```

PEDERSON | NEESE

PEDERSON: The available approaches for calculating ZFS with DFT each differ subtly from the others. We believe that the method proposed by van Wüllen and coworkers^{Page 253, 11 12} is the most theoretically complete but it may be that for certain systems the other approaches are more accurate. The van Wüllen formulation is the default but if the PEDERSON keyword is included then the equation proposed by Pederson and Khanna⁶ is used. NEESE: If the NEESE keyword is included then the equation for ZFS proposed by Neese⁷ is used.

ANALYSIS | FULLANALYSIS

ANALYSIS: Neese has presented some interesting analyses of ZFS⁷. If the ANALYSIS keyword is invoked then the contributions to the ZFS are divided into terms from alpha-beta, alpha-alpha, beta-beta and beta-alpha one-electron excitations. FULLANALYSIS: The output requested by the ANALYSIS keyword is further extended to analyze each of the alpha-beta, alpha-alpha, beta-beta and beta-alpha contributions in terms of the individual one-electron excitations.

⁶ M.R. Pederson, S.N. Khanna, *Magnetic anisotropy barrier for spin tunneling in Mn₁₂ O₁₂ molecules*, Physical Review B 60, 9566 (1999) (<https://doi.org/10.1103/PhysRevB.60.9566>)

⁷ F. Neese, *Calculation of the zero-field splitting tensor on the basis of hybrid density functional and Hartree-Fock theory*, Journal of Chemical Physics 127, 164112 (2007) (<https://doi.org/10.1063/1.2772857>)

¹¹ C. van Wüllen, *Magnetic anisotropy from density functional calculations. Comparison of different approaches: Mn₁₂ O₁₂ acetate as a test case*, Journal of Chemical Physics 130, 194109 (2009) (<https://doi.org/10.1063/1.3134430>)

¹² S. Schmitt, P. Jost, C. van Wüllen, *Zero-field splittings from density functional calculations: Analysis and improvement of known methods*, Journal of Chemical Physics 134, 194113 (2011) (<https://doi.org/10.1063/1.3590362>)

7.10 Nuclear Quadrupole Interaction (EFG)

QTENS

This key activates the computation of the Nuclear Electric Quadrupole Hyperfine interaction. It can be applied to open-shell and to closed-shell systems. QTENS gives you the Nuclear Electric Quadrupole Hyperfine interaction (Q-tensor)¹. The latter is directly related to the Electric Field Gradient (EFG). The Q-tensor elements (in MHz) equal the electric field gradient tensor elements (in a.u.) times 234.9647 times the nuclear quadrupole moment (NQM in barn units, 1 barn = 10⁻²⁸m² = 10⁻²⁴cm²) and divided by 2I(2I-1), where I is the nuclear spin. The Nuclear Quadrupole Coupling Constant (NQCC) (in MHz) is the largest value of the principal values of the EFG (in a.u.) times 234.9647 times the nuclear quadrupole moment (in barn units). The electric field gradient tensor is printed next to the Q-tensor.

In the case of ZORA the program will calculate the EFG in the so-called ZORA-4 approximation, which includes a small component density ("picture-change correction"), see [Page 254, 1](#). If you also want to calculate the EFG using the ZORA density, thus in the Foldy-Wouthuysen picture, include the keywords:

PRINT FWPICTURE

In case QTENS is used for ⁵⁷Fe, ¹¹⁹Sn, ¹²⁵Te, ¹⁹³Ir, and ¹⁹⁷Au, quadrupole splittings are written in units of mm/s, used in Mössbauer spectroscopy.

Analysis of the EFG

With the EFG keyword in AOResponse a Mulliken-type analysis of the EFG principal components, and an analysis in terms of canonical MOs, can be performed. Required is symmetry NOSYM. This is not implemented in case of spin-orbit coupling. For an NBO analysis of the EFG, see the [section on NBO analysis](#) (page 311). For an explanation of the output and a general usage tutorial, see². Further references and recommended citations, see³.

```
Symmetry NOSYM
Aoresponse
  efg NUC
end
```

efg NUC

Here NUC is the number of the nucleus at which the EFG is to be computed (ADF internal atom ordering). Available for one nucleus at a time.

7.11 Mössbauer spectroscopy

Isomer shifts

By default the electron density at the nuclei is calculated; no input key is required. In the implementation in ADF, the electron density is not calculated exactly at the center of the nucleus, however, at points on a small sphere around the center of a nucleus. The printed electron density in the output of ADF is the average electron density on these points. The radius of the sphere is an approximated finite nuclear radius. The electron density at the nuclei could be used for the interpretation of isomer shifts in Mössbauer spectroscopy. Typically one needs to perform a fit of the experimentally measured isomer shifts and calculated electron densities, for example as done in Ref.¹.

¹ E. van Lenthe and E.J. Baerends, *Density functional calculations of nuclear quadrupole coupling constants in the zero-order regular approximation for relativistic effects*, *Journal of Chemical Physics* 112, 8279 (2000) (<https://doi.org/10.1063/1.481433>)

² J. Autschbach, S. Zheng, and R.W. Schurko, *Analysis of Electric Field Gradient Tensors at Quadrupolar Nuclei in Common Structural Motifs*, *Concepts in Magnetic Resonance Part A* 36A, 84 (2010) (<https://doi.org/10.1002/cmr.a.20155>)

³ A.J. Rossini, R.W. Mills, G.A. Briscoe, E.L. Norton, S.J. Geier, I. Hung, S. Zheng, J. Autschbach, and R.W. Schurko, *Solid-State Chlorine NMR of Group IV Transition Metal Organometallic Complexes*, *Journal of the American Chemical Society* 131, 3317 (2009) (<https://doi.org/10.1021/ja808390a>)

¹ W.-G. Han, T. Liu, T. Lovell and L. Noodleman, *DFT calculations of ⁵⁷Fe Mössbauer isomer shifts and quadrupole splittings for iron complexes in polar dielectric media: Applications to methane monooxygenase and ribonucleotide reductase*, *Journal of Computational Chemistry* 27, 1292 (2006)

One should use all-electron basis sets for the Mössbauer active elements. It is important to use the same basis set, same exchange-correlation functional, same integration accuracy, and same nuclear model (see key [NUCLEARMODEL](#)) if electron densities at nuclei in different molecules are compared. Note that the absolute electron density at a nucleus heavily depends on the accuracy of the basis set in the core region of this nucleus, especially if relativistic effects are included.

In case of ZORA the electron density at the nuclei is calculated with the ZORA-4 method, which includes a small component density. Previously it was using the ZORA density, which does not include a small component density. If you also want to calculate this ZORA density at the nuclei, include the keywords:

```
PRINT FWPICTURE
```

Instead of SAPA (the Sum of neutral Atomic potential Approximation) MAPA is used by default for ZORA in ADF2017. The MAPA (the Minimum of neutral Atomic potential Approximation) at a point is the minimum of the neutral atomic potentials at that point. The advantage of MAPA over SAPA is that the gauge dependence of ZORA is reduced. The ZORA gauge dependency is small for almost all properties, except for the electron density very close to a heavy nucleus.

A ZORA calculation gives a too large density at the nucleus compared to a relativistic Dirac calculation, mostly due to the 1s-orbital. If one performs a fit of the experimentally measured isomer shifts against calculated electron densities, the fact that the ZORA electron density is too large is not so important. If an absolute value of the electron density at the nucleus is important one may use the relativistic X2C method; see key [RELATIVITY](#) (page 106). Note that one then needs large basis sets with tight STO 1s-functions to get accurate results (for example the basis sets in the TZ2P-J or QZ4P-J directory).

Quadrupole splittings

For the calculation of Mössbauer quadrupole splittings see the key [QTENS](#) (page 254).

Nuclear resonance vibrational spectroscopy (NRVS)

The nuclear resonance vibrational spectroscopy (NRVS) experiment can be thought of as Mössbauer spectroscopy with vibrational sidebands. The NRVS experiment provides the complete set of bands corresponding to modes that involve motion of the Mössbauer active atoms. In order to calculate this with the ADF program a partial vibrational density of states (PVDOS) has been implemented. A PVDOS factor for a given atom is the ratio of this atom's nuclear kinetic (vibrational) energy to the total vibrational energy of all nuclei, for a given mode. PVDOS factors for every atom and every mode are written to adf.rkf if [IR Frequencies](#) (page 169) are calculated. To visualize the calculated PVDOS with the AMS-GUI use AMSspectra: select the PVDOS spectrum type. Next select one or more atoms to get the PVDOS spectrum generated by the selected atoms. This is useful for analysis of NRVS spectra in bioinorganic chemistry for NRVS-active nuclei.

7.12 GW

7.12.1 General

Warning: In AMS2023.102 (or bug-fixed AMS2023 binary with r112249 or higher) a bug was fixed in ADF regarding GW. An incorrect Fermi energy was used. This is especially important in case the Fermi energy is not close to zero.

This page describes the basic procedure, usage, and scope of a GW calculation. Technical details of the algorithm can be tweaked in the [MBPT input block](#) (page 387). In AMS2020, G_0W_0 is implemented. In AMS2021, evGW and evGW₀ are implemented. In AMS2022, qsGW, qsGW₀, and G3W2 are implemented. In AMS2023, GW (G_0W_0 , evGW, evGW₀, qsGW, qsGW₀, and G3W2) with spin-orbit coupling is implemented.

(<https://doi.org/10.1002/jcc.20402>)

See also:

Tutorial: Accurate Ionization Potential and Electron Affinity with GW

Examples GW (page 1022)

The GW method is a relatively accurate method to obtain information about so-called charged excitations, or single-particle excitations. We refer to them as quasiparticle energies. These are especially important to interpret and predict the outcome of direct and inverse photo-emission spectroscopy and can be used to obtain, for example, very accurate ionization potentials and electron affinities which give access to the so-called fundamental gap (not to be confused with the optical gap).

GW can be used with scalar and spin-orbit coupled relativistic effects within the ZORA, X2C, or RA-X2C formalism.

In practice, fully self-consistent GW is rarely used for molecular systems. Instead, perturbative approximations, so-called quasiparticle GW methods are used since they are cheaper and also more accurate than fully self-consistent GW. The most popular approach is G_0W_0 ¹, in which quasiparticle energies are obtained as a one-shot perturbative correction to KS eigenvalues. A downside of this approach is the rather pronounced starting-point dependence. This can be overcome to a large extent in eigenvalue-only self-consistent GW (evGW), in which the quasiparticle energies (but not the density) are iteratively updated until self-consistency is reached. In quasiparticle self-consistent GW, also the density is updated in each iteration, so that the results become completely starting-point independent. The partially self-consistent GW variants usually converge within 6-12 iterations, which makes these approaches a factor of 6-12 more expensive than G_0W_0 .

A GW calculation as implemented in ADF proceeds in five steps as has been described in detail in a series of papers.^{Page 256, 156} The technique is also known as the GW space-time method. Our implementation is closely related to the scheme outlined in⁴. A GW implementation in ADF for closed-shell molecules that includes spin-orbit coupling is described in Ref.¹⁴.

- A DFT single-point calculation is performed. This can be an LDA, GGA, or hybrid calculation. At the moment, ADF does not support the use of XCfun, but LibXC is supported. Valid choices could be LDA, PBE, BLYP, PBE0, BHandHLYP, and many more. The default is LDA. As usual, the functional to be used during the SCF is requested in the *XC input block* (page 80) block. The following requests a G_0W_0 calculation with default settings using a PBE reference:

```
XC
  GGA PBE
END

GW
End
```

- From the KS orbitals and orbital energies, a Green's function (G) is evaluated and from the Green's function, the so-called independent-particle polarizability is calculated. This is done in imaginary time.
- The polarizability is Fourier transformed to the imaginary frequency axis where the screened Coulomb potential (W) is evaluated using the Coulomb potential and the polarizability.
- The screened Coulomb potential is Fourier transformed to imaginary time. Here, the self-energy is calculated using G and W (that's why it is called GW), which gives access to spectroscopic properties.

¹ Arno Förster, Lucas Visscher, *Low-order scaling G0W0 by pair atomic density fitting*, Journal of Chemical Theory and Computation 16 (12), 7381–7399 (2020) (<https://doi.org/10.1021/acs.jctc.0c00693>)

⁵ Arno Förster, Lucas Visscher, *GW100: A Slater-Type Orbital Perspective*, Journal of Chemical Theory and Computation 17 (8), 5080–5097 (2021) (<https://doi.org/10.1021/acs.jctc.1c00308>)

⁶ Arno Förster, Lucas Visscher, *Low-Order Scaling Quasiparticle Self-Consistent GW for Molecules*, Frontiers in Chemistry 9, 736591 (2021) (<https://doi.org/10.3389/fchem.2021.736591>)

⁴ J. Wilhelm, D. Golze, L. Talirz, J. Hutter, C.A. Pignedoli, *Toward GW Calculations on Thousands of Atoms*, Journal of Physical Chemistry Letters 9 (2), 306–312 (2012) (<https://doi.org/10.1021/acs.jpclett.7b02740>)

¹⁴ A. Förster, E. van Lenthe, E. Spadetto, L. Visscher, *Two-Component GW Calculations: Cubic Scaling Implementation and Comparison of Vertex-Corrected and Partially Self-Consistent GW Variants*, Journal of Chemical Theory and Computation 19, 5958 (2023) (<https://doi.org/10.1021/acs.jctc.3c00512>)

- The self-energy is transformed to the molecular orbital basis from where it is Fourier transformed to the imaginary frequency axis from where it is analytically continued to the complex plane. Along the real frequency axis, the quasiparticle energies are evaluated.
- In case of evGW (evGW₀), the input KS eigenvalues are replaced by the quasiparticle energies from the previous iteration and the scheme is iterated until self-consistency in the quasiparticle energies is reached.
- In case of qsGW (qsGW₀), a non-local, Hermitian, and static exchange-correlation potential is constructed from the self-energy. This exchange-correlation potential replaces the KS exchange-correlation potential. Diagonalization gives a new set of single-particle orbitals and quasiparticle energies. The procedure is repeated until self-consistency is reached.
- By default, the DIIS algorithm is used to accelerate and stabilize convergence of the self-consistent GW schemes. A linear-mixing scheme can also be used.

The GW space-time method has the distinct advantage that it can be very fast, while a full frequency, conventional GW calculation scales to the 6th power of the system size and is prohibitive for systems larger than a few tens of atoms. ADF uses advanced density fitting options to accelerate the space-time method further and in practice nearly quadratic scaling can be reached. This enables the routine application of the method to systems of several hundreds of atoms. A G_0W_0 calculation (without the preceding SCF) is usually not much slower than a hybrid calculation. The downside of the approach is that the analytical continuation technique produces large errors (up to several eV) for core states which are, for example, important in X-ray spectroscopy. Thus, the GW implementation in ADF should only be used to predict quasiparticle energies for states in the valence region. In fact, we have only tested it for HOMO and LUMO states (which are arguably most important).

The states of interest can be requested in the GW block:

```
GW
  nStates 5
End
```

This is the default and calculates five occupied and five unoccupied states.

```
GW
  nStates 1
End
```

calculates the HOMO and LUMO quasiparticle energy only.

7.12.2 Levels of self-consistency

Eigenvalue-only self-consistent GW

An evGW calculation is requested by

```
GW
  SelfConsistency evGW
End
```

One can also only iterate G by keeping W fixed, which reduces the cost of each iteration by roughly 50 %. This is requested by

```
GW
  SelfConsistency evGW0
End
```


On the other hand, much of the starting-point dependence of the G_0W_0 method remains in the $evGW_0$ method and it is generally not recommended.

Quasiparticle self-consistent GW

A qsGW calculation is requested by

```
GW
  SelfConsistency qsGW
End
```

One can also only iterate G by keeping W fixed, which reduces the cost of each iteration by roughly 50 %. This is requested by

```
GW
  SelfConsistency qsGW0
End
```

On the other hand, much of the starting-point dependence of the G_0W_0 method remains in the $qsGW_0$ method and it is generally not recommended.

More options:

QPHamiltonian

In quasiparticle self-consistent GW, the frequency-dependent self-energy is mapped to a static exchange-correlation potential in each iteration. The mapping is not unique and different schemes have been suggested. They differ in the way the frequency dependence of the self-energy is treated. In ADF, two variants can be used: KSF1 and KSF2 are both from the paper by Kotani et al.⁷. KSF1 refers to Eq. 10 therein and is most commonly implemented, KSF2 refers to Eq. 11 therein. KSF2 is the default in ADF since it is numerically more stable when qsGW is implemented together with the analytical continuation algorithm. In case the analytical integration algorithm is used, only KSF1 is currently supported. ADF also supports a variant denoted as LQSGW, which has been suggested by Kutepov et al.⁸. It uses a first-order expansion around the chemical potential. This is also similar to the approach implemented in VASP.

FixedGrids

By default, the imaginary frequency and imaginary time grids used in the GW calculation are updated in each iteration in a qsGW calculation since this is necessary to make the results strictly starting-point independent. This can also be turned off, and fixed grids are used throughout. This might be helpful in case of convergence problems.

Convergence

The self-consistency can be controlled by a few parameters: For example

```
GW
  Converge HOMO=5e-3
End
```

requests that the $evGW(0)$ calculation is considered converged if the difference between the HOMO quasiparticle energies of 2 consecutive iterations does not change by more than 5 meV. The default is 1 meV which is in practice usually a little too tight. We recommend adjusting this parameter according to your requirements, for example the experimental resolution you would like to match.

⁷ A.L. Kutepov, V.S. Oudovenko, G. Kotliar, *Linearized self-consistent quasiparticle GW method: Application to semiconductors and simple metals*, *Computer Physics Communications* 407-414 (2017) (<https://dx.doi.org/10.1016/j.cpc.2017.06.012>)

⁸ Takao Kotani, Mark Van Schilfgaarde, Sergey V. Faleev, *Quasiparticle self-consistent GW method: A basis for the independent-particle approximation*, *Physical Review B* 76 (16) 1-24 (2007) (<https://doi.org/10.1103/PhysRevB.76.165106>)

For qsGW (qsGW₀), the change in the norm of the density matrix is used as an additional criterion to control convergence. In evGW (evGW₀) it is ignored.

```
GW
  Converge Density=1e-07
End
```

is the default. For very large systems and when QZ basis sets are used, it is recommended to decrease that value, for example to

```
GW
  Converge Density=1e-08
End
```

```
GW
  linearmixing 0.2
End
```

turns off DIIS and requests to use linear mixing instead with a mixing parameter of 0.2. This can be useful if, for some reason, convergence using DIIS cannot be achieved. However, it is usually better to adjust the number of vectors in the DIIS expansion. This is achieved by (for example)

```
GW
  DIIS 5
End
```

The default is 10 expansion vectors.

7.12.3 Vertex corrections beyond GW

Starting from ADF2022 and with many additions in ADF2025, it is possible to go beyond the GW approximation for the self-energy using vertex corrections. This is possible in several ways, but not all are recommended. The algorithms and methods implemented in AMS (all of these methods can be used with both the ADF and the BAND engine) have been described in a series of publications.¹⁰¹¹¹²¹³

The easiest way to go beyond the GW is to also calculate the next term in the self-energy, often called G3W2. For the full G3W2 term, two nested and slowly converging frequency integrals have to be performed.^{Page 259, 11} However, there are possible approximations to it, for instance, the SOSEX and 2SOSEX approximations which only require a single frequency integration.¹¹ It is also possible to apply a static approximation to this term which avoids frequency integrations completely.¹⁰

None of these variants is recommended. They are expensive, and it can be shown that they always perform worse than a reasonable GW calculation.¹¹ The reason for this is that additional terms in the self-energy beyond GW should always be combined with additional terms in the polarizability. Additional self-energy terms always lower the HOMO, increase the LUMO, and therefore open the fundamental gap. Additional terms in the polarizability do the opposite. It can be shown that they largely cancel,¹² but the remaining effect improves results. This has been shown for a Hartree-Fock starting point (not recommended for G0W0, but with additional vertex corrections the performance is very good)¹² and for qsGW.¹³

ADF/BAND implements four possibilities to go beyond the simple RPA polarizability:

¹⁰ A. Förster, L. Visscher, *Exploring the statically screened G3W2 correction to the GW self-energy : Charged excitations and total energies of finite systems*, Physical Review B 105, 125121 (2022) (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.105.125121>)

¹¹ F.Bruneval, A. Förster, *Fully Dynamic G3W2 Self-Energy for Finite Systems: Formulas and Benchmark*, Journal of Chemical Theory and Computation 20 (8), 3218-3230 (2024) (<https://doi.org/10.1021/acs.jctc.4c00090>)

¹² A. Förster, F.Bruneval, *Why Does the GW Approximation Give Accurate Quasiparticle Energies? The Cancellation of Vertex Corrections Quantified*, The Journal of Physical Chemistry Letters 15, 12526-12534 (2024) (<https://doi.org/10.1021/acs.jpclett.4c03126>)

¹³ A. Förster, *Beyond quasi-particle self-consistent GW for molecules with vertex corrections*, arXiv:2412.01581 (2024) (<https://arxiv.org/abs/2412.01581>)

```

GW
  Polarizability {RPA|G4V1|G4W1|TDHF|BSE}
End

```

- **RPA** : Standard (direct) RPA without exchange. This is the default.
- **G4V1** : This evaluates the RPA polarizability and adds the G4V1 term. This is the next-to-leading order term beyond RPA in the bare Coulomb interaction V .¹²
- **G4W1** : This evaluates the RPA polarizability and adds the G4W1 term. This is the next-to-leading order term beyond RPA in the statically screened Coulomb interaction W .^{Page 259, 12}
- **TDHF** : Here, instead of improving the RPA polarizability order by order, one adds an infinite order correction. TDHF solves the usual TDHF linear response equations to calculate the reducible polarizability which is then used to calculate the screening. The G4V1 term is the first-order approximation to TDHF.^{Page 259, 12}
- **BSE** : This is the recommended option. BSE solves the usual BSE linear response equations with the statically screened exchange kernel to calculate the reducible polarizability which is then used to calculate the screening. This is also the BSE which is usually solved in the GW-BSE method. The G4W1 term is the first-order approximation to TDHF.^{Page 259, 12}
- Both **BSE** and **TDHF** have to be solved in the MO basis using analytical integration. This does not have to be specified in the input since ADF selects this automatically.
- Both **G4V1** and **G4W1** have to be solved in the MO basis using analytical continuation. This does not have to be specified in the input since ADF selects this automatically.

These polarizability terms should always be combined with the compatible additional terms in the self-energy.^{Page 259, 12} Compatible means that it makes sense physically. Most of these options can be combined at will, and you will get a result. It just might not make sense.

```

GW
  SelfEnergy {HF|G3W2dynamic|G3W2|GW|SOSEX|GWGamma|GWGammaInf|GWGammaInfDyn}
End

```

- **HF** : This uses the GW code to perform a HF calculation. Not recommended.
- **G3W2dynamic** : This is the fully G3W2 dynamical self-energy. Very expensive and bad. **Not recommended**.^{Page 259, 11}
- **G3W2** : This is the fully statical G3W2 self-energy. **Not recommended**.^{Page 259, 10}
- **GW** : This is the default.
- **SOSEX** : This is the SOSEX approximation to G3W2. Should be combined either with the **G4V1** or the **TDHF** polarizabilities.^{Page 259, 11}
- **GWGamma** : This is the GWGamma approximation to G3W2. In case the **G4V1** or the **TDHF** polarizability is used, it defaults to SOSEX. In case the **G4W1** or the **BSE** polarizabilities are used, it does something that looks like SOSEX, but the bare V in SOSEX is replaced by the statically screened Coulomb interaction W . This makes this option compatible with all options for the polarizability (except for the default, RPA).^{Page 259, 12}
- **GWGammaInf** : Similar to TDHF or BSE, it resums the additional self-energy terms beyond GW to infinite orders. This is the **recommended** choice whenever the TDHF or BSE polarizability is used.^{Page 259, 12}
- **GWGammaInfDyn** : Finally, we have an option which first performs a **GWGammaInf** calculation, and adds a first-order dynamical correction. This is not recommended at the moment but could be combined with a first-order dynamical correction to the polarizability. However, this is not yet implemented.
- In summary, we do recommend the following combinations:^{Page 259, 12Page 259, 13}

```

GW
  Polarizability {BSE|TDHF}
  SelfEnergy GWGammaInf
End

```

- Both options give similar results.^{Page 259, 12} In principle, BSE should be better, and only slightly more expensive. Both options are relatively expensive anyway since a full linear response problem has to be solved completely.
- This should either be used with a Hartree-Fock starting point, or combined with a qsGW calculation. The latter will give very accurate results (possibly the best you can get), but it is expensive. You might be able to apply it to systems < 20 atoms in a TZ basis set on a standard node. Larger systems are potentially possible if run on a high-memory node. Other KS starting points can be used, and this could potentially work well. But this has not been tested yet.

7.12.4 Embedding

The GW method can be combined with both the **COSMO**, **DIM**, and **FQ** embedding methods¹⁶ This coupling is only available for the G_0W_0 level of approximation and is highly experimental, therefore users should exercise caution in interpreting the results. The implementation is based on the work by Duchemin et al.¹⁵ on the combination of GW with the polarizable continuum model, which we further extended to the DIM method.

To add embedding effects in a GW calculation, simply include the corresponding keywords in the input file as is done for regular DFT calculations.

7.12.5 Recommendations

Basis sets

The recommended numerical settings depend strongly on the basis set. The recommended basis set depends on system size and the property of interest. The following are recommendations which should be seen as guidelines and not as definite. We recommend to always verify the basis set convergence for the property of interest. Details about basis set convergence can be found in this paper^{Page 259, 13}.

Basis sets

All-electron: All-electron calculations have to be used.

Basis set size: Larger basis sets are needed to achieve the same accuracy as in a DFT calculation.

Augmented basis sets: Should only be used if absolutely necessary. However, they are often necessary for an accurate description of the electron affinity for molecules with LUMO above the vacuum level.

Ionization Potentials: QZ4P or larger

Electron affinities, bound LUMO: Corr/TZ3P or larger

Electron affinities, unbound LUMO: AUG/ATZ2P or larger

Fundamental Gaps: Triple-zeta quality basis sets are typically sufficient.

¹⁶

G. Nottoli, P. Lafiosca, F.E.Q. Rodríguez, F. Egidi, A. Förster, C. Cappelli, *GW Approximation Coupled with Classical Fluctuating Charges and Dipoles*, *Journal of Chemical Theory and Computation* 22 (2026) 371–384 (<https://doi.org/10.1021/acs.jctc.5c01722>)

¹⁵ I. Duchemin, D. Jacquemin, X. Blase, *Combining the GW formalism with the polarizable continuum model: A state-specific non-equilibrium approach*, *The Journal of Chemical Physics* 144, 164106 (2016) (<https://dx.doi.org/10.1063/1.4946778>)

The GW-BSE excitation energies and the screened Coulomb interaction only depend on the QP gaps and not on their absolute values. Therefore, triple-zeta quality basis sets are typically sufficient.

For **highly accurate results** we recommend performing an extrapolation to the complete basis set limit: for this, perform two calculations using the Corr/TZ3P and Corr/QZ6P. The basis set limit is then calculated according to

$$\epsilon_n^{CBS} = \epsilon_n^{QZ} - \frac{1}{N_{bas}^{QZ}} \frac{\epsilon_n^{QZ} - \epsilon_n^{TZ}}{\frac{1}{N_{bas}^{QZ}} - \frac{1}{N_{bas}^{TZ}}}$$

The values for N_{bas}^{TZ} and N_{bas}^{QZ} can be found in the `adf.rkf` file in the GW section under the entry `nBas`. Additional explanations can be found in the references³ and [Page 259, 13](#). Alternatively, this basis set extrapolation can be performed with the BAND code and the Dunning basis sets cc-pVTZ and cc-pVQZ.

Numerical aspects

- According to the choice of basis set, the recommended numerical settings can differ. For a discussion, see the [MBPT page](#) (page 387).
- qsGW has higher requirements on the numerical parameters than evGW and G_0W_0 . Usually, it is necessary to use a larger value in the `Dependency` key; see the [MBPT page](#) (page 387). Note that starting from AMS2022 ADF will use a `Dependency bas=5e-3` and `RIHartreeFock DependencyThreshold=5e-3` in case of (any variant of) GW. One can override these values in the input.
- The implemented GW algorithm is very sensitive to numerical noise and depending on the numerical settings and/or the underlying exchange-correlation functional, (occupied) quasiparticle energies from partially self-consistent GW calculations performed on different hardware can differ by a few meV. The discrepancies are generally more pronounced for core states for which the analytical continuation technique is not applicable. Here, the analytical integration algorithm should be used.
- In our experience, these differences only occur with large basis sets (QZ4P or larger) and when Minnesota functionals (we tested M06, M06-2X and M06-HF) are used to calculate the KS reference. When the DIIS algorithm is used to converge the quasiparticle energies, the number of iterations needed for convergence can then differ as well.
- The analytical integration solution of GW is numerically more stable since there are no problems due to frequency integration, analytical continuation, or time-to-frequency Fourier transforms.
- If the RI formalism is used, one avoids time-to-frequency Fourier transforms. This can sometimes help in case of unexpected results with the analytical continuation based algorithm.

Choosing the KS reference

- As for ground-state properties, it is far from trivial to recommend a universal functional. However, for G_0W_0 calculations, a few general guidelines can be offered. A good discussion is found in². It should be noted that GGA functionals should not be used, even though a PBE starting point is a popular choice. We rather recommend using a hybrid functional. The relevant parameter in the choice of the hybrid is usually the fraction of exact exchange. In our experience, PBE0 with 40-50 % exact exchange is a good choice. You might also use a range-separated hybrid via LibXC, for example LRC-wPBEH.
- If in doubt, one of the partially self-consistent schemes should be used. evGW is almost starting-point independent and qsGW is completely starting-point independent. Therefore, for qsGW, it is in principle irrelevant what starting

³ M.J. Van Setten, F. Caruso S. Sharifzadeh X. Ren M. Scheffler F. Liu J. Lischner L. Lin J. Deslippe S.G. Louie C. Yang F. Weigend J.B. Neaton F. Evers P. Rinke, *GW100: Benchmarking G_0W_0 for Molecular Systems*, *Journal of Chemical Theory and Computation* 11 (12), 5665-5687 (2015) (<https://doi.org/10.1021/acs.jctc.5b00453>)

² F. Bruneval, M.A.L., Marques, *Benchmarking the starting points of the GW approximation for molecules*, *Journal of Chemical Theory and Computation* 9 (1), 324-329 (2013) (<https://dx.doi.org/10.1021/ct300835h>)

point is chosen. Convergence properties can in principle be affected, although the number of iterations until convergence is reached is also more or less independent of the starting point^{Page 256, 6}. Also for evGW, starting from a hybrid functional or a range-separated functional usually results in the highest accuracy.

- A Hartree-Fock starting point can be used in G_0W_0 , but in that case a vertex correction should be applied. See above.

7.12.6 GW key

```

GW
  nStates integer
  Polarizability [RPA | BSE | G4W1 | G4V1 | TDHF]
  SelfEnergy [HF | GW | G3W2 | SOSEX | GWGamma | G3W2dynamic | GWGammaInf | ↵
↵GWGammaInfDyn]
  SelfConsistency [G0W0 | EVGW0 | EVGW | QSGW0 | QSGW]
  QPHamiltonian [KSF1 | KSF2 | SRG | LQSGW]
  AnalyticalIntegration
    Enabled Yes/No
    SpectralFunctionResolution integer
    TDA Yes/No
    eta float
  End
  nIterations integer_list
  Converge
    Density float_list
    HOMO float
  End
  LinearMixing float_list
  AdaptiveMixing float_list
  DIIS integer
  LinearizeQPequations Yes/No
  ScissorShift Yes/No
End

```

GW

Type

Block

Description

Perform a GW calculation. G0W0 is the default for GW%SelfConsistency.

nStates

Type

Integer

Default value

5

GUI name

N states

Description

Number of Quasiparticle States to be printed to output.

The default is 5 states which in this case means that $\min(5, \text{Number of particle states})$ occupied and $\min(5, \text{Number of hole states})$ hole states are printed. The whole list of states can be printed by setting this parameter to -1'

Polarizability**Type**

Multiple Choice

Default value

RPA

Options

[RPA, BSE, G4W1, G4V1, TDHF]

Description

Sets the expression for the Polarizability used in the GW calculation.

RPA is the Default and amounts to a standard GW calculation.

BSE denotes screening in the Bethe-Salpeter-equation formalism.

SelfEnergy**Type**

Multiple Choice

Default value

GW

Options

[HF, GW, G3W2, SOSEX, GWGamma, G3W2dynamic, GWGammaInf, GWGammaInfDyn]

Description

Controls the form of the self-energy.

GW is the default and corresponds to the standard GW calculation.

G3W2 is a GW calculation plus a perturbative second-order statically screened exchange correction (second order expansion in the self-energy). Note, that there the self-energy is always static.

SelfConsistency**Type**

Multiple Choice

Default value

G0W0

Options

[G0W0, EVGW0, EVGW, QSGW0, QSGW]

Description

Sets the level of self-consistency in a GW calculation.

G0W0 calculates a one-shot, perturbative correction to the KS eigenvalues.

In evGW and evGW0, the quasi-particle energies are updated until self-consistency is reached.

evGW0 requests that the Green's function is evaluated self-consistently but not the screened interaction.

In qsGW, the density is updated as well, however, the self-energy is mapped to a static effective potential and the Dyson equation is solved by diagonalization instead of inversion. The results

of a qsGW are independent of the choice of the underlying exchange-correlation functional and are usually the most accurate ones.

The same is done in qsGW0, but the screened interaction is not updated.

QPHamiltonian

Type

Multiple Choice

Default value

KSF2

Options

[KSF1, KSF2, SRG, LQSGW]

Description

The quasi-particle Hamiltonian can be constructed in different ways.

KSF1 refers to the original construction by Kotani, Van Schilfgaarde and Faleev (KSF) which is also implemented in TURBOMOLE.

KSF2 refers to an alternative construction by KSF.

KSF1 is not recommended since it is numerically less stable than KSF2 in case analytical continuation is used (the default).

In case the analytical integration algorithm is used, only KSF1 is implemented. Therefore, make sure that KSF1 is specified. The results are typically very similar.

The QP energies at which the matrix elements are evaluated can be tweaked further, see the two subsequent keys: However, KSF2 is recommended since it typically leads to QP energies with the best agreement with experiment.

Ignored when not a quasi-particle self-consistent GW calculation is performed

AnalyticalIntegration

Type

Block

Description

Use analytical integration to calculate the self-energy. Very slow, unless the system is very small but useful to check the accuracy of the frequency integration

Enabled

Type

Bool

Default value

No

GUI name

analytical integration

Description

Enable the calculation of the GW quasi-particle energies via analytical integration.

SpectralFunctionResolution

Type

Integer

Default value

800

Description

Number of points at which spectral function is evaluated.

TDA**Type**

Bool

Default value

No

Description

Solve the linear response equations in the Tamm-Dancoff approximation.

eta**Type**

Float

Default value

0.001

Description

Artificial (positive) broadening parameter for evaluation of self-energy in analytical integration.

Ideally should be as small as possible but this might lead to convergence issues in partially self-consistent approaches.

In this case, a value of up to 0.1 is possible.

nIterations**Type**

Integer List

Default value

[10]

GUI name

Number of iterations

Description

The maximum number of iterations within the (partially or fully) self-consistent GW calculation has to converge.

Ignored when Formalism is set to G0W0

Converge**Type**

Block

Description

Sets convergence criteria for the GW calculation in self-consistent case

Density**Type**

Float List

Default value

[1e-08, 1e-05]

Description

First Criterion for self-consistency procedure to terminate.

Criterion is the trace of the density matrix. Ignored in non-selfconsistent Calculation and in eigenvalue self-consistent GW

It is possible to run a qsGW calculation with an inner SCF loop which updates the static part of the elf-energy only. This can be useful to accelerate the convergence in case linear mixing is used. It is not recommended to use linear mixing, so it is also not recommended to use that inner loop as well. The second number in this list specifies the convergence criterion for the inner SCF loop.

HOMO**Type**

Float

Default value

0.003

Unit

eV

GUI name

HOMO energy convergence

Description

Criterion for self-consistency procedure to terminate.

The self-consistent GW calculation terminates, when the difference between the HOMO QP energies between 2 consecutive iterations is below this number.

The LUMO energy converged faster than the HOMO energy so when the HOMO energy is converged according to this criterion, the LUMO energy will be converged as well.

In non-selfconsistent Calculation, this criterion is ignored.

LinearMixing**Type**

Float List

Description

Requests to use linear mixing instead of DIIS and sets the mixing parameter for linear mixing of Green's function in case of self-consistency.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

AdaptiveMixing**Type**

Float List

Description

Requests to use adaptive mixing instead of DIIS and sets the starting mixing parameter for mixing of Green's function in case of self-consistency.

Adaptive mixing is recommended in case a qsGW calculation does not converge with DIIS.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

DIIS

Type

Integer

Default value

10

Description

Requests to use DIIS. This is the Default. Number of expansion coefficients can be requested as well. Ignored in non-selfconsistent calculation

LinearizeQPequations**Type**

Bool

Default value

No

Description

Instead of solving the non-linear QP equations in a G0W0 (or evGW calculation) by bisection exactly, linearize them by first-order Taylor expansion.

This is not recommended since it does not save computational time when used together with analytical continuation (as implemented in AMS). It might however be useful for benchmarking or for validating results.

If the results of the linearization differ by a lot (for instance, more than 0.1 eV in frontier QP energies) from the non-linearized results, this might indicate that the GW calculation is not reliable.

ScissorShift**Type**

Bool

Default value

No

Description

Only calculate the HOMO and LUMO QP energies and shift the remaining QP energies by the same amount.

This is a rather crude approximation and not recommended.

It might again be useful for benchmarking purposes.

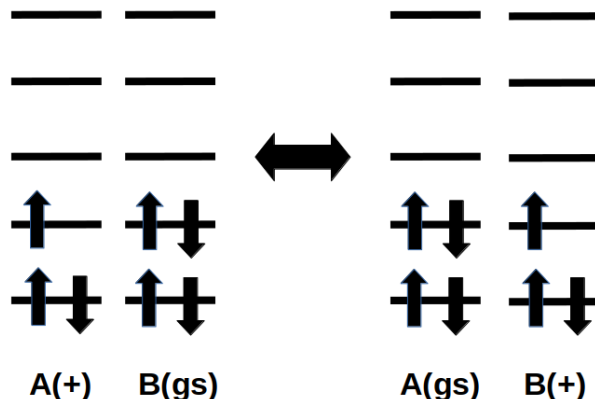
TRANSPORT PROPERTIES

See also:

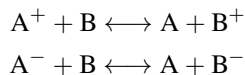
Examples: *transport properties* (page 1032)

8.1 Charge transfer integrals (transport properties)

ADF can provide input parameters, such as charge transfer integrals, that are needed in approximate methods that model charge transport properties. ADF has the unique feature that it can also calculate such transfer integrals based on the direct method by the use of its unique fragment approach.



Example electron configuration for charge hopping from A to B or back, where A and B are nearby molecules, or different parts of a complex AB. The hopping can occur from the diabatic state where A is charged and B is in the ground state to the diabatic state where A is in the ground state and B is charged (or back).



In theoretical models of charge transport in organic materials, see Refs.^{6,7,8}, the whole system is divided into fragments,

⁶ M.D. Newton, *Quantum chemical probes of electron-transfer kinetics: the nature of donor-acceptor interactions*, *Chemical Reviews* 91, 767 (1991) (<https://doi.org/10.1021/cr00005a007>).

⁷ K. Senthilkumar, F.C. Grozema, F.M. Bickelhaupt, and L.D.A. Siebbeles, *Charge transport in columnar stacked triphenylenes: Effects of conformational fluctuations on charge transfer integrals and site energies*, *Journal of Chemical Physics* 119, 9809 (2003) (<https://doi.org/10.1063/1.1615476>).

⁸ K. Senthilkumar, F.C. Grozema, C. Fonseca Guerra, F.M. Bickelhaupt, F.D. Lewis, Y.A. Berlin, M.A. Ratner, and L.D.A. Siebbeles, *Absolute Rates of Hole Transfer in DNA*, *Journal of the American Chemical Society* 127, 14894 (2005) (<https://doi.org/10.1021/ja054257e>).

in which an electron or hole is localized on a fragment, and can hop from one fragment to another. In the tight-binding approximation that is used in these models the electron or hole is approximated with a single orbital, and it is assumed that only the nearest neighboring fragments can couple. The models require accurate values of electronic couplings for charge transfer (also referred to as charge transfer integrals or hopping matrix elements) and site energies (energy of a charge when it is localized at a particular molecule) as a function of the geometric conformation of adjacent molecules. Charge transfer integrals for hole transport can be calculated from the energetic splitting of the two highest-occupied molecular orbitals (HOMO and HOMO-1) in a system consisting of two adjacent molecules, also called the Energy Splitting In Dimer (ESID) method. For electron transport these can be calculated from the two lowest-unoccupied orbitals (LUMO and LUMO+1) in this ESID method. ADF can also calculate transfer integrals based on the direct method by the use of its unique fragment approach; see Refs. [Page 269, 7](#) [Page 269, 8](#). ADF allows one to use molecular orbitals on individual molecules as a basis set in calculations on a system composed of two or more molecules. The charge transfer integrals obtained in this way differ significantly from values estimated from the energy splitting between the highest occupied molecular orbitals in a dimer. The difference is due to the nonzero spatial overlap between the molecular orbitals on adjacent molecules. Also, ADF's methods are applicable in cases where an orbital on one molecule couples with two or more orbitals on another molecule.

8.1.1 Charge transfer integrals with the TRANSFERINTEGRALS key

In this method the matrix elements of the molecular Kohn-Sham Hamiltonian H^{KS} in the basis of fragment orbitals are used to calculate site energies and charge transfer integrals. Likewise the overlap integrals between fragment orbitals are calculated. No explicit electrons are removed or added in this method. For electron mobility calculations the fragment LUMOs are considered. For hole mobility calculations the fragment HOMOs are considered.

To calculate the charge transfer integrals, spatial overlap integrals, and site energies, include the key TRANSFERINTEGRALS in the input for ADF. Symmetry NOSYM should be used. The molecular system typically should be built from two fragments. In the fragment calculation full symmetry can be used.

```
TRANSFERINTEGRALS
Symmetry NOSYM
Fragments
  frag1 frag1.results/adf.rkf
  frag2 frag2.results/adf.rkf
End
```

By default, integrals are calculated only for the HOMO (LUMO) of the fragments, and possibly HOMO-1, HOMO-2 (LUMO+1, LUMO+2) if the energy of those fragment orbitals are close to the HOMO (LUMO) of that fragment. To calculate the matrix elements and overlap integrals based on all fragment orbitals, one can use the key:

```
PRINT FMATSFO
```

The method described here to calculate charge transfer integrals is more approximate than the next method that uses FDE. The major difference is how effects of a localized charge are included.

If two fragments are used the electronic coupling V (also known as effective (generalized) transfer integrals J_{eff}) for hole transfer or electron transfer is calculated as $V = (J - S(e_1 + e_2)/2)/(1 - S^2)$. Here e_1 and e_2 are the site energies of fragment 1 and 2, respectively. J is the charge transfer integral, and S the overlap integral.

$$\begin{aligned} e_1 &= \langle \phi_1 | H^{KS} | \phi_1 \rangle \\ e_2 &= \langle \phi_2 | H^{KS} | \phi_2 \rangle \\ J &= \langle \phi_1 | H^{KS} | \phi_2 \rangle \\ S &= \langle \phi_1 | \phi_2 \rangle \\ V &= \frac{J - S(e_1 + e_2)/2}{1 - S^2} \end{aligned}$$

In case of electron mobility calculations ϕ_1 is the LUMO of fragment 1 and ϕ_2 is the LUMO of fragment 2. In case of hole mobility calculations ϕ_1 is the HOMO of fragment 1 and ϕ_2 is the HOMO of fragment 2. The electronic coupling between the HOMO of the donor fragment and the LUMO of the acceptor fragment and vice versa is also calculated, which represents the probability of a charge recombination process.

If there is (near) degeneracy in the fragment HOMO and/or LUMO, multiple electronic couplings V_i are printed. A total electronic coupling is calculated as

$$V_{tot} = \sqrt{\sum_{deg} V_i^2}$$

TIdegeneracyThreshold float

TIdegeneracyThreshold

Type

Float

Default value

0.1

Unit

eV

Description

If the orbital energy of the fragment MO is within this threshold with fragment HOMO or LUMO energy, then this fragment MO is included in the calculation of the transfer integrals. Relevant in case there is (near) degeneracy.

8.1.2 Charge transfer integrals with FDE

Overview

The ELECTRONTRANSFER keyblock invokes the calculation of Hamiltonian (site energies and couplings) and overlap matrix elements with FDE-derived localized states. Two FDE calculations are (not strictly) needed before running the ELECTRONTRANSFER calculation. The calculated matrix elements are theoretically similar to the ones obtained with the TRANSFERINTEGRALS keyword. A review casts ELECTRONTRANSFER in the state-of-the-art of methods for computing charge transfer couplings, and provides a step-by-step guide for computing such couplings with ADF¹.

Features

- Effects of orbital relaxation due to localized charges, Refs.^{9,2}.
- Effects of polarization due to molecules in the environment, Ref.^{Page 271, 2}.
- ELECTRONTRANSFER is linear scaling in the number of fragments when the system is composed of more than one fragment.
- The code can tackle hole transfer, electron transfer, charge separation and charge recombination processes³.

¹ P. Ramos, M. Mankarious, M. Pavanello, *A critical look at methods for calculating charge transfer couplings fast and accurately*, in *Practical Aspects of Computational Chemistry IV*, Jerzy Leszczynski and Manoj Shukla (eds.), 2016, Springer (https://doi.org/10.1007/978-1-4899-7699-4_4)

⁹ M. Pavanello and J. Neugebauer, *Modelling charge transfer reactions with the frozen density embedding formalism*, *Journal of Chemical Physics* 135, 234103 (2011) (<https://doi.org/10.1063/1.3666005>)

² M. Pavanello, T. Van Voorhis, L. Visscher, and J. Neugebauer, *An accurate and linear-scaling method for calculating charge-transfer excitation energies and diabatic couplings*, *Journal of Chemical Physics* 138, 054101 (2013) (<https://doi.org/10.1063/1.4789418>)

³ A. Solovyeva, M. Pavanello, J. Neugebauer, *Describing Long-Range Charge-Separation Processes with Subsystem Density-Functional Theory*, *J. Chem. Phys.* 140, 164103 (2014) (<https://doi.org/10.1063/1.4871301>)

- Can compute transfer integrals from diabats obtained with the Constrained DFT method (i.e., invoked by using the experimental CDFT keyword of ADF). This includes calculation of couplings between diabats made of a single fragment.
- It is possible to include the effect of the environment on CDFT diabats by coupling it with an FDE calculation⁴.
- The performance of ElectronTransfer in the evaluation of the hole transfer coupling was benchmarked against wave function methods, with an error below 7%. PBE, PW91, B3LYP and PBE0 functionals, with PW91k for the non-additive component of the kinetic energy and a TZP basis set, are recommended to obtain the FDE-derived localized states⁵.
- The code was parallelized in ADF2018.

Limitations

- Hybrid functionals are not yet supported
- adf.rkf (TAPE21) files with charge or spin-localized states with specific names are needed

These two limitations do not apply to the method with the TRANSFERINTEGRALS key, but the TRANSFERINTEGRALS method has many other limitations. Like the method with the TRANSFERINTEGRALS key, fragments are needed.

ELECTRONTRANSFER input

The minimum input for the ELECTRONTRANSFER key is:

```
FRAGMENTS
frag1 FragFile1
...
fragN FragFileN
END
ELECTRONTRANSFER
NumFrag N
END
```

where frag1 ... fragN are the labels of the fragments in the calculation, and FragFile1 ... FragFileN are the adf.rkf (TAPE21) files of spin-restricted calculations of the isolated fragments, N is the total number of fragments employed in the calculation.

Files and file names

The fragment files to be used in the ELECTRONTRANSFER calculation are generally different from the adf.rkf (TAPE21) files used in the FRAGMENTS key block. Two types of fragment adf.rkf (TAPE21) files are needed by the calculation:

- The isolated closed-shell TAPE files for the FRAGMENTS keyblock
- The adf.rkf (TAPE21) files of the charge or spin localized states (which can be obtained with an FDE calculation as done in the example below)

There are two charge localized states. They are labeled with A and B. The respective adf.rkf (TAPE21) files must be named as follows:

```
fragA1.t21, fragA2.t21, ... , fragAN.t21 (for state A)
fragB1.t21, fragB2.t21, ... , fragBN.t21 (for state B)
```

⁴ P. Ramos, M. Pavanello, *Constrained Subsystem Density Functional Theory*, *Physical Chemistry Chemical Physics* 18, 21172 (2016) (<https://doi.org/10.1039/C6CP00528D>).

⁵ P. Ramos, M. Papadakis, M. Pavanello, *Performance of Frozen Density Embedding for Modeling Hole Transfer Reactions*, *Journal of Physical Chemistry B* 119, 7541 (2015) (<https://doi.org/10.1021/jp511275e>)

The above files should be copied to the working folder of the ADF calculation prior to executing ADF.

Options

```
ELECTRONTRANSFER
  NumFrag N
  {Joint|Disjoint}
  {Debug}
  {Print EIGS|SAB}
  {FDE}
  {INVTHR threshold}
  {CDFT}
  {KNADD}
END
```

Joint|Disjoint

The default is “Joint”. Joint is always recommended. The “Disjoint” formalism is described in Ref.² and is much faster than the “Joint” formalism when more than 2 fragments are considered. Joint and Disjoint are equivalent for systems composed of only 2 fragments. Disjoint should only be used if the fragment files are obtained in an FDE calculation (see FDE below).

Debug

The code performs additional checks (determinants, diagonalizations, inversions, traces, etc.). Substantial increase in the output should be expected.

Print

If EIGS, it will print the (unformatted) matrix of the MO coefficient in the AO representation. If SAB, it will print the (unformatted) matrix of the diagonal and transition overlap matrix in the MO representation.

FDE

An FDE calculation including more than two fragments must include the following key block:

```
ELECTRONTRANSFER
  FDE
END
```

and the numerical integration precision in the *last* FDE calculation for every subsystem should be set to no less than:

```
BeckeGrid
  Quality Good
End
```

if in the subsequent ELECTRONTRANSFER calculation the DISJOINT subkey is used.

Invthr threshold

Default 1.0e-3, is a threshold for the Penrose inversion of the transition overlap matrix. If warnings about density fitting are printed, invthr may be increased up to 1.0e-2. Larger invthr might affect the quality of the calculated couplings and excitation energies.

CDFT

If disjoint is selected, this keyword must be selected if the evaluation of the electronic coupling is sought between diabats located on the same CDFT fragment. In this case, the CDFT fragment has to be always first under the ATOMS keyword.

KNADD

If disjoint is selected, this allows the kinetic energy of each fragment to be obtained locally without using the full grid. This keyword is recommended when there are many tens of subsystems, such as systems with several solvent molecules.

Output

The output of the example in \$AMSHOME/examples/adf/ElectronTransfer_FDE_H2O is discussed here. This example involves the calculation of electronic coupling, site energies and charge-transfer excitation energy for the hole transfer in a water dimer.

```
===== Electron Transfer RESULTS =====

Electronic Coupling =      0.000000 eV
Electronic Coupling =     -0.003569 cm-1
H11-H22            =     -1.396546 eV
Excitation Energy  =      1.396546 eV
Overlap            =      0.000000
H11 H22 H12 =   -152.443000816341   -152.391678701092   -151.743979368040 Eh
S11 S22 S12 =      0.981795415192      0.981006454450      -0.000000023700

===== END Electron Transfer RESULTS =====
```

Due to symmetry, the overlap is almost diagonal (Overlap = 0.00), thus the transition density is evaluated with one less electron as explained in Ref.^{Page 271, 2}.

The electronic coupling between the state with a positive charge localized on one water molecule and another with the charge localized on the other water molecule is given by “Electronic Coupling” and is reported in eV and cm⁻¹.

“H11-H22” is the difference of the site energies in eV. Values of the site energies are given by the first two values of “H11 H22 H12” in atomic units.

“Excitation Energy” reports the value of the transfer excitation energy as calculated by diagonalization of the 2x2 generalized eigenvalue problem in the basis of the charge-localized states, see Refs.^{Page 271, 2Page 271, 9}.

“S11 S22 S12” are the values of the non-normalized overlaps.

8.1.3 Charge transfer integrals with FOCDFT

FOCDFT can be used to calculate charge transfer integrals. *FOCDFT* (page 78) is a fragment orbital based method for constraining (integer) charges and spins on fragments. It uses the (localized) Löwdins that ADF makes to constrain charges and spins on fragments. This method can be used to specify 2 different electron configurations of the same complex, such that a charge on the first fragment in the first calculation is transferred to the second fragment in the second calculation.

The two electron configurations calculated with FOCDFT will lead to two one-determinantal wave functions with occupied orbitals, which are not necessarily mutually orthonormal. Löwdin’s pairing theorem (see for example Ref.¹⁰) is used to make a set of occupied orbitals that are orthonormalized and ‘paired’, and which do not change the resulting two one-determinantal wave functions. Because FOCDFT uses the (localized) Löwdins that ADF makes, and charge is transferred from one fragment to the other, the two one-determinantal wave functions are orthonormal and there is at least one pair of ‘corresponding orbitals’ that have zero overlap. These two ‘corresponding orbitals’ a_i (of the first calculation) and b_i (of the second calculation) are used to calculate an approximation to the electronic coupling by calculating

$$\langle a_i | 0.5F^A + 0.5F^B | b_i \rangle$$

where F^A is the Fock matrix in the first calculation and F^B is the off-diagonal Fock matrix in the second calculation. The off-diagonal Fock matrix is the off-diagonal part of the Fock matrix between Löwdins on the first fragment and Löwdins on the second fragment, before it is set to zero in *FOCDFT* (page 78). The overlap of the other paired orbitals is taken into account in the final electronic coupling.

¹⁰ I. Mayer, *Löwdin’s pairing theorem and some of its applications*, *Molecular Physics*, 108, 3273 (2010) (<https://doi.org/10.1080/00268976.2010.508473>)

In FOCDFT electron transfer effects of orbital relaxation due to localized charges are included and effects of polarization due to molecules in the environment can be included. FOCDFT electron transfer can tackle hole transfer and electron transfer. Hybrid functionals are supported. FOCDFT electron transfer is not benchmarked against wave function methods.

For the calculation of electronic couplings between locally excited states and charge separated states see the section on *exciton transfer integrals with FOCDFT* (page 278).

With the proper input ADF will do the 2 FOCDFT calculations on the 2 diabatic states on the same complex consecutively and print the site energies and electronic coupling to output. In case of hole charge transfer in the ADF part of the input one should use something like:

```
fragments
  Frag1 Frag1.results/adf.rkf
  Frag2 Frag2.results/adf.rkf
end
spinpolarization 1
unrestricted
FOCDFT
  charge 1 0
  spinpolarization 1 0
  electrontransfer
    charge 0 1
    spinpolarization 0 1
  end
end
```

The FOCDFT and FOCDFT%ElectronTransfer keys in more detail:

```
FOCDFT
  Charge float_list
  SpinPolarization float_list
  ElectronTransfer
    Charge float_list
    OffDiagonalHF Yes/No
    OffDiagonalHFValue float
    SpinPolarization float_list
  End
End
```

FOCDFT

Type

Block

Description

Localize orbitals on fragments and constrain charge and spin polarization on fragments.

Charge

Type

Float List

Description

Constrain charge on fragments. Number of charges should be the same as number of fragments, and sum should add up to total charge.

SpinPolarization

Type

Float List

Description

Constrain spin polarization on fragments. Number of spin polarization values should be the same as number of fragments, and sum should add up to total spin polarization. Calculation should be spin unrestricted.

ElectronTransfer**Type**

Block

Description**Charge****Type**

Float List

Description

Constrain charge on fragments for the second calculation. Number of charges should be the same as number of fragments, and sum should add up to total charge.

OffDiagonalHF**Type**

Bool

Default value

No

GUI name

Off diagonal HF

Description

Off diagonal HF matrix elements.

OffDiagonalHFValue**Type**

Float

Default value

1.0

GUI name

Off diagonal HF value

Description

Amount of HF in case off diagonal HF matrix elements.

SpinPolarization**Type**

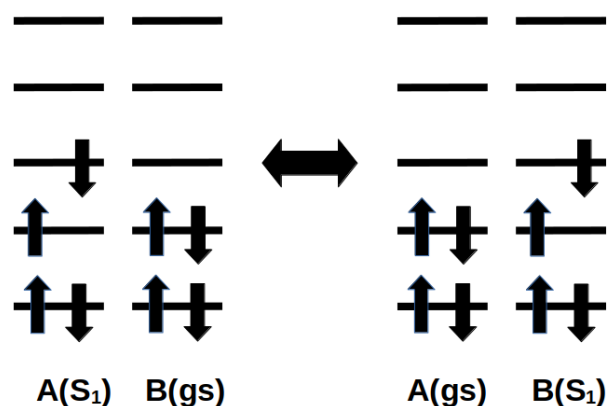
Float List

Description

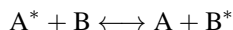
Constrain spin polarization on fragments for the second calculation. Number of spin polarization values should be the same as number of fragments, and sum should add up to total spin polarization. Calculation should be spin unrestricted.

8.2 Exciton transfer integrals

ADF can provide input parameters, such as exciton transfer integrals, that are needed in approximate methods that model exciton transport properties, like Förster and Marcus theory.



Example electron configuration for exciton hopping from A to B or back, where A and B are nearby molecules, or different parts of a complex AB. The hopping can occur from the diabatic state where A is in an excited state and B is in the ground state to the diabatic state where A is in the ground state and B is in an excited state (or back).



In theoretical models of exciton hopping, the whole system is divided into fragments, in which an exciton is localized on a fragment (diabatic state), and can hop from one fragment to another. The models require accurate values of excitonic couplings for exciton transfer (also referred to as exciton transfer integrals) and exciton site energies (energy of an exciton when it is localized at a particular molecule) as a function of the geometric conformation of adjacent molecules. Exciton transfer integrals can be calculated from the energetic splitting of excitation energies in a system consisting of two adjacent molecules, also called “Davydov splitting”. ADF can also calculate exciton transfer integrals by the use of its unique fragment approach. ADF allows one to use molecular orbitals on individual molecules as a basis set in calculations on a system composed of two or more molecules. Also, ADF’s methods are applicable in cases where an orbital on one molecule couples with two or more orbitals on another molecule.

8.2.1 Exciton transfer integrals with FDE

The linear-response *subsystem TDDFT* (page 153) code couples the monomer excitations to obtain the excited states of the total system (often denoted as coupled frozen density embedding, FDEc). It can be used, for example, to calculate singlet energy transfer integrals. For a complete description, see the *FDE part* (page 144) of the ADF manual, and in particular the part about *subsystem TDDFT* (page 153).

8.2.2 Exciton transfer integrals with ROSE or FOCDFT

The methods used for calculating exciton transfer integrals with *ROSE* (page 300) and *FOCDFT* (page 78) are very similar. However, the ROSE localized orbitals and FOCDFT localized orbitals may be quite different. Note that the methods used here can also be used solely for analysis of the character of the excited states, especially if `Excitations%descriptors` is included.

ROSE localized orbitals

The ROSE localized orbitals can be used to calculate exciton transfer integrals. *ROSE* (page 300) is a method that calculates a set of re-canonicalized intrinsic localized molecular orbitals (RILMOs), see also Ref.¹. While almost fully localized on individual fragments, RILMOs are delocalized within a fragment and can be interpreted as perturbed fragment orbitals. The ROSE localized occupied orbitals and the localized valence virtual orbitals are not very basis set dependent. The rest of the ROSE virtuals, the so-called hard virtuals, are (typically) more basis-set dependent. The occupied RILMOs span the occupied space of the supermolecular calculation exactly. As ROSE truncates the virtual space, one may need to vary the value of the `Additional_virtuals_cutoff` key to check convergence of results that depend on electronically excited states.

In combination with the `EXCITATIONS` and `EXCITONTRANSFER` key one can use the localized orbitals (RILMOs) that ROSE makes to calculate localized excitations on fragments (quasi-diabatic states) and calculate electronic couplings between them. The Tamm–Dancoff approximation (TDA) is required. Symmetry cannot be used. All-electron basis sets should be used.

FOCDFT localized orbitals

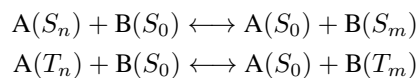
FOCDFT can be used to calculate exciton transfer integrals. *FOCDFT* (page 78) is a fragment orbital based method for constraining (integer) charges and spins on fragments. It uses the (localized) Lowdins that ADF makes to constrain charges and spins on fragments. In practice this method works best if there are no covalent bonds or if one does not want covalent bonds between the fragments. The FOCDFT localized occupied orbitals are not very basis-set dependent. The FOCDFT localized virtual orbitals, on the other hand, are much more basis-set dependent. The occupied FOCDFT orbitals span a different space than the occupied orbitals coming from a supermolecular calculation, because of the constraints used in FOCDFT. If one has a neutral complex and the constraints are that there should be zero charge and spin on all the fragments, this difference may not be so large. However, FOCDFT allows one also to constrain a charge on one of the fragments, whereas a calculation on the whole complex with the same charge would most likely give a much more delocalized charge. FOCDFT does not truncate the virtual space.

In combination with the `EXCITATIONS` and `EXCITONTRANSFER` key one can use the localized orbitals that FOCDFT makes to calculate localized excitations on fragments (diabatic states) and calculate electronic couplings between them. The Tamm–Dancoff approximation (TDA) is required. Symmetry can be used. Frozen core basis sets are allowed.

Exciton transfer integrals

Because charge-transfer (CT) excitations are calculated in ROSE or FOCDFT TD-DFT excitation calculations, it is best to use an XC functional that can calculate CT excitations reasonably accurately, such as range-separated hybrids.

One can study, for example, singlet energy transfer (SET) or triplet energy transfer (TET) with ROSE or FOCDFT.



including couplings to charge separated states, since CT states are calculated in this method.

¹ S. Sen, B. Senjean, L. Visscher, *Characterization of excited states in time-dependent density functional theory using localized molecular orbitals*, *Journal of Chemical Physics* 158, 054115 (2023) (<https://doi.org/10.1063/5.0137729>)

One possibility using the ExcitonTransfer key is to make purely local excitations (LEs) and purely charge-transfer (CT) excitations, if one sets the subkey ExcitonTransfer%Localize to OccupiedAndVirtual. The calculated LEs are then linear combinations of single-orbital transitions from occupied orbitals on one fragment to virtual orbitals on the same fragment. The calculated CT excitations are linear combinations of single-orbital transitions from occupied orbitals on one fragment to virtual orbitals on a different fragment. This is how excitations were analyzed in Ref. [Page 278, 1](#) using ROSE localized orbitals. The ROSE localized occupied orbitals and localized ‘hard virtual’ orbitals are not very basis-set dependent. In many cases excitations from occupied to the ‘hard virtual’ orbitals are the more interesting ones.

One can calculate an effective excitonic coupling between local diabatic states that include intermediate CT states by means of second-order perturbation corrections. This is only possible if the Localize keyword is set to OccupiedAndVirtual, the key SecondOrder is included, and the key Output is set to FilteredCouplings or AllAndFilteredCouplings. In case of a direct coupling between two local diabatic states, a second-order correction (involving a sum over diabatic CT states) is then added.

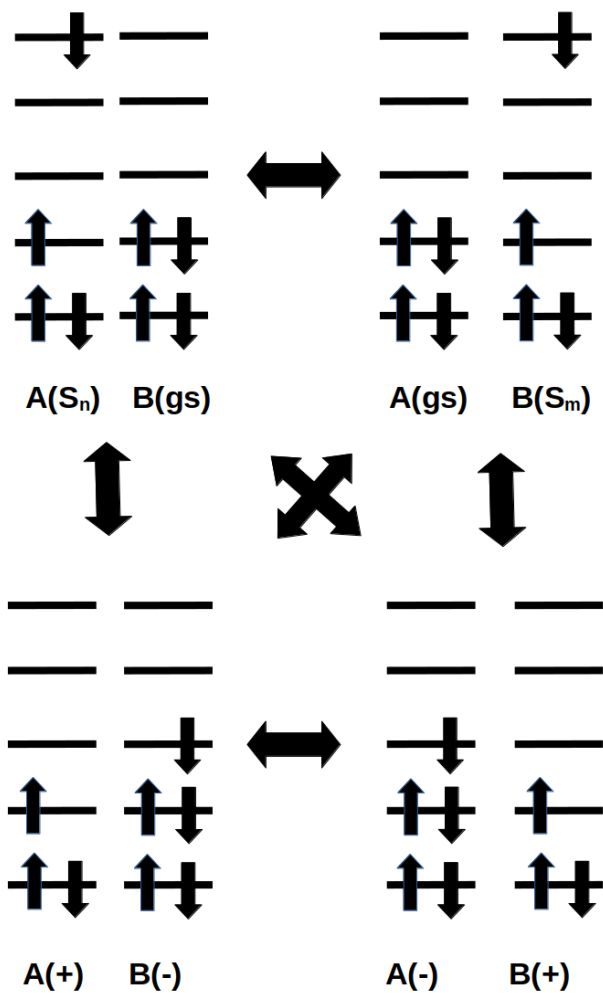
Part of the Engine ADF input in case of ROSE could look like:

```
Basis
  ...
  Core None
End
ROSE
  FragmentFile Frag1.results/adf.rkf
  FragmentFile Frag2.results/adf.rkf
End
TDA
Excitations
  descriptors
End
ExcitonTransfer
  Localize      OccupiedAndVirtual
  SecondOrder  True
  Output        AllAndFilteredCouplings
End
```

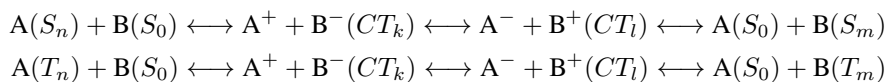
This method, which in many cases is adequate for ROSE, is not the recommended way if one uses FOCDFDFT localized orbitals, since all FOCDFDFT localized virtual orbitals are rather basis set dependent. In order to make LEs and CT excitations that are less basis-set dependent, a method has been implemented that combines the LEs from one fragment and CT excitations coming from the same fragment. This method will be used if one sets the subkey ExcitonTransfer%Localize to OccupiedOnly. The calculated excitations are, in this case, linear combinations of single-orbital transitions from occupied orbitals on one fragment to virtual orbitals on all fragments. Of course, this method can also be used for ROSE localized orbitals. One needs to use the Excitations%descriptors key to see whether an excitation is mostly an LE or a CT excitation.

Part of the Engine ADF part of the input in case of FOCDFDFT could look like:

```
Fragments
  Frag1 Frag1.results/adf.rkf
  Frag2 Frag2.results/adf.rkf
End
FOCDFT
End
TDA
Excitations
  descriptors
End
ExcitonTransfer
  Localize OccupiedOnly
End
```



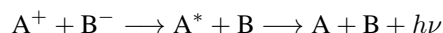
Example electron configuration for charge or exciton hopping from molecule A to molecule B or back. The hopping can occur from the diabatic state where A is in an excited state and B is in the ground state to the diabatic state where A is in the ground state and B is in an excited state or to a diabatic state where both A and B are charged (CT state).



With ROSE or FOCDFDFT, oscillator strengths can be calculated for the absorption of light to localized diabatic states. Thus, with ROSE or FOCDFDFT it is possible to investigate, for example, the absorption process where A is locally excited, which is followed by a charge-separation process (like in photosynthesis):



One could also study a reverse process (like in OLED devices):



In order to calculate couplings from LEs from one fragment and CT excitations coming from the same fragment, it is best to set the subkey `ExcitonTransfer%Localize` to `OccupiedAndVirtual`.

ExcitonTransfer key

```
ExcitonTransfer
  CoupleFinalStates Yes/No
  FilteredCouplings
    MaxEnergy float
    MaxEnergyDiff float
    MinCoupling float
    MinEnergy float
  End
  FullRun Yes/No
  LocalCouplingsOnly Yes/No
  Localize [OccupiedOnly | OccupiedAndVirtual]
  Lowest integer_list
  LowestCT integer_list
  Output [AllCouplings | FilteredCouplings | AllAndFilteredCouplings]
  SecondOrder Yes/No
End
```

ExcitonTransfer

Type

Block

Description

Block key for exciton transfer integrals with ROSE or FOCDFDFT.

CoupleFinalStates

Type

Bool

Default value

No

Description

Calculate delocalized excited states in the basis of the localized excited states that are calculated, thus couple the localized excited states.

FilteredCouplings**Type**

Block

Description

Details on filter used for electronic couplings in the output

MaxEnergy**Type**

Float

Default value

10.0

Unit

eV

Description

Max. energy (in eV) of diabatic states

MaxEnergyDiff**Type**

Float

Default value

0.5

Unit

eV

Description

Max. energy difference (in eV) between diabatic states

MinCoupling**Type**

Float

Default value

0.1

Description

Min. coupling value (in meV) that is printed

MinEnergy**Type**

Float

Default value

0.0

Unit

eV

Description

Min. energy (in eV) of diabatic states

FullRun**Type**

Bool

Default value

No

Description

Include run without restriction of localization of occupied and/or virtual orbitals.

LocalCouplingsOnly**Type**

Bool

Default value

No

Description

Only account for couplings between local diabatic states

Localize**Type**

Multiple Choice

Default value

OccupiedOnly

Options

[OccupiedOnly, OccupiedAndVirtual]

Description

Localize OccupiedAndVirtual means that separately purely localized excitations and purely charge-transfer excitations are calculated. Localize OccupiedOnly means that an excitation may have local and charge-transfer character, but the excitation only has contributions from occupied orbitals on one fragment. Only relevant in case block key FOCDFE is used or ROSE orbitals are used.

Lowest**Type**

Integer List

GUI name

Number of excitations

Description

Number of lowest excitations to compute for each fragment. These are purely local excitations if the Localize OccupiedAndVirtual key is specified.

LowestCT**Type**

Integer List

GUI name

Number of charge-transfer excitations

Description

Number of lowest charge-transfer excitations to compute for each fragment. Only relevant if the Localize OccupiedAndVirtual key is also specified.

Output**Type**

Multiple Choice

Default value

AllCouplings

Options

[AllCouplings, FilteredCouplings, AllAndFilteredCouplings]

Description

Amount of output

SecondOrder**Type**

Bool

Default value

No

Description

Include 2nd-order correction to electronic couplings

8.3 GREEN: Non-self-consistent Green's function calculation

green is an auxiliary program which can be used to calculate the density of states (DOS) and transmission of molecules connected to semi-infinite contacts. The transmission is the electron transmission through a molecule connected to semi-infinite contacts. The calculation is based on the non-self-consistent Green's function method, which is an approximation to the non-equilibrium Green's function (NEGF) method. The details of this method can be found in chapter 2 and appendix C of the PhD thesis of Jos Seldenthuis (2011) (<https://downloads.scm.com/Doc/Seldenthuis2011.pdf>). See Ref.¹ for more details on the applicability of the wide-band limit approximation. We suggest considering the NEGF implementation in the periodic program BAND; see the [BAND manual](#), since it might give better results.

8.3.1 Introduction

The utility program *green* calculates the density of states (DOS) and zero-bias transmission of a molecule connected to two semi-infinite contacts. A typical calculation consists of two parts. The first is the calculation of the effect of the semi-infinite contacts, contained in the so-called self-energy matrix. The second is the calculation of the desired properties of the molecule with the self-energies.

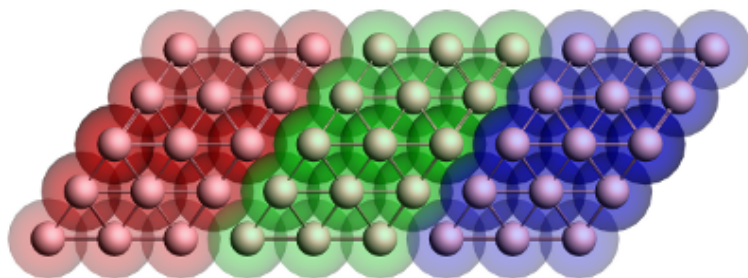
Self-energy

Figure 1: Geometry of the gold contact used in the calculation of the self-energy. The lead consists of two surface layers, left (red) and right (blue), and a bulk layer (green). Each principal layer in turn consists of three atomic layers. This should be sufficient to ensure that the Hamiltonian of the central (green) layer is a bulk Hamiltonian.

¹ C.J.O. Verzijl, J.S. Seldenthuis, and J.M. Thijssen, *Applicability of the wide-band limit in DFT-based molecular transport calculations*, *Journal of Chemical Physics* 138, 094102 (2013) (<https://doi.org/10.1063/1.4793259>)

Since the contacts are semi-infinite, the calculation of their self-energy is effectively a bulk calculation. Since ADF only works with systems of finite size, approximations have to be made. Fig. 1 shows the typical geometry used in the calculation of a gold contact. The geometry consists of three parts, the so-called principal layers. These layers should be large enough that the atoms on one side are not influenced by whatever is attached to the other side. Three atomic layers usually suffice. The green region is the bulk layer. The red and blue regions are the surface layers. Note that the blue region corresponds to the left contact of a molecule and the red region to the right contact.

To calculate the self-energy, we first need to do a single-point calculation of a principal layer. This layer is then used as a fragment in the following calculations. Note that all ADF calculations have to be performed with SYMMETRY NOSYM. We then build up the contact geometry from three copies of the layer fragment as in Fig. 1 and perform another single-point calculation. This results in a Hamiltonian describing the three contact layers and the coupling between them.

From the `adf.rkf` (TAPE21) file *green* can now calculate the self-energy matrices with the SURFACE key. This has to be done once for every energy for which we want to calculate the DOS or transmission. For the left contact of the molecule, *green* needs the blue and green fragments. The self-energy is calculated by taking the (blue) surface layer and iteratively adding more (green) bulk layers until matrices converge to the semi-infinite result. The self-energy of the right contact is similarly calculated from the red and green fragments. Since the self-energy describes the effect of an infinite chain of (green) bulk regions on a (red or blue) surface layer, this calculation does not depend on whatever is attached to the contacts. The self-energy matrices can therefore be reused for different molecules.

DOS and transmission

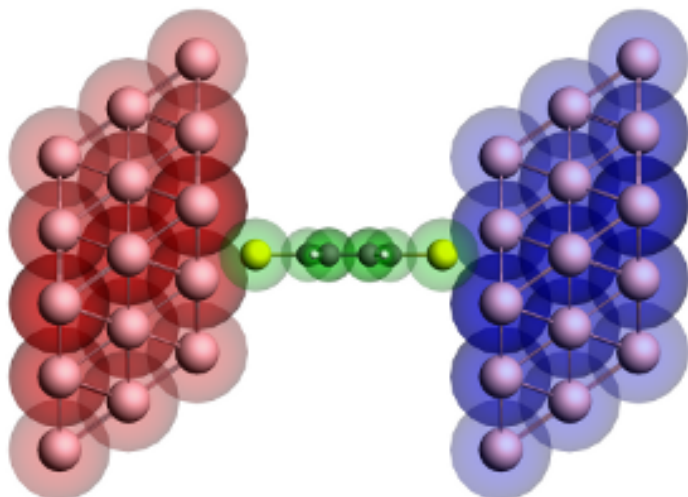


Figure 2: Geometry of the extended molecule used in the calculation of a benzenedithiol junction. The molecule is shown in green, while the left and right contact regions are shown in red and blue, respectively. Note that the red region corresponds to the blue surface layer in Figure 1 and vice versa.

Once the self-energy matrices have been calculated for the desired energies, we can compute the DOS and transmission of a molecule. However, since the self-energy matrices couple to the surface layers of the contacts, we need to include those surface layers in the calculation of the molecule (see Fig. 2). We therefore first perform a single-point calculation with ADF of the isolated molecule. The result is then used as a fragment and combined with the fragments of the surface layers to construct the so-called extended molecule. We then perform another single-point calculation of the final geometry.

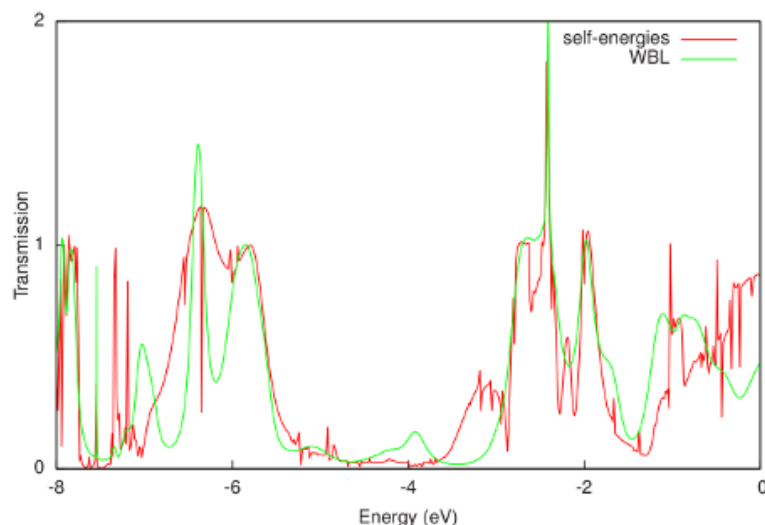
From the self-energies of the contacts and the `adf.rkf` file of the extended molecule, *green* can now compute the DOS and transmission. This calculation is non-self-consistent since the ADF calculations are all performed on finite instead of semi-infinite systems. This will result in certain artifacts in the DOS and transmission spectra, but those can be made arbitrarily small by choosing the principal layers large enough.

8.3.2 Wide-band-limit

In the wide-band limit (WBL) the coupling to the leads is assumed to be independent of energy. Therefore one does not need to calculate any self-energies. This also means that the eigenspace of the Green's function is independent of energy. It can therefore be diagonalized in advance, greatly speeding up the calculation of the DOS and the transmission. See Ref. [Page 284, 1](#) for more details on the applicability of the wide-band limit in DFT-based molecular transport calculations.

In the example `$AMSHOME/examples/adf/green_Al/green_WBL.run` of *green*, the transmission of *benzenedithiol junction* (page 1100) in the wide-band limit (WBL) is calculated. In order to model the molecule-metal interface, we do need to include a few gold layers in the calculation. However, unlike *before* (page 1089), only a single atomic layer as the principal layer is used. Because a single atomic layer is an unnatural configuration for gold, a minor amount of smearing is necessary to make the calculation converge. The molecule is sandwiched between the electrodes just like before (see Fig. 2 in *the example for benzenedithiol* (page 1100)). However, this time each atomic layer of gold gets its own fragment. The reason for this configuration is that if the WBL is used on the entire gold contact the result is an unphysical coupling to the leads; even the gold atoms contacting the molecule would have a direct coupling to the environment. A much better result can be obtained by only using the WBL on the back-most atomic layer and letting the electrons propagate naturally through the rest of the contact. Because the WBL is computationally so inexpensive, we can easily calculate the DOS and transmission for 10,000 points instead of 1000.

A comparison of the resulting transmission with the calculation with self-energies is shown in the following figure:



The WBL shows good agreement with the non-WBL transmission around the Fermi energy (-0.195 Hartree or -5.306 eV). Note that the quality of the WBL depends on the choice of the coupling (ETA). For this particular contact geometry we obtain good agreement for $\text{ETA} = 0.02$ Hartree, but a better value may be found for other electrodes. Finally, the WBL can be incrementally improved by adding more gold layers to the extended molecule. For many layers it converges to the calculation with full self-energies.

8.3.3 Input options

The input for *green* is keyword oriented and is read from the standard input. *green* is typically first used to calculate the self-energy matrices of the left and right contacts (with the SURFACE key), and then to calculate the density of states (DOS) and transmission (with the DOS and TRANS keys, respectively), using those self-energies. The only keyword required to be present in all calculations is the EPS keyword, which specifies the energy range.

```
$AMSBIN/green << eor
EPS mineps maxeps numeps
{ETA eta}
```

(continues on next page)

(continued from previous page)

```

{SO sh sl {moc}}
{SURFACE filename
  FRAGMENTS f1 f2
  END}
{DOS filename}
{TRANS
  LEFT filename
  FRAGMENT fragment
  ETA eta
  END
  RIGHT filename
  FRAGMENT fragment
  ETA eta
  END}
eor

```

EPS mineps maxeps numeps

The energy range for which either the self-energy matrices or the DOS and transmission have to be calculated. The range consists of numeps (≤ 1) points running from mineps to maxeps inclusive.

(optional) ETA eta

The imaginary energy, or the distance from the real axis, in the calculation of the Green's function. The value needs to be a small positive number to prevent singularities in the calculation. The default value (10^{-6} Hartree) is sufficient for most calculations.

(optional) SO sh sl {moc}

The shifts for the scissors operator. All occupied orbitals (HOMO and below) are shifted by sh, while the unoccupied orbitals (LUMO and above) are shifted by sl. Orbitals are considered occupied if their (possibly fractional) occupation is larger than moc (default 0). The scissor operator can partially remedy the underestimation of the HOMO-LUMO gap in DFT. The sh and sl shifts generally have the same magnitude, but opposite sign (with sh usually being negative and sl positive). A good estimate for the magnitude is the sum of the ionization potential and the energy of the HOMO of the *free* molecule. This can be improved by including image charge effects. For more details, see Ref.². By default, sh=sl=0.

(optional) SURFACE

```

SURFACE filename
  FRAGMENTS f1 f2
  END

```

The SURFACE block key enables the calculation of the self-energy matrices. The filename specifies the adf.rkf file resulting from an ADF calculation of the contacts. This calculation has to be performed with SYMMETRY NOSYM. The FRAGMENTS key is used to specify the two principal layers between which the surface is defined. The resulting self-energy matrices (one for every energy point given by EPS) are stored in a binary KF file named SURFACE.

(optional) DOS filename

The DOS key enables the calculation of the density of states. The filename specifies the adf.rkf file containing the result of an ADF calculation of the extended molecule (performed with SYMMETRY NOSYM). Two text files will be generated: DOS_A and DOS_B, containing, respectively, the DOS of the spin-A and spin-B electrons. In the case of a spin-unrestricted calculation, DOS_A and DOS_B might differ. If only the DOS of the spin-A electrons is required, the calculation can be sped up by specifying NOSAVE DOS_B. The DOS key requires the presence of the LEFT and RIGHT keys.

² S.Y. Quek, L. Venkataraman, H.J. Choi, S.G. Louie, M.S. Hybertsen and J.B. Neaton, *mine-Gold Linked Single-Molecule Circuits: Experiment and Theory*, *Nano Letters* 7, 3477 (2007) (<https://doi.org/10.1021/nl072058i>)

(optional) TRANS

The TRANS key enables the calculation of the transmission. The filename specifies the adf.rkf file containing the result of an ADF calculation of the extended molecule (performed with SYMMETRY NOSYM). Two text files will be generated: TRANS_A and TRANS_B, containing, respectively, the transmission of the spin-A and spin-B electrons. In the case of a spin-unrestricted calculation, TRANS_A and TRANS_B might differ. If only the transmission of the spin-A electrons is required, the calculation can be sped up by specifying NOSAVE TRANS_B. The TRANS key requires the presence of the LEFT and RIGHT keys.

LEFT/RIGHT

```
LEFT filename
  FRAGMENT fragment
  ETA eta
END
```

The LEFT and RIGHT block keys specify the left and right self-energies used in a calculation of the DOS and transmission. If a filename is specified, the self-energy matrices are read from that file. The energy range of the self-energies has to be consistent with the range specified by the EPS keyword. The FRAGMENT key is used to denote the fragment in the extended molecule (given by the argument to the DOS or TRANS key) to which the self-energy couples. If no filename is specified, the wide-band limit is used. The ETA key can then be used to specify the magnitude of the coupling (10^{-3} Hartree by default).

8.3.4 Output

After a successful calculation of the self-energy matrices, *green* produces a binary KF file named SURFACE containing two sections. The Surface section contains the energy range:

contents of Surface	comments
mineps	start of the energy range
maxeps	end of the energy range
numeps	number of points

The Sigma section contains the real and imaginary parts of the self-energy matrices:

contents of Sigma	comments
nfo	number of fragment orbitals (dimension of the self-energy matrices)
Re(Sigma_%d)	the real part of the %d self-energy matrix (numbered from 1 up to numeps)
Im(Sigma_%d)	the imaginary part of the %d self-energy matrix (numbered from 1 up to numeps)

A successful calculation of the density of states (DOS) or transmission results in the text files DOS_A and DOS_B, and TRANS_A and TRANS_B, respectively. The suffixes _A and _B denote the different spins. The text files contain the DOS and transmission for every energy point and can be plotted with, for example, gnuplot.

8.3.5 GREEN with ADF-GUI

In ADF2017 the ADF-GUI can be used to set up a GREEN calculation, and look at the results. Note, however, that not all GREEN options are supported with the ADF-GUI. For example, one cannot use unrestricted or wide-band-limit calculations with the ADF-GUI. GUI tutorials exist for NEGF with DFTB or BAND. Suggestion is to consider using the NEGF implementation in the periodic program BAND, see the [BAND manual](#), since it might give better results.

ANALYSIS

See also:ADF-GUI tutorial: [all ADF tutorials](#), [fragment analysis](#)Examples: [analysis](#) (page 1108)

9.1 Molecules built from fragments

ADF analyzes the results in terms of user-specified subsystems from which the total system is built. The program tells you how the ‘Fragment orbitals’ (FOs) of the chemically meaningful subunits mix with FOs on other fragments to combine to the final molecular orbitals.

ADF builds a molecule from user-defined fragments, which may be single atoms or larger moieties, for example, ligands, functional groups, or complete molecules in a donor-acceptor complex. In practice, this means that the results of the ADF calculation on a fragment are saved on a file and that the fragment files are then used in setting up the calculation on the overall system. The fragment orbitals (FOs), i.e., the MOs from the calculations on the fragments, are employed as basis functions in the new calculation. This does not imply a basis set truncation or contraction because the virtual FOs are included: the FOs constitute only a transformation of the basis set. If there are symmetry-equivalent fragments, for example, the six CO molecules in octahedral $\text{Cr}(\text{CO})_6$, the program generates symmetry combinations of the FOs and uses the symmetrized fragment orbitals (SFOs) as basis functions. The SFOs transform as the irreducible representations (irreps) of the molecule, allowing a symmetry-driven analysis of the results. In the absence of any symmetry the SFOs are identical to the FOs.

The fragment approach offers considerable advantages. It enhances the interpretative power of ADF as it leads to a more transparent picture of bonding, which reduces from a complicated mixing of many primitive basis functions (possessing little physical relevance) to a few key interactions between meaningful fragment (frontier) orbitals. The fragment approach also improves the numerical precision. In ADF, energies are calculated directly, with respect to the fragments, by one single numerical integral of the difference energy density $\epsilon[\rho, \mathbf{r}] - \sum_A \epsilon_A[\rho_A, \mathbf{r}]$ between the overall molecule and the constituting fragments.

$$\Delta E[\rho] = \int d\mathbf{r} \left(\epsilon[\rho, \mathbf{r}] - \sum_A \epsilon_A[\rho_A, \mathbf{r}] \right)$$

In other words, we evaluate the energy of the overall molecule, $E[\rho] = \int d\mathbf{r} \epsilon[\rho, \mathbf{r}]$, and the energies of each of the fragments, say the atoms that constitute the overall molecule, $E_A[\rho] = \int d\mathbf{r} \epsilon_A[\rho_A, \mathbf{r}]$, in the same numerical integration grid. This provides more accurate relative energies than subtracting total energies from separate calculations, because the same relative numerical integration error applies to a much smaller quantity, yielding, in turn, a much smaller absolute error.

Note that the user has the freedom to make their own choice of fragments. This is, however, not a matter of plain arbitrariness, and it does not make the analysis tools less meaningful. On the contrary, this freedom simply reflects the many perspectives from which a particular chemical phenomenon can be viewed.

In practice, many calculations are performed using as fragments the so-called basic atoms, which are the smallest possible building blocks in ADF. The basic atoms are not necessarily physically realistic objects - indeed, usually they are not, as they must be spin-restricted and spherically symmetric. The computed (bonding) energy with respect to basic atoms, then, does not yield quantities that can be compared to experimental data directly. Rather, one must correct for the true ground state of the isolated single atoms.

Text is mostly taken from: *Chemistry with ADF* G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler *Journal of Computational Chemistry* 22, 931 (2001) (<https://doi.org/10.1002/jcc.1056>).

Link: [How to make molecular fragments](#) (page 53)

Tutorial: [ADF fragment analysis](#)

Examples: [analysis options](#) (page 1108)

9.2 Bond energy analysis

No special input keys are required. However, if you have open-shell fragments, see the UNRESTRICTEDFRAGMENTS or FRAGOCCUPATIONS key.

ADF calculates various chemically meaningful terms that add up to the bond energy, with an adaptation of Morokuma's bond energy decomposition to the Kohn-Sham MO method. The individual terms are chemically intuitive quantities such as electrostatic energy, Pauli repulsion, and orbital interactions. The latter are symmetry decomposed according to the Ziegler transition state method. For a discussion of bond energy decompositions and applications, see, for example, Refs.^{1,2,3,12,13,14,15,16,17,18}. For a discussion of forming electron pair bonding between open-shell molecules, see Ref.⁴. For an ETS-NOCV analysis of the orbital interaction, see Ref.⁵.

¹ T. Ziegler and A. Rauk, *On the calculation of Bonding Energies by the Hartree Fock Slater method. I. The Transition State Method*, *Theoretica Chimica Acta* 46, 1 (1977) (<https://doi.org/10.1007/BF00551648>)

² T. Ziegler and A. Rauk, *A theoretical study of the ethylene-metal bond in complexes between copper(1+), silver(1+), gold(1+), platinum(0) or platinum(2+) and ethylene, based on the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* 18, 1558 (1979) (<https://doi.org/10.1021/ic50196a034>)

³ F.M. Bickelhaupt, N.M. Nibbering, E.M. van Wezenbeek and E.J. Baerends, *The Central Bond in the Three CN Dimers NC-CN, CN-CN, and CN-NC: Electron Pair Bonding and Pauli Repulsion Effects**, *Journal of Physical Chemistry* 96, 4864 (1992) (<https://doi.org/10.1021/j100191a027>)

¹² K. Kitaura and K. Morokuma, *A new energy decomposition scheme for molecular interactions within the Hartree-Fock approximation*, *International Journal of Quantum Chemistry* 10, 325 (1976) (<https://doi.org/10.1002/qua.560100211>)

¹³ T. Ziegler and A. Rauk, *Carbon monoxide, carbon monosulfide, molecular nitrogen, phosphorus trifluoride, and methyl isocyanide as sigma donors and pi acceptors. A theoretical study by the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* 18, 1755 (1979) (<https://doi.org/10.1021/ic50197a006>)

¹⁴ H. Fujimoto, J. Osamura and T. Minato, *Orbital interaction and chemical bonds. Exchange repulsion and rehybridization in chemical reactions*, *Journal of the American Chemical Society* 100, 2954 (1978) (<https://doi.org/10.1021/ja00478a004>)

¹⁵ S. Wolfe, D.J. Mitchell and M.-H. Whangbo, *On the role of steric effects in the perturbational molecular orbital method of conformational analysis*, *Journal of the American Chemical Society* 100, 1936 (1978) (<https://doi.org/10.1021/ja00474a055>)

¹⁶ A.J. Stone and R.W. Erskine, *Intermolecular self-consistent-field perturbation theory for organic reactions. I. Theory and implementation; nucleophilic attack on carbonyl compounds*, *Journal of the American Chemical Society* 102, 7185 (1980) (<https://doi.org/10.1021/ja00544a003>)

¹⁷ F. Bernardi, A. Bottoni, A. Mangini and G. Tonachini, *Quantitative orbital analysis of ab initio SCF=MO computations : Part II. Conformational preferences in H2N-OH and H2N-SH*, *Journal of Molecular Structure: THEOCHEM* 86, 163 (1981) ([https://doi.org/10.1016/0166-1280\(81\)85082-8](https://doi.org/10.1016/0166-1280(81)85082-8))

¹⁸ P.J. van den Hoek and E.J. Baerends, *Chemical bonding at metal-semiconductor interfaces*, *Applied Surface Science* 41/42, 236 (1989) ([https://doi.org/10.1016/0169-4332\(89\)90063-9](https://doi.org/10.1016/0169-4332(89)90063-9))

⁴ F.M. Bickelhaupt, M. Solà, C. Fonseca Guerra, *Highly polar bonds and the meaning of covalency and ionicity - structure and bonding of alkali metal hydride oligomers*, *Faraday Discussions* 135, 451 (2007) (<https://doi.org/10.1039/B606093E>)

⁵ M. Mitoraj, A. Michalak and T. Ziegler, *A Combined Charge and Energy Decomposition Scheme for Bond Analysis*, *Journal of Chemical Theory and Computation* 5, 962 (2009) (<https://doi.org/10.1021/ct800503d>)

In ADF2012 the calculation of the Pauli repulsion for meta-GGAs and meta-hybrids is implemented. Note that for hybrids this was already implemented before in the case of closed-shell fragments. In ADF2012, for hybrids, meta-GGAs, and meta-hybrids the calculation of the Pauli repulsion is also implemented if one is simulating an unrestricted fragment with the key FRAGOCCUPATIONS.

In ADF2012, for hybrids the exact exchange contribution to the Pauli term is isolated and the contributions to the orbital term are divided among orbital symmetries.

In ADF2026, in the case of a non-atomic fragment calculation, the bond energy with respect to atomic create runs is printed in the output. This bond energy is computed as an energy difference between the full molecule and single atoms (create runs), where in the create runs the atoms are usually calculated as spherical spin-restricted neutral atoms.

9.2.1 Bond energy details

In the framework of Kohn-Sham MO theory and in conjunction with the fragment approach, one can decompose the bond energy between the fragments of a molecular system - say, a base and a substrate for E2 elimination - into contributions associated with the various orbital and electrostatic interactions. In ADF, we follow a Morokuma-type energy decomposition method. The overall bond energy ΔE is divided into two major components. First, the preparation energy ΔE_{prep} corresponding to the amount of energy required to deform the separated fragments A and B, say, from their equilibrium structure to the geometry they acquire in the overall molecule ($\Delta E_{\text{prep,geo}}$), and to excite them to their valence electronic configuration ($\Delta E_{\text{prep,el}}$). Second, the interaction energy ΔE_{int} between the prepared fragments.

$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} = \Delta E_{\text{prep,geo}} + \Delta E_{\text{prep,el}} + \Delta E_{\text{int}}$$

In the next step, the interaction energy ΔE_{int} is further decomposed into three physically meaningful terms, which are printed in the ADF output file.

$$\Delta E_{\text{int}} = \Delta V_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} = \Delta E^0 + \Delta E_{\text{oi}}$$

The term ΔV_{elst} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments as they are brought together at their final positions, giving rise to an overall density that is simply a superposition of fragment densities $\rho_A + \rho_B$. (Note that we use the convention that energy terms containing potential energy only, kinetic energy only, or both kinetic and potential energy are indicated by V, T, and E, respectively.) For neutral fragments, ΔV_{elst} is usually attractive. The Pauli repulsion ΔE_{Pauli} arises as the energy change associated with going from $\rho_A + \rho_B$ to the wave function $\Psi^0 = N A[\Psi_A \Psi_B]$ that properly obeys the Pauli principle through explicit antisymmetrization (A operator) and renormalization (N constant) of the product of fragment wave functions. It comprises the destabilizing interactions between occupied orbitals, and is responsible for any steric repulsion. In case of neutral fragments, it can be useful to combine ΔV_{elst} and ΔE_{Pauli} in a term ΔE_0 which, in the past, has been conceived as the steric interaction. However, we prefer to reserve the designation steric interaction or repulsion for ΔE_{Pauli} because that is, as already mentioned, the only source of net repulsive interactions between molecular fragments. Finally, the wave function is allowed to relax from Ψ^0 to the fully converged wave function Ψ . The associated orbital interaction energy ΔE_{oi} accounts for electron pair bonding, charge transfer (e.g., HOMO-LUMO interactions), and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). In a symmetric molecule this can be further decomposed into the contributions from the distinct irreducible representations Γ of the interacting system using the extended transition state method. In systems with a clear σ/π separation, this symmetry partitioning proves to be very informative.

$$\Delta E_{\text{oi}} = \sum_{\Gamma} \Delta E_{\text{oi},\Gamma}$$

An alternative, which can also be used in asymmetric molecules, is the ETS-NOCV analysis, which decomposes the bonding interactions in the context of natural orbitals for chemical valence, see Refs. [Page 292, 567](#).

⁶ M. Mitoraj, A. Michalak and T. Ziegler, *On the Nature of the Agostic Bond between Metal Centers and Beta-Hydrogen Atoms in Alkyl Complexes. An Analysis Based on the Extended Transition State Method and the Natural Orbitals for Chemical Valence Scheme (ETS-NOCV)*, *Organometallics* 28, 3727 (2009) (<https://doi.org/10.1021/om900203m>)

⁷ M. Mitoraj, and A. Michalak, *Natural orbitals for chemical valence as descriptors of chemical bonding in transition metal complexes*, *Journal of Molecular Modeling* 13, 347 (2007) (<https://doi.org/10.1007/s00894-006-0149-4>)

The pure orbital interaction effect of forming electron pair bonding between open-shell molecules can approximately be calculated with a bond energy analysis in which all virtual orbitals are removed from the fragments, see Ref. [Page 292, 4](#).

An extensive discussion of the physical meaning of all the terms in the energy decomposition is given in F.M. Bickelhaupt and E.J. Baerends, *Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry*, In: Rev. Comput. Chem.; Lipkowitz, K. B. and Boyd, D. B., Eds.; Wiley-VCH: New York, 2000, Vol. 15, 1-86.

Text is mostly taken from: *Chemistry with ADF*, G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *Journal of Computational Chemistry* 22, 931 (2001) (<https://doi.org/10.1002/jcc.1056>).

9.2.2 Notes on double-hybrid functionals and MP2

Since ADF2019.3, double-hybrid density functionals have been implemented in ADF. These include contributions from virtual orbitals from a *MP2 calculation* (page 387). The evaluation of MP2 energies requires orbital energies as input, which, however, are not available for orthogonal fragments. Thus, whenever a double-hybrid calculation is carried out, the bond energy with respect to the individual fragments is calculated and printed out. However, all terms which rely on the orthogonal fragment density (e.g. Pauli repulsion terms) do not include the MP2 part of the double-hybrid.

9.2.3 Total energy evaluation

ADF normally does not calculate the total energy of a system (the energy with respect to bare nuclei and free electrons). However, ADF calculates the energy of the system with respect to fragment energies. By default, these fragments are the spherical spin-restricted neutral atoms, but one can also use larger fragments. For this reason total energies from other programs cannot be compared to ADF directly. Note, however, that only energy difference comparisons are meaningful. These are the only energies that play a role in chemistry, of course, and for this one does not need total energies.

If you really want to calculate the total energies, there are two options in ADF:

Total energy by adding the binding energy of the atoms

There is a work-around to calculate the total energy of a system: calculate the total energies of the atomic fragments and add them to the bonding energy. Because the total energy of an atom is, by definition, the energy difference between the atom and the (nucleus+free electrons) system, one can calculate it by calculating a single atom with the charge equal to the number of electrons. The ‘bonding energy’ of such an ‘atom’ will then be equal to the negative of the total energy of the atomic fragment. Care should be taken to apply this procedure to frozen-core fragments. In this case, it only makes sense to remove the valence electrons and leave the frozen core.

TOTALENERGY keyword

The total energies have not been tested extensively and should therefore be used with caution. In addition to bond energies, it is now possible to compute total energies with ADF by including the keyword TOTALENERGY in the input. This work is in progress.

TOTALENERGY

The total energy will be computed for the chosen XC functional (LDA, GGA, hybrid functionals, or Hartree-Fock). Meta-GGA functionals, (ZORA) scalar relativistic and relativistic spin-orbit calculations, electric fields, and QM/MM are not yet supported.

In particular the requirements for integration accuracy are somewhat higher than for bond energies. It is recommended to use an integration grid (BeckeGrid) of quality “Good”. If in doubt, a convergence test with respect to the integration accuracy is recommended.

9.2.4 Interacting Quantum Atoms (IQA)

Note: The use of **symmetry keyword** is allowed (however, all the points of the grid will be used) and the code has been extended to **open-shell systems** (AMS2023). **Scalar relativistic calculations (ZORA)** are now allowed (AMS2026). Due to gauge dependence with ZORA, only interatomic interactions are calculated. Please note that spin-orbit calculations are not allowed with IQA.

The interacting quantum atoms approach (IQA) has been developed by Angel Martín Pendás and coworkers in the framework of real-space partitions of the molecular space^{8,9,19}. This can be seen as an alternative to the Bickelhaupt-Baerends' bond energy decomposition scheme but for the **total energy** of the molecular system. A full IQA decomposition is the default procedure (except for scalar ZORA calculations), including both intra-atomic and interatomic interactions.

In a wavefunction context, the IQA QTAIM partition of the molecular energy leads exactly to:

$$E = \sum_A (T^A + E_{Ne}^{AA} + E_{eeCl}^{AA} + E_{eeXC}^{AA}) + \frac{1}{2} \sum_{A \neq B} (E_{NN}^{AB} + E_{eN}^{AB} + E_{Ne}^{AB} + E_{eeCl}^{AB} + E_{eeXC}^{AB})$$

The first four terms of the right-hand side in the equation above correspond to intra-atomic (also coined 'self') terms for each atom 'A': the atomic kinetic energy (T^A), the interaction energy between the nucleus and the electron density inside basin A (E_{Ne}^{AA}), and the repulsion energy between electrons in A, decomposed into classical electrostatic (E_{eeCl}^{AA}) and exchange-correlation contributions (E_{eeXC}^{AA}).

The last sum in the equation corresponds to the interactions between each atom pair 'AB' (bonded or not bonded by a bond path): the repulsion energy between nuclei in A and B (E_{NN}^{AB}), the attraction of the electrons in A by the nucleus in B (E_{eN}^{AB}), the attraction of the electrons in B by the nucleus in A (E_{Ne}^{AB}), and the repulsion energy between electrons in A with those in B, which can be split into a classical electrostatic contribution (E_{eeCl}^{AB}) and an exchange-correlation one (E_{eeXC}^{AB}).

Within a Kohn-Sham DFT framework, the implementation of this partition is not straightforward (see Ref.¹⁰ for more details). For any atom-atom pair 'AB', we evaluate:

$$E_{inter}^{AB} = E_{NN}^{AB} + E_{eN}^{AB}[\rho] + E_{Ne}^{AB}[\rho] + E_{eeCl}^{AB}[\rho] + E_{eeX}^{AB}[\{\psi_i^{KS}\}]$$

where $E_{eeX}^{AB}[\{\psi_i^{KS}\}]$ corresponds to the full exact exchange ('HF-like') interacting energy between the two atoms. Tognetti and Joubert have shown that despite underlying approximations, this expression can be safely used at least for semi-quantitative purposes¹¹.

Three energetic terms are printed for each atom pair. The first one corresponds to the *total* interaction energy between the two atoms (E_{inter}^{AB}). This energy is then split into two contributions: the 'covalent part' corresponds to the exchange energy between the two atomic basins ($E_{eeX}^{AB}[\{\psi_i^{KS}\}]$), while the 'noncovalent one' is the sum of all remaining electrostatic contributions ($E_{NN}^{AB} + E_{eN}^{AB} + E_{Ne}^{AB}[\rho] + E_{eeCl}^{AB}[\rho]$). This last term also includes a dispersion correction (if and only if dispersion is a posteriori requested in the DFT calculation). It should be noticed that here, *noncovalent* is to be understood as the sum of all contributions that are not covalent (and not only London-type interactions). To summarize, when no dispersion correction of the Grimme type is added, the *noncovalent* is equal to the classical electrostatic part (previously coined *ionic*), while when Grimme's D3 is used, *noncovalent* is the sum of this ionic part and of the dispersion correction.

As already mentioned, a full IQA decomposition is now automatically performed, including intra-atomic terms. Choosing the **verbose mode** allows you to get more details about the energy decomposition (all terms are detailed in this case and described in the output itself). This is now the default option.

⁸ M.A. Blanco, A.M. Pendás and E. Francisco, *Interacting Quantum Atoms: a correlated energy decomposition scheme based on the quantum theory of atoms in molecules*, Journal of Chemical Theory and Computation 1, 1096 (2005) (<https://doi.org/10.1021/ct0501093>).

⁹ A.M. Pendás, M.A. Blanco and E. Francisco, *A molecular energy decomposition scheme for atoms in molecules*, Journal of Chemical Theory and Computation 2, 90 (2006) (<https://doi.org/10.1021/ct0502209>).

¹⁹ J.M. Guevara-Vela, E. Francisco, T. Rocha-Rinza and A.M. Pendás, *Interacting Quantum Atoms - A review*, Molecules 25, 4028 (2020) (<https://doi.org/10.3390/molecules25174028>).

¹⁰ V. Tognetti and L. Joubert, *On Atoms-in-Molecules Energies from Kohn-Sham calculations*, ChemPhysChem 18, 2675 (2017) (<https://doi.org/10.1002/cphc.201700637>).

¹¹ V. Tognetti and L. Joubert, *On the physical role of exchange in the formation of an intramolecular bond path between two electronegative atoms*, Journal of Chemical Physics 138, 024102 (2013) (<https://doi.org/10.1063/1.4770495>).

Tip: If you need to extract relevant IQA terms along a PES Scan, see also the [REG/IQA tutorial](#)

You can activate the full IQA analysis via the IQA input block:

```
IQA
  Enabled Yes/No
  Print [normal | verbose]
  AtomsToDo integer_list
End
```

IQA

Type

Block

Description

Total energy decomposition based on the interacting quantum atoms (IQA) approach and using QTAIM real-space partition.

Enabled

Type

Bool

Default value

No

GUI name

Calculate: Interacting Quantum Atoms (IQA)

Description

Calculate the total energy decomposition using the interacting quantum atoms (IQA) approach and the QTAIM real-space partitioning.

Print

Type

Multiple Choice

Default value

normal

Options

[normal, verbose]

Description

Minimal output (default) or verbose mode (detailed energy decomposition)

AtomsToDo

Type

Integer List

GUI name

Include atoms

Description

Define a subset of atoms for which the IQA atom-atom interactions are calculated (no intra-atomic terms).

If left empty, all atoms will be included (full IQA).

9.3 Localized Molecular Orbitals

9.3.1 Boys-Foster and Pipek-Mezey localization

With the LOCORB key ADF provides the Boys-Foster method and Pipek-Mezey method for localization of molecular orbitals¹²³. This implies a unitary transformation of the occupied molecular orbitals as computed in the SCF procedure, with the objective of obtaining a (transformed) set of orbitals that represent exactly the same charge density but with molecular orbitals that are more localized in space than the original MOs.

These localization methods cannot be used in case of spin-orbit coupling.

The goal of orbital localization lies in analysis: the localized orbitals provide an easier-to-interpret picture. The localized molecular orbitals can be visualized with the ADF-GUI.

Orbital localization procedures require a measure of the localization of the orbitals which can then be optimized in the space of the allowed unitary transformations. Methods advocated in the literature differ in the definition of this measure. The Boys-Foster method minimizes the mean extension of the occupied orbitals around their center of gravity; see the literature for details. The Pipek-Mezey localization maximizes the sum of orbital-dependent partial charges on the nuclei, see the literature for details. Both Boys-Foster localization method and Pipek-Mezey localization method have been implemented in ADF, see Ref.^{Page 297, 1}.

Occasionally it is useful to apply the localization only to a subset of the MOs, with the objective to expose certain features better. This is accomplished by performing the localization in a number of distinct steps, where at each step the localization is restricted by keeping a subset of the MOs frozen. A case is worked out in the Examples document.

The computation of localized orbitals is controlled with the block-type key. By default (if the key is not supplied in input) no orbital localization is carried out.

```
LOCORB {nopop store}
  {Criterion <BOYS|PM>}
  Spintype FrozenMOs
  Spintype FrozenMOs
  ...
End
```

nopop

Specifies that no SFO population analysis is to be carried out on the localized MOs. By default this population analysis will be printed in the output file.

store

Specifies that the transformation from MOs to localized MOs is stored on adf.rkf (TAPE21).

Criterion <BOYS|PM>

By default the Boys-Foster localization method is used if Criterion is not specified and in case 'Criterion BOYS' is specified. If 'Criterion PM' is specified, the Pipek-Mezey localization method is used.

Spintype

Must be either alfa or beta (not case sensitive) and refers to spin-A and spin-B orbitals respectively. In a spin-restricted run beta records are meaningless and must not be used.

FrozenMOs

A list (possibly empty) of integers, referring to a list of MOs from the SCF, and/or labels of irreducible representations. The integers and/or labels may be given in any order.

¹ J. Autschbach and H.F. King, *Analyzing molecular static linear response properties with perturbed localized orbitals*, Journal of Chemical Physics 133, 044109 (2010) (<https://doi.org/10.1063/1.3455709>)

² C. Edmiston and K. Rudenberg, *Localized Atomic and Molecular Orbitals*, Reviews of Modern Physics 35, 457 (1963) (<https://doi.org/10.1103/RevModPhys.35.457>)

³ J.M Foster and S.F. Boys, *Canonical Configurational Interaction Procedure*, Reviews of Modern Physics 32, 300 (1960) (<https://doi.org/10.1103/RevModPhys.32.300>)

Each record Spintype FrozenMOs in the data block defines a localization *cycle* in which the localization procedure is carried out on all orbitals (of the indicated spin), except those indicated by the FrozenMOs.

For either spin at least one localization cycle is carried out. If no data record for that spin is found in the data block, a full localization is performed, without any MOs excluded.

The data block may be completely empty (but the record end must be supplied since the key is block-type) and would be equivalent with specifying two records, one for either spin, without any FrozenMOs:

```
LOCORB {nopop}  
End
```

is equivalent with

```
LOCORB {nopop}  
  alfa  
  beta  
End
```

The integers in FrozenMOs refer to an overall list of SCF MOs consisting of all valence MOs in each symmetry representation up to and including the highest non-empty one. So, when for instance in the first irrep MO #4 is the highest non-empty one and in the second irrep mo #2 is the highest non-empty one, then in the overall list the first 4 are the orbitals of the first irrep, the no.s 5 and 6 are from the second irrep, et cetera.

Each symmetry label in FrozenMOs collectively denotes in one stroke all molecular orbitals of that representation up to and including the highest occupied one (in that symmetry). The label may be the name of an irreducible representation or of a subspecies. In the former case all partner representations are denoted collectively. In an atom symmetry for instance, specifying P would be equivalent to P:x P:y P:z.

Note that if the final SCF has in any symmetry representation empty orbitals *below* the highest non-empty orbital in that symmetry - violating the Aufbau principle - then these empty orbitals are included in the above-defined overall list and hence a FrozenMOs specification is necessary, namely to avoid mixing MOs with different occupation numbers in the localization.

Note: It is imperative that in a particular localization cycle only MOs from the SCF are combined that have identical occupation numbers. If this is violated the program will carry out the localization without error message, but the results are incorrect in the sense that the density defined by the localized orbitals is *not* the same anymore as the SCF density.

So, if any of the MOs in the overall list defined above is not fully occupied (open shell, excited state, ...) you need to define precisely the localization cycles - localizing in each cycle only MOs with identical occupations and freezing all others - in order to obtain sensible results.

In the output file the localized MOs are printed as expansions in SFOs and (optionally) a population analysis is given, again in terms of the SFOs. Furthermore, each localized MO has associated with it an energy value and an occupation number. The energy is the expectation value of the Fock operator for the orbital. The occupation number is obtained as a weighted sum from the SCF MOs that were combined into the localized orbital. As mentioned before one should combine only SCF MOs with identical occupations into a localized orbital, in which case its occupation number will be the same. The printout of the occupation number of the localized orbital allows therefore a verification that a correct localization procedure has been carried out.

Perturbed Localized Molecular Orbitals

Perturbed localized molecular orbitals, correct to first order in an applied field, can be calculated in case of AORESPONSE. Can be used if the applied field changes the density in first order. Ref.¹ describes this functionality and the implementation in ADF in detail, and gives some examples. The perturbed localized molecular orbitals can be visualized with the ADF-GUI. In addition to the AORESPONSE and the LOCORB key one has to specify the PERTLOC key in order to calculate these perturbed localized molecular orbitals. The optional subkeywords of the block key PERTLOC are described below.

```
LOCORB ..
  ..
End
AORESPONSE
  ..
End
PERTLOC
  efield
  bfield
  alfa
  gprime
  beta
  <static|dynamic>
  <diag|fulltens>
End
```

efield

The perturbation is an electric field (default).

bfield

The perturbation is a magnetic field. Should be consistent with AORESPONSE.

alfa

Analyze the static or dynamic polarizability.

gprime

Analyze the G' (gyration) tensor, for optical rotation dispersion. Requires a frequency dependent perturbation field, with a frequency (omega) unequal to zero.

beta

Analyze the optical rotation parameter beta. The relation to G' is $\beta = -G'/\omega$. The optical rotation parameter beta is calculated directly⁴ and has a well-defined static limit, i.e. omega can be zero or non-zero.

<static|dynamic>

The static or dynamic (frequency dependent) subkeyword should be consistent with what is used in AORESPONSE. Static is default, should be used for a static field. Dynamic should be used for a frequency dependent perturbation field.

<diag|fulltens>

Diag is default, which will only analyze the diagonal of the response tensor. If fulltens is specified the full tensor is analyzed.

⁴ S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *A Density Functional Theory study of frequency-dependent polarizabilities and van der Waals dispersion coefficients for polyatomic molecules*, *Journal of Chemical Physics* 103, 9347 (1995) (<https://doi.org/10.1063/1.469994>)

9.3.2 Reduction of Orbital Space Extent (ROSE)

ROSE (Reduction of Orbital Space Extent) aims at constructing intrinsic fragment orbitals (IFOs), see Ref.⁵, and recanonicalized intrinsic localized molecular orbitals (RILMOs), see Ref.⁶. With the external ROSE package (see https://gitlab.com/quantum_rose/rose, this package is not distributed by SCM), one can calculate such orbitals for different types of basis functions. In AMS2025 the ROSE functionality relating to Slater-Type Orbitals has been made available inside ADF.

The basic idea used in ROSE is to define an intrinsic minimal basis set of polarized orbitals which span the occupied space exactly and also covers the valence part of the unoccupied, or virtual, orbital space. These intrinsic fragment orbitals are localized and not very basis set dependent and therefore form a good starting point for analysis. They are furthermore used as a reference in a localization procedure in which the occupied orbitals are unitarily transformed into RILMOs that typically resemble the occupied MOs of the reference fragment calculations. The same localization procedure is also applied to localize the valence virtuals that together with the occupied RILMOs span the IFO space. As the thus generated virtual space is too small to reach quantitative accuracy in TDDFT calculations, it is necessary to also add the so-called ‘hard’ virtuals, see Ref.^{Page 300, 6}, to the virtual space. This is done, slightly different from the procedure reported in Ref.⁶, by defining a set of reference virtuals on the fragments. The generation of localized hard virtuals follows then in mathematically exactly the same way as the construction of valence intrinsic fragment orbitals. The difference is that an energy-truncated space, complementary to the already localized valence space, is now the target. This procedure combines energy localization and spatial localization to allow for subsystem TDDFT treatments, see section on *exciton transfer integrals with ROSE* (page 278) and Ref.⁶.

Next we only discuss the functionality of ROSE that is available inside ADF. In this implementation spin-orbit coupling cannot be used, spin-restricted orbitals should be used, and all-electron basis sets should be used.

Starting point for ROSE calculations is always to divide the target molecule or complex into 2 or more chemically relevant fragments. One needs to calculate these fragments using SYMMETRY NOSYM, and the fragment nuclear coordinates should match the corresponding coordinates in the full molecule or complex. The subsequent ADF calculation on the full molecule or complex should also use symmetry NOSYM. It is convenient to use the same basis set as used in the fragments to make sure that the reference virtual space is large enough to cover the (energy-truncated) supermolecular virtual space.

An input that calculates localized orbitals with the ROSE implementation in ADF could look like

```
AMS_JOBNAME=Frag1 $AMSBIN/ams <<eor
System
  atoms
    coordinates Frag1
  end
end
Task SinglePoint
Engine ADF
  basis
    ...
    core None
  end
  symmetry nosym
  ...
EndEngine
eor

AMS_JOBNAME=Frag2 $AMSBIN/ams <<eor
System
```

(continues on next page)

⁵ B. Senjean, S. Sen, M. Repisky, G. Knizia, and L. Visscher, *Generalization of Intrinsic Orbitals to Kramers-Paired Quaternion Spinors, Molecular Fragments, and Valence Virtual Spinors*, *Journal of Chemical Theory and Computation* 17, 1337 (2021) (<https://doi.org/10.1021/acs.jctc.0c00964>)

⁶ S. Sen, B. Senjean, L. Visscher, *Characterization of excited states in time-dependent density functional theory using localized molecular orbitals*, *Journal of Chemical Physics* 158, 054115 (2023) (<https://doi.org/10.1063/5.0137729>)

(continued from previous page)

```

atoms
  coordinates Frag2
end
end
Task SinglePoint
Engine ADF
  basis
    ...
    core None
  end
  symmetry nosym
  ...
EndEngine
eor

$AMSBIN/ams <<eor
System
  atoms
    coordinates Frag1
    coordinates Frag2
  end
end
Task SinglePoint
Engine ADF
  basis
    ...
    core None
  end
  symmetry nosym
  ROSE
    fragmentfile Frag1.results/adf.rkf
    fragmentfile Frag2.results/adf.rkf
  End
  ...
EndEngine
eor

```

The calculated intrinsic orbitals can be visualized with the AMS-GUI.

The ROSE block key should contain the FragmentFile key. Other keys are optional.

```

ROSE
  Additional_virtuals_cutoff float
  Exponent integer
  Frag_bias float_list
  Frag_threshold float
  Frag_valence integer_list
  FragmentFile string
  Version [Stdrrd_2013 | Simple_2013 | Simple_2014]
  nfragments integer
End

```

ROSE

Type
Block
Description

Options for orbital localization

Additional_virtuals_cutoff**Type**

Float

Default value

2.0

Unit

Hartree

GUI name

Additional virtuals cutoff

Description

Specifies the energy threshold to determine the number of additional hard virtuals to localize for the supermolecule. If not specified the default value is used.

Exponent**Type**

Integer

Description

The value of the exponent (for the default Pipek-Mezey type of localization, the exponent is equal to 2. A higher value of 3 or 4 is sometimes useful.).

Frag_bias**Type**

Float List

Description

Expert key. Specifies the bias applied to each fragment when assigning the localized orbitals to a particular fragment. Use a negative value for default behavior for a given fragment. If not specified, or if the number of items is unequal the number of fragments, a default bias is used.

Frag_threshold**Type**

Float

Default value

10.0

Unit

Hartree

GUI name

Frag threshold

Description

Specifies energy threshold to determine number of reference hard virtuals to use for the fragments (needed to localize the additional hard virtuals). The total number of reference virtuals should be larger than the number of virtual MOs to localize (similar to having more reference valence orbitals than occupied valence orbitals to localize), so it is advisable to use a relatively high value for this parameter. If not specified the default value is used.

Frag_valence**Type**

Integer List

Description

Expert key. Specifies the number of valence orbitals for each fragment. Use a negative value for default behavior for a given fragment. If not specified, or if the number of items is unequal the number of fragments, by default the code generates the valence space for each fragment as the sum of valence orbitals of individual atoms within each fragment.

FragmentFile**Type**

String

Recurring

True

Description

Path (either absolute or relative) of each fragment file. The number of fragments used to project on will be number of occurrences of this key.

Version**Type**

Multiple Choice

Options

[Stdndr_2013, Simple_2013, Simple_2014]

Description

Expert key, specifies version of the IAO generation. If not specified a default value is used.

nfragments**Type**

Integer

Default value

2

Description

Expert key, preferably use the FragmentFile key for each fragment instead, and do not use this key. If the FragmentFile key is not used, then with this key one can specify the number of fragments used to project on. If this key is used the fragment file names should be called frag1.rkf, frag2.rkf, etcetera, and should be present at the directory where ams is started.

9.3.3 Natural Bond Orbitals (NBO)

See the section on *NBO analysis* (page 309) for localized orbitals that are calculated in case of NBO.

9.4 Advanced charge density and bond order analysis

In addition to Mulliken charge analysis, ADF calculates several atomic charges that do not share the flaws of Mulliken (strong basis set dependence). The multipole-derived charge analysis exactly reproduces dipole and higher multipole moments of the molecule. Other charge analysis methods (Voronoi deformation density and Hirshfeld) provide atomic charges that agree well with chemical intuition. Nalewajski bond orders can be calculated and show good agreement with experimental trends and chemical intuition, even for transition metal compounds.

Note that the amount of data can be controlled with the keys PRINT, NoPrint, EPrint, and Debug.

9.4.1 Charges, Populations

Mulliken populations

See the input key *EPRINT* (page 328). See also the *section on Mulliken populations* (page 336).

Hirshfeld charges, Voronoi deformation density (VDD)

No special input key is required, except for `PRINT VDDANALYSIS` for a symmetry decomposed VDD analysis. See also the *section on Hirshfeld charges, Voronoi deformation density* (page 336).

Multipole derived charges

No special input key required. See also the *section on MDC* (page 338).

ESP-CHELPG and ESP-RESP charges

Charges derived from the Electrostatic Potential Grid (ChElPG) are calculated with the key

```
ESP-CHELPG
```

RESP (Restrained Electrostatic Potential Charge) is calculated with

```
ESP-RESP
```

See also the *section on CHELPG and RESP* (page 338).

Charge model 5 (CM5)

Charges calculated with CM5 are activated by the keyword

```
CM5
```

See also the *section on CM5* (page 338).

QTAIM

QTAIM charges are calculated if QTAIM is enabled, and the `AnalysLevel` is at least extended. See also the *section on QTAIM* (page 315).

Charges for AMS

Only one of the charges above can be returned to the AMS driver if charges are needed at the driver level or explicitly requested with `Properties%Charges` in the AMS driver input. The choice for which charge analysis scheme is used for the returned charges is made with the `AtomicChargesTypeForAMS` keyword. This key will also set the required input for the chosen charge analysis scheme.

```
AtomicChargesTypeForAMS [Mulliken | Hirshfeld | CM5 | Voronoi | MDC-M | MDC-D | MDC-Q | QTAIM | ESP-CHELPG | ESP-RESP]
```

AtomicChargesTypeForAMS

Type

Multiple Choice

Default value

Mulliken

Options

[Mulliken, Hirshfeld, CM5, Voronoi, MDC-M, MDC-D, MDC-Q, QTAIM, ESP-CHELPG, ESP-RESP]

GUI name

Atomic charges for AMS

Description

Type of atomic charges to be used by AMS.

Note that some of these atomic charges are computed and printed by default in ADF.

Hirshfeld charges are available only for default atomic fragments.

9.4.2 Bond orders

There are several ways to calculate bond orders with ADF. See also the [section on bond order analysis](#) (page 338) for how bond orders are calculated.

Bond Orders with atomic fragments

The calculation of bond orders can be requested at the AMS driver level (see the [Properties section of the AMS driver manual](#)), if atomic fragments are used:

```
$AMSBIN/ams << eor
...
Properties
  BondOrders Yes
End

Engine ADF
...
EndEngine
eor
```

The bond order analysis is based on SFOs. The symmetry used in the calculation should be NOSYM.

By default, bond orders are computed using the Nalewajski-Mrozek³⁴³⁷³⁸³⁹ method. There are three alternative definitions of the valence and bond order indices within the Nalewajski-Mrozek approach. By default, the values obtained from partitioning of $\text{Tr}(\mathbf{P} \Delta \mathbf{P})$ (i.e. Nalewajski-Mrozek-3) are calculated and printed in the output. For more information on alternative Nalewajski-Mrozek bond order indices, see the [section on bond order analysis](#) (page 338).

In the Engine ADF part of the input, you can specify the following options:

```
BondOrders
  Calculate Yes/No
  PrintAll Yes/No
  PrintTolerance float
  TypeForAMS [Nalewajski-Mrozek-1 | Nalewajski-Mrozek-2 | Nalewajski-Mrozek-3 | ↵
↵Mayer |
              Gopinathan-Jug]
End
```

BondOrders

³ A. Michalak, R.L. De Kock and T. Ziegler, *Bond Multiplicity in Transition-Metal Complexes: Applications of Two-Electron Valence Indices*, *Journal of Physical Chemistry A* 112, 7256 (2008) (<https://doi.org/10.1021/jp800139g>)

⁴ R.F. Nalewajski, J. Mrozek and A. Michalak, *Two-electron valence indices from the Kohn-Sham orbitals*, *International Journal of Quantum Chemistry* 61, 589 (1997) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1997\)61:3%3C589::AID-QUA28%3E3.0.CO;2-2](https://doi.org/10.1002/(SICI)1097-461X(1997)61:3%3C589::AID-QUA28%3E3.0.CO;2-2))

³⁷ R.F. Nalewajski and J. Mrozek, *Modified valence indices from the two-particle density matrix*, *International Journal of Quantum Chemistry* 51, 187 (1994) (<https://doi.org/10.1002/qua.560510403>)

³⁸ R.F. Nalewajski, J. Mrozek and A. Michalak, *Exploring Bonding Patterns of Molecular Systems Using Quantum Mechanical Bond Multiplicities*, *Polish Journal of Chemistry* 72, 1779 (1998) (<https://ichf.edu.pl/pjch/pj-1998/pj07s98.htm#1779>)

³⁹ R.F. Nalewajski, J. Mrozek and G. Mazur, *Quantum chemical valence indices from the one-determinantal difference approach*, *Canadian Journal of Chemistry* 74, 1121 (1996) (<https://doi.org/10.1139/v96-126>)

Type

Block

Description

Options for the calculation of bond orders. Note: the calculation of bond orders should be requested via the Properties%BondOrders input option in the AMS driver input.

Calculate**Type**

Bool

Default value

No

Description

Whether or not the bond orders should be calculated. This is for internal use/debug purposes, except for multi-atomic fragments. In case of atomic fragments one should request the bond orders at the AMS driver level via the Properties%BondOrders input option. For multi-atomic fragments, however, one should not request the bond orders at the AMS driver level, but instead use this key.

PrintAll**Type**

Bool

Default value

No

Description

If 'Yes', all five types of bond orders (i.e. Nalewajski-Mrozek-1,2 & 3, Mayer and Gopinathan-Jug) will be printed to the output. Otherwise only the Nalewajski-Mrozek-3 and the type requested in BondOrders%TypeForAMS will be printed.

PrintTolerance**Type**

Float

Default value

0.2

Description

Only bond orders larger than this threshold will be printed in the output (this threshold applies only to the printing in the 'BOND-ORDER ANALYSIS' section of the ADF output).

TypeForAMS**Type**

Multiple Choice

Default value

Nalewajski-Mrozek-3

Options

[Nalewajski-Mrozek-1, Nalewajski-Mrozek-2, Nalewajski-Mrozek-3, Mayer, Gopinathan-Jug]

GUI name

Bond order type for AMS

Description

The type of bond order that will be saved, printed and used by AMS.

Nalewajski-Mrozek-1,2: bond orders calculated from two-electron valence indices based on partitioning of $\text{tr}(\Delta_P^2)$ using 3-index set or 4-index set respectively. Nalewajski-Mrozek-3: bond-orders calculated from valence indices based on partitioning of $\text{tr}(P \cdot \Delta_P)$. Inter-atomic bond orders are not defined with non-atomic fragments.

Bond Orders with multi-atomic fragments

The bond analysis may also be used for multi-atomic fragments. The fragment-fragment bond orders are printed in such a case. Note that in the present implementation all fragment types should be different. Symmetry should be NOSYM. In this case you may not specify the Properties%BondOrders key in the AMS part of the input, because AMS wants a bond analysis based on atomic fragments. However, you should specify BondOrders%Calculate in the Engine ADF part of the input:

```
$AMSBIN/ams << eor
...
Engine ADF
  BondOrders
    Calculate Yes
    ...
  End
  Fragments
    ...
  End
  Symmetry NOSYM
EndEngine
eor
```

ExtendedPopan

Mayer bond orders and Mulliken atom-atom populations per l-value can be enabled using the ExtendedPopan key. Symmetry can be used. The atom-atom bond orders are printed, also if one uses multi-atomic fragments.

```
ExtendedPopan Yes/No
```

ExtendedPopan**Type**

Bool

Default value

No

GUI name

: Extended population analysis

Description

Calculate the Mayer bond orders and Mulliken atom-atom populations per l-value

9.4.3 ETS-NOCV: Natural Orbitals for Chemical Valence

With the ETS-NOCV charge and energy decomposition scheme, the deformation density is partitioned into the different components (σ , π , δ) of the chemical bond. The energy contributions to the total bond energy are calculated for each specific orbital interaction between fragments, giving insight into the orbital interactions also for non-symmetric molecules. The ETS-NOCV analysis offers a compact quantitative picture of the chemical bond, which is also qualitatively attractive to chemists.

Tip: See also the [EDA-NOCV tutorial](#)

The Natural Orbitals for Chemical Valence (NOCV) approach has been derived from the Nalewajski-Mrozek valence theory^{Page 305, 3Page 305, 4}. From the mathematical point of view, each NOCV ψ_i is defined as an eigenvector of the deformation density matrix in the basis of fragment orbitals.

$$\Delta P \Psi_i = \nu_i \Psi_i$$

Thus, the deformation density $\Delta\rho$ can be expressed in the NOCV representation as a sum of pairs of complementary eigenfunctions (ψ_{-k} , ψ_k) corresponding to eigenvalues $-\nu_k$ and ν_k with the same absolute value but opposite signs:

$$\Delta\rho(r) = \sum \Delta\rho_k(r) = \sum \nu_k (-\Psi_{-k}^2(r) + \Psi_k^2(r))$$

Here, k goes over the pairs of NOCVs.

In the combined ETS-NOCV scheme, the orbital interaction term ΔE_{orb} is expressed in terms of NOCVs as⁵⁶:

$$\Delta E_{\text{orb}} = \sum \Delta E_k^{\text{orb}} = \sum \nu_k (-F_{-k}^{\text{TS}} + F_k^{\text{TS}})$$

Here, $-F_{-k}^{\text{TS}}$ and F_k^{TS} are diagonal transition-state Kohn-Sham matrix elements corresponding to NOCVs with eigenvalues $-\nu_k$ and ν_k , respectively. The advantage of this expression is that usually only a few complementary NOCV pairs significantly contribute to the total ΔE_{orb} . Another advantage of this approach is that not only can each $\Delta\rho_k(r)$ be visualized but there is also a well-defined bonding energy contribution ΔE_k^{orb} corresponding to it.

Further decomposition of ΔE_k^{orb} into ΔT_k^{orb} and ΔV_k^{orb} components is possible as the Fock matrix can be decomposed into kinetic and potential energy matrices⁵³:

$$\Delta E_{\text{orb}} = \sum \nu_k (-F_{-k}^{\text{TS}} + F_k^{\text{TS}}) = \sum \nu_k (-T_{-k}^{\text{TS}} - V_{-k}^{\text{TS}} + T_k^{\text{TS}} + V_k^{\text{TS}}) = \sum (\Delta T_{\text{orb}} + \Delta V_{\text{orb}})$$

where T_{-k}^{TS} and V_{-k}^{TS} are diagonal elements of T and V matrices corresponding to F^{TS} matrix.

Remarks

The ETS-NOCV analysis is often not very useful when atomic fragments are used. No symmetry should be used in the final calculation, so use the `Symmetry NOSYM` keyword if your molecule is symmetric. The analysis is not completely implemented for meta-GGAs and meta-hybrids. In the case of meta-GGAs and meta-hybrids the so-called MetaGGA correction or MetaHybrid correction part of the orbital interaction term is not taken into account when calculating energy contributions.

Improvements in ADF2012 to both the ETS and NOCV analysis with hybrids. ETS: Now the exact exchange contribution to the Pauli term is isolated and the contributions to the orbital term are divided among orbital symmetries. NOCV: The

⁵ M. Mitoraj, A. Michalak and T. Ziegler, *A Combined Charge and Energy Decomposition Scheme for Bond Analysis*, *Journal of Chemical Theory and Computation* 5, 962 (2009) (<https://doi.org/10.1021/ct800503d>)

⁶ M. Mitoraj, A. Michalak and T. Ziegler, *On the Nature of the Agostic Bond between Metal Centers and Beta-Hydrogen Atoms in Alkyl Complexes. An Analysis Based on the Extended Transition State Method and the Natural Orbitals for Chemical Valence Scheme (ETS-NOCV)*, *Organometallics* 28, 3727 (2009) (<https://doi.org/10.1021/om900203m>)

⁵³ F. Sagan and M. Mitoraj, *Kinetic and Potential Energy Contributions to a Chemical Bond from the Charge and Energy Decomposition Scheme of Extended Transition State Natural Orbitals for Chemical Valence*, *Journal of Physical Chemistry A* 123, 4616 (2019) (<https://doi.org/10.1021/acs.jpca.9b01420>)

exact exchange contribution to the Fock operator is included when calculating energy contributions. These changes do not apply to meta-hybrids.

In case of bonding between closed-shell molecular fragments, the set of NOCVs originating from the total deformation density matrix $\Delta P = (\Delta P_\alpha + \Delta P_\beta)$ will be printed out. See *the example of carbene bonding between closed shell CH₂ and Cr(CO)₅* (page 1160). In case of bonding between open-shell molecular fragments, two sets of NOCVs originating from ΔP_α and ΔP_β will be printed out. See *the example of CH₃-CH₃ bonding between two CH₃ radicals with opposite spins* (page 1162) using the key *FRAGOCCUPATIONS* (page 71), or *the example of CH₃I bonding between the CH₃ radical and I* (page 1140) using the key *UNRESTRICTEDFRAGMENTS* (page 70).

Usage

In order to perform the ETS-NOCV analysis, include the block key ETSNOCV:

```
ETSNOCV
  {RHOKMIN rhokmin}
  {EKMIN ekmin}
  {ENOCV enocv}
  {TVANALYSIS}
End
```

ETSNOCV

The ETSNOCV keyword specifies thresholds for printing NOCV-related information. All three arguments are optional and when all three are omitted, only the NOCVs corresponding to eigenvalues $abs(\nu_k) \geq 0.05$ are included in the analysis.

RHOKMIN

The threshold for population analysis of each deformation density contribution in terms of individual SFOs.

EKMIN

The threshold for orbital interaction energy contributions corresponding to deformation density components originating from each NOCV pair.

ENOCV

The threshold for NOCV eigenvalues.

TVANALYSIS

Enable T/V decomposition of energy contributions.

PRINT NOCVHirshfeld

The NOCVs can be integrated per fragment using the Hirshfeld partitioning scheme. Using these integrals, you can distinguish between inter- and intra-fragment NOCVs. An inter-fragment NOCV has a nonzero integral Hirshfeld ΔQ value and corresponds to a charge transfer between fragments. An intra-fragment NOCV has a small ΔQ value and corresponds to polarization of the fragments. When `PRINT NOCVHirshfeld` is specified, the $\int \Delta \rho = -\Delta Q$ values per NOCV are printed to the output file in the “Hirshfeld partitioning” table at the end of the ETS-NOCV section.

9.4.4 Adfnbo, gennbo: NBO analysis

- (PDF) NBO manual

Dr. Autschbach, SCM, and Prof. Weinhold have collaborated to prepare a simple input file generator, called `adfnbo`, for the GENNBO program of Prof. Weinhold's Natural Bond Orbital (NBO) package. In ADF2013 and later, the NBO 6.0 version is supported <https://nbo6.chem.wisc.edu>.

The GENNBO executable is included in the ADF distribution and can be enabled via the license file for all those who buy an NBO license from SCM (info@scm.com). An extensive documentation of GENNBO is part of the NBO manual. The application of ADFNBO to frozen-core basis sets needs to be further tested. Usage can be found below and in the Examples Document.

Next a brief summary of the capabilities of GENNBO is given (by Prof. Weinhold). GENNBO implements most capabilities of the full NBO 6.0 program suite as described on the NBO website: <https://nbo6.chem.wisc.edu>. These include the determination of natural atomic orbitals (NAOs), bond orbitals (NBOs), and localized MOs (NLMOs), as well as the associated NPA (atomic charges and orbital populations) and NRT (resonance structures, weightings, bond orders) valence descriptors, for a wide variety of uncorrelated and correlated (variational, perturbative, or density functional) theoretical levels. GENNBO-supported options include all keywords except those explicitly requiring interactive communication with the host electronic structure system (viz., \$DEL deletions, NEDA, NCS, NJC). The GENNBO program typically sits conveniently on the PC desktop, ready to analyze (or re-analyze at will, with altered options) the final results of a complex ADF calculation performed on a remote cluster.

GENNBO “communicates” with the original ADF calculation through an archive file (JOB.47 file, preserving all necessary details of the final density) that is initially generated by ADF and subsequently becomes the input file for GENNBO. The .47 file contains a standard \$NBO ... \$END keylist that can be edited with a standard word processor or text editor to include chosen NBO keyword options, just as though they might have appeared in the original input stream of an interactive ADFNBO run. The stand-alone GENNBO program therefore allows many alternative NBO analysis options to be explored at leisure, without costly re-calculation of the wave function.

In ADF2018 the NBO 6.0 version in the ADF distribution is updated to the March 2017 version; see also <https://nbo6.chem.wisc.edu>: “The 14-Mar-2017 distribution includes a number of other features of interest to general NBO users: The default NAO search algorithm has been modified to better preserve core-valence separation in rare cases where numerical near-degeneracies can lead to unphysical core-valence mixing. The numerical effects are generally negligible except where they become necessary. The “OLDNAO” keyword restores the legacy NAO algorithm for comparison purposes.”

Usage

ADF needs to write some data to file, which is done by including FULLFOCK, AOMAT2FILE, SAVE TAPE15, and SYMMETRY NOSYM in the input file for ADF. An all-electron basis set is needed. Use the key `spherical` in the `adfnbo` input. A file named `FILE47` is generated by `adfnbo`, which is an input file for the general NBO program `gennbo6`. Thus the usage is like

```
$AMSBIN/ams <<eor
...
Engine ADF
  Basis
    ...
    Core None
  End
  FullFock
  AOMat2File
  Save TAPE15
  Symmetry Nosym
EndEngine
eor

$AMSBIN/adfnbo <<eor
  ADFfile ams.results/adf.rkf
  TAPE15file ams.results/TAPE15
  write
  fock
  spherical
eor

$AMSBIN/gennbo6 FILE47
```

In order to get, for example, the second order perturbation theory analysis of the Fock matrix in the NBO basis, you should include the keyword `FOCK` in the `adfnbo` that is performed before `gennbo6` is called. Remark: it was noted that the `gennbo6` results for heavy elements related to the Fock matrix calculated with ADF do not seem to make sense. That is

why the key FOCK is not included in this adfnbo call if AMSinput (GUI module) is used. The key Fock is not necessary to calculate the NBOs or NLMOs.

The default for the so-called NBO key list that adfnbo puts on FILE47 is: BNDIDX NBONLMO=W AONBO=W AONLMO=W NLMOMO=W STERIC DIST. You can also write a user-defined NBO keylist in FILE47 using the key NBOkeylist in adfnbo, for example like

```
$AMSBIN/adfnbo <<eor
  ADFfile ams.results/adf.rkf
  TAPE15file ams.results/TAPE15
  write
  fock
  spherical
  NBOkeylist BNDIDX NBONLMO=W AONBO=W AONLMO=W NLMOMO=W NAOMO=PVAL NRT STERIC CMO
  →3CBOND DIST
eor

$AMSBIN/gennbo6 FILE47
```

Note that here NRT is included. The calculation of NRT (natural resonance theory) with gennbo6 can be very expensive for larger systems (or may fail to converge) and/or gennbo6 may try to allocate too much memory. Thus it is not recommended to include this key NRT in the NBOkeylist for larger systems.

NBO analysis of EFG, NMR chemical shifts, NMR spin-spin coupling

For certain molecular properties it is possible to perform detailed analyses in terms of Natural Bond Orbitals (NBOs) and Natural Localized Molecular Orbitals (NLMOs). These features generally require a sequence of ADF and/or property code runs. An initial non-relativistic or scalar relativistic ADF run, followed by the generation of NBO and NLMO data, is required, and the resulting data files need to be present in subsequent property calculations, along with a keyword indicating that the NBO analysis is requested in the property module.

We have noted in the past some slight loss of numerical accuracy of the results after going through the various orbital transformations in the NBO-NLMO sequence. It is important that you verify in each case that the total contributions from the analysis are in agreement with the total calculated property, within the numerical integration accuracy limits. In order to assist with this, the analysis program always prints the total analysis contributions, including small non-printed values.

Moreover, there appears to be a problem with the analysis of the Fock matrix in the NBO program in conjunction with ADF calculations. Therefore, do not use the Fock matrix second order perturbation theory analysis in NBO at this time. We will remove this disclaimer once the issue has been fixed. Applications of the NBO-NLMO property analysis codes have so far given no indication that the Fock matrix issue interferes with the analysis.

Important note: If properties are analyzed from within spin-orbit relativistic computations, the NBO/NLMO analysis is performed in terms of scalar (spin-free) relativistic orbitals, as detailed in the technical references. The results from these analyses are exact in the sense that they fully reproduce the final spin-orbit property result, and they allow you to dissect the property in terms of more intuitive one component real scalar relativistic localized orbitals. Typically, the property analysis in a spin-orbit calculation involves contributions from unoccupied scalar NLMOs, whereas there are no such contributions if a non-relativistic or scalar relativistic property is analyzed.

Available properties for NBO analysis: EFG, NMR chemical shifts, and NMR spin-spin coupling.

NBO analysis of EFG

EFGs: non-relativistic and scalar ZORA, in ADF/AOResponse. Requires an initial ADF run with

```
AOresponse
  donothing
End
```

in order to generate orbitals that are equivalent to those generated in the subsequent ADF run where the EFG is calculated. Alternatively, simply calculate the EFG twice, once before the NBO generation step, and once afterward.

The next step (see below) is to create the NBOs and the required data files for the analysis. Afterward, in the second ADF run, use

```
AOresponse
  efg NUC nbo
End
```

efg NUC nbo

Here NUC is the number of the nucleus at which the EFG is to be computed (ADF internal atom ordering). Example: efg 1 nbo.

The threshold for printing the EFG-NBO contributions to output can be adjusted via the `Tresh` options. The default is 0.05, which means that only orbitals with absolute value contribution larger than 5% of the total EFG are printed. To increase the number of contributions printed, specify a smaller threshold. For example:

```
AOresponse
  efg 1 nbo Tresh 0.01
End
```

In addition to the optional NBO analysis, the EFG program in AOResponse prints a Mulliken-type analysis of the EFG principal components, and an analysis in terms of canonical MOs.

WARNING: The ordering of the principal components is lowest to highest including the sign. That is, we have $V_{11} \leq V_{22} \leq V_{33}$. This does not conform to the usual convention of $|V_{11}| \leq |V_{22}| \leq |V_{33}|$. Please make sure you select the right component for your analysis.

Example job: \$AMSHOME/examples/adf/AICl3_efgnbo. For an explanation of the output and a general usage tutorial, see⁷. For further references and recommended citations, see⁸.

NBO analysis of NMR Chemical shift

An implementation is currently available for spin-orbit ZORA computations. If scalar ZORA calculations are to be analyzed, provide the input keyword

```
FAKESO
```

in the NMR input (outside of the `NMR` keyword). If this feature is requested you should restrict the calculation to a single shielding tensor per NMR run. It would be good practice to check the results against regular NMR calculations where the analysis feature is not requested. No ZORA scaling is applied in the analysis results. The data should be equivalent to a regular computation in the NMR input with

```
NMR
  ulk best
  calc all
END
```

Depending on whether scalar or spin-orbit calculations are to be analyzed, the sequence of calculations is different:

scalar:

1. ADF, scalar ZORA, symmetry NOSYM, closed shell
2. generate NBOs and required data files for analysis

⁷ J. Autschbach, S. Zheng, and R.W. Schurko, *Analysis of Electric Field Gradient Tensors at Quadrupolar Nuclei in Common Structural Motifs, Concepts in Magnetic Resonance Part A* 36A, 84 (2010) (<https://doi.org/10.1002/cmr.a.20155>)

⁸ A.J. Rossini, R.W. Mills, G.A. Briscoe, E.L. Norton, S.J. Geier, I. Hung, S. Zheng, J. Autschbach, and R.W. Schurko, *Solid-State Chlorine NMR of Group IV Transition Metal Organometallic Complexes*, *Journal of the American Chemical Society* 131, 3317 (2009) (<https://doi.org/10.1021/ja808390a>)

3. NMR with FAKESO and analysis keywords, use adf.rkf (previously known as TAPE21), TAPE10 from step 1.

spin-orbit:

1. ADF, scalar ZORA, closed shell
2. generate NBOs and required data files for analysis
3. delete adf.rkf, TAPE10, TAPE15
4. ADF, spin-orbit ZORA, symmetry NOSYM, closed shell
5. NMR with analysis keywords, using adf.rkf, TAPE10 from step 4

In the NMR run, in addition to the NMR keyword, provide the following

```
analysis
print 0.01
canonical
nbo
components
end
```

The optional canonical keyword can be used independently from the NBO analysis features. It enables an analysis of the shielding in terms of the canonical MOs. The components keyword is optional and enables an analysis not only of the isotropic shielding but also of each principal component of the tensor. The print keyword selects printout of contributions relative to the total diamagnetic and paramagnetic terms. In the example, only contributions greater than 1% are printed. Set to zero to print all contributions.

Example job: \$AMSHOME/examples/adf/CH4_nmrnbo. References⁴⁰⁴¹⁴².

NBO analysis of NMR spin-spin coupling (J-coupling)

Non-relativistic, scalar ZORA, spin-orbit ZORA

The sequence of jobs is similar to those in the NMR section.

scalar or non-relativistic:

1. ADF, scalar ZORA or nonrel.
2. generate NBOs and required data files for analysis
3. CPL with analysis keyword, use adf.rkf (previously known as TAPE21), TAPE10 from step 1.

spin-orbit:

1. ADF, scalar ZORA
2. generate NBOs and required data files for analysis
3. delete adf.rkf, TAPE10, TAPE15
4. ADF, spin-orbit ZORA
5. CPL with analysis keyword, using adf.rkf, TAPE10 from step 4

In the CPL run provide the following `contributions` keyword to enable the analysis

⁴⁰ J. Autschbach, *Analyzing NMR shielding tensors calculated with two-component relativistic methods using spin-free localized molecular orbitals*, *Journal of Chemical Physics* 128, 164112 (2008) (<https://doi.org/10.1063/1.2905235>)

⁴¹ J. Autschbach and S. Zheng, *Analyzing Pt chemical shifts calculated from relativistic density functional theory using localized orbitals: The role of Pt 5d lone pairs*, *Magnetic Resonance in Chemistry* 46, S45 (2008) (<https://doi.org/10.1002/mrc.2289>)

⁴² J. Autschbach and S. Zheng, *Relativistic computations of NMR parameters from first principles: Theory and applications*, *Annual Reports on NMR Spectroscopy* 67, 1 (2009) ([https://doi.org/10.1016/S0066-4103\(09\)06701-5](https://doi.org/10.1016/S0066-4103(09)06701-5))

```
nmrcoupling
... other options
contributions 1E19 nbo
End
```

The numerical value selects a print threshold in SI units of T^{*2}/J for the analysis. Increase the value to obtain less detail in the analysis. By default, `contributions` triggers an analysis of the J-coupling in terms of canonical MOs. The `nbo` keyword enables the NBO-NLMO analysis in addition.

Please note that due to the history of how the program was developed, the output from the scalar/nrel. analysis and from the spin-orbit calculations differs somewhat. The qualitative content is the same.

In scalar ZORA or non-relativistic CPL calculations without the SD term, an orbital-based analysis is only performed for the Fermi-contact mechanism. If you also need an analysis for the PSO and SD mechanisms but do not want to run a spin-orbit calculation with ADF, please use the SD or NOSD keywords which will cause the spin-orbit branch of the CPL code to be used. In ZORA spin-orbit calculations the FC, SD, PSO, and cross terms are analyzed together by default. You can selectively switch them on or off in order to get individual mechanism analyses. The DSO mechanism is often negligible. An analysis tool for this mechanism has therefore not yet been developed.

Example job: \$AMSHOME/examples/adf/CPL_CH3OH_NBO. References NMR spin-spin couplings with NBO analysis^{Page 313, 42434445}.

Generation of NBOs

How to generate the NBOs, NLMOs, and the data files needed for these calculations (step 2 below is step 2 in the examples above):

1. run ADF with scalar ZORA or non-relativistic options, and keep `adf.rkf` and TAPE15.

```
AMS_JOBNAME=Scalar $AMSBIN/ams <<eor
...
eor
```

- 2.

```
# run adfnbo in WRITE mode to create the gennbo input file FILE47
# and one of the required property analysis files, adfnbo.kf

$AMSBIN/adfnbo << eor
ADFfile Scalar.results/adf.rkf
TAPE15file Scalar.results/TAPE15
write
spherical
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48
$AMSBIN/gennbo6 << FILE47

# run adfnbo in COPY mode to create the second property analysis
# file, adfnbo2.kf
```

(continues on next page)

⁴³ J. Autschbach, *Analyzing molecular properties calculated with two-component relativistic methods using spin-free Natural Bond Orbitals: NMR spin-spin coupling constants* *Journal of Chemical Physics* 127, 124106 (2007) (<https://doi.org/10.1063/1.2768363>)

⁴⁴ J. Autschbach and B. Le Guennic, *Analyzing and interpreting NMR spin-spin coupling constants from molecular orbital calculations*, *Journal of Chemical Education* 84, 156 (2007) (<https://doi.org/10.1021/ed084p156>)

⁴⁵ A.M.A. Boshala, S.J. Simpson, J. Autschbach and S. Zheng, *Synthesis and Characterization of the Trihalophosphine Compounds of Ruthenium [RuX₂(η^6 -cymene)(PY₃)] (X = Cl, Br, Y = F, Cl, Br) and the Related PF₂(NMe₂) and P(NMe₂)₃ Compounds; Multinuclear NMR Spectroscopy and the X-ray Single Crystal Structures of [RuBr₂(η^6 -cymene)(PF₃)], [RuBr₂(η^6 -cymene)(PF₂{NMe₂})], and [RuI₂(η^6 -cymene)(P{NMe₂})₃]*, *Inorganic Chemistry* 47, 9279 (2008) (<https://doi.org/10.1021/ic800611h>)

(continued from previous page)

```

$AMSBIN/adfnbo << eor
  ADFfile Scalar.results/adf.rkf
  TAPE15file Scalar.results/TAPE15
  spherical
  copy
eor

# run adfnbo in READ mode: prepare locorb on TAPE21

$AMSBIN/adfnbo << eor
  ADFfile scalar.results/adf.rkf
  TAPE15file scalar.results/TAPE15
  spherical
  read
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48

# keep the adf.rkf after this sequence in order to
# be able to plot the NBOs and NLMOs with amsview

# clean up, keep adfnbo*.kf for any NBO property analyses.

```

9.4.5 QTAIM: Atoms in Molecules

One can calculate local and atomic properties using a real-space partition of the electronic density. It is based on the quantum theory of atoms in molecules (QTAIM) developed by Richard Bader⁹. Another possibility for Bader analysis is to use the adf2aim utility with a third-party program such as Xaim.

Local, atomic, and non-local properties

The QTAIM input block replaces the *Bader* keyword. The former *Bader Reactivity* option now corresponds to the *ConceptualDFT* block (see below).

The QTAIM functionality encompasses two different but related features: a topological analysis of the electron density gradient field¹⁰, and a calculation of condensed atomic properties by integrating various local functions over atomic basins^{46,47}. The topological analysis is performed at all levels of the analysis (normal, extended, or full) and it produces a list of the molecule's electron density critical points and bond paths that can be visualized by the AMSview GUI module. In addition, the following properties at the critical points are calculated: electron density, its Laplacian and Hessian matrix, ellipticity, Jenkins' metallicity index¹², reduced density gradient, DFT energy density variation rates¹³, and Abramov's local energy components¹⁴. At the *Extended* analysis level the following condensed atomic properties are calculated: charges, density Laplacian, dipole and quadrupole moments, Shannon and Renyi entropies, spatial distribution of the

⁹ P.L.A. Popelier, *Atoms in Molecules An Introduction*, Pearson Education, Harlow, 2000.

¹⁰ J.I. Rodríguez, *An Efficient Method for Computing the QTAIM Topology of a Scalar Field: The Electron Density Case*, *Journal of Computational Chemistry* 34, 681 (2013) (<https://doi.org/10.1002/jcc.23180>)

⁴⁶ J.I. Rodríguez, A.M. Köster, P.W. Ayers, A. Santos-Valle, A. Vela and G. Merino, *An efficient grid-based scheme to compute QTAIM atomic properties without explicit calculation of zero-flux surfaces*, *Journal of Computational Chemistry* 30, 1082 (2009) (<https://doi.org/10.1002/jcc.21134>)

⁴⁷ J.I. Rodríguez, R.F.W. Bader, P.W. Ayers, C. Michel, A.W. Götz and C. Bo, *A high performance grid-based algorithm for computing QTAIM properties*, *Chemical Physics Letters* 472, 149 (2009) (<https://doi.org/10.1016/j.cplett.2009.02.081>)

¹² P.W. Ayers, S. Jenkins, *Bond metallicity measures*, *Comput. Theor. Chem.* 1053, 112 (2015) (<https://doi.org/10.1016/j.comptc.2014.10.040>)

¹³ V. Tognetti, L. Joubert, *Density functional theory and Bader's atoms-in-molecules theory: towards a vivid dialogue*, *Phys. Chem. Chem. Phys.* 16, 14539 (2014) (<https://doi.org/10.1039/C3CP55526G>)

¹⁴ Y.A. Abramov, *On the Possibility of Kinetic Energy Density Evaluation from the Experimental Electron-Density Distribution*, *Acta Cryst.* A53, 264 (1997) (<https://doi.org/10.1107/S010876739601495X>)

molecular orbitals over atomic basins. If the *Energy* keyword is specified, the atomic energies¹¹ are also calculated. At the *Full* level, the atom-atom matrix elements of the localization (LI) and delocalization (DI) indices^{48,49} are computed. In ADF2023, we also added the (optional) calculation of the Source Function introduced by Gatti and Bader^{54,55}. This function is evaluated for each bond or ring critical point of the molecule, allowing a decomposition of the values of the electron density at these points as a sum of atomic contributions. Since this calculation requires the integration of the Laplacian of the electron density, we strongly recommend a numerical quality set (at least) to *Good* (or higher).

QTAIM

Type

Block

Description

This block is used to request a topological analysis of the gradient field of the electron density, also known as the Bader's analysis. If this block is specified without any sub-key, only local properties are calculated.

AnalysisLevel

Type

Multiple Choice

Default value

Normal

Options

[Normal, Extended, Full]

Description

Set the level of the QTAIM analysis:

Normal - topology analysis and properties at the density critical points,

Extended - same as Normal plus condensed atomic descriptors, plus basin information on TAPE10

Full - same as Extended plus non-local descriptors.

Source

Type

Bool

Default value

No

GUI name

Source Function

Description

Calculate the Source Function at BCPs and RCPs.

AtomsToDo

¹¹ J.I. Rodríguez, .W. Ayers, A.W. Götz, and F.L. Castillo-Alvarado, *Virial theorem in the Kohn-Sham density-functional theory formalism: Accurate calculation of the atomic quantum theory of atoms in molecules energies*, *Journal of Chemical Physics* 131, 021101 (2009) (<https://doi.org/10.1063/1.3160670>)

⁴⁸ X. Fradera, M.A. Austen, *The Lewis model and beyond*, R.F.W. Bader, *J. Phys. Chem. A* 103, 304 (1999) (<https://doi.org/10.1021/jp983362q>).

⁴⁹ J. Poater, M. Solà, M. Duran, X. Fradera, *The calculation of electron localization and delocalization indices at the Hartree-Fock, density functional and post-Hartree-Fock levels of theory*, *Theor. Chem. Acc.* 107, 362 (2002) (<https://doi.org/10.1007/s00214-002-0356-8>).

⁵⁴ R.F.W. Bader, C. Gatti, *A Green's function for the density*, *Chem. Phys. Lett.* 287, 233 (1998) ([https://doi.org/10.1016/S0009-2614\(97\)01457-7](https://doi.org/10.1016/S0009-2614(97)01457-7))

⁵⁵

C. Gatti, F. Cargnoni, L. Bertini, *Chemical information from the source function*, *J. Comput. Chem.* 24, 422 (2003) (<https://doi.org/10.1002/jcc.10205>)

Type

Integer List

GUI name

Include atoms

Description

List of atoms for which condensed descriptors are to be calculated. By default all atoms are included.

Spacing**Type**

Float

Default value

0.5

Unit

Bohr

Description

Specifies spacing of the initial Cartesian grid when searching for critical points. It may be useful to specify a smaller value than the default if some critical points are missed. This will result in a more accurate but slower calculation.

Note that the accuracy of condensed atomic properties can be estimated by integrating the Laplacian of the electron density over a given basin, which, ideally, must vanish. The accuracy of the method can be improved by using a larger integration grid (NumericalQuality). Usually, the default grid is sufficient to achieve the accuracy of 10^{-3} a.u. (differences of milliHartree in the energies). Unfortunately, the convergence of the electron density Laplacian integral with the grid size is not monotonous. Therefore this type of Bader atomic property calculation should be considered for applications where computational efficiency is critical and moderate accuracy is sufficient.

Note: The *Energy* keyword is now obsolete (AMS2023). The (virial) atomic energies are now automatically calculated at the *Extended* or *Full* level except for relativistic calculations. However, the other QTAIM properties *are* correct for such calculations (they depend on the sole electron density; see reference¹⁵). Please note that the atomic energies are correct only at equilibrium geometries (the virial theorem is used).

ADF2AIM

The ADF utility adf2aim (original name rdt21) developed by Xavi Lopez, Engelber Sans and Carles Bo converts an ADF `adf.rkf` (formerly known as TAPE21) to WFN format (for Bader analysis).

The program rdt21 is now called adf2aim and is part of the ADF package.

The WFN file is an input file for the third-party program Xaim (see <http://www.quimica.urv.es/XAIM> for details), which is a graphical user interface to programs that can perform the Bader analysis. Usage of adf2aim can be found in the Examples Document.

¹⁵ J.S.M. Anderson, J.I. Rodriguez, P.W. Ayers, and A.W. Götz, *Relativistic (SR-ZORA) Quantum Theory of Atoms in Molecules Properties*, *Journal of Computational Chemistry* 82, 81 (2017) (<https://doi.org/10.1002/jcc.24520>)

Aromaticity index with QTAIM

The cyclic delocalization of mobile electrons in two or three dimensions is probably one of the key aspects that characterize aromatic compounds. However, aromaticity cannot be measured directly by any physical or chemical experiment because it is not a well-defined magnitude. One can define indicators of aromaticity, some of which are implemented in ADF. The matrix of localization/delocalization indices (LI-DI) and the following from it Iring (ring index) and MCI (multi center index) aromaticity indices (see Ref.¹⁶) can be computed for rings specified by the user. The rings are specified using the AROMATICITY input block, one line per ring.

```
Aromaticity
  RingAtoms integer_list
End
```

Aromaticity

Type

Block

Description

Calculate aromaticity indicators, i.e. the matrix of localization/delocalization indices (LI-DI), Iring (ring index) and MCI (multi center index) aromaticity indices.

RingAtoms

Type

Integer List

Recurring

True

Description

List of the atom numbers that form a ring. For each ring a separate line.

For example, for a benzene molecule where atoms 1-6 are carbon atoms the input would look like this:

```
AROMATICITY
  ringatoms 1 2 3 4 5 6
END
```

The program does not check whether the atoms in the AROMATICITY input block are connected, so it is the responsibility of the user to specify them correctly. Moreover, for the Iring index to be calculated correctly the atoms must be listed in the order they are connected in the ring.

Calculation of the aromaticity indices invokes the QTAIM analysis automatically and uses its results, so all accuracy considerations for the QTAIM key above are also valid here. This feature requires that the calculation is performed without symmetry (Symmetry NOSYM).

Results of the calculation are printed to the output under the “Aromaticity Index” header. The first table presents the total number of electrons per atom and their breakdown in “localized” and “delocalized”. Note: the total number of electrons per atom $N_{total} = N_{loc} + N_{deloc}/2$ since delocalized electrons are counted twice. The second table presents the Iring and MCI ring indices for each ring specified in the AROMATICITY block. These results (and the original LiDi matrix from which they are computed) are stored in the Properties section in the t21 file.

¹⁶ F. Feixas, E. Matito, J. Poater and M. Sola, *Quantifying aromaticity with electron delocalisation measures*, Chem. Soc. Rev. 44, 6434 (2015) (<https://doi.org/10.1039/c5cs00066a>)

9.4.6 Conceptual DFT

Global, atomic, and non-local descriptors

The *ConceptualDFT* block replaces and extends the set of features behind the *Bader Reactivity* keyword found in the ADF versions before ADF2019. The frontier molecular orbital (FMO) approximation is used for all calculations. Orbital degeneracy is taken into account following Martinez¹⁷. All these descriptors are described in Ref.¹⁸. Which descriptors are calculated depends on the *AnalysisLevel* key:

- *Normal*: global conceptual DFT descriptors, i.e. electronic chemical potential, electronegativity (its opposite), hardness and softness, hyperhardness¹⁹, electrophilicity index²⁰, dissociation energies (nucleofuge and electrofuge, see Ref.²¹), electrodonating and electroaccepting powers²² and the net electrophilicity²³. Also, global descriptors called *global dual descriptors* $\Delta f+$ and $\Delta f-$ are calculated²⁴, which correspond to the spatial integral of the positive (electrophilic) or negative (nucleophilic) regions of the original dual descriptor, respectively. These descriptors allow for comparing total reactivity of molecules, in contrast with Fukui functions or the original dual descriptor that integrate over the whole space to 1 or 0 for all molecules.
- *Extended*: both global and atomic properties, including condensed (QTAIM) descriptors in both canonical and grand canonical ensembles. More precisely, the following properties are computed: condensed Fukui functions²⁶, dual descriptor^{25,27} and some of their composite functions^{50,51,52}, as well as condensed local electrophilicity and nucleophilicity²⁸.
- *Full*: all properties are calculated, including non-local ones, such as the condensed linear response function²⁹ and the softness kernel³⁰.

Please note that atomic electronegativities³¹ are calculated separately with an optional *Electronegativity* keyword. In contrast with other properties, it requires all-electron basis sets and triggers the *TotalEnergy* keyword.

¹⁷ J. Martínez, *Local Reactivity Descriptors from Degenerate Frontier Molecular Orbitals*, Chem. Phys. Lett. 478, 310-322 (2009) (<https://doi.org/10.1016/j.cplett.2009.07.086>)

¹⁸ G. Hoffmann, V. Tognetti and L. Joubert, *Can molecular and atomic descriptors predict the electrophilicity of Michael acceptors?*, J. Mol. Model. 24, 281 (2018) (<https://doi.org/10.1007/s00894-018-3802-9>).

¹⁹ C. Morell, A. Grand, A. Toro-Labbé, *Is hyper-hardness more chemically relevant than expected ?*, J. Mol. Model. 19, 2893 (2013) (<https://doi.org/10.1007/s00894-013-1778-z>)

²⁰ R.G. Parr, L.v. Szentpály, S. Liu, *Electrophilicity index*, J. Am. Chem. Soc. 121, 1922 (1999) (<https://doi.org/10.1021/ja983494x>)

²¹ P.W. Ayers, J.S.M. Anderson, J.I. Rodriguez, Z. Jaweda, *Indices for predicting the quality of leaving groups*, Phys. Chem. Chem. Phys. 7, 1918 (2005) (<https://doi.org/10.1039/b500996k>)

²² J.L. Gázquez, A. Cedillo, A. Vela, *Electrodonating and electroaccepting powers*, J. Phys. Chem. A 111, 1966 (2007) (<https://doi.org/10.1021/jp065459f>)

²³ P.K. Chattaraj, A. Chakraborty, S. Giri, *Net electrophilicity*, J. Phys. Chem. A 113, 10068 (2009) (<https://doi.org/10.1021/jp904674x>)

²⁴ F. Guégan, P. Mignon, V. Tognetti, L. Joubert, C. Morell, *Dual descriptor and molecular electrostatic potential: complementary tools for the study of the coordination chemistry of ambiphilic ligands*, Phys. Chem. Chem. Phys. 16, 15558 (2014) (<https://doi.org/10.1039/c4cp01613k>)

²⁶ R.G. Parr, W.T. Yang, *Density functional approach to the frontier-electron theory of chemical reactivity*, J. Am. Chem. Soc. 106, 4049 (1984) (<https://doi.org/10.1021/ja00326a036>)

²⁵ F. Zielinski, V. Tognetti, L. Joubert, *Condensed descriptors for reactivity: A methodological study*, Chem. Phys. Lett. 527, 67 (2012) (<https://doi.org/10.1016/j.cplett.2012.01.011>)

²⁷ C. Morell, A. Grand, A. Toro-Labbé, *New Dual Descriptor for Chemical reactivity*, J. Phys. Chem. A 109, 205 (2005) (<https://doi.org/10.1021/jp046577a>)

⁵⁰ A. Toro-Labbé, P. Jaque, J.S. Murray and P. Politzer, *Connection between the average local ionization energy and the Fukui function*, Chem. Phys. Lett. 407, 143 (2005) (<https://doi.org/10.1016/j.cplett.2005.03.041>)

⁵¹ J. Padmanabhan, R. Parthasarathi, M. Elango, V. Subramanian, B.S. Krishnamoorthy, S. Gutierrez-Oliva, A. Toro-Labbé, D. R. Roy, P. K. Chattaraj, *Multiphilic descriptor for chemical reactivity and selectivity*, J. Phys. Chem. A 111, 130 (2007) (<https://doi.org/10.1021/jp0718909>)

⁵² P.K. Chattaraj, B. Maiti, U. Sarkar, *Philicity: A unified treatment of chemical reactivity and selectivity*, J. Phys. Chem. A 107, 4973 (2003) (<https://doi.org/10.1021/jp034707u>)

²⁸ C. Morell, J.L. Gázquez, A. Vela, F. Guégan, H. Chermette, *Revisiting electroaccepting and electrodonating powers: proposals for local electrophilicity and local nucleophilicity descriptors*, Phys. Chem. Chem. Phys. 16, 26832 (2014) (<https://doi.org/10.1039/c4cp03167a>)

²⁹ P. Geerlings, S. Fias, Z. Boisdenghien, F. De Proft, *Conceptual DFT: chemistry from the linear response function*, Chem. Soc. Rev. 43, 4989 (2014) (<https://doi.org/10.1039/C3CS60456J>)

³⁰ S. Fias, F. Heidar-Zadeh, P. Geerlings, P.W. Ayers, *Chemical transferability of functional groups follows from the nearsightedness of electronic matter*, PNAS 114, 11633 (2017) (<https://doi.org/10.1073/pnas.1615053114>)

³¹ V. Tognetti, C. Morell, L. Joubert, *Atomic electronegativities in molecules*, Chem. Phys. Lett. 635, 111 (2015) (<https://doi.org/10.1016/j.cplett.2015.05.057>)

ConceptualDFT**Type**

Block

Description

Conceptual DFT Properties

AnalysisLevel**Type**

Multiple Choice

Default value

Normal

Options

[Normal, Extended, Full]

Description

Set the level of the ConceptualDFT analysis:

Normal - global descriptors only,

Extended - both global and condensed (QTAIM) local descriptors,

Full - all descriptors including non local ones.

Electronegativity**Type**

Bool

Default value

No

GUI name

Atomic electronegativities

Description

Calculate atomic electronegativities. Requires an all-electron calculation (no frozen core), triggers the TotalEnergy and increases the [AnalysisLevel] to at least Extended.

AtomsToDo**Type**

Integer List

GUI name

Include atoms

Description

Define a subset of atoms for which properties are calculated. If the [Domains] block is present then this list specifies which atoms are used to define the domains bounding box.

For more information about *Conceptual DFT*, we suggest reading these excellent reviews: Refs.³³ and³².

³³ H. Chermette, *Chemical reactivity indexes in density functional theory*, J. Comput. Chem. 20, 129 (1999) ([https://doi.org/10.1002/\(SICI\)1096-987X\(19990115\)20:1%3C129::AID-JCC13%3E3.0.CO;2-A](https://doi.org/10.1002/(SICI)1096-987X(19990115)20:1%3C129::AID-JCC13%3E3.0.CO;2-A))

³² P. Geerlings, F. de Proft, W. Langenaeker, *Conceptual Density Functional Theory*, Chem. Rev. 103, 1793 (2003) (<https://doi.org/10.1021/cr990029p>)

Domains of the dual descriptor

In a paper³⁴, Tognetti et al. proposed a real-space partitioning scheme of the dual descriptor (DD) into chemically meaningful *reactivity domains*. Basically, a predominantly electrophilic (nucleophilic) DD domain constitutes a region of space where this function remains positive (negative). They can be visualized using the GUI and quantitative information can be obtained using the additional *Domains* key block.

Note: This analysis requires that the calculation is performed without symmetry (Symmetry NOSYM).

ConceptualDFT

Type

Block

Description

Conceptual DFT Properties

Domains

Type

Block

Description

Calculate integrated properties for the domains (same sign) of the dual descriptor.

Border

Type

Float

Default value

7.0

Unit

Bohr

Description

Set the extent of the Cartesian grid. Extent is the distance between a face of the grid's bounding box and the most outlying atom in the corresponding direction. If the [AtomsToDo] key is present, the bounding box is created around the specified atoms.

Display

Type

Float

Default value

0.005

Description

Domains for which the integrated DD value is smaller (in magnitude) than the specified value are omitted from the printed output.

Enabled

Type

Bool

³⁴ V. Tognetti, C. Morell, L. Joubert, *Quantifying electro/nucleophilicity by partitioning the dual descriptor*, J. Comput. Chem. 36, 649 (2015) (<https://doi.org/10.1002/jcc.23840>)

Default value

No

GUI name

Properties of reactivity domains

Description

Calculate properties of reactivity domains.

Ensemble**Type**

Multiple Choice

Default value

Canonical

Options

[Canonical, GrandCanonical]

Description

Statistical ensemble for DD domains. Canonical: DD values are calculated using the statistical canonical ensemble. GrandCanonical: DD values are calculated using the statistical grand canonical ensemble. The grand canonical DD corresponds to $(S^2 f(2) - (\gamma/\eta^3) f^0)$, where $f(2)$ is the canonical DD, γ and η - the hyper-hardness and hardness of the chemical system, respectively, and f^0 is the mean Fukui function. This statistical ensemble is a natural choice when comparing two chemical systems with a different number of electrons.

Radius**Type**

Float

Default value

0.0

Description

This option adds a sphere around each nucleus, excluding all points inside it. This can help to separate domains around an atom or to exclude core electrons. Be careful when using this option. In particular, the radius of the sphere should exceed two or three times the [Spacing] value to be effective. By default, no spheres are added.

Spacing**Type**

Float

Default value

0.1

Unit

Bohr

Description

Specifies spacing (distance between neighboring points) of the rectangular Cartesian grid used when searching for DD domains. It may be useful to specify a smaller value (or increase the size of the grid, see [Border] key) if a substantial part of the electronic density is accounted for.

Threshold

Type

Float

Default value

0.001

Description

Arbitrary value of dual descriptor used to separate DD domains (values below this threshold are ignored).

9.4.7 adf2damqt: DAMQT interface

Interface (adf2damqt) to the third-party DAMQT 2.0 package³⁵, which can analyze the electron density in molecules, and related quantities. DAMQT includes the method of deformed atoms in molecules (DAM). The DAMQT 2.0 package is described in Ref.^{Page 323, 35}. In the ADF calculation, TAPE15 and adf.rkf need to be saved. The executable adf2damqt can be run with up to three optional arguments. If no argument is supplied, “ADF” is chosen as default root name (fname) for files generated by the interface, and files containing electron density matrix (fname.den) and molecular orbitals (fname.SLorba and, eventually, fname.SLorbb) will be created in a format suitable to be read by DAMQT.

```
$AMSBIN/ams << eor
...
Engine ADF
...
    SAVE TAPE15
EndEngine
eor
mv ams.results/adf.rkf TAPE21
mv ams.results/TAPE15 TAPE15
$AMSBIN/adf2damqt {fname {SPIN} {NOORBITALS}}
```

fname

If a specific name is desired for the files (fname), it must be supplied as first optional argument, provided that the name does not coincide with any of the two additional options SPIN and NOORBITALS.

SPIN

SPIN: for storing spin density matrix in fname.den file (instead of total electron density, which is the default).

NOORBITALS

NOORBITALS: to prevent generation of files with molecular orbitals (by default orbitals are generated).

SPIN and NOORBITALS are case insensitive and can be given in any order (but always after optional fname when required).

9.4.8 FOD: fractional orbital density

Following the analysis method by Grimme and Hansen (Ref.³⁶) a fractional occupation number weighted electron density (FOD) can be plotted with AMSview. The scalar field is obtained by finite-temperature DFT calculations with pre-defined electronic temperature T_{el} , typically $T_{el} = 5000$ K, and for hybrids $T_{el} = 20000 * (\text{amount of HF exchange}) + 5000$, see Ref.³⁶. This analysis tool can be used to determine whether static electron-correlation effects are important.

```
OCCUPATIONS ELECTRONICTEMPERATURE=5000
```

³⁵ R. López, J.F. Rico, G. Ramírez, I. Ema, D. Zorrilla, *DAMQT 2.0: A new version of the DAMQT package for the analysis of electron density in molecules*, *Computer Physics Communications* 192, 289 (2015) (<https://doi.org/10.1016/j.cpc.2015.02.027>)

³⁶ S. Grimme and A. Hansen, *A Practicable Real-Space Measure and Visualization of Static Electron-Correlation Effects*, *Angewandte Chemie International Edition* 54, 12308 (2015) (<https://doi.org/10.1002/anie.201501887>)

The NFOD (integrated FOD) is written in the output of ADF. The FOD can be visualized with AMSview. The contour surface value in AMSview should be set to 0.005 ($e/(bohr)^3$).

9.5 Controlling printed output

The amount of printed output is regulated with the keys Print, NoPrint, EPrint, and Debug. (No)Print and Debug are simple keys; EPrint is a block-type key.

Many print options pertain to debugging situations and are included here only for completeness. This section is intended to give a survey of all possibilities. Some items may be mentioned again in other sections where the subject of a particular print switch is discussed.

9.5.1 Print / NoPrint

```
PRINT Argumentlist
Print Argumentlist
NoPrint Argumentlist
```

Argumentlist

A sequence of names separated by blanks or commas. The keys Print and NoPrint may occur any number of times in the input file. The names in the argument list may refer to various items. For some of them printing is normally on, and you can turn them off with NoPrint. For others the default is not printing; use Print to override that.

The following is a list of the recognized items that are applicable in the argument lists, with a short explanation and defaults. Item names must be used exactly as given in the table - abbreviated or elongated forms will not be recognized - but they are not case-sensitive.

Items

Atdist

Default: No

Interatomic distance matrix at each new geometry (in an optimization)

Bas

Default: Yes

General control of output related to elementary basis functions (bas).

Character-Table

Default: No

Table of characters for the irreducible representations of the point group symmetry.

Computation

Default: Yes

Reports progress of the computation, with (concise) info about each SCF cycle.

Core

Default: No

Description of the frozen core: frozen core expansion functions (corbas) and the expansion coefficients for the frozen orbitals. This printing can only be activated if Functions is also *on*, otherwise it is ignored.

CoreOrt

Default: No

The valence basis set contains auxiliary Core Functions. They are not degrees of freedom but are used solely to ensure orthogonalization of the valence set to the frozen Core Orbitals. The orthogonalization coefficients and some related overlap matrices are printed.

CoreTable

Default: No

Internally the charge density and potential of the atomic frozen cores are processed as tables with values for a sequence of radial distances. A few initial and a few final values from these tables are printed, along with the (radial) integral of the core density, which should yield the number of core electrons.

EKin

Default: No

At the end of SCF: Kinetic energy of each occupied MO.

EPauli

Default: Yes

The repulsive Pauli term in the bonding energy (also called exchange repulsion) with its decomposition in density functional (lda and nl) and Coulomb terms.

Fit

Default: Yes

General control of output related to the density fitting.

Fmat

Default: No

Fock matrix computed at each cycle of the SCF.

FmatSFO

Default: No

Fock matrix (and overlap matrix) in the basis of symmetrized fragment orbitals (SFOs). This option requires the FULLFOCK and ALLPOINTS keyword to be present in the input. The matrix is printed only at the last SCF cycle. Use 1 iteration in the SCF for the Fock matrix at the first SCF cycle.

Frag

Default: No

General control of output related to build-molecule-from-fragments.

Functions

Default: Yes

List of employed Slater-type exponential basis functions and fit functions.

Group-Operators

Default: No

3x3 matrices of point group symmetry operators, with the axis and angle of rotation.

Irrep-Matrices

Default: No

Irreducible representation matrices

Logfile

Default: Yes

At the end of the calculation a copy of the log file is appended to standard output.

low

Default: No

Construction of the LOW basis from the elementary BAS functions and from the SFOs: combination coefficients

lowMO

Default: No

MOs are printed in the LOW (Lowdin) representation, in the RESULTS section

Ov1BAS

Default: No

Overlap matrices processed during the construction of the LOW basis. Only printed in case OLDORTHON is used in the input.

Pmat

Default: No

The density matrix (in Lowdin representation) in each cycle of the SCF.

QMpot

Default: Yes

At the end of the SCF, for each atom the electrostatic potential at its nucleus (excluding its own contribution of course).

SCF

Default: Yes

Controls the information about progress of the SCF procedure. Applies only if the print switch Computation is on.

sdiis

Default: No

Expansion coefficients applied by the DIIS procedure during the SCF.

sdiismat

Default: No

Turns on sdiis (see above) *and* prints the *error vector* constructed by the DIIS routine (this is the commutator of the Fock matrix and the Density matrix). This is used to determine the DIIS expansion coefficients and to assess convergence.

SFO

Default: depends on system size

General control of SFO-related output (if SFO subkey of key EPRINT is used). If turned off, (almost) all such output is suppressed. If on, such printing is controlled by the eprint subkey SFO. The default depends on the system size: if the number of primitive STOs < 1000, the default is Yes, else No.

SFOsiteEnergies

Default: No

The site energy of an SFO is defined as the diagonal Fock matrix element of the Fock matrix of the full complex in SFO representation.

Smat

Default: No

Overlap matrix of BAS functions.

Smearg

Default: No

Smear parameter - if and when applied - used in the determination of electronic occupation numbers for the MOs, with details of how it works out at every cycle of the SCF. For debugging purposes.

SpinOrbit

Default: No

Detailed information about how double-group symmetry representations are related to the single group representations.

Tails

Default: No

In each block of integration points (see Blocks) the evaluation of (Slater-type) exponential functions (basis, fit) is skipped when the function has become negligible for all points in that block due to the distance of those points from the atom where the function is centered. The relative savings due to this distance screening is printed at the first geometry cycle (use debug for printing at all cycles).

TechPar

Default: Yes

Technical parameters such as maximum vector length in vectorized numerical integration loops, SCF parameters.

Arguments for the keys PRINT and NOPRINT.

For print switches Frag, Fit, Repeat, SCF, SFO, TF, see the key EPRINT below.

9.5.2 Debug

The key DEBUG is used to generate extensive output that is usually only relevant for debugging purposes. It operates exactly like the PRINT key but there is no converse: nodebug is not recognized; it would be irrelevant anyway because by default all debug print switches are off.

A list of the possible items for the DEBUG key is given below.

All items of the print list can also be used with the debug key. If they are not mentioned in table III, the meaning is the same as for the print key, but the corresponding output may be generated more often, for instance at every SCF cycle rather than at the last one only.

Table 9.1: Table III. Arguments for the print key DEBUG. All debug switches are by default off.

Item	Explanation
Basis	Construction of the orthonormal LOW basis from elementary (BAS) and fragment (FO) basis.
Core	Core Orthogonalization procedure
Ekin	Kinetic energy matrices. (compare the print switches EKIN)
Fit	Construction of the symmetry adapted fit functions
Fitint	Construction of integrals used in the Fit procedure.
Gradients	The gradients split out in parts.
Pmat	P-matrix (density matrix) during SCF and in the ETS analysis program in the BAS representation.
Rhofih	Computation of fit coefficients during the SCF.
SCF	Extensive output during the SCF procedure about many different items. See also EPRINT, subkey SCF.
SDIIS	All data concerning the DIIS as used during the SCF.
TransitionField	The Transition State procedure to compute and analyze certain terms in the bonding energy. The distinct components, the involved transition field Fock matrices, etc.

9.5.3 EPrint

The key EPRINT is an extended version of the (no)print key, employed for print switches that require more specification than just off or on.

Contrary to what is the case for the keys print and noprint, the key EPRINT must occur only once in the input file; any subsequent occurrences are incorrect and ignored or lead to abort.

```
EPRINT
  subkey
  subkey
  ...
end
```

subkey

A subkey-type structure: it consists of a keyword followed by data, so that it functions as a simple (sub)key, *or* it is a keyword followed by a data *block* which must then end with the word subend.

The subkeys used in the EPRINT data block are called Eprint keys. A complete list of them is given below. All available EPRINT keys are discussed in the schemes below. The enclosing records EPRINT and end are omitted in these schemes.

Table 9.2: Table IV. List of EPRINT subkeys.

EPRINT keys	sub-	Subject
<i>AtomPop</i> (page 336)		Mulliken population analysis on a per-atom basis
<i>BASPop</i> (page 334)		Mulliken population analysis on a per-bas-function basis
<i>Eigval</i> (page 333)		One-electron orbital energies
<i>Fit</i> (page 329)		Fit functions and fit coefficients
<i>Frag</i> (page 329)		Building of the molecule from fragments.
<i>FragPop</i> (page 334)		Mulliken population analysis on a per fragment basis
<i>OrbPop</i> (page 330)		(Mulliken type) population analysis for individual MOs
<i>OrbPopEr</i> (page 330)		Energy Range (ER) in hartree units for the OrbPop subkey
<i>Repeat</i> (page 330)		repetition of output in Geometry iterations (SCF, optimization, ...)
<i>SCF</i> (page 331)		Self Consistent Field procedure
<i>SFO</i> (page 332)		Information related to the Symmetrized Fragment Orbitals and the analysis
<i>TF</i> (page 332)		Transition Field method.

9.5.4 Eprint subkeys vs. Print switches

Several EPRINT subkeys are merely shortcuts for normal (no)print switches. All such simple subkeys are used in the following way:

```
EPRINT
  ESUBKEY argumentlist
END
```

Esubkey

One of the following EPRINT subkeys: Fit, Frag, Repeat, SCF, sdiis, SFO, TF.

argumentlist

A sequence of names, separated by delimiters. Each of these names will be concatenated with the esubkey and the combination will be stored as a normal print switch. Example: Frag rot, SFO will be concatenated to fragrot and fragsfo and both will be stored as print switches. All such combinations can also be specified directly with the key PRINT. The example is therefore exactly equivalent with the input specification: print FragRot, Fragsfo****

If any of the names starts with the two characters no, the *remainder* of the name will be concatenated with the EPRINT, but now the result will be stored and treated as a noprint switch. Items that are on by default can in this way be turned off. Example:

```
EPRINT
  FRAG noRot Eig
END
```

This turns Rot *off* and Eig *on* for the EPRINT subkey Frag. Equivalent would be:

```
NOPRINT FragRot
Print FragEig
```

Follows a description of all simple EPrint subkeys:

Fit

The subkey fit controls output of how the elementary fit functions are combined into the symmetric (A1) fit functions. It controls also printing of the initial (start-up) and the final (SCF) fit coefficients.

```
EPRINT
  FIT list
END
```

list

A list of items, separated by blanks or commas. The following items are recognized: Charge, Coef, Comb.

Charge

The amount of electronic charge contained in the fit (start-up), total and per fragment.

Coef

The fit coefficients that give the expansion of the charge density in the elementary fit functions.

Comb

The construction of the totally symmetric (A1) fit function combinations from the elementary fit functions.

By default all options are off.

Frag

The subkey frag controls output of how the molecule is built up from its fragments.

```
EPRINT
  FRAG list
END
```

list

A list of items, separated by blanks or commas. The following items are recognized: Eig, Fit, Rot, SFO.

Eig

The expansion coefficients in elementary functions (bas) of the fragment Molecular Orbitals as they are on the fragment file.

Rot

The rotation (and translation) required to map the master fragment (i.e. the geometrical data on the fragment file)

onto the actual fragment which is part of the current molecule. N.B.: if eig and rot are both *on*, the rotated fragment orbitals are printed also.

Fit

The fit coefficients that describe the fitted charge density of the fragments after the rotation from the *master* fragment on file to the actual fragment. These are the molecular fit coefficients that are used (by default) to construct the total molecular start-up (fitted) charge density and hence the initial Coulomb and XC potential derived from it.

SFO

The Symmetry-adapted combinations of Fragment Orbitals that are used in the current calculation. This feature ensures that the definition of the SFOs is printed. This will happen anyway whenever the EPRINT subkey SFO itself is activated. By default all options are off. Remark: SFO analysis in a Spin-Orbit relativistic calculation is implemented only in the case there is one scalar relativistic fragment, which is the whole molecule.

OrbPop

Specifies that (Mulliken type) population analysis should be printed for individual MOs, both on a per-SFO basis and on a per-bas function basis. The format of the subkey is as follows:

```
EPRINT
  ORBPOP TOL=X Nocc Nunocc
    subspecies orbitals
    subspecies orbitals
    ...
  SUBEND
END
```

X is the threshold for the SFO coefficient value to include in the listing for the per-SFO analysis. Nocc is the number of the highest occupied and Nunocc is the number of the lowest unoccupied orbitals to analyze.

subspecies

One of the subspecies of the molecular symmetry group. Can not be used in a Spin-Orbit coupled calculation.

orbitals

A list of integers denoting the valence orbitals (in energy ordering) in this subspecies that you want to analyze. This overrules the Nocc, Nunocc specification for that symmetry representation. In an unrestricted calculation two sequences of integers must be supplied, separated by a double slash (/).

OrbPopEr

Specifies the energy range for the MOs to which the OrbPop key applies. The default range is from -0.7 below the HOMO to 0.2 Hartree above the LUMO. Usage:

```
EPRINT
  OrbPopER minEn maxEn
END
```

where minEn and maxEn are both in Hartree, and have the defaults just specified. In order to get information on many more orbitals, simply specify a large negative value for minen and a large positive value to maxen.

Repeat

Control the repetition of output in Geometry iterations: optimization, computation of frequencies, transition state search.

```
EPRINT
  Repeat list
END
```

list

contains one or more of the following items: NumInt, SCF.

NumInt

Output from the numerical integration procedure, like parameters, numbers of points generated, test data is controlled by the *numint* subkey (see below). The *repeat* subkey controls whether the output is repeated for all geometries (if the flag is on) or only for the first (if the flag is off). Some concise info is produced (repeatedly) anyway if the print switch computation is on.

SCF

Controls similarly the SCF output, like population analysis and orbital eigenvalues. If the flag is on, these items are printed at the last SCF cycle in every geometry, otherwise only at the last geometry.

By default both options are off.

SCF

Output during the SCF procedure.

```
EPRINT
  SCF list
END
```

list

is a list of items, separated by blanks or commas. The following items are recognized: Eigval, Eigvec, Err, Fmat, Keeporb, MOPop, Occ, Pmat, Pop, Start.

Eigval

Eigenvalues of the one-electron orbitals at the last SCF cycle. In a run with multiple SCF runs (Geometry Optimization,...) this printing occurs only for the last SCF procedure. See also the eigval subkey of EPRINT. (Use the *repeat* subkey of EPRINT to get output for the last SCF procedure at each SCF run, use DEBUG SCFEIGVAL to get output on all SCF cycles).

Eigvec

MO eigenvector coefficients in the BAS representation. Only printed on the last SCF cycle.

Err

SCF error data which are checked for convergence. By default this takes effect after cycle 25 of the SCF. If the key is set it takes effect at the first cycle. Optionally one may type ErrN, where n is an integer (written directly after Err without a blank in between), in which case the key takes effect at cycle n.

Fmat

Fock matrix in the low representation.

Keeporb

If the KeepOrbitals option is activated (see the key SCF), output is generated whenever this option actually results in a change of occupation numbers as regards the energy ordering.

Occ

concise output of SCF occupation numbers on last SCF cycle if no eigenvalues are printed (see: Eigval).

moPop

Mulliken populations in terms of the elementary basis functions (bas), per MO, for input-specified MOs (see the EPRINT subkey *orbpop*)

Pmat

Density matrix

Pop

General control of bas Mulliken populations. This supervises all printing (whether populations are printed or not) according to the EPRINT subkeys *atompop*, *fragpop*, *orbpop* (the latter only as regards the bas population analysis at the end of the SCF procedure).

Start

Data pertaining to the *first* SCF cycle (of the *first* SCF procedure, in case of an optimization; use *repeat* to get this for *all* SCFs).

By default Eigval, Keeporb, Occ, and Pop are on, the others off.

SFO

Information pertaining to the use of Symmetrized Fragment Orbitals (for analysis purposes).

```
EPRINT
  SFO list
END
```

list

A list of items, separated by blanks or commas. The following items are recognized: eig, eigcf, orbpop, grosspop, fragpop, ovl.

Eig

The MO coefficients in terms of the SFOs.

Eigcf

idem, but now also containing the coefficients pertaining to the CoreFunctions.

OrbPop

population analysis of individual orbitals. The orbitals analyzed are set with the EPRINT subkey *orbpop*.

GrossPop

Gross populations of the SFOs, split out in symmetry representations. GrossPop is automatically turned on when OrbPop is activated.

FragPop

Population analysis on a per-FragmentType basis. This analysis does in fact not depend on the SFOs (ie, the result does not depend on how the SFOs are defined), but the computation of these populations takes place in the SFO-analysis module, which is why it is controlled by the SFO print option. FragPop output is given per orbital when OrbPop is activated, per symmetry representation when GrossPop is activated, and as a sum-over-all-orbitals-in-all-irreps otherwise (if FragPop is active).

Ov1

Overlap matrix of the SFO basis, separately for each symmetry representation.

By default orbpop is on, the other options off.

In a Spin-Orbit calculation the SFO analysis is not yet implemented completely.

Remark: the options eig and eigcf replace the previous (now disabled) simple print options eigsfo and eigsfo.

Note that the simple print key SFO controls whether or not the EPRINT subkey *sfo* is effective at all.

TransitionField

Part of the bonding energy is computed and analyzed by the so-called Transition State procedure^{2,3}. This has nothing to do with physical transition states, but is related to the Fock operator defined by an average charge density, where the average is taken of the initial (sum-of-orthogonalized-fragments) and the final (SCF) charge density. There is also an analogous term where the average is taken of the sum-of-fragments and the sum-of-orthogonalized-fragments. Various terms, Fock operators and Density Matrices used in this approach may be printed. To avoid confusion with real Transition States (saddle points in the molecular Energy surface) the phrase TransitionField is used here.

² T. Ziegler and A. Rauk, *On the calculation of Bonding Energies by the Hartree Fock Slater method. I. The Transition State Method*, *Theoretica Chimica Acta* 46, 1 (1977) (<https://doi.org/10.1007/BF00551648>)

³ T. Ziegler and A. Rauk, *A theoretical study of the ethylene-metal bond in complexes between copper(1+), silver(1+), gold(1+), platinum(0) or platinum(2+) and ethylene, based on the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* 18, 1558 (1979) (<https://doi.org/10.1021/ic50196a034>)

```
EPRINT
  TF list
END
```

List

A list of items, separated by blanks or commas. The following items are recognized: Energy, Fmat, DiagFmat, FragPmat, DiagFragPmat, F*dPmat, DiagF*dPmat, OrbE.

Energy

Energy terms computed from the TransitionField.

Fmat

TransitionField Fock matrices.

DiagFmat

Idem, but only the diagonal elements.

FragPmat

The molecular P-matrix constructed from the sum-of-fragments.

DiagFragPmat

idem, but only the diagonal elements.

F*dPmat

The TransitionField energy term can be expressed as a Fock operator times the difference between two P-matrices (initial and final density).

DiagF*dPmat

only diagonal elements

OrbE

Orbital energies in the TransitionField.

By default all options are off.

9.5.5 Other Eprint subkeys

We discuss now the remaining EPRINT sub keys that are not simple shortcuts for print switches.

```
EPRINT
  Eigval noccup {nvirtual}
END
```

This specifies the *number* of one-electron orbitals for which in the SCF procedure energies and occupation numbers are printed whenever such data is output: the highest noccup occupied orbitals and the lowest nvirtual empty orbitals. Default values are noccup=10, nvirtual=10. If only one integer is specified it is taken as the noccup value and nvirtual is assumed to retain its standard value (10). Printing can be turned off completely with the EPRINT sub key SCF, see above.

Mulliken Population Analysis

All population subkeys of EPRINT refer to *Mulliken* type populations.

```
EPRINT
  ATOMPOP level
END
```

Populations accumulated per atom.

level must be none, gross or matrix. none completely suppresses printing of the populations; gross yields the gross populations; matrix produces the complete matrix of net and overlap populations. Default value: matrix.

```
EPRINT
  BASPop level
END
```

Populations are printed per elementary (bas) basis function. The level options are none, short, gross, matrix. none, gross and matrix are as for atompop.

short yields a summary of BAS gross populations accumulated per angular momentum (l) value and per atom.

Default value: gross.

```
EPRINT
  FragPop level
END
```

Completely similar to the atompop case, but now the populations per *fragment*. Of course in the case of single-atom fragments this is the same as atompop and only one of them is printed. Default: matrix.

For all three population keys atompop, fragpop and baspop, specification of a higher level implies that the lower-level data, which are in general summaries of the more detailed higher level options, are also printed.

Printing of any populations at the end of the SCF procedure is controlled with the EPRINT sub key *SCF* (pop).

Population Analysis per MO

A very detailed population analysis tool is available: the populations *per orbital* (MO). The printed values are independent of the occupation numbers of the MOs, so they are not populations in a strict sense. The actual populations are obtained by multiplying the results with the orbital occupations.

The analysis is given in terms of the SFOs and provides a very useful characterization of the MOs at the end of the calculation, after any geometry optimization has finished. This feature is now also available in a Spin-Orbit coupled relativistic calculation, in the case there is one scalar relativistic fragment, which is the whole molecule.

The same analysis is optionally (see EPRINT subkey *SCF*, option mopop also provided in terms of the elementary basis functions (bas).

```
EPRINT
  OrbPop {noccup {nvirtual}} {tol=tol}
    subspecies orbitals
    subspecies orbitals
    ...
  subend
END
```

noccup

Determines how many of the highest occupied orbitals are analyzed in each irrep. Default noccup=10.

nvirtual

Determines in similar fashion how many of the lowest virtual orbitals are analyzed in each irrep. Default nvirtual=4.

tol

Tolerance parameter. Output of SFO contributions smaller than this tolerance may be suppressed. Default: 1e-2.

subspecies

One of the subspecies of the molecular symmetry group. Can not be used (yet) in a Spin-Orbit coupled calculation.

orbitals

A list of integers denoting the valence orbitals (in energy ordering) in this subspecies that you want to analyze. This overrules the noccup,nvirtual specification for that symmetry representation. In an unrestricted calculation two sequences of integers must be supplied, separated by a double slash (/).

Any subset of the subspecies can be specified; it is not necessary to use all of them. No subspecies must occur more than once in the data block. This can not be used in a Spin-Orbit coupled equation (yet).

A total SFO gross populations analysis (from a summation over the occupied MOs) and an SFO population analysis per fragment type are preformed unless *all* MO SFO-populations are suppressed.

9.5.6 Reduction of output

One of the strong points of ADF is the analysis in terms of fragments and fragment orbitals (SFOs) that the program provides. This aspect causes a lot of output to be produced, in particular as regards information that pertains to the SFOs.

Furthermore, during the SCF and, if applicable, geometry optimizations, quite a bit of output is produced that has relevance merely to check progress of the computation and to understand the causes for failure when such might happen.

If you dislike the standard amount of output you may benefit from the following suggestions:

If you are not interested in info about progress of the computation:

```
NOPRINT Computation
```

If you'd like to suppress only the SCF-related part of the computational report:

```
NOPRINT SCF
```

If you don't want to see any SFO stuff:

```
NOPRINT SFO
```

To keep the SFO *definitions* (in an early part of output) but suppress the SFO-mo coefficients and the SFO overlap matrix:

```
EPRINT
  SFO noeig, noovl
END
```

Note: the SFO-overlap matrix is relevant only when you have the SFO-MO coefficients: the overlap info is needed then to interpret the bonding/anti-bonding nature of the various SFO components in an MO.

If you are not interested in the SFO *populations*:

```
EPRINT
  SFO noorbpop
END
```

9.6 Results on Output

The (standard) output file contains information on the main characteristics of the run, the SCF and geometry optimization results, bonding energy and population analyses. Major parts of output can be regulated with print switches, see section *Controlling printed output* (page 324).

By default the program produces quite a bit of output, for a large part related to (Mulliken-type) population analyses of the molecule in total, as well as of individual orbitals, both in terms of the elementary basis functions and in terms of the SFOs, the symmetry-adapted Fragment Orbitals.

The fragment-oriented approach of ADF is very suitable for a thorough chemical analysis of molecular orbital properties and a conceptual representation of results. New users are advised to spend time and get familiar with the SFO-type

analysis. It is a much more powerful tool to understand the electronic structure of the molecule than the classical atomic orbital populations.

The results for structure and reactivity, spectroscopic properties, transport properties that are printed are meant to be self-explanatory. See also the input options for each of these properties.

9.6.1 Electronic Configuration

The direct results from the SCF are the orbital energies and occupation numbers. This defines the electronic configuration: the occupation numbers and HOMO and LUMO energies for instance show whether or not the Aufbau principle is satisfied in the final situation.

The energies of the Core Orbitals can be used to interpret for instance XPS (X-ray Photoelectron Spectroscopy) data: from Koopman's theorem these core orbital energies are an approximation to the core ionization energies. This neglects the effect of relaxation upon the ionization so that absolute energy values may not be very good; relative values, however, should be fair and can therefore be used to study (relative) chemical shifts.

9.6.2 Mulliken populations

Mulliken populations are based on the elementary atomic basis functions (bas). The individual BAS populations are printed together with summaries of the populations in all basis functions with the same angular momentum quantum number on the same atom. A final summary is obtained by adding all functions on each atom, yielding the atom-atom populations. The atom-atom populations per l-value can be obtained if the key EXTENDEDPOPAN is included. The atomic gross charges are derived from the net and the overlap populations in the usual way. In addition, a population analysis may be given of individual MOs (by default this is suppressed). See the EPrint keys SCF (option mopop) and orbpop.

Mulliken-type populations are computed and printed at various levels of refinement (ranging from *per-basis function* to *per-fragment type*, data for the whole molecule as well as for individual MOs), and in two different representations, one based on the elementary basis functions (bas), the other on SFOs (Symmetrized Fragment Orbitals). This is potentially a very large amount of data. Precisely what is printed by default, and how this can be modified so as to suppress output or, alternatively, to get more information, is regulated by the print keys (print, eprint).

9.6.3 Hirshfeld charges, Voronoi deformation density

Mulliken populations can be summarized to yield atomic charges. Alternative methods exist to deduce atom charges from the self-consistent results of a molecular calculation. Several of those alternatives are provided by ADF: Hirshfeld analysis, Voronoi analysis, multipole derived charges, and charge model 5.

Of the methods applied in ADF to compute charges (Mulliken, Hirshfeld, Voronoi) we recommend the Hirshfeld analysis^{2,3} and the analysis based on Voronoi *deformation* density (VDD) charges^{1,4}, see below. The fragments to which the Hirshfeld charges apply are enumerated in the early geometry part of the output file, where for each fragment the numbers of the atoms are given that belong to the fragment. The sum of the Hirshfeld charges may not add up to the analytical net total charge of the molecule. Any deviation from this is caused by numerical integration precision (small effect) and the neglect of long-distance terms that ADF uses to speed up the integral evaluations. This approximation does not affect very much the energy and molecular orbital properties, but it does show up in the sum-of-charges somewhat more. It does not indicate an error (unless the deviation is really large, say in the order of 1‰ of the total number of electrons).

² F.L. Hirshfeld, *Bonded-atom fragments for describing molecular charge densities*, *Theoretica Chimica Acta* 44, 129 (1977) (<https://doi.org/10.1007/BF00549096>)

³ K.B. Wiberg and P.R. Rablen, *Comparison of atomic charges derived via different procedures*, *Journal of Computational Chemistry* 14, 1504 (1993) (<https://doi.org/10.1002/jcc.540141213>)

¹ G. te Velde, *Numerical integration and other methodological aspects of bandstructure calculations*, in *Chemistry*. 1990, Vrije Universiteit: Amsterdam.

⁴ F.M. Bickelhaupt, N.J.R. van Eikema Hommes, C. Fonseca Guerra and E.J. Baerends, *The Carbon-Lithium Electron Pair Bond in (CH₃Li)_n (n = 1, 2, 4)*, *Organometallics* 15, 2923 (1996) (<https://doi.org/10.1021/om950966x>)

The Hirshfeld analysis produces a charge value per fragment, computed as the integral of the SCF charge density over space, in each point weighted by the relative fraction of the (initial) density of that fragment in the total initial (sum-of-fragments) density:

$$Q^{\text{frag}(i)} = \int \rho^{\text{SCF}} \rho^{\text{initial frag}(i)} / \sum_j \rho^{\text{initial frag}(j)} \quad (5.1.1)$$

The VDD method is based on the *deformation* density and a rigorous partitioning of space into non-overlapping atomic areas, the so-called Voronoi cells^{Page 336, 1Page 336, 45}. The Voronoi cell of an atom *A* is the region in space closer to nucleus *A* than to any other nucleus (cf. Wigner-Seitz cells in crystals). The VDD charge of an atom *A* monitors the *flow* of charge into, or out of the atomic Voronoi cell as a result of ‘turning on’ the chemical interactions between the atoms. The VDD method summarizes the three-dimensional deformation density on a per-atom basis. It is conceptually simple and affords a transparent interpretation based on the plausible notion of charge redistribution due to chemical bonding, i.e. the gain or loss of charge in well-defined geometrical compartments of space. For the use of VDD in analyses involving molecular fragments, see Ref.⁶.

In the same fashion as for the Hirshfeld analysis, a summation over all atoms is given which should yield zero (for a neutral molecule). The deviation from zero is caused by numerical integration and by neglect-of-long-distance-terms; the same remarks apply as for the Hirshfeld analysis above.

The partitioning of space, using mid-way separation planes, is inappropriate to produce useful absolute numbers when neighboring atoms have very different sizes, for instance, Hydrogen and a heavy metal. However, *changes* in the density analyzed in this way do give a reasonable general insight in the effect of bonding on the location of charge densities, in particular because the Voronoi data per atom are split up in contributions within the atomic sphere and the rest of its Voronoi cell.

For symmetric molecules one can do a (partial) symmetry partitioning of the Voronoi deformation density if one includes

PRINT VDDANALYSIS

This analysis is especially useful if all fragments are calculated in the same symmetry as the full molecule, which is not always possible or useful, for example, symmetry NOSYM does not provide any extra information.

Hirshfeld and Voronoi charge analyses are printed at the end of the SCF (of the last geometry, in case of an optimization).

The Hirshfeld analysis in ADF produces charges *per fragment*, so that *atomic* charges are obtained only if single-atom fragments are used. This limitation does not apply to Voronoi charges (data per atom). Mulliken charges are given both per atom *and* per fragment.

In the printout of charges per fragment (as for the Hirshfeld analysis), you have to be aware of the *ordering* of fragments. A complete list of fragments is printed in the early GEOMETRY section of standard output, where you also find which atom(s) correspond(s) to which fragment. Note that even when you use single-atom fragments only, the order of fragments is usually quite different from the order of atoms in your input file. Typically (but not necessarily exactly in each case), when you use single-atom fragments: consider the first non-dummy atom in your ATOMS block. This defines the first atom *type*. Then browse the ATOMS list until you find an atom of a different type. This defines the second atom type, and so on. The single-atom fragment list will often be such that you first get *all* atoms of the first atom type, then all atoms of the second type, and so on. Check the printed list-of-fragments always, to avoid mistakes in assigning Hirshfeld charges to atoms (fragments).

⁵ C. Fonseca Guerra, J.-W. Handgraaf, E. J. Baerends and F. M. Bickelhaupt, *Voronoi Deformation Density (VDD) charges. Assessment of the Mulliken, Bader, Hirshfeld, Weinhold and VDD methods for Charge Analysis*, *Journal of Computational Chemistry* 25, 189 (2004) (<https://doi.org/10.1002/jcc.10351>)

⁶ C. Fonseca Guerra, F.M. Bickelhaupt, J.G. Snijders and E.J. Baerends, *The Nature of the Hydrogen Bond in DNA Base Pairs: The Role of Charge Transfer and Resonance Assistance*, *Chemistry - A European Journal* 5, 3581 (1999) ([https://doi.org/10.1002/\(SICI\)1521-3765\(19991203\)5:12%3C3581::AID-CHEM3581%3E3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1521-3765(19991203)5:12%3C3581::AID-CHEM3581%3E3.0.CO;2-Y))

9.6.4 Multipole derived charges

The multipole derived charges (MDC) analysis⁷ uses the atomic multipoles (obtained from the fitted density) up to some level X, and reconstructs these multipoles exactly (up to level X) by distributing charges over all atoms. This is achieved by using Lagrange multipliers and a weight function to keep the multipoles local. Since the atomic multipoles are reconstructed up to level X, the molecular multipoles are represented also up to level X. The recommended level is to reconstruct up to quadrupole: MDC-q charges. The SCF should have converged for a meaningful MDC analysis.

9.6.5 Charges Derived from the Electrostatic Potential

Charges derived from the electrostatic potential (ESP) are available for partial charge analysis. Two different charges are available in ADF: ChEIPG and RESP.

ChEIPG is the acronym for ‘Charges derived from the Electrostatic Potential Grid’. They are defined by fitting point charges to the electron density, on a real-space atom-centric Lebedev grid outside the van der Waals region subject to the constraint that the ChEIPG charges must equal the total charge of the molecule. For input use the keyword *ESP-CHELPG* (page 304).

RESP is the acronym for ‘Restrained Electrostatic Potential Charges’. RESP charges are the same as ChEIPG charges but with a harmonic restraint (0.05) to keep the charges and dipole moments as small as possible. RESP charges are typically more physically reasonable and robust than CHELPG charges. For input use the keyword *ESP-RESP* (page 304).

NUMERICALQUALITY (page 367) good is recommended. These charges can be used in the *3D-RISM* (page 155) and *SM12* (page 118) solvation models.

9.6.6 Charge model 5

The charge model 5 (CM5)⁸⁹ uses the Hirshfeld analysis in combination with a parametrization to yield atomic charges that can accurately reproduce dipole moments obtained from experimental results. CM5 charges can be used in the *SM12* (page 118) solvation model. For input use the keyword *CM5* (page 304).

9.6.7 Bond order analysis

The bond order analysis (see *Bond orders* (page 305)). produces the output in which the bond order values are printed for each pair of atoms for which the Nalewajski-Mrozek bond order value is larger than the threshold that can be specified with the keyword BONDORDER. For convenience the printed bond orders are accompanied by the corresponding interatomic distance. In the Nalewajski-Mrozek approach^{11 12 16 17 18 19} the bond order indices b_{AB} are calculated based on the

⁷ M. Swart, P.Th. van Duijnen and J.G. Snijders, *A charge analysis derived from an atomic multipole expansion*, *Journal of Computational Chemistry* 22, 79 (2001) ([https://doi.org/10.1002/1096-987X\(20010115\)22:1%3C79::AID-JCC8%3E3.0.CO;2-B](https://doi.org/10.1002/1096-987X(20010115)22:1%3C79::AID-JCC8%3E3.0.CO;2-B))

⁸ A.V. Marenich, S.V. Jerome, C.J. Cramer, D.G. Truhlar, *Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases*, *Journal of Chemical Theory and Computation* 8, 527 (2012) (<https://doi.org/10.1021/ct200866d>)

⁹ C.A. Peebles and G. Schreckenbach, *Implementation of the SM12 Solvation Model into ADF and Comparison with COSMO*, *Journal of Chemical Theory and Computation* 12, 4033 (2016) (<https://doi.org/10.1021/acs.jctc.6b00410>)

¹¹ A. Michalak, R.L. De Kock and T. Ziegler, *Bond Multiplicity in Transition-Metal Complexes: Applications of Two-Electron Valence Indices*, *Journal of Physical Chemistry A* 112, 7256 (2008) (<https://doi.org/10.1021/jp800139g>)

¹² M.S. Gopinathan and K. Jug, *Valency. I. A quantum chemical definition and properties*, *Theoretica Chimica Acta* 1983 63, 497 (1983) (<https://doi.org/10.1007/BF00552652>)

¹⁶ R.F. Nalewajski and J. Mrozek, *Modified valence indices from the two-particle density matrix*, *International Journal of Quantum Chemistry* 51, 187 (1994) (<https://doi.org/10.1002/qua.560510403>)

¹⁷ R.F. Nalewajski, J. Mrozek and A. Michalak, *Two-electron valence indices from the Kohn-Sham orbitals*, *International Journal of Quantum Chemistry* 61, 589 (1997) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1997\)61:3%3C589::AID-QUA28%3E3.0.CO;2-2](https://doi.org/10.1002/(SICI)1097-461X(1997)61:3%3C589::AID-QUA28%3E3.0.CO;2-2))

¹⁸ R.F. Nalewajski, J. Mrozek and A. Michalak, *Exploring Bonding Patterns of Molecular Systems Using Quantum Mechanical Bond Multiplicities*, *Polish Journal of Chemistry* 72, 1779 (1998) (<https://ichf.edu.pl/pjch/pj-1998/pj07s98.htm#1779>)

¹⁹ R.F. Nalewajski, J. Mrozek and G. Mazur, *Quantum chemical valence indices from the one-determinantal difference approach*, *Canadian Journal of Chemistry* 74, 1121 (1996) (<https://doi.org/10.1139/v96-126>)

one- and two-center valence indices

$$b_{AB} = V_{AB} + W_A^{AB} V_A + W_B^{AB} V_B$$

with the weighting factors for one-center indices given by

$$W_X^{XY} = \frac{V_{XY}^{\text{COV}}}{\sum_Z V_{XZ}^{\text{COV}}}$$

Unlike other definitions of covalent bond orders, the Nalewajski-Mrozek valence indices comprise both, covalent and ionic contributions. There exist three alternative sets of the Nalewajski-Mrozek valence indices^{Page 338, 11}Page 338, 12Page 338, 16Page 338, 17Page 338, 18Page 338, 1910. The bond order indices calculated from each set of the valence indices differ slightly due to arbitrariness in the way of splitting the one-center terms between bonds. More detailed description of alternative valence indices and their physical meaning is summarized in^{Page 338, 11}; see also original papers^{Page 338, 12}Page 338, 16Page 338, 17Page 338, 18Page 338, 19.

By default the bond order indices based on the valence indices obtained from partitioning of $\text{Tr}(P\Delta P)$ are printed in the ADF output. Note that in this version the covalent two-center part (also printed in the output) is equal to the Gopinathan-Jug^{Page 338, 12} bond order. The default values are:

$$\begin{aligned} V_A &= V_A^{\text{ion}} + V_A^{\text{COV}} \\ V_A^{\text{ion}} &= \sum_{a \in A} (P_{aa}^{\alpha} \Delta P_{aa}^{\alpha} + P_{aa}^{\beta} \Delta P_{aa}^{\beta}) \\ V_A^{\text{COV}} &= 2 \sum_{a \in A} \sum_{a' \in A, a < a'} (P_{aa'}^{\alpha} \Delta P_{a'a}^{\alpha} + P_{aa'}^{\beta} \Delta P_{a'a}^{\beta}) \\ V_{AB}^{\text{COV}} &= 2 \sum_{a \in A} \sum_{b \in B} (P_{ab}^{\alpha} \Delta P_{ba}^{\alpha} + P_{ab}^{\beta} \Delta P_{ba}^{\beta}) \end{aligned}$$

To produce the values from all alternative versions of Nalewajski-Mrozek valence indices, accompanied by the Gopinathan-Jug^{Page 338, 12} and Mayer¹⁰ bond orders, see the keyword BONDORDER.

The Mayer¹⁰ bond orders can also be calculated (see *BondOrders%PrintAll* (page 305)). The two implementations of calculating the Mayer bond orders differ slightly if one uses frozen cores. They should agree exactly in all electron calculations.

9.6.8 Dipole moment, Quadrupole moment, Electrostatic potential

Dipole moment. Note that in an ion the value of the dipole moment depends on the choice of the origin, as follows from elementary electrostatic theory.

Quadrupole moment. Note that the value of the quadrupole moment often depends on the choice of the origin, as follows from elementary electrostatic theory.

Electrostatic potential at the nuclei: the Coulomb potential of the molecule at the nuclear positions, where the contribution from the nucleus itself is omitted.

¹⁰ I. Mayer, *Charge, bond order and valence in the ab initio SCF theory*, Chemical Physics Letters 97, 270 (1983) ([https://doi.org/10.1016/0009-2614\(83\)80005-0](https://doi.org/10.1016/0009-2614(83)80005-0))

9.6.9 Fragments and Basis Functions

SFOs

SFOs: the Symmetry combinations of Fragment Orbitals. The SFOs are the basic conceptual entities for the analysis of MOs and other results. Note: The FO *coefficients* that expand the SFOs are normalized in the sense that they add up (squared) to unity. The resulting SFO *function* is not necessarily a normalized function. The FOs are normalized, so it depends on the *overlap* between the FOs what the self-overlap and hence the norm of the SFO is. Also printed are, for each subspecies in each irrep separately, the indices of the elementary basis functions from which the FOs and hence the SFOs are built up. (The overlap matrix of SFOs is printed much later, in the SFO Populations section after everything (SCF, Geometry) has cycled to convergence).

Elementary basis functions (BAS)

First the lists of function *sets*, defined by radial behavior and the angular quantum number, are printed for all atom types on which the functions are centered. Thereafter follows the complete BAS list where the function sets have been expanded over all atoms (the *sets* are printed only for the atom *types*) and also over all Cartesian harmonics (6, not 5 *d*-functions, et cetera). In this printout the numbering can be found to which the SFO survey above refers.

9.6.10 MO analysis

MOs expanded in SFOs

This gives a useful characterization of the character of the self-consistent molecular orbitals. Additional information is supplied by the SFO population analysis, see below. The definition of the SFOs in terms of the Fragment MOs has been given in an earlier part of output (section build). The SFO occupation numbers that applied in the fragments are printed. This allows a determination of the orbital interactions represented in a MO. Be aware that the bonding/antibonding nature of a SFO combination in a MO is determined by the relative signs of the coefficients *and* by the overlap of the SFOs. This overlap *may be negative!* Note also that SFOs are generally *not* normalized functions. The SFO overlap matrix is printed later, in the SFO-populations part below.

SFO population analysis

For each irrep:

- Overlap matrix of the SFOs. Diagonal elements are not equal to 1.0 if the SFO is a linear combination of two or more Fragment Orbitals. The Fragment Orbitals themselves are normalized so the diagonal elements of the SFO overlap matrix give information about the overlap of the Fragment Orbitals that were combined to build the SFO.
- Populations on a per-fragment basis for a selected set of MOs (see EPrint, subkey *OrbPop*). This part is by default *not* printed, see EPRINT subkey *SFO*.
- SFO contributions per MO: populations for each of the selected MOs. In these data the MO occupation numbers are not included, so that also useful information about the virtual MOs is obtained. The printout is in matrix form, with the MOs as columns. In each printed matrix a row (corresponding to a particular SFO) is omitted if all populations of that SFO are very small in all of the MOs that are represented in that matrix. See eprint, subkey *orbpop*. Note that this method to define SFO populations (for orbitals) is very similar to the classical Mulliken type analysis, in particular regarding the aspect that *gross* populations are obtained as the diagonal (*net*) populations plus half of the related off-diagonal (overlap) populations. Occasionally this may result in negative (!) values for the population of certain SFOs, or in percentages higher than 100%. If you have such results and wonder if they can be right, work out one of the offending cases by hand, using the printed SFO overlap matrix and the printed expansion of the MOs in SFOs to compute 'by hand' the population matrix of the pertaining MO. To avoid doing large calculations it is usually sufficient to take only the few largest MO expansion coefficients; this should at least qualitatively give the correct outcomes.
- Total SFO gross populations in a symmetry representation: from a summation over all MOs (not only those analyzed in the previous section of output) in the symmetry representation under consideration. In the gross populations the MO occupation numbers have been included.

- (Per spin): A full list of all MOs (combining all symmetry representations), ordered by energy, with their most significant SFO populations. Since there might be several significant SFO populations for a particular MO, and an SFO may actually be a linear combination of several (symmetry-related) Fragment Orbitals, this table could get quite extensive. In order to confine each SFO population specification to one line of output, the SFOs are indicated by the characteristics of the first term (Fragment Orbital) of its expansion in Fragment Orbitals. So, if you see the SFO given as the '2 P:x on the first Carbon fragment', it may actually refer to the symmetry combination of, for instance, 2P:x and 2P:y orbitals on the first, second and third Carbon fragments. A full definition of all SFOs in terms of the constituting Fragment Orbitals is given in an early part of the output.

9.6.11 Bond energy analysis

The bond energy and its decomposition in conceptually useful terms: Pauli (exchange) repulsion, total steric repulsion, orbital interactions (partitioned into the contributions from the distinct irreducible representations), and corrections for some approximations (fitting and Transition State analysis procedure). For a discussion of bonding energy decompositions and applications see e.g. refs.^{13 14 15 20 21 22 23 24 25 26}.

The program prints the bonding energy (not in a Create or Frequencies run) and its decomposition in terms that are useful for chemical interpretation. The *total* energy is not computed. The bonding energy is defined relative to the fragments. When *basic atoms* are employed as fragments one should realize that these do not represent the atomic ground state since they are computed as spin-restricted and spherically symmetric objects, with possibly fractional occupation numbers. The correct multiplet state is not computed. To obtain the bonding energy with respect to isolated atoms you should therefore add atomic correction terms to account for spin polarization and the multiplet state. See also the SLATERDETERMINANTS key and the discussion on multiplet states.

The spin polarization energy can be computed by running the single atom unrestricted, using as fragment the corresponding (restricted) basic atom. The true multiplet state is not necessarily obtained in this way.

For the comparison of computed bonding energies with experimental data one should furthermore be aware of any aspects that are not represented in the computational formalism, such as zero-point motions and environment (solvent) effects.

In a Geometry Optimization or Transition State search, the program may print a bonding energy evaluation at each geometry (depending on print switches). A test-energy value is written in the log file. This is *not* the bonding energy, although the difference is usually small. The test-energy printed in the log file is the energy expression from which the energy gradients are computed. The true bonding energy contains in addition a few (small) correction terms that are mostly related to the fit incompleteness. These correction terms are usually very small.

¹³ T. Ziegler and A. Rauk, *On the calculation of Bonding Energies by the Hartree Fock Slater method. I. The Transition State Method*, *Theoretica Chimica Acta* 46, 1 (1977) (<https://doi.org/10.1007/BF00551648>)

¹⁴ T. Ziegler and A. Rauk, *A theoretical study of the ethylene-metal bond in complexes between copper(1+), silver(1+), gold(1+), platinum(0) or platinum(2+) and ethylene, based on the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* 18, 1558 (1979) (<https://doi.org/10.1021/ic50196a034>)

¹⁵ F.M. Bickelhaupt, N.M. Nibbering, E.M. van Wezenbeek and E.J. Baerends, *The Central Bond in the Three CN Dimers NC-CN, CN-CN, and CN-NC: Electron Pair Bonding and Pauli Repulsion Effects**, *Journal of Physical Chemistry* 96, 4864 (1992) (<https://doi.org/10.1021/j100191a027>)

²⁰ K. Kitaura and K. Morokuma, *A new energy decomposition scheme for molecular interactions within the Hartree-Fock approximation*, *International Journal of Quantum Chemistry* 10, 325 (1976) (<https://doi.org/10.1002/qua.560100211>)

²¹ T. Ziegler and A. Rauk, *Carbon monoxide, carbon monosulfide, molecular nitrogen, phosphorus trifluoride, and methyl isocyanide as sigma donors and pi acceptors. A theoretical study by the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* 18, 1755 (1979) (<https://doi.org/10.1021/ic50197a006>)

²² H. Fujimoto, J. Osamura and T. Minato, *Orbital interaction and chemical bonds. Exchange repulsion and rehybridization in chemical reactions*, *Journal of the American Chemical Society* 100, 2954 (1978) (<https://doi.org/10.1021/ja00478a004>)

²³ S. Wolfe, D.J. Mitchell and M.-H. Whangbo, *On the role of steric effects in the perturbational molecular orbital method of conformational analysis*, *Journal of the American Chemical Society* 100, 1936 (1978) (<https://doi.org/10.1021/ja00474a055>)

²⁴ A.J. Stone and R.W. Erskine, *Intermolecular self-consistent-field perturbation theory for organic reactions. I. Theory and implementation; nucleophilic attack on carbonyl compounds*, *Journal of the American Chemical Society* 102, 7185 (1980) (<https://doi.org/10.1021/ja00544a003>)

²⁵ F. Bernardi, A. Bottoni, A. Mangini and G. Tonachini, *Quantitative orbital analysis of ab initio SCF=MO computations : Part II. Conformational preferences in H2N—OH and H2N—SH*, *Journal of Molecular Structure: THEOCHEM* 86, 163 (1981) ([https://doi.org/10.1016/0166-1280\(81\)85082-8](https://doi.org/10.1016/0166-1280(81)85082-8))

²⁶ P.J. van den Hoek and E.J. Baerends, *Chemical bonding at metal-semiconductor interfaces*, *Applied Surface Science* 41/42, 236 (1989) ([https://doi.org/10.1016/0169-4332\(89\)90063-9](https://doi.org/10.1016/0169-4332(89)90063-9))

If Electric Fields are used in the computation (homogeneous and/or point charges), the printed Bonding Energy is the energy of the molecule in the field minus the energy of the fragments in the same field. The energy terms due to the field are also printed separately so that one can subtract them from the total bonding energy to obtain the energy-change without field-terms.

9.7 Densf: Volume Maps

densf is an auxiliary program to generate values of molecular orbitals, charge densities, and potentials on a user-specified grid, typically for plotting or graphical display. The TAPE41 result file can be used directly by the AMSview program to visualize these properties.

densf requires an ASCII input file where you specify the grid and the items to calculate on the grid, plus the standard result file `adf.rkf` (TAPE21) from an *adf* calculation. *densf* writes a summary of the requested items to standard output, together with some general information.

densf produces a (binary) KF file TAPE41, see the OUTPUTFILE keyword below. TAPE41 is a KF file and all KF utilities can be used to inspect and process its data.

densf can also read and write cube files. See the CUBINPUT and CUBOUTPUT input options for details.

Examples of using *densf* are contained in the set of sample runs; see the [ADF Examples](#) (page 471).

9.7.1 Input

The input for *densf* is keyword oriented. The keywords may be specified in any order.

Below follows a list of the allowed keywords with their description.

```
$AMSBIN/densf << eor
ADFFILE {file}
OUTPUTFILE {file}
VTKFILE {file}
CUBINPUT {file}
CUBOUTPUT {file}
GRID ...
UNITS ...
Density ...
KinDens ...
Laplacian ...
DenGrad ...
DenHess ...
Potential ...
Orbitals ...
NOCV ...
NCI ...
SEDD
DualDescriptor
POLTDDFT ...
eor
```

Input/Output files

```
ADFFILE {file}
```

ADFFILE keyword specifies the path to the `adf.rkf` file from which *densf* reads the input data. Absence of the keyword is treated as if **ADFFILE TAPE21** has been specified.

```
OUTPUTFILE {file}
```

OUTPUTFILE keyword specifies the path to the (possibly existing) TAPE41 file. If the file exists, *densf* will read grid specifications from it, ignoring the GRID keyword in the input. Computed quantities are saved in the file, overwriting existing data with the same name, if any.

```
VTKFILE {file}
```

VTKFILE keyword specifies the path to a file in the format readable by VTK directly. This option exists primarily for better integration with ADF-GUI and you should not specify it.

```
CUBINPUT {file}
```

If the CUBINPUT keyword is present, then the grid as specified in the **file** is used to calculate all requested quantities. Any volume data found in the cube file are also saved in the output file. NOTE: The CUBINPUT option cannot be used with a pre-existing TAPE41 file because they both specify the grid, which may lead to a conflict.

```
CUBOUTPUT {file}
```

The CUBOUTPUT keyword tells *densf* to save all computed quantities as cube files using **file** as filename prefix. The prefix can also contain a complete path including directories. For example, specifying the following in the *densf* input

```
CUBOUTPUT /home/myhome/H2O
Density SCF
```

will result in a file `/home/myhome/H2O%SCF%Density.cub` being created containing volume data for the total SCF density. One file per requested quantity is created.

The OUTPUTFILE, CUBOUTPUT, and VTKFILE options are mutually exclusive. Absence of any of these options is treated as if **OUTPUTFILE TAPE41** has been specified.

Grid

The grid can be specified using the GRID block key.

In its simplest form the block can be written as follows:

```
GRID {save} {coarse|medium|fine}
END
EXTEND grid_extent
```

If the word *save* is specified, the program will store all grid points on TAPE41 (in addition to the specification of the grid that is always stored). The default is **not** to store all the grid points.

Either coarse, medium, or fine may be specified. This instructs the program to generate the grid automatically within a box enclosing all atoms of the molecule. The distance between grid points is 0.5, 0.2, or 0.1 bohr for the coarse, medium, and fine grid, respectively. Obviously, the size of the result file TAPE41 depends strongly on this specification. By default a coarse grid is generated. The size of the grid box is determined by the atomic coordinates and the grid extent. The

latter is by default equal to 4.0 Bohr and can be changed using the EXTEND keyword, in which case it is affected by the unit_of_length value specified in the UNITS block (see below).

For more detailed grid specification the following GRID block can be used:

```
Grid {save}
  x0 y0 z0
  n1 [n2 [n3]]
  v1x v1y v1z length1
  [v2x v2y v2z length2]
  [v3x v3y v3z length3]
END
```

The rows of the GRID block are specified as follows:

- Row 1: three coordinates for the origin (one of the corners) of the grid.
- Row 2: up to three integers specifying the numbers of points in each direction. The number of integers defines the dimensionality of the grid.
- Rows 3 to 5: up to three rows, one per grid dimension. Each row contains components of the direction vector and the length of the grid in this dimension. The absolute magnitude of the vector components is irrelevant as it will be scaled to fit the given number of points into the grid length in this dimension. The unit of length for the grid size is by default angstrom. The default can be overridden by using the input key UNITS, see below.

Notes:

- The second row ('three integers...') specifies the number of grid *points* in the different directions. The corresponding number of steps or intervals is one less!
- If the TAPE41 result file is to be used by AMSview, the grid must be a 3-dimensional orthogonal one, with the same step size for all three dimensions.
- If the output TAPE41 file already exists and it contains valid grid data or if CUBINPUT is specified then the GRID input is ignored.
- The unit of length used in the input file has no relation to how the data are stored on the result file and how the program processes the data internally. Internal processing and storage on file is in bohr (atomic units).

Inline Grid

DENSF can read the grid as a list of points. When specifying an inline grid the GRID keyword should look as follows:

```
Grid Inline
  x1 y1 z1
  x2 y2 z2
  ...
  xN yN zN
End
```

Here, x#, y#, and z# are coordinates of points at which requested properties will be calculated. This feature may be used, for example, by external programs to calculate various properties at a number of points exactly and avoid interpolation with its inaccuracy. This feature should be used only when the output file has a TAPE41 format.

Units

The unit of length can be set with the Units block:

```
UNITS
  Length unit_of_length
END
```

The unit of length will apply to the grid specification in the input file. The default is Angstrom.

Density

Generates the charge density on the grid. It is a simple keyword (not block-type).

```
density {fit} {frag} {ortho} {scf} {trans}
```

The word *fit* specifies that all densities specified in this record will be computed from the fit functions (an approximation to the exact density), rather than from the occupied molecular orbitals.

frag, *ortho*, *scf*, and *trans* cause each of the corresponding densities to be computed. *frag* stands for the sum-of-fragments (i.e. the initial) density, *scf* for the final result of the *adf* calculation, *ortho* for the orthogonalized fragments (orthogonalization to account for the Pauli repulsion, see the ADF User's Guide), and *trans* for excitation transition density.

Transition density is a product of the initial and final states of an excitation. In the simplest case when initial and final states consist of one molecular orbital each, the corresponding transition density is a product of the two MOs. To obtain transition densities you need to perform an excitation calculation with ADF; see the EXCITATIONS keyword in the ADF User's Guide. Transition densities for all excitations found in the input `adf.rkf` (TAPE21) file will be calculated. The transition densities are always fit densities.

If both the exact and the fit densities are required, the density keyword must be repeated, once with and once without the fit option specified.

The default (when the DENSITY key does not occur in the input file) is to calculate the final SCF density and the sum-of-fragments density.

The frozen core density is calculated with:

```
density core
```

Kinetic Energy Density and Electron Localization Function (ELF)

```
KinDens {frag} {orth} {scf}
```

Generates the kinetic energy density and electron localization function on the grid.

Any of these keywords requests calculation of the two quantities (KinDens and ELF) based on the corresponding density: sum-of-fragments, orthogonalized fragments, or SCF, respectively. If none of the options is present, *scf* is assumed.

Laplacian of the Density

The Laplacian of the exact SCF density is calculated with:

```
Laplacian
```

The Laplacian of the fitted SCF density is calculated with:

```
Laplacian fit
```

The LAPLACIAN key can occur multiple times. The LAPLACIAN feature is also supported by AMSview.

Gradient of the Density

The gradient of the exact SCF density is calculated with:

```
DenGrad
```

The gradient of the fitted SCF density is calculated with:

```
DenGrad fit
```

The gradient of the frozen core density is calculated with:

```
DenGrad core
```

The DENGRADE key can occur multiple times. This feature should be used only when the output file has a TAPE41 format.

Hessian of the Density

The Hessian of the exact SCF density is calculated with:

```
DenHess
```

The Hessian of the fitted SCF density is calculated with:

```
DenHess fit
```

The Hessian of the frozen core density is calculated with:

```
DenHess core
```

The DENHESS key can occur multiple times. This feature should be used only when the output file has a TAPE41 format.

Potential

Generates the Coulomb and/or exchange-correlation potential on the grid.

```
potential {coul / XC} {frag} {ortho} {scf}
```

frag, ortho, and scf are as for the density: at least one must be specified.

coul and XC specify that the Coulomb potential, respectively the exchange-correlation potential, must be computed. Precisely one of these options must be specified in the record. If both potential types are required, another input record with the potential key must be used.

In the present release the XC option is not yet operational.

The default (when the POTENTIAL key does not occur in the input) is to calculate the SCF Coulomb potential.

Orbitals

A block-type key in which the required molecular orbitals are specified. The key can be repeated in the input any number of times; all occurrences are read and applied.

```
Orbitals {GRAD} type
  (data)
END
```

The argument of the orbitals key (type) must be `scf` (for the SCF orbitals) or `loc` (for the localized molecular orbitals, see the ADF User's Guide) or `generic` (see separate section).

The SCF type can have an optional GRAD specifier, which requests calculation of the MO gradients.

In many data records in the ORBITALS block, as noted in the description of these data records, you may specify a HOMOLUMO range.

A HOMOLUMO range is the following:

```
{HOMO{-}n} {LUMO{+}n}
```

HOMO: the highest occupied orbital HOMO-*n*, with *n* an integer: the highest (*n*+1) occupied orbitals. LUMO: the lowest virtual orbital LUMO+*n*, with *n* an integer: the lowest (*n*+1) virtual orbitals.

The HOMO part, or the LUMO part, or both must be specified. The integer *n* with sign is always optional, and the sign is always optional (and has no meaning, it is intended to enhance readability).

Thus, as an example,

```
HOMO-1 LUMO+1
```

means a range of 4 orbitals: the two highest occupied ones, and the two lowest virtuals.

Each data record in the orbitals block must have either of the following formats:

the word alpha or beta.

This specifies that subsequent records refer to spin-alpha or spin-beta orbitals respectively. In a restricted calculation this has no meaning and beta must not be specified. alpha and/or beta may occur any number of times in the orbitals block. All records until the first occurrence of alpha or beta are assumed to refer to spin-alpha orbitals.

label n1, n2, n3, ...

label is one of the subspecies of the point group symmetry used in the adf calculation and n1 etc. are indices of the molecular orbitals (in that subspecies) that are to be computed. This format is meaningless and must not be used for the loc orbitals type, because localized orbitals do not (necessarily) belong to a particular symmetry.

label HOMOLUMO

label is one of the subspecies of the point group symmetry used in the calculation, the orbitals follow from the HOMOLUMO range.

label occ or label virt

occ specifies all orbitals (in that symmetry representation) up to and including the highest occupied one. virt specifies all orbitals above the highest occupied one. In this context partially occupied orbitals are considered occupied. Note carefully that if in a particular symmetry representation an empty orbital is computed below the highest occupied one in that same representation (excited state), that particular empty one is included in the list of occ. Again, this format is meaningless and must therefore not be used for the loc type of orbitals.

all occ or all virt or all HOMOLUMO

Specifies for each symmetry representation:

- all orbitals up to and including the highest occupied one (in that symmetry), or
- all orbitals above the highest occupied one, or
- all orbitals defined by the HOMOLUMO range.

This form is not to be used for the LOC type of orbitals. However, using this for LOC will not result in an error but will be interpreted as identical to the following format.

all

This format must be used only for the LOC type of orbitals and simply means: all computed localized orbitals (irrespective of occupation numbers).

n1, n2, ...

a simple list of integer indices. This format must be used only for the loc type of orbitals since no reference is made to any symmetry representation. The indices refer to the list of localized orbitals as computed by ADF.

The default value used when the ORBITALS key is not present is:

```
Orbitals SCF
All HOMO-1 LUMO+1
End
```

NOCV

In ADF2009.01, it is possible to use DENSF to calculate $\epsilon^* \phi^2$ values of Natural Orbitals for Chemical Valence (NOCVs). Additional information on NOCVs is available in Ref.¹.

The relevant part of the DENSF input is as follows:

For spin-unrestricted:

```
NOCV
Alpha
N1:math:`\alpha`
N2:math:`\alpha`
...
Beta
N1:math:`\beta`
N2:math:`\beta`
...
END
```

¹ A. Michalak, M. Mitoraj, and T. Ziegler, *Bond Orbitals from Chemical Valence Theory*, Journal of Physical Chemistry A 112, 1933 (2008) (<https://doi.org/10.1021/jp075460u>)

For spin-restricted:

```
NOCV
  N1
  N2
  ...
END
```

N1, N2, etc. specify sequential numbers of the orbitals for which $\epsilon^* \phi^2$ is to be calculated.

Alpha and *Beta* specify that the numbers that follow refer to spin α and β , respectively. Both *Alpha* and *Beta* are optional, *Alpha* being assumed if omitted. The NOCV input block must be closed with “END”.

Alternatively, one can specify to calculate all (alpha- or beta-) NOCVs:

For spin-unrestricted:

```
NOCV
  Alpha
  ALL
  Beta
  ALL
END
```

For both spin-restricted and spin-unrestricted:

```
NOCV
  ALL
END
```

The last and probably the most convenient form of the NOCV input blocks lets you specify an NOCV eigenvalue threshold as a criterion for selecting orbitals:

For spin-unrestricted:

```
NOCV
  Alpha
    THRESH threshold
  Beta
    THRESH threshold
END
```

For both spin-restricted and spin-unrestricted:

```
NOCV
  THRESH threshold
END
```

When this form of the input is used, only those NOCVs will be included whose absolute eigenvalue is equal to or larger than the given *threshold*.

NOCV profile

It is possible to compute an integral profile of the NOCV $\epsilon^* \phi^2$ function along a given line. To calculate a single point of the profile the $\epsilon^* \phi^2$ is integrated in the plane orthogonal to the profile axis and passing through the point. In addition to the input above used for selecting NOCVs, the following input is required to calculate the profile:

```
NOCV
  PROFILE
END
LINE
  x1 y1 z1
  x2 y2 z2
  delta
END
```

The LINE input block is used to define the axis along which the profile will be generated. The $(x1,y1,z1)$ point defines the origin of the profile axis and $(x2,y2,z2)$ defines the second point of the line and the positive direction. The distance between the points does not matter. The *delta* value is the distance between two points in the profile. All values are given in the units specified in the UNITS input block. The positions of the left- and rightmost profile points depend on the coordinates of the atoms and the grid extent value (specified by the EXTEND keyword, see above).

Generic orbitals

There is also a possibility to calculate any orbital as long as it is present in the t21 file in the BAS representation. The input syntax is as follows:

```
Orbitals GenBas
  section1%variable1
  section2%variable2
End
```

In the example above, each line contains the section and variable name of the orbital in the input t21 file. The length of the variable should be equal to the number of atomic functions (naos) and it is supposed to contain expansion coefficients of the orbital on the basis of atomic (primitive) functions.

The calculation results are stored in the output file in sections and variables with exactly the same names as specified in the input. The section and variable names may contain spaces although the leading and trailing spaces are discarded.

NCI

The areas of non-covalent interactions (NCI), see Refs.^{4,5}, can be recognized by a low value of the electron density coupled with a low value of RDG (reduced density gradient $s = 1/2 (3 \pi^2)^{-1/3} |\nabla \rho| \rho^{-4/3}$) and a negative (or a small positive) value of the second eigenvalue of the Hessian of the electron density (λ_2). The regions of significant hydrogen bonding are recognized by strictly negative λ_2 while in the regions of VdW interactions it may be slightly positive. The relevant DENSF input keyword is:

```
NCI {BOTH|FIT} {RHOVDW=*RhoVdW*} {RDG=*Rdg*}
```

All arguments are optional.

⁴ E.R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García A.J. Cohen, and W. Yang, *Revealing Non-Covalent Interactions*, *Journal of the American Chemical Society* 132, 6498 (2010) (<https://doi.org/10.1021/ja100936w>)

⁵ J. Contreras-García E.R. Johnson, S. Keinan, R. Chaudret, J-P. Piquemal, D.N. Beratan, and W. Yang, *NCIPLOT: A Program for Plotting Noncovalent Interaction Regions*, *Journal of Chemical Theory and Computation* 7, 625 (2011) (<https://doi.org/10.1021/ct100641a>)

By default, the exact density is used to calculate the NCI properties. If FIT is specified, then the fitted density is used to calculate the fields and their names are prepended with “Fit”. If BOTH is specified, then the NCI properties are calculated using both the exact and the fitted density. Again, names of the fields calculated from the fitted density start with “Fit”.

The remaining arguments set relevant thresholds (all in atomic units): *RhoVdW*: density threshold for detection of weak interaction regions (default 0.02); *Rdg*: threshold on the reduced density gradient value s (default 0.5). A point is considered for NCI only if s value is smaller than *Rdg*.

DENSF creates three variables per density type (exact or fitted) when NCI is present in the input: *SCF%RDG* (or *SCF%FitRDG*): the reduced density gradient value s ; *SCF%DenSigned* (or *SCF%FitDenSigned*): the $\text{sign}(\lambda_2) \rho$ value for regions where $s < \text{Rdg}$; *SCF%NCI* (or *SCF%FitNCI*): the NCI flag value, see below;

If the point is considered for NCI (that is if $s < \text{Rdg}$), the $\text{sign}(\lambda_2) \rho$ value (or ρ) is tested against *RhoVdW*. If $\rho < \text{RhoVdW}$ then the NCI value is set to 1 to flag a VdW interaction region. If $\text{sign}(\lambda_2) \rho < -\text{RhoVdW}$ then the NCI value is set to -1 to flag a hydrogen bonding region. In all other cases the NCI value is zero.

AMView visualization of NCI: use `Isosurface:with phase isosurface` of property NCI (at 0.5). Alternative visualization of NCI: use a colored isosurface with isosurface of property *RDGforNCI* (at 0.5) colored with NCI (range -0.5 to 0.5). The value of *RDGforNCI* is the same as *RDG* (reduced density gradient) except in regions where the density is larger than 0.05, in order to get rid of surfaces around atoms that would otherwise appear when using an isosurface of *RDG*. One may need a medium or fine grid for best visualization.

SEDD

The single exponential decay detector (SEDD), see Ref.², extracts information about bonding and localization in atoms, molecules, or molecular assemblies. The practical evaluation of SEDD does not require any explicit information about the orbitals. The only quantity needed is the electron density (calculated or experimental) and its derivatives up to the second order. For the exact equation to be used, and pictures, see Ref.^{Page 351, 2}.

Specifying SEDD in the input also invokes calculation of the Density Overlap Regions Indicator (DORI)³. The DORI is best visualized as a 0.9 isosurface colored with the $\text{sign}(\lambda_2) \rho$ value (see the *DenSigned* variable from the NCI keyword above). AMView visualization of DORI: use a colored isosurface with isosurface of property DORI (at 0.9) colored with *DenSigned* (range -0.02 to 0.02). One may need a medium or fine grid for best visualization.

DualDescriptor

Calculate the dual descriptor (DD) in the frontier molecular orbitals approximation. The DD is essentially a difference between (an average of) the square of the lowest unoccupied and the highest occupied molecular orbitals: $DD = \frac{1}{N_{LUMO}} (\sum_i^{N_{LUMO}} \psi_i^2) - \frac{1}{N_{HOMO}} (\sum_j^{N_{HOMO}} \psi_j^2)$, where i and j are indices of orbitals within 10^{-3} Hartree of the LUMO and HOMO, respectively. Please note that this method will produce incorrect results for molecules with fractional occupation numbers.

² P. de Silva, J. Korchowiec, T.A. Wesolowski, *Revealing the Bonding Pattern from the Molecular Electron Density Using Single Exponential Decay Detector: An Orbital-Free Alternative to the Electron Localization Function*, *ChemPhysChem* 13, 3462 (2012) (<https://doi.org/10.1002/cphc.201200500>)

³ P. de Silva and C. Corminboeuf, *Simultaneous Visualization of Covalent and Noncovalent Interactions Using Regions of Density Overlap*, *Journal of Chemical Theory and Computation* 10, 3745 (2014) (<https://doi.org/10.1021/ct500490b>)

PoITDDFT

ADF can calculate the complex dynamical polarizability with *PoITDDFT* (page 222), which can be used to calculate the photoabsorption and CD spectra. With *densf*, you can calculate for a given frequency the three components of the induced (first-order perturbed) density (relevant for polarizability), the three components of the transition (first-order perturbed) density (relevant for absorption), and the three components of the rotator strength density (relevant for CD), see Ref.⁶.

```
POLITDDFT n
```

Here *n* is the *n*'th frequency in the list of requested frequencies.

9.7.2 Result: TAPE41

Below is a description of the contents of TAPE41. We start with a brief discussion of the sections. At the end, you can find an uncommented list of all variables and sections. Note that some data are only generated when certain keywords are provided.

Sections on TAPE41

Grid

This is a general section. It contains the grid data and some more general information.

The grid characteristics are stored as:

- The 'origin' of the grid.
- The numbers of points in three independent directions.
- Three vectors, called 'x-vector', 'y-vector' and 'z-vector'. They are the *steps* in the three independent directions that define the grid.

If the save option was used in the input (key GRID), all grid coordinates are stored: for each point three coordinates (xyz), also if only a 2-dimensional or 1-dimensional grid has been generated (a 2D grid does not necessarily lie in the xy-plane).

Note that the grid values are now stored in a simpler manner than in previous (prior to 2004) versions of densf, because the 'x values', 'y values', and 'z values' now each have their own, separate sections.

The remaining (general) data in this section comprise:

- The number of subspecies ('symmetries') for which data such as Molecular Orbitals may be present.
- The names of the subspecies.
- A logical with the name 'unrestricted', which flags whether the data pertain to an unrestricted calculation.
- The total number of grid points.

SumFrag

Contains grid data of the Sum-of-fragments (charge density, Coulomb potential, kinetic energy density, ELF, etc.).

Ortho

Contains similar data for the orthogonalized-fragments.

SCF

Contains the (spin) density, potential, etc. of the final (scf) solution.

⁶ L. Chang, O. Baseggio, L. Sementa, D. Cheng, G. Fronzoni, D. Toffoli, E. Aprà, M. Stener, and A. Fortunelli, *Individual Component Map of Rotatory Strength and Rotatory Strength Density Plots As Analysis Tools of Circular Dichroism Spectra of Complex Systems*, *Journal of Chemical Theory and Computation* 14, 3703 (2018) (<https://doi.org/10.1021/acs.jctc.8b00250>)

Core

Contains grid data of the frozen core (charge density, gradients, Hessian).

TransDens_L1_L2

Contains grid data for electron transition densities. L1 is either SS or ST, and L2 is a symmetry label for all transitions in the section. Here SS and ST stand for Singlet-Singlet and Singlet-Triplet, respectively. Variables in each section are Fitdensity_N and Coulpot_N for the density and Coulomb potential for excitation N within this spin and symmetry.

SCF_label

‘Label’ is one of the symmetry subspecies.

Each such section contains the total number of orbitals in that subspecies (as used in the *adf* calculation), with their occupation numbers and energy eigenvalues.

In addition it contains the grid-values of the (user-specified subset of) MOs in that subspecies. The variable name corresponding to an orbital is simply its index in the energy-ordered list of all orbitals (in that subspecies): ‘1’, ‘2’, etc.

In case of spin-orbit coupling, spinors are calculated. The label is one of the double group symmetry subspecies, and the square root of the density of the spinor is calculated with an approximate phase factor. The full description of the spinor can be found in the section SO_label.

SO_label

‘Label’ is one of the double group symmetry subspecies.

The grid values of the (user-specified subset of) spinors in that subspecies. A spinor is a two-component complex wave function which can be described with four real functions: real part alpha, real part beta, imaginary part alpha, and imaginary part beta. The variable name corresponding to a spinor is its index in the energy-ordered list of all orbitals (in that subspecies), combined with the real alpha part, the real beta part, the imaginary alpha part, or the imaginary beta part: ‘1_alpha_R’, ‘1_beta_R’, ‘1_alpha_I’, ‘1_beta_I’, ‘2_alpha_R’, etc.

LocOrb

Values of the localized orbitals.

NOCV

Values related to the NOCVs.

Profile

Values related to the NOCV profile. The variables whose names start with “Dif” contain the in-plane integral (in e/Bohr) for the given point on the profile axis. A variable without “Dif” in the name contains the integral (in electrons) of the corresponding “Dif” variable on the (-infinity, x) interval.

Geometry

Some general geometric information: the number of atoms (not counting any dummy atoms that may have been used in the *adf* calculation), their Cartesian coordinates (in bohr) and nuclear charges.

Note: the *order* of the atoms here is not necessarily identical to the input list of atoms: they are grouped by atom type.

- In an unrestricted calculation the section SCF_label is replaced by SCF_label_A and SCF_label_B for the spin-alpha and spin-beta data, respectively, and similarly for LocOrb: LocOrb_A and LocOrb_B.
- One or more subspecies may not have been used in the *adf* calculation. This happens when the basis set used in that calculation does not contain the necessary functions to span symmetry-adapted combinations of basis functions for that subspecies. In such a case the corresponding section on TAPE41 will not be created by *densf*.
- If you want to verify the contents of TAPE41, use the *pkf* utility to obtain a survey or *dmpkf* to get a complete ASCII printout.

The information is presented in three columns. In the left-most column, section and variable names are printed, variable names being indented. In the middle column, variable's type and size is given. If the type is omitted, double precision floating point is assumed. The right-most column contains comments, if any.

Note that the name of a section of variable may consist of more than one word and that blanks in such names are significant. Furthermore, they are case-sensitive. Each line below contains the name of only one section or variable.

NAME	length	Comment
Grid		
Start_point	(3)	
nr of points x	(one integer)	
nr of points y	(idem)	
nr of points z	(idem)	
total nr of points	(idem)	
x-vector	(3)	
y-vector	(3)	
z-vector	(3)	
nr of symmetries	(one integer)	
labels	(nr of symmetries160 characters)	
unrestricted	(one logical)	
SumFrag		
CoulPot	(total nr of points)	
XCPot_A	(idem)	spin-restricted: XCPot
XCPot_B	(idem)	
Density_A	(idem)	spin-restricted: Density
Density_B	(idem)	
Fitdensity_A	(idem)	spin-restricted: Fitdensity
Fitdensity_B	(idem)	
Kinetic Energy Density_A	(idem)	spin-restricted:
		Kinetic Energy Density
Kinetic Energy Density_B	(idem)	
ELF_A	(idem)	spin-restricted: ELF
ELF_B	(idem)	
Ortho		
Same variables as in SumFrag		
SCF		
Same variables as in SumFrag and Ortho, and:		
DensityLap_A	(idem)	spin-restricted: DensityLap
DensityLap_B	(idem)	
DensityGradX_A	(idem)	spin-restricted: DensityGradX
DensityGradX_B	(idem)	
DensityGradY_A	(idem)	spin-restricted: DensityGradY
DensityGradY_B	(idem)	
DensityGradZ_A	(idem)	spin-restricted: DensityGradZ
DensityGradZ_B	(idem)	
DensityHessXX_A	(idem)	spin-restricted: DensityHessXX
DensityHessXX_B	(idem)	
DensityHessXY_A	(idem)	spin-restricted: DensityHessXY
DensityHessXY_B	(idem)	
DensityHessXZ_A	(idem)	spin-restricted: DensityHessXZ
DensityHessXZ_B	(idem)	
DensityHessYY_A	(idem)	spin-restricted: DensityHessYY
DensityHessYY_B	(idem)	
DensityHessYZ_A	(idem)	spin-restricted: DensityHessYZ
DensityHessYZ_B	(idem)	
DensityHessZZ_A	(idem)	spin-restricted: DensityHessZZ
DensityHessZZ_B	(idem)	
DenSigned	(idem)	sign(:math:`\lambda` `^2`) :math:`\rho`

(continues on next page)

(continued from previous page)

```

FitDenSigned      (idem)
RDG               (idem)    reduced density gradient
FitRDG           (idem)
NCI              (idem)    +/-1 flag for non-covalent interaction regions
FitNCI           (idem)
SEDD             (idem)    single exponential decay detector
DORI             (idem)    density overlap regions indicator
Core
Density          (total nr. of points)
DensityGradX     (idem)
DensityGradY     (idem)
DensityGradZ     (idem)
DensityHessXX    (idem)
DensityHessXY    (idem)
DensityHessXZ    (idem)
DensityHessYY    (idem)
DensityHessYZ    (idem)
DensityHessZZ    (idem)
TransDens_L1_L2  (L1: SS or ST; L2 is excitation's symmetry)
Fitdensity_1     (total nr. of points)
Fitdensity_2     (idem)
Fitdensity_3     (idem)
Coulpot_1        (idem)
Coulpot_2        (idem)
Coulpot_3        (idem)
SCF_label_A
  (label is a symmetry subspecies.
  Spin-restricted: SCF_label)
nr of orbitals   (one integer)
Occupations      (nr of orbitals)
Eigenvalues      (idem)
1                (total nr of points)
2                (idem)
3                (idem)
  (as many as there are Molecular Orbitals in that
  symmetry representation for the indicated spin)
SCF_label_B
  (only if spin-unrestricted same variable as
  in SCF_label_A)
SO_label
  (label is a double group symmetry subspecies.)
1_alpha_R       (total nr of points) real alpha part of the 1st spinor
1_beta_R        (idem) real beta part of the 1st spinor
1_alpha_I       (idem) imaginary alpha part of the 1st spinor
1_beta_I        (idem) imaginary beta part of the 1st spinor
2_alpha_R       (idem) real alpha part of the 2nd spinor
2_beta_R        (idem) real beta part of the 2nd spinor
2_alpha_I       (idem) imaginary alpha part of the 2nd spinor
2_beta_I        (idem) imaginary beta part of the 2nd spinor
  (as many as there are spinors in that
  double group symmetry representation)
LocOrb_A        if unrestricted, otherwise
                  LocOrb
nr of orbitals   (one integer)
1                (total nr. of points)
2                (idem)
(etc)

```

(continues on next page)

(continued from previous page)

```

NOCV
  Dens_A number(occupation number)      (total nr. of points)
  Dens_B number(occupation number)      (idem)
  (etc)
Profile
  DifDens_A number*(NOCV eigenvalue)    (number of profile points)
  DifDens_B number*(NOCV eigenvalue)    (idem)
  DifSumDens_A number                    (idem)
  DifSumDens_B number                    (idem)
  DifRestSumDensities_A                  (idem)
  DifRestSumDensities_B                  (idem)
  DifSumBelow_A                          (idem)
  DifSumBelow_B                          (idem)
  Dens_A number*(NOCV eigenvalue)        (idem)
  Dens_B number*(NOCV eigenvalue)        (idem)
  SumDens_A number                       (idem)
  SumDens_B number                       (idem)
  RestSumDensities_A                     (idem)
  RestSumDensities_B                     (idem)
  SumBelow_A                             (idem)
  SumBelow_B                             (idem)
POLTDFFT
  InducedDensX_number                    (total nr of points)  Induced (first-order perturbed)
  ↳density in the X-direction
  InducedDensY_number                    (idem)                Induced (first-order perturbed)
  ↳density in the Y-direction
  InducedDensZ_number                    (idem)                Induced (first-order perturbed)
  ↳density in the Z-direction
  TransDensX_number                      (idem)                Transition (first-order
  ↳perturbed) density in the X-direction
  TransDensY_number                      (idem)                Transition (first-order
  ↳perturbed) density in the Y-direction
  TransDensZ_number                      (idem)                Transition (first-order
  ↳perturbed) density in the Z-direction
  RotatorStrengthDensX_number (idem)      Rotator strength density in the X-
  ↳direction
  RotatorStrengthDensY_number (idem)      Rotator strength density in the Y-
  ↳direction
  RotatorStrengthDensZ_number (idem)      Rotator strength density in the Z-
  ↳direction
Geometry
  nnuc                                  (one integer)
  (nr of nuclei, omitting dummy atoms)
  xyznuc                                (nnuc times 3)
  (the atoms are not in the same order as in the adf input
  file. Rather they are grouped by atomtype.)
  qtch                                  (nnuc)      Atomic charges
x values
  x values                              (total nr. of points)
y values
  y values                              (idem)
z values
  z values                              (idem)

```

9.8 DOS: Density of States

The auxiliary program *dos* computes various types of densities-of-states (DOS) for a user-specified energy interval.

dos cannot be used in case of spin-orbit coupling

dos requires an ASCII input file where the user specifies the items to be calculated and computational details, plus the standard result file *adf.rkf* (TAPE21) from an *adf* calculation. The latter file must be present as a local file with name TAPE21 in the directory where *dos* is executed, or one can use the key *adffile* to point to the *adf.rkf* file,

dos produces as result one or more ASCII files with the density-of-states values. Error messages and computational info (if any) are written to standard output.

9.8.1 Introduction

The program *dos* gives information on the number and character of one-electron levels (molecular orbitals) as a function of the (orbital) energy. The total density of states $N^*(E)$ is a well-known concept in electronic structure theory of infinite systems (crystals). $N^*(E)dE$ denotes the number of one-electron levels (orbitals) in the infinitesimal energy interval dE . The total density of states (TDOS) at energy E is usually written as

$$N(E) = \sum_i \delta(E - \epsilon_i) \quad (4.5.1)$$

where the ϵ_i denote the one-electron energies. So the integral of $N(E)$ over an energy interval E_1 to E_2 gives the number of one-electron states in that interval. Usually the δ -functions are broadened to make a graphical representation possible.

When the δ -functions are multiplied by a weight factor that describes some property of the one-electron state ϕ_i at energy ϵ_i various types of densities-of-states are obtained that provide a graphical representation of the state character (orbital character) as a function of one-electron energy.

In calculations on finite molecules the total density of states as a function of (orbital) energy may also be useful, but the main use of various types of densities-of-states is to provide a pictorial representation of Mulliken populations. The weight factors employed are related to the orbital character determined by means of a Mulliken population analysis *per orbital* (see below). The program *dos*, therefore, provides the same information as can be generated by the ADF program (a population analysis per orbital) but *dos* enables an easy graphical representation and is particularly useful when there are many one-electron levels, for instance in calculations on clusters. You can obtain a simple view of the character of the orbitals in a certain energy range. You can also find out in which orbitals (at which energies) certain basis functions or fragment orbitals give a large contribution, and whether such contributions are bonding, nonbonding or antibonding with respect to particular bonds. Such information is provided by *dos* in the form of (weighted) density of states values over a user-specified energy range, which can for instance be plotted by *gnuplot*.

The following options are available for computations by *dos*:

- TDOS: Total Density of States
- GPDOS: Gross Population Density of States
- OPDOS: Overlap Population Density of States
- PDOS: Projected Density of States

The total density of states (TDOS) has large values at energies where there are many states per energy interval.

The GPDOS (Gross Population based Density Of States) of a function χ_μ (or a sum of such functions) has large values at energies where this function (these functions) occur(s) in the molecular orbitals.

The PDOS of a function χ_μ provides similar information, but with the projection of χ_μ onto the orbital ϕ_i as weight factor for the importance of χ_μ in the orbital ϕ_i .

The OPDOS (Overlap Population based Density Of States) between χ_μ and χ_ν has large positive values at energies where the interaction between them is bonding, and negative values where the interaction is anti-bonding. An example of the use of these plots is provided in¹.

We review below the Mulliken population analysis, and then describe the forms of density of states analysis performed by DOS. Finally an input description of DOS is given.

9.8.2 Mulliken population analysis

The orbitals ϕ_i with energies ϵ_i are expanded in basis functions χ_μ , which leads to the definition of density matrices P_i describing orbital densities, from which the total density matrix can be constructed:

$$\begin{aligned}\phi_i(r) &= \sum_{\mu} \chi_{\mu}(r) C_{\mu i} \\ \rho_i(r) &= \int |\phi_i(r)|^2 = \sum_{\mu\nu} P_{i,\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \\ P_{i,\mu\nu} &= C_{\mu i} C_{\nu i} \\ \rho(r) &= \sum_i n_i \rho_i(r) = \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \\ P_{\mu\nu} &= \sum_i n_i C_{\mu i} C_{\nu i} \quad (4.5.2)\end{aligned}$$

Here μ and ν run over the basis functions, which may be either primitive functions, or combinations of primitive functions, for instance the SCF orbitals of atoms or larger fragments.

The Mulliken population analysis provides a partitioning of either the total charge density or an orbital density. The total density is written as

$$\begin{aligned}\rho(r) &= \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \\ &= \sum_{A \leq B} \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \\ &= \sum_{A \leq B} \rho_{AB} \quad (4.5.3a) \\ \rho_{AB} &= \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \quad (4.5.3b)\end{aligned}$$

The total number of electrons, $N = \int \rho(r) dr$, is now partitioned over the atoms by assigning an overlap population $P_{\mu\nu} S_{\mu\nu} + P_{\nu\mu} S_{\nu\mu}$ for one half to the atom A of χ_{μ} and one half to atom B of χ_{ν} ,

$$N = \int \rho(r) dr = \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} = \sum_{\mu} G P_{\mu} \quad (4.5.4a)$$

$$G P_{\mu} = \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \quad (4.5.4b)$$

$G P_{\mu}$ is the gross population of χ_{μ} . It contains the net population $P_{\mu\mu}$ and half of each total overlap population $P_{\mu\nu} S_{\mu\nu} + P_{\nu\mu} S_{\nu\mu}$ between χ_{μ} and χ_{ν} . Summing the gross population over the functions $\mu \in A$ yields the total number of electrons assigned to atom A, or the gross population of atom A, $G P_A$, and hence the gross charge Q_A of atom A,

$$G P_A = \sum_{\mu \in A} G P_{\mu} \quad (4.5.5a)$$

¹ P.J. van den Hoek, E.J. Baerends, and R.A. van Santen, *Ethylene epoxidation on silver(110): the role of subsurface oxygen*, *Journal of Physical Chemistry* 93, 6469 (1989) (<https://doi.org/10.1021/j100354a038>)

$$Q_A = Z_A - GP_A \quad (4.5.5b)$$

The overlap population $OP_{\mu\nu}$ between two functions and the overlap population Q_{AB} between two atoms are defined in an analogous manner,

$$OP_{\mu\nu} = P_{\mu\nu}S_{\mu\nu} + P_{\nu\mu}S_{\nu\mu} \quad (4.5.6a)$$

$$Q_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} OP_{\mu\nu} \quad (4.5.6b)$$

These quantities can be evaluated for a single orbital density, $N = 1 = \int |\phi_i(r)|^2 dr$. The gross population $GP_{i,\mu}$ of a function in a specific orbital density $|\phi_i(r)|^2$ is then associated with the fraction of the orbital density belonging to that function (or the percentage χ_μ character of orbital ϕ_i , and the overlap population $OP_{i,\mu\nu}$ gives an indication of the strength of bonding or anti-bonding between χ_μ and χ_ν in orbital ϕ_i ,

$$GP_{i\mu} = \sum_{\nu} P_{i,\mu\nu}S_{\mu\nu} = \sum_{\nu} C_{\mu i}C_{\nu i}S_{\mu\nu} \quad (4.5.7a)$$

$$OP_{i,\mu\nu} = P_{i,\mu\nu}S_{\mu\nu} + P_{i,\nu\mu}S_{\nu\mu} = 2C_{\mu i}C_{\nu i}S_{\mu\nu} \quad (4.5.7b)$$

9.8.3 Density of states analyses based on Mulliken population analysis

Total density of states

The total density of states TDOS at energy E is written as

$$TDOS : N(E) = \sum_i \delta(E - \epsilon_i)$$

so the integral of $N(E)$ over an energy interval E_1 to E_2 gives the number of one-electron states in that interval. In practice the delta functions are approximated by Lorentzians,

$$TDOS : N(E) = \sum_i L(E - \epsilon_i) = \sum_i \left(\frac{\sigma}{\pi} \frac{1}{(E - \epsilon_i)^2 + \sigma^2} \right)$$

A plot of $N(E)$ versus E reveals energetic regions where many levels are located. The width parameter σ determines of course the appearance of the plot. A typical value is 0.25 eV (used as default in *dos*).

Partial (gross population and projected) density of states

In order to find out if a given function χ_μ contributes strongly to one-electron levels at certain energies, one may weigh a one-electron level with the percentage χ_μ character. We usually determine the χ_μ character by the gross populations, obtaining the GPDOS form of the partial density of states,

$$GPDOS : N_\mu(E) = \sum_i GP_{i,\mu} L(E - \epsilon_i)$$

If the weight factor is determined by projection of ϕ_i against χ_μ , we obtain the projected density of states PDOS,

$$PDOS : N_\mu(E) = \sum_i |\langle \chi_\mu | \phi_i \rangle|^2 L(E - \epsilon_i)$$

One should not use the PDOS for d-type or f-type primitive basis functions ("BAS"). A d-type function consists of 6 Cartesian functions, while there can of course be only 5 true d-type functions among them: one (linear combination) of them is in fact an s-type function ($x^2+y^2+z^2$). Similarly, there are 10 f-type Cartesian functions, 3 of which are in fact p-functions. The PDOS is calculated for the 6 d-type and 10 f-type Cartesian functions, which leads to undesired results. A PDOS for SFOs does not suffer from this problem.

Overlap population density of states (OPDOS)

If the delta function representing orbital ϕ_i is weighed with the overlap population between χ_μ and χ_ν in ϕ_i , the overlap population density of states OPDOS is obtained,

$$OPDOS : N_{\mu\nu}(E) = \sum_i OP_{i,\mu\nu} L(E - \epsilon_i)$$

If an orbital ϕ_i at energy ϵ_i is strongly bonding between χ_μ and χ_ν the overlap population is strongly positive and OPDOS(e) will be large and positive around $E = \epsilon_i$. Similarly, OPDOS(E) will be negative around energy ϵ_i when there is antibonding between χ_μ and χ_ν in ϕ_i .

The OPDOS(E) has been used under the name coop (crystal orbital overlap population) in Extended-Hückel solid state calculations by Hoffmann and coworkers [2].

[2] R. Hoffmann, *A chemist's view of bonding in extended structures* (VCH Publishers, New York, 1988).

9.8.4 Generalizations of OPDOS, GPDOS, PDOS

As observed above, the basis functions in the above expressions may be primitive basis functions ('Slater type orbitals'), but of course the formulas are equally applicable for other types of MO expansions. In *dos* the user may select either the expansion in primitive basis functions ('BAS') or the expansion in SFOs (Symmetrized Fragment Orbitals) for the DOS analyses.

It is also possible in DOS to treat a *set* of basis functions simultaneously. For instance, the GPDOS for a set of basis functions $\mu_1, \mu_2, \dots$ is simply defined as the summation of the corresponding single-function GPDOS(E) values

$$N_{\mu-set}(E) = \sum_{\mu \in \mu-set} \sum_i GP_{i,\mu} L(E - \epsilon_i)$$

In a similar fashion the OPDOS can be defined for *two sets* of basis functions $\mu_1, \mu_2, \dots$ and $\nu_1, \nu_2, \dots$ as

$$N_{\mu-set, \nu-set}(E) = \sum_{\nu \in \nu-set} \sum_{\mu \in \mu-set} \sum_i OP_{i,\mu\nu} L(E - \epsilon_i)$$

and finally for the PDOS we get in similar fashion

$$N_{\mu-set}(E) = \sum_{\mu \in \mu-set} \sum_i |\langle \chi_\mu | \phi_i \rangle|^2 L(E - \epsilon_i)$$

9.8.5 Input

The (ASCII) input for *dos* is keyword oriented. Reading input by *dos* terminates whenever it finds a line END INPUT or the end-of-file, whichever comes first.

Follows a list of keywords with their meaning. Generally keys may occur more than once and *the order in which they appear is relevant in some cases*. For instance the key energyrange (which defines for what energy values to compute densities-of-states, see below) applies to all items that come after it in input until the next occurrence of energyrange.

```
$AMSBIN/dos << eor
ADFFILE adffile
ENERGYRANGE {Npoint=nr} {E-start=e1} {E-end=e2 / E-step=de}
LORENTZIAN width=width
FILE file
TDOS { title }
OPDOS ...
GPDOS ...
PDOS ...
eor
```

ADFFILE adffile

```
ADFFILE adffile
```

Specifies a (relative) path to an adf.rkf file. If not specified dos requires a file named TAPE21 in the current directory.

Energy scan values

```
ENERGYRANGE {Npoint=nr} {E-start=e1} {E-end=e2 / E-step=de}
```

This specifies for which energy values the densities-of-states are computed that are specified *after* it in the input file and *until* the next occurrence of ENERGYRANGE.

ENERGYRANGE specifies the lower bound, upper bound and number of equidistant energy values (including end-points). All items are optional with defaults applying for those omitted.

The E end and E-step values determine one another and must therefore not be specified both (or be consistent).

The initial defaults are:

```
nr=301
e1=-20
de=0.1
```

All energy data are in eV.

When values have been changed with the key ENERGYVALUE, the so-modified values are the defaults for the next occurrence of ENERGYVALUE.

Peak widening

The peaks in the DOS curves corresponding to the energies of the molecular orbitals are widened by a Lorentzian curve, the width of which can be adjusted.

```
LORENTZIAN width=width
```

Initial default width is 0.25 (eV).

As for ENERGYRANGE, the key LORENTZIAN may occur more than once and each occurrence sets the width for all items after it.

Result files

The computed densities-of-states are stored on one or more ASCII files, which have to be specified in input.

```
FILE file
```

The key FILE may occur any number of times in input. Each time it occurs the specified file is opened by *dos*. The file must not yet exist and the new file will accumulate (ASCII) the densities-of-states data of all DOS items subsequently specified, until the next occurrence of FILE. The first occurrence of the key FILE must be given before any DOS specification (by the keys TDOS, OPDOS, GPDOS, PDOS, see below).

The format of the result file is such that it can be fed directly into *gnuplot*.

Densities of States

Total density of states.

```
TDOS { title }
```

TDOS

instructs the program to compute the total density of states.

title (optional)

will appear as title to the section of corresponding Density-of-States data in the result file.

The other types of densities-of-states require block-type keyword input.

```
OPDOS { title }  
Ftype numbers  
Ftype numbers  
...  
*SUBEND*  
Ftype numbers  
Ftype numbers  
...  
END
```

Ftype

Specifies the type of basis functions to use in the MO expansions. If the primitive basis functions are to be used Ftype must be bas. For the SFO representation Ftype must be one of the irreducible representations of the point group symmetry. All Ftype values in the data block must be consistent: either all are bas or all are irrep labels. The scope of this consistency requirement is the data block of the current key: in a next OPDOS data block, for instance, a different choice may be made.

numbers

Must be a sequence of integers referring to the basis functions to be selected, i.e. the ‘ μ -set’ and ‘ ν -set’ in (4.5.13) etc. If bas-type basis functions are selected the numbers refer to the overall list of all basis functions as printed in the output file of the adf run. If SFOs are selected the numbers refer to the SFO list of the pertaining symmetry representation without the core functions, see the adf output file.

SUBEND

Must be typed as such and separates the ‘ μ -set’ and the ‘ ν -set’: all records before subend specify together the ‘ μ -set’ and all records below subend comprise the ‘ ν -set’. Each of these two sections may consist of any number of records.

The input for GPDOS and PDOS are similar, but simpler because only one set of functions (‘ μ -set’) has to be specified, so there is no subend in the data blocks for these keys.

```
GPDOS { title }  
Ftype numbers  
Ftype numbers  
...  
END
```

```
PDOS { title }  
Ftype numbers  
Ftype numbers  
...  
END
```

The keys GPDOS, OPDOS, PDOS and (TDOS) may occur any number of times in input and in any order. Each time the DOS key occurs the current energyrange and lorentzian settings apply and the results are written to the current file.

9.9 VCD Analysis: VCDtools

The auxiliary program *VCDtools* provides insight into the origin of the VCD intensity of a given normal mode. This is done by analyzing and visualizing the various contributions to the total electric (E) and magnetic (M) dipole transition moments (DTM), e.g., the contributions from atoms, electrons, nuclei, and molecular fragments. The *VCDtools* program is accessible through the AMS-GUI. Documentation can be found in:

- [VCDtools section of the AMS manual](#).

9.10 PyFrag: Activation Strain Model Analysis

The standalone script PyFrag allows one to analyze various quantities along a trajectory with ADF. Usually such a trajectory results from either an internal reaction coordinate (IRC) or a linear transit (LT) calculation and is analyzed in the context of the Extended Activation Strain Model (ASM).

See also:

Example: Activation Strain Model Analysis using PyFrag (page 1146)

9.10.1 Requirements

The trajectory can thereby either be a file containing concatenated molecular geometries in the XYZ format (see example below) or a T21 binary output file from a previous LT or IRC calculation with ADF. ASM is based on the concept of molecular fragments, which have to be defined by specifying the corresponding atomic indices for each fragment. Furthermore, frequently used ADF input options can be imported from a separate input file (see [example](#) (page 1146)).

9.10.2 Running PyFrag

Running PyFrag is done by starting the corresponding Python script as follows:

```
$AMSBIN/amspython $AMSHOME/scripting/standalone/pyfrag/PyFrag.py [options]
```

where the details of possible [options] are explained in the following

9.10.3 Specifying the Trajectory

The trajectory is specified by one of the following:

```
--xyzpath <PATH>/trajectory.xyz
--irct21 <PATH>/IRCtrajjectory.T21
--lt <PATH>/LTtrajectory.T21
```

9.10.4 Molecular Fragments

The system can be split into an arbitrary number of disjoint subsystems, fragments. Each fragment is defined by its own argument `--fragment` followed by the indices of atoms in that fragment:

```
--fragment 1 3 4 5 6 --fragment 2
```

9.10.5 ADF Options

The settings for the ADF calculations are retrieved from either a PyFrag-specific settings file `adfsettings` (see *example* (page 1146)).

```
--adfinputfile adfsettings
```

or by individual command line arguments for each option, e.g.:

```
--adfinput basis.type=TZ2P
```

9.10.6 Analysis Options

The following options control the quantities reported by PyFrag in the final results table:

Offsets for the strain energies in kcal/mol of the fragments (one argument for each fragment, corresponding to the order of the fragment definition above):

```
--strain <StrainEnergy Fragment1> --strain <StrainEnergy Fragment2>
```

Bond length between selected pairs of atoms and equilibrium offset value in Angstrom

```
--bondlength <AtomIndex1> <AtomIndex2> <offset value>
```

Angle between selected triples of atoms and equilibrium offset value in degrees

```
--angle <AtomIndex1> <AtomIndex2> <AtomIndex3> <offset value>
```

Hirshfeld charges of fragments

```
--hirshfeld frag<FragmentNumber>
```

Atomic charges (Voronoi deformation density charges, VDD)

```
--VDD <AtomIndex1> [<AtomIndex2> [...]]
```

Orbital interaction energies for orbitals belonging to a point group symmetry irrep (specified by its symbol) of the whole system

```
--irrepOI <IrrepSymbol>
```

Orbital energies within fragments can be specified for a certain orbital in a given irrep or specifically for HOMO and LUMO levels in each fragment

```
--orbitalenergy <IrrepSymbol> <FragmentNumber> <OrbitalIndexWithinIrrep>
--orbitalenergy frag<FragmentNumber> HOMO
--orbitalenergy frag<FragmentNumber> LUMO
```

Orbital population numbers within fragments can again be specified for a certain orbital in an irrep or for the HOMO or LUMO in each fragment

```
--population <IrrepSymbol> frag<FragmentNumber> <OrbitalIndexWithinIrrep>  
--population frag<FragmentNumber> HOMO  
--population frag<FragmentNumber> LUMO
```

Orbital overlaps between pairs of orbitals, e.g.

```
--overlap frag<FragmentNumber> HOMO frag<FragmentNumber> LUMO
```

or

```
--overlap <IrrepSymbol> frag<FragmentNumber> <OrbitalIndexWithinIrrep> <IrrepSymbol> ↵  
↵frag<FragmentNumber> <OrbitalIndexWithinIrrep>
```


ACCURACY AND EFFICIENCY

See also:

Examples: *accuracy* (page 1188)

10.1 Precision and Self-Consistency

The precision of a calculation is determined by

- The function sets (basis sets, levels of frozen core approximation, and fit sets for the computation of the Coulomb potential)
- Numerical integration settings in real space
- The accuracy of the density fitting procedure
- Convergence criteria (for the SCF procedure and the geometry optimization)
- A few more items that are rather technical and usually irrelevant (these are not discussed here).

The fragments you attach determine, through the fragment files, the function sets. Since each fragment traces back to one or more Create runs, the employed database files in the Create runs determine the function sets that are ultimately used.

In this section we examine numerical integration, density fitting, and the SCF procedure.

Numerical Quality

With the key `NUMERICALQUALITY` one can set the density fitting quality (`ZlmFit`) and the numerical integration quality (`BeckeGrid`) simultaneously.

```
NUMERICALQUALITY [basic|normal|good|verygood|excellent]
```

Note that the so-called Excellent quality is only meant for debugging purposes. In case of real numerical issues the results with Excellent should not be trusted more than those with VeryGood.

10.1.1 SCF

The SCF procedure is regulated with keys that set the maximum number of iterations, the convergence criterion, and various items that control the iterative update method. Molecules may display wildly different SCF-iteration behavior, ranging from easy and rapid convergence to troublesome oscillations. We expect that the default settings take care of most cases, but one should realize that this is a difficult and tricky subject. The user has a few main options to adapt the procedure to the situation at hand: simple damping or one of the SCF acceleration schemes.

See also:

In case of SCF convergence problems, see *SCF Convergence Guidelines for ADF* (page 412)

At each cycle the electron density is computed as a sum of occupied orbitals squared; the new density defines the potential from which the orbitals are re-computed. The cycle is repeated until convergence is reached. To speed up convergence and to avoid non-convergent oscillatory behavior the values at the next iteration are constructed as a mixture of the computed new data and those used in previous cycles. This may involve only the previous cycle and is then called *damping*. Alternatively some sort of DIIS (direct inversion in iterative space) or LIST (Linear-expansion Shooting Technique) procedure can be invoked, which is a generalization of damping to include more previous iterations.

Starting from ADF2016, the SCF module has been rewritten from scratch. The old SCF is still available and it can be switched on using the `OldSCF` keyword. The description below refers to the new SCF code only. User documentation for the OldSCF module is available in the ADF2014 User's Guide.

There are various SCF acceleration techniques implemented in ADF. By default the mixed ADIIS+SDIIS method by Hu and Wang¹ is used, unless the number of DIIS expansion vectors is set to zero (see the `DIIS N` key below) or `NoADIIS` is specified. Here, SDIIS stands for the original Pulay DIIS scheme. Other available methods mostly belong to the LIST family developed in the group of Y.A. Wang. The ARH and Energy-DIIS methods are available with the OldSCF method only.

Main options

Subkeys in the data block of the master key SCF control the aspects mentioned above. Each subkey is optional. Curly brackets are not part of the key. Omission means the application of default values. Omission of the SCF block altogether implies defaults for all subkeys.

```
SCF
  Iterations Niter
  Converge SCFconv { sconv2 }
  AccelerationMethod { ADIIS | LISTi | LISTb | fDIIS | LISTf | MESA | SDIIS }
  MESA [NoFDIIS] [NoLISTb] [NoLISTf] [NoLISTi] [NoSDIIS] [NoADIIS]
  ADIIS
    {THRESH1 a1}
    {THRESH2 a2}
  End
  NoADIIS
  DIIS
    {N n}
    {OK ok}
    {cyc cyc}
  End
  Mixing mix
  Mixing1 mix1
```

(continues on next page)

¹

X. Hu and W. Yang, *Accelerating self-consistent field convergence with the augmented Roothaan-Hall energy function*, *Journal of Chemical Physics* 132, 054109 (2010) (<https://doi.org/10.1063/1.3304922>)

(continued from previous page)

```
OldSCF
End
```

Iterations Niter**Niter**

The maximum number of SCF cycles allowed. In case of Geometry Optimizations it applies separately to each of the SCF procedures that are executed. Default is 300. The program executes at least one cycle, even if you specify a non-positive number.

Converge SCFcnv { sconv2 }**SCFcnv**

The criterion to stop the SCF updates. The tested error is the commutator of the Fock matrix and the P-matrix (=density matrix in the representation of the basis functions) from which the F-matrix was obtained. This commutator is zero when absolute self-consistency is reached. Convergence is considered reached when the maximum element falls below SCFcnv and the norm of the matrix below 10*SCFcnv. The default is 1e-6 (in Create mode: 1e-8).

sconv2

A second criterion which plays a role when the SCF procedure has difficulty converging. When in any SCF procedure the currently applicable criterion does not seem to be achievable, the program stops the SCF. When the secondary criterion (sconv2) has been met, only a warning is issued and the program continues normally. If the secondary criterion was not met either, the program terminates any further geometry optimizations, frequency steps, etc. You can prevent the program from terminating in such a case with the key ALLOW. The default for sconv2 is 1e-3.

AccelerationMethod

Specify which SCF acceleration method must be invoked. By default the ADIIS+SDIIS method (denoted as ADIIS) is used and normally it results in optimal performance. In some cases it may be useful to use one of the methods from the LIST family or fDIIS. The LIST family methods have been implemented following publications by the group of Y.A. Wang^{2,3,4}. The number of vectors to store specified by DIIS N also applies to the LIST methods. This number is a very important parameter and it is worthwhile increasing or decreasing it in case of SCF convergence problems. A word of caution: do not just blindly increase the number for every system. Testing showed that a large number breaks convergence for some, mainly small, systems.

MESA

The MESA method has also been developed in the group of Y.A. Wang^{Page 369, 34}. It combines several other acceleration methods (currently ADIIS, fDIIS, LISTb, LISTf, LISTi, and SDIIS). In order to improve the method's performance, some of the components can be disabled by specifying the corresponding "No" argument. For example, to remove SDIIS from MESA specify MESA NoSDIIS. Specifying this key invokes the MESA method regardless of the AccelerationMethod's value.

ADIIS

This key has effect only if ADIIS acceleration method is used. The THRESH1 and THRESH2 arguments correspond to values of the maximum element of the [F,P] commutator matrix, ErrMax. If $\text{ErrMax} \geq a1$ then only A-DIIS coefficients are used to determine the next Fock matrix. If $\text{ErrMax} \leq a2$ then only SDIIS coefficients are used. For ErrMax between $a2$ and $a1$ the total DIIS coefficients are calculated from SDIIS and A-DIIS values weighted proportionally according to the ErrMax value. Thus, the weight of A-DIIS coefficients decreases as the

² Y.A. Wang, C.Y. Yam, Y.K. Chen, G. Chen, *Communication: Linear-expansion shooting techniques for accelerating self-consistent field convergence*, *Journal of Chemical Physics* 134, 241103 (2011) (<https://doi.org/10.1063/1.3609242>)

³ M.A. Garcia-Chavez, *Numerical methods in quantum chemistry to accelerate SCF convergence and calculate partial atomic charges*, PhD Thesis, University of British Columbia, (2018), (<https://dx.doi.org/10.14288/1.0372885>)

⁴

M. A. Garcia-Chavez, A. Yakovlev, Y. K. Chen, and Y. A. Wang, *General Linear-Expansion Shooting Techniques Based on Minimization of Intra-Iteration Errors.*, *Progress in Theoretical Chemistry and Physics* 34, 47 (2024) (https://doi.org/10.1007/978-3-031-52078-5_4)

ErrMax value becomes smaller. The default values for a1 and a2 are 0.01 and 0.0001, respectively. In difficult SCF cases, especially when the Pulay DIIS appears to be unstable, it may be worth trying to decrease the thresholds and let A-DIIS approach the final solution on its own.

NoADIIS

If OldSCF is not set, specifying NoADIIS has the same effect as setting AccelerationMethod to SDIIS. It disables A-DIIS and switches SCF to a damping+SDIIS scheme. In this scheme, SCF starts with simple damping (a.k.a. mixing) and continues until the maximum element value of the [F,P] commutator drops below the DIIS OK parameter but for no more than DIIS Cyc iterations. After this, the pure SDIIS scheme becomes effective until the end of the SCF procedure. If OldSCF is set then specifying NoADIIS disables the automatic switching to ADIIS+SDIIS in case of a difficult SCF convergence.

DIIS

The DIIS sub-block specifications can be given to control the SCF acceleration procedure. All these specifications are optional. Normally, ADIIS+SDIIS is activated starting from the 2nd iteration regardless of the OK and Cyc settings below. The two settings become effective only when NoADIIS is specified.

N

The number of expansion vectors used for accelerating the SCF. The number of previous cycles taken into the linear combination is then n-1 (the new computed potential is also involved in the linear combination). By default n=10. An input value smaller than 2 disables the DIIS. Note that this number applies not only to Pulay DIIS scheme but also to other DIIS-like methods, such as A-DIIS and LIST methods. It should be noted that methods from the LIST family are quite sensitive to the number of expansion vectors used. For this reason, these methods have a built-in limit on the number depending on the iteration number and the degree of convergence. The number of vectors in LIST increases when approaching convergence but it is always limited by DIIS N, which is a hard limit. It may be useful to set DIIS N to a value larger than 10 when using a LIST method with a difficult to converge system. A value between 12 and 20 can sometimes get the job done.

OK

The SDIIS starting criterion, when A-DIIS is disabled, by default 0.5 a.u.

Cyc

When A-DIIS is disabled, the SDIIS will start at this iteration (by default 5) irrespective of the DIIS OK value above.

Mixing mix**mix**

When none of the SCF acceleration methods is active, the next Fock matrix is determined as $F = mix F_n + (1 - mix) F_{n-1}$. The default value is 0.2.

Mixing1 mix1**mix1**

A different mixing parameter value for the first SCF cycle. By default, equal to Mixing.

OldSCF

Enforce the old SCF procedure. It will also be used automatically when one of the following is true: Occupations Steep is specified, level-shifting is enabled (see the Lshift key below), the augmented Roothaan-Hall method is enabled (see the ARH key below), the Energy-DIIS method is enabled (see the EDIIS key below), the RESTOCC key is specified.

Lshift vshift

Level shifting is currently not implemented in the new SCF, therefore specifying Lshift enables OldSCF automatically.

VShift

The level shifting parameter. The diagonal elements of the Fock matrix, in the representation of the orbitals of the previous iteration, are raised by vshift hartree energy units for the virtual orbitals. This may help to solve

convergence problems when during the SCF iterations charge is sloshing back and forth between different orbitals that are close in energy and all located around the Fermi level. Level shifting is not supported in the case of Spin-Orbit coupling. **At the moment properties that use virtuals, like excitation energies, response properties, NMR calculations, will give incorrect results if level shifting is applied.**

Lshift_err Shift_err

Shift_err

Specifies that level shifting will be turned off by the program as soon as the SCF error drops below a threshold; default value: 0.

Lshift_cyc Shift_cyc

Shift_cyc

Specifies that level shifting is not turned on before the given SCF cycle number (for the start-up geometry); default value: 1.

Note: *Electron smearing* may be used to overcome convergence difficulties. The idea is to distribute electron occupations fractionally over the states around the Fermi level using the Fermi distribution function. This aspect is controlled by the Smear or the ElectronTemperature option of the Occupations key. See the Occupations key for more details.

Note: A-DIIS is not compatible with enforced non-Aufbau electronic configurations and it is disabled in such a case automatically. A non-Aufbau electronic configuration may be enforced using a block form of the Occupations key, but it may also result from the KeepOrbitals (a.k.a. orbital tracking) feature.

Energy-DIIS

```
SCF
  EDIIS
  ...
End
```

Energy-DIIS is implemented following the paper by Kudin, Scuseria, and Cancès⁵. The method is invoked by specifying an EDIIS keyword in the SCF block. Please note that, similar to ARH and unlike the standard SCF procedure in ADF, this method requires energy evaluation at each SCF cycle, which makes it significantly slower compared to energy-free SCF. You might need a higher integration accuracy to get an accurate total energy. The same restrictions apply as for the key *TOTALENERGY* (page 294). The EDIIS method will start at the second SCF cycle, and the size of the DIIS space will be the same as for the normal DIIS. This subkey EDIIS can be used in addition to the other subkeys of the block key SCF. This method has been superseded by A-DIIS and the LIST family methods.

⁵ K.N. Kudin, G.E. Scuseria and E. Cancès, *A black-box self-consistent field convergence algorithm: One step closer*, Journal of Chemical Physics 116, 8255 (2002) (<https://doi.org/10.1063/1.1470195>)

Augmented Roothaan-Hall (ARH)

The Augmented Roothaan-Hall method has been developed by T. Helgaker and coworkers and is extensively discussed in Ref.⁶. The basic idea of the method is that the density matrix is optimized directly to minimize total energy. At each step, the new density matrix is parametrized in terms of matrix exponent:

$$P_{\text{new}} = \exp(-X) P_{\text{old}} \exp(X),$$

here, X is an anti-symmetric step matrix subject to the following conditions:

$X = \text{argmin}\{E(P(X))\}$ - X minimizes the energy

$|X| < h$ - length of X is smaller than or equal to some trust radius

The optimal X is found using a Conjugate Gradient method, possibly with pre-conditioning. The trust radius is updated based on how well the energy change is predicted.

ARH Input

The ARH procedure is invoked by including the ARH block in the SCF input block. This subkey ARH can be used in addition to the other subkeys of the block key SCF.

```
SCF
  ARH
    {CONV conv}
    {ITER iter}
    {NSAVED nsaved}
    {START start}
    {FINAL} ...
  End
  ...
End
SYMMETRY NOSYM
```

All parameters in the ARH keyword are optional. The following arguments determine the main parameters of the ARH procedure.

CONV conv

ARH convergence criterion. When the RMS gradient and its maximum components are both lower than the criterion, the ARH procedure will be considered converged. The default value is 10^{-4} .

ITER iter

Maximum number of ARH iterations to perform. Please note that in difficult cases a large number of iterations may be required for complete SCF convergence. The default value is 500.

FINAL

Determines whether SCF is continued after ARH has completed. If this option is set, one Fock matrix diagonalization will be performed to get orbitals and the SCF procedure will be halted. By default this option is OFF.

START start

Sets the SCF cycle number on which the ARH method is invoked. The default value is 2. Using a larger value may provide a better starting guess for the ARH minimization.

NSAVED nsaved

Sets the number of saved density and Fock matrices used for augmentation of the electronic Hessian. The default value is 8. A larger nsaved value should be used in difficult cases when the number of orbitals very close to the Fermi level is large.

⁶ S. Høst, J. Olsen, B. Jansík, L. Thøgersen, P. Jørgensen and T. Helgaker, *The augmented Roothaan-Hall method for optimizing Hartree-Fock and Kohn-Sham density matrices*, Journal of Chemical Physics 129, 124106 (2008) (<https://doi.org/10.1063/1.2974099>)

The default minimization method is Untransformed Pre-conditioned Conjugate Gradient. The following two parameters may be used to change this.

NOPRECOND

Disables pre-conditioning during the CG minimization. This option should not be used if atoms heavier than the second-row elements are present.

TRANSPCG

Specifying this option will enable the use of the Transformed Pre-conditioned CG method, which may result in better SCF convergence in some cases.

At each SCF step, the procedure begins by performing usual CG minimization keeping track of the total step length. If at some micro-iteration the step length exceeds the trust radius, the procedure switches to trust-radius optimization in the reduced space, which, in turn, is halted as soon as the level-shift parameter *mu* has converged. The final step is then calculated as a Newton step in the reduced space of all the trial vectors generated during CG minimization. The following options may be used to modify this behavior.

NOSWITCHING

Setting this option turns OFF the switching from the normal CG to a trust-radius minimization in reduced space. Using this option helps to reduce the total number of SCF cycles in some cases.

SHIFTED

Setting this option will turn ON the trust-radius optimization from the first micro- iteration.

CGITER=cgiter

Sets the maximum number of micro-iterations.

The next two options determine the trust radius.

TRUSTR=trustr

Initial value for the trust radius. Default: 0.5

MAXTRUSTR=maxtrustr

The maximum trust radius value. This is set to 0.5 by default and should never be changed.

ARH Notes and Recommendations

Restriction: The method currently works for symmetry NOSYM calculations only. The NOSYM requirement comes from the fact that during direct optimization of the density matrix it may have a symmetry lower than that of the molecule.

The method requires the total energy to be calculated at each step, which makes it much more expensive compared to the standard SCF procedure that does not need the energy. Therefore, the method should only be used when the standard SCF procedure fails. Another complication caused by the use of the total energy is that somewhat higher integration accuracy may be required to get stable SCF convergence, and that the method may not be applicable in all cases. It is also recommended to use the [ADDDIFFUSEFIT](#) (page 383) keyword or a higher ZlmFit quality setting to increase accuracy of the total energy and, thus, improve convergence. Please refer to the [TOTALENERGY](#) (page 294) keyword for more information.

10.1.2 Numerical Integration

Many integrals in ADF are calculated via numerical integration. The integration grid used for computing these integrals is therefore an important technical aspect of an ADF calculation, affecting both the accuracy of the results and the computation time.

Becke Grid

The default numerical integration grid is a refined version of the fuzzy cells integration scheme developed by Becke¹. The implementation in ADF is described in Ref.².

The quality of the Becke integration grid can be changed within the BECKEGRID block key:

```
BECKEGRID
  Quality [basic|normal|good|verygood|excellent]
End
```

Quality

Default: Normal. For a description of the various “qualities” and the associated numerical accuracy, see Ref. [Page 374, 2](#). The integration grid quality defined in the BECKEGRID block key overrides the *NumericalQuality* (page 367).

Advanced options:

```
BECKEGRID
  {QualityPerRegion
    Region myregion
    Quality {Basic|Normal|Good|VeryGood|Excellent}
  }
  {qpnear qpnear}
  {RadialGridBoost boost}
End
```

QualityPerRegion

One can overwrite the integration grid quality for atoms in a particular region. *Example: Multiresolution* (page 1202) illustrates how to use this option.

qpnear

Default: 4.0 Angstrom. Only relevant if you have specified point charges in the input file. ADF generates grids only around those point charges that are close to any real atoms. The criterion, input with the qpnear subkey, is the closest distance between the point charge at hand and any real atom. Any input value is interpreted in the unit of length specified with the Units key.

RadialGridBoost

Default: 1.0 (or 3 if a numerically sensitive functional is used). The number of radial integration points will be boosted by this factor. Some XC functionals require very accurate radial integration grids, so ADF will automatically *boost* the radial grid for the following numerically sensitive functionals: LibXC M05, LibXC M05-2X, LibXC M06-2X, LibXC M06-HF, LibXC M06-L, LibXC M08-HX, LibXC M08-SO, LibXC M11-L, LibXC MS0, LibXC MS1, LibXC MS2, LibXC MS2H, LibXC MVS, LibXC MVSH, LibXC N12, LibXC N12-SX, LibXC SOGGA11, LibXC SOGGA11-X, LibXC TH1, LibXC TH2, LibXC WB97, LibXC WB97X, MetaGGA M06L, MetaHybrid M06-2X, MetaHybrid M06-HF, MetaGGA MVS

Notes:

- The space-partition function used in ADF differs from the one described in Ref.². The unnormalized partition function used in the program is defined as (Ω_I is an element-dependent parameter: 0.1 Bohr for H, 0.3 Bohr for He-Xe and 0.6 Bohr for Cs-Og):

¹ A.D. Becke, *A multicenter numerical integration scheme for polyatomic molecules*, Journal of Chemical Physics 88, 2547 (1988) (<https://doi.org/10.1063/1.454033>)

² M. Franchini, P.H.T. Philipsen, L. Visscher, *The Becke Fuzzy Cells Integration Scheme in the Amsterdam Density Functional Program Suite*, Journal of Computational Chemistry 34, 1818 (2013) (<https://doi.org/10.1002/jcc.23323>).

$$\mathcal{P}_{i,U} = \begin{cases} 1 & \text{if } r_{i,U} < \Omega_I \\ 0 & \text{if } \exists j : r_{j,U} < \Omega_J \\ \eta_i \frac{e^{-2(r_{i,U}-\Omega_I)/a_0}}{(r_{i,U}-\Omega_I)^2} & \text{elsewhere} \end{cases}$$

- If either the (block) key `INTEGRATION` or the key `NOBECKEGRID` are used in the input, the Voronoi grid is used:

```
NOBECKEGRID
```

- A Becke grid of normal quality is roughly equivalent (in both absolute accuracy and computation time) to `INTEGRATION 4` (Voronoi scheme), and a Becke grid of good quality is roughly equivalent to `INTEGRATION 6` (Voronoi scheme).
- The Becke grid is not very well suited to calculate Voronoi deformation density (VDD) charges. For accurate calculation of VDD charges the Voronoi integration scheme is recommended.

Voronoi grid (deprecated)

In ADF2012 and previous versions, the default integration scheme was the cellular Voronoi quadrature scheme, implemented by te Velde and Baerends^{3,4}. Starting from ADF2013 this method is no longer the default scheme for integration. The so-called Becke grid is the default; see the key `BECKEGRID`. If the key `INTEGRATION` is used, the Voronoi scheme will be used. Thanks to a smoother behavior of the relative integration error as a function of the nuclear coordinates, the Becke grid is better suited for geometry optimization and TS search compared to the Voronoi scheme.

The Voronoi integration method requires only one input parameter which determines the precision of numerical integrals and derives from that the number of integration points.

```
INTEGRATION
  accint value
End
```

accint

A positive real number: the numerical integration scheme generates points and weights such that a large number of representative test integrals are evaluated with an accuracy of `accint` significant digits. The default `accint` is 4.0 (10.0 in Create runs).

The *number* of integration points varies strongly with `accint`, and this determines to a large extent the computational effort. Decreasing `accint` from 4.0 to 3.0 for instance roughly halves the number of points (this depends somewhat on the molecule).

The defaults should yield good precision for the very large majority of applications. Lower values (3.0 or even 2.0) can be used if precision is not crucial and the purpose is to get an impression. We recommend that you experiment for yourself to get a feel for how results may vary in quality and computing time.

The default in Create mode is very large: 10.0. This is computationally no problem thanks to the simplicity of the single atom case, in particular due to the high symmetry. There is no reason to override the default integration settings when creating basic atoms.

We have now only explained the normal, simple application of the Integration key, which we hope and expect is adequate for all your computations. Next additional details will be discussed. The distribution of points over space is internally regulated by quite a few parameters. Each of these parameters can be controlled in input. By default they depend on one another, and all of them depend on the main parameter `accint`. Advanced users may wish to experiment and override the default relations between the parameters.

³ P.M. Boerrigter, G. te Velde and E.J. Baerends, *Three-dimensional Numerical Integration for Electronic Structure Calculations*, *International Journal of Quantum Chemistry* 33, 87 (1988) (<https://doi.org/10.1002/qua.560330204>)

⁴ G. te Velde and E.J. Baerends, *Numerical Integration for Polyatomic Systems*, *Journal of Computational Physics* 99, 84 (1992) ([https://doi.org/10.1016/0021-9991\(92\)90277-6](https://doi.org/10.1016/0021-9991(92)90277-6))

You may also have rather non-standard applications where the default relations are less adequate. A thorough understanding of the underlying method is required to make a sensible choice for all parameters^{Page 375, 4, 5}.

More options can be defined in the `Integration` block. Consult the literature for detailed information about the various schemes.

```
Integration
  ACCINT float_list
  ACCOUT float
  ACCPYR float
  ACCPYU float
  ACCPYV float
  ACCPYW float
  ACCSPH float
  DISHUL float
  FRANGE float
  LINROT integer
  LINTEG integer_list
  NOUTER integer
  OUTPAR float
  OUTRAD float
  QPNEAR float
  RSPHER float_list
End
```

Integration

Type

Block

Description

Options for the Voronoi numerical integration scheme

ACCINT

Type

Float List

Description

The main precision parameter. Its value defines the number of significant digits by which an internal set of standard integrals must be evaluated. The number and distribution of integration points is tuned accordingly. For normal applications this should yield a nearly optimal (given the underlying method) generation of points and weights. The default depends on the run type.

ACCOUT

Type

Float

Description

The region of space further away from the atoms, outside the polyhedrons, has its own precision parameter. By default `accout=accint`.

ACCPYR

Type

Float

⁵ G. te Velde, *Numerical integration and other methodological aspects of bandstructure calculations*, in *Chemistry*. 1990, Vrije Universiteit: Amsterdam.

Description

Similarly this subkey sets the test level for the parts of the pyramids outside the atomic sphere.
Default: accpyr=accint.

ACCPYU**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. Accpyw controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal accpyr.

ACCPYV**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. Accpyw controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal accpyr.

ACCPYW**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. Accpyw controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal accpyr.

ACCSPH**Type**

Float

Description

The polyhedron method of generating integration points partitions space in atomic polyhedrons, partitioned in pyramids with their tops at the atom in the center of the polyhedron. A core like atomic sphere is constructed around the atom; this truncates the tops of the pyramids. accsph specifies the test precision for the generation of points within the spheres. By default accsph=accint.

DISHUL**Type**

Float

Unit

Bohr

Description

Sets the distance between the outermost nuclei of the molecule and the boundary planes that

define the boundary between the polyhedrons and the outer region. By default dishul=2.3*R, where R is the radius of the largest atomic sphere in the molecule.

FRANGE**Type**

Float

Unit

Bohr

Description

The outward range of the outer region: integration is not performed to infinity but to a distance frange from the outermost atoms, where all functions can be assumed to be essentially zero. By default frange is derived both from accint, the general precision parameter, and from the present chemical elements: heavier atoms have longer-range functions than hydrogen say. The precise relations can be found in the implementation.

LINROT**Type**

Integer

Description

This parameter is significant only for symmetries with an axis of infinite rotational symmetry: C and D. It is the highest rotational quantum number around this axis that occurs among the integrands. This depends on the employed basis functions and fit functions. By default the program finds this out for itself.

LINTEG**Type**

Integer List

Description

The maximum angular momentum quantum number of integrands centered on an atom of that type (one value for each atom type). This depends on the basis functions and on the fit functions. By default the program checks the function sets and sets the linteg values accordingly. This subkey is applied for the generation of grid points in the atomic spheres.

NO OUTER**Type**

Integer

Description

This outer region is treated by a product formula: outwards times parallel. The latter involves two dimensions: the surface of the molecule say. The outward integration is performed with Gauss-Legendre quadrature, in a few separate steps. The lengths of the steps are not equal, they increase by constant factors. The total length is fixed. The number of steps is controlled with this subkey; default: 2.

OUTPAR**Type**

Float

Description

Similarly the integration in the directions parallel to the surface of the atomic system is controlled by a parameter. See the implementation for details.

OUTRAD

Type

Float

Description

The parameter that defines the number of Gauss-Legendre integration points for each outward step. The precise relation between the actual number of points and this subkey, and the default relation between outrad and accout can be found in the implementation.

QPNEAR**Type**

Float

Unit

Angstrom

Description

If you specify point charges in the input file, there are two considerations implied for the numerical integration grid. First, since the point charges create a Coulomb singularity. The integrands (of for instance the basis function products against the Coulomb potential) can only be evaluated with high precision if the grid around the point charges has spherical symmetry and uses local spherical coordinates, exactly as is done for the atomic nuclei. Second, the point charges do not carry fit or basis functions, hence they play only a role in the more diffuse tails of the actual functions involved in integrals. Therefore, a relative low precision of the integral part close to the point charge may have little effect on the total integration accuracy. Since additional 'spherical centers' with their own surrounding grids increase the total number of points significantly, typically a few thousands per Coulomb center, this may result in high computational effort. Therefore, the program generates spherical grids only about those point charges that are close to the other atoms. The criterion, input with the qpnear subkey, is the closest distance between the point charge at hand and any real atom. Default 4.0 Angstrom.

RSPHER**Type**

Float List

Unit

Bohr

Description

Gives the radii of the atomic spheres, one value for each atom type. By default, the radii are derived from the chemical element (heavier atoms get larger spheres) and from the environment: the sphere must not be too large for the atomic cell (polyhedron).

Atomic radial grid

For each atom the charge densities and the Coulomb potentials of frozen core and valence electrons are computed in a radial grid and stored on `adf.rkf`. The values in the points of the molecular numerical integration grid are then evaluated by interpolation from the table of radial values.

The radial grid consists of a sequence of r-values, defined by a smallest value, a constant multiplication factor to obtain each successive r-value, and the total number of points. Equivalently it can be characterized by the smallest r-value, the largest r-value, and the number of points; from these data the program computes then the constant multiplication factor. The characteristics are set with

```
RADIALCOREGRID {nrad=points} {rmin=rmin} {rmax=rmax}
```

points

The number of radial grid points; default: 5000.

rmin

The shortest distance used in the radial grid; default 1e-6 Angstrom.

rmax

The largest distance in the radial grid; default: 100 Angstrom.

rmin and rmax, when specified, are interpreted as specified in units of length defined by Units.

The keyword name RADIALCOREGRID has historical reasons: in earlier releases the radial grid was used only for the frozen core density and potential.

10.1.3 Density fitting

Zlm Fit: density fitting with radial spline functions and real spherical harmonics

Note: In ADF2013 and previous versions, a different density-fitting scheme (pair fit) was used. Include the key STOFIT if you want to use the old fitting scheme.

The basic ideas behind the so-called Zlm Fit can be described as follows. The total electron density is split into atomic densities (in a similar way as the volume is partitioned for the Becke grid). These atomic densities are then approximated by a combination of radial spline functions and real spherical harmonics (Zlm). The implementation in ADF is described in Ref.². The algorithm that is used in ADF is related to the procedures proposed by Becke³ and Delley¹.

The Zlm Fit scheme (which is the default fitting scheme in ADF2016) offers certain advantages compared to the old pair-fit method, especially the possibility to calculate the Coulomb potential to very high precision.

```
ZLMFIT
  Quality {Basic|Normal|Good|VeryGood|Excellent}
  {QualityPerRegion
    Region myregion
    Quality {Basic|Normal|Good|VeryGood|Excellent}
  }
End}
End
```

Quality

The default quality of the Zlm Fit is Normal. It can be changed with the subkey Quality.

QualityPerRegion

You can override the Zlm Fit quality for atoms in a particular region. *Example: Multiresolution* (page 1202) illustrates how to use this option.

The Zlm Fit method can be used for most features of the ADF program. For the calculation of Hartree-Fock exchange integrals, ADF uses a different fitting method, see *the section on Hartree-Fock exchange* (page 382).

Pair fit: symmetric density fit

The non-default density fitting procedure in ADF, called the pair fit method, is carried out separately for each pair of atoms. To use it, one needs to include the keyword STOFIT.

² M. Franchini, P.H.T. Philipsen, E. van Lenthe, L. Visscher, *Accurate Coulomb Potentials for Periodic and Molecular Systems through Density Fitting*, *Journal of Chemical Theory and Computation* 10, 1994 (2014) (<https://doi.org/10.1021/ct500172n>)

³ A.D. Becke, R.M. Dickson, *Numerical solution of Poisson's equation in polyatomic molecules*, *Journal of Chemical Physics* 89, 2993 (1988) (<https://doi.org/10.1063/1.455005>)

¹ B. Delley, *An all-electron numerical method for solving the local density functional for polyatomic molecules*, *Journal of Chemical Physics* 92, 508 (1992) (<https://doi.org/10.1063/1.458452>)

STOFIT

The implemented approach has several advantages in efficiency, but it has a drawback in that it necessitates the use of all available fit functions rather than only the symmetric combinations, although the final result of course needs only a symmetric fit because the total density is a symmetric (A1) function. For atoms far apart the density fitting is performed with only symmetric functions. Given the implemented algorithm this entails an approximation which can be tuned:

AlFIT atomicseparation

atomicseparation

The threshold distance between atoms, *in Angstrom*. The symmetric fit approximation is applied only for atoms farther apart. Default is 10.0 Angstrom.

Pair fit: fit integrals

STOFIT

For the computation of the Coulomb potential with the pair fit method the program uses a large number of so-called *fit integrals*: the overlap integrals of a fit function with a *product* of two basis functions, where at least two of the involved three functions are centered on the same atom. In fact these are ordinary overlap integrals of STOs because the fit and basis functions are all STOs and a product of STOs on a center is itself also an STO. To use this STO fitting method, which was previously the default, use the key STOFIT in the input of ADF (also include it in the Create mode of an atom, if that is explicitly used). For the bond energy a first-order fit correction term is included, which makes the bond energy accurate to first order in the fit.

Obviously, when the two involved atoms are far enough apart, such overlap integrals become negligibly small. All fit integrals that are smaller (according to a rough but reasonable estimate) than a preset threshold are ignored and not computed.

The value of this threshold can be set via input, using the subkey CUTOFF_FIT of the [LINEARSCALING](#) (page 396) block keyword.

True density in XC potential

For the computation of the exchange-correlation potential (XC-potential) the program uses the fitted density by default. This is an approximation. For the XC potential the true density can be used if one includes the keyword EXACTDENSITY:

EXACTDENSITY

Using the EXACTDENSITY keyword makes the calculation more time-consuming but more accurate in the following cases:

- calculations that require accurate description of virtual orbitals, such as most of the TDDFT;
- when studying systems where weak interactions, such as van der Waals forces and hydrogen bonds, are important. For example, EXACTDENSITY should be switched on when performing a geometry optimization of DNA pairs.

Precision of density fitting on standard output

In the output file of the ADF calculation you can find, at the end of the SCF, concise information about the density-fit precision: the error integral for the SCF density. The error integral is the integral of the difference between the exact density and the fit density, squared. Such values have very little to do with numerical integration; rather they show whether or not the employed set of fit functions is adequate to describe the SCF density. Error integral values that significantly exceed $1e-4$ times the number of atoms are suspicious and may indicate some deficiency in the fit set for the actual calculation. On the last geometry (in an optimization) the fit-error integrals are also printed for the initial (sum-of-fragments) density and the orthogonalized fragments. In the bond energy analysis a first-order fit-correction term is given.

10.1.4 Hartree-Fock RI scheme

The implementation in ADF of the calculation of exact exchange (**Hartree-Fock exchange**), which is needed for the hybrid functionals, is based on work by Watson et al., Ref.¹. This procedure is generally referred to as **resolution of the identity** (abbreviated as **RI**). It employs an auxiliary set of functions (**fit functions**) to efficiently approximate the Hartree-Fock exchange matrix.

Technical aspects of the RI scheme can be tweaked in the `RIHartreeFock` key block:

```
RIHartreeFock
  UseMe                {True|False}
  Quality              {Auto|Basic|Normal|Good|VeryGood}
  FitSetQuality        {VeryBasic|Basic|Normal|Good|VeryGood}
  DependencyThreshold rVal
  QualityPerRegion
    Region myregion
    Quality {VeryBasic|Basic|Normal|Good|VeryGood}
  End
End
```

UseMe

Default: True. Set to False if you want to use the old RI scheme.

Quality

Default: Auto. Set the quality of the **FitSet** and of other RI-specific technical procedures, including numerical integration and linear scaling parameters. If `Auto`, the quality defined in *NumericalQuality* (page 367) will be used.

FitSetQuality

The quality of the auxiliary fit set used in the RI scheme. If both `RIHartreeFock%Quality` and `RIHartreeFock%FitSetQuality` are specified, the value specified in `RIHartreeFock%FitSetQuality` is used. Normal quality is generally sufficient for basis sets up to and including TZ2P. Numerical issues have been found, especially if the molecule has symmetry NOSYM and a basis set larger than TZ2P is used. For larger basis sets (or for benchmarking purposes), a Good or VeryGood fit set is recommended. For basis sets larger than TZ2P, it is recommended to include the `DEPENDENCY` key with a larger-than-default criterion for the basis set dependence, namely `bas=5e-4`. **Note that FitSetQuality strongly influences the computational cost.**

DependencyThreshold

Default: 1.0E-3. To improve numerical stability, almost linearly dependent combinations of basis functions are removed from the Hartree-Fock exchange matrix. If you obtain unphysically large bond energy in a hybrid calculation, you might try setting the `DependencyThreshold` to a larger value (e.g. 3.0E-3). Starting from AMS2022, ADF uses `DependencyThreshold=5e-3` for any variant of GW if it is not specified in the input.

QualityPerRegion

You can override the fit set quality (`FitSetQuality`) for atoms in a particular region. *Example: Multiresolution* (page 1202) illustrates how to use this option.

In ADF2019.3 the fit set for quality GOOD has been improved by adding more diffuse l=0 fit functions.

Note:

- In ADF2019.3 the fit set for `FitSetQuality Good` has been improved.
- In ADF2017 and previous versions, a different implementation of the Hartree-Fock RI scheme was used by default. See *Old Hartree-Fock RI scheme* (page 383).

¹ M.A. Watson, N.C. Handy and A.J. Cohen, *Density functional calculations, using Slater basis sets, with exact exchange*, *Journal of Chemical Physics* 119, 6475 (2003) (<https://doi.org/10.1063/1.1604371>)

Old Hartree-Fock RI scheme

To use the old Hartree-Fock RI scheme, specify:

```
RIHartreeFock
  UseMe False
End
```

In ADF2017 and previous versions, a different implementation of the Hartree-Fock RI scheme was used by default.

The old Hartree-Fock RI uses a smaller fit set than the default scheme and does not include H and I fit functions; the new scheme should give more accurate results, especially for f-block elements.

Memory usage

Calculation of the Hartree-Fock exchange may require a lot of memory. Shared memory is used to buffer the data used by all processes on a multi-processor node. By default, ADF will use 30% of the total physical memory of the computer for this buffer, which may be more than is desirable or possible. This amount, in megabytes, can be set using the HFMAXMEMORY input keyword.

```
HFMaxMemory mbytes
```

The amount of memory used is related to how many atoms can be processed in a single pass. Another way to limit the amount of memory used by ADF is to limit the number of atoms done per pass. The latter can be done using the HFATOMSPERPASS keyword. The safest, but also the slowest, is to set HFATOMSPERPASS to 1.

```
HFAtomsPerPass AtomsPerPass
```

If both HFMAXMEMORY and HFATOMSPERPASS are present, the value specified in HFATOMSPERPASS takes precedence. To debug memory usage in the Hartree-Fock routine, you can use a PRINT HARTREEFOCK keyword.

Numerical issues

Numerical problems have been found with the present implementation of Hartree-Fock or (meta-)hybrids during the SCF, especially if the molecule has symmetry NOSYM and a basis set TZP or larger is used. A workaround is to always use the DEPENDENCY key with rather strict criteria for the basis set dependence, namely bas=4e-3. In ADF2010 these numerical problems have been reduced. The DEPENDENCY key is automatically switched on in the case of a Hartree-Fock or a (meta-)hybrid potential. The result of the DEPENDENCY key is that linear dependence of the basis set is reduced by removing linear combinations that correspond to eigenvalues in the virtual SFOs overlap matrix, which are smaller than, in this case, 4e-3. Note that this is a rather large value, such that it will have an effect on the bonding energy. For DZ and DZP basis sets this value will normally not result in reduction of the virtual space. However, for TZP, TZ2P, QZ4P, and larger this will often result in reduction of the basis set, which will have an effect on the accuracy of the bonding energy. In these cases you can try a smaller value than 4e-3, but be aware that numerical problems may occur. If the molecule has symmetry, the numerical problems are reduced.

The origin of this problem is that for an accurate description of Hartree-Fock exchange, you need more (diffuse) fit functions in the fit procedure used in ADF, which uses only fit functions on the two centers of the two STOs. You can get more diffuse fit functions if you add the following key in the Create run of an atom:

```
AddDiffuseFit
```

If the BASIS key is used, you can also add this key in the molecular calculation (the scripts in ADF will then automatically add this in the Create runs of the atoms). If you add this key, preliminary results indicate that you can lower the value for the dependency key to bas=1e-4. Such a low value for the dependency key normally means that the basis set is not reduced for basis sets of TZP or TZ2P quality.

A different way to add fit functions that is useful for standard basis sets DZ, DZP, TZP, and TZ2P is to add the subkey `FitType QZ4P` in the `BASIS` key, thus:

```
BASIS
  Type ...
  Core ...
  FitType QZ4P
End
```

In ADF2013 use is made of distance cut-offs for the calculation of the HF exchange integrals. This can reduce computation time and memory usage, especially for large molecules; however, this can also reduce the precision, which can lead to numerical problems. It is possible to set the distance cut-off threshold (starting from ADF2013.01b) for the calculation of the HF exchange integrals. A value of 99 for `hffit` virtually excludes the possibility that something will be neglected:

```
LINEARSCALING
  HF_FIT hffit
END
```

SCF problems

However, for larger molecules and in case the molecule contains heavy elements ($Z > 36$), you should still use rather strict criteria for the basis set dependence, such as `bas=4e-3`.

In case of SCF problems that might be related to numerical issues, you can try one or more of the following, which were discussed above.

```
LINEARSCALING
  HF_FIT 99
END
Basis
  FitType QZ4P
End
AddDiffuseFit
Dependency bas=5e-3
```

10.1.5 MBPT scheme

Note: This page describes technical aspects of the MBPT (Many-Body Perturbation Theory) module which is used in double-hybrid and MP2, RPA, GW and GW-BSE calculations. In order to use double-hybrids, MP2, or RPA in your calculation you should request it in the *XC input block* (page 80). In order to perform a GW calculation, you should request it in the *GW input block* (page 263).

ADF implements RPA, GW, and SOS-MP2 (spin-opposite-scaled) using a newly designed algorithm which in all cases scales quadratically with system size¹³. Full MP2 is at the moment only implemented using the canonical RI algorithm which scales to the fifth power with system size. Thus, we strongly discourage using full MP2 or double-hybrids employing full MP2 for systems larger than 1000-1500 basis functions. At the moment ADF features a large number of double-hybrids using SOS-MP2 only (for a list of implemented functionals see *XC input block* (page 80)) which are significantly faster than conventional double-hybrids while offering the same level of accuracy².

¹ A. Förster, M. Franchini, E. van Lenthe, L. Visscher, *A Quadratic Pair Atomic Resolution of the Identity Based SOS-AO-MP2 Algorithm Using Slater Type Orbitals*, *Journal of Chemical Theory and Computation* 16 875-891 (2020) (<https://doi.org/10.1021/acs.jctc.9b00854>)

³ A. Förster, L. Visscher, *Low-order scaling |GOW0| by pair atomic density fitting*, *Journal of Chemical Theory and Computation* 16 (12), 7381 (2020) (<https://doi.org/10.1021/acs.jctc.0c00693>)

² A. Förster, L. Visscher, *Double hybrid DFT calculations with Slater type orbitals*, *Journal of Computational Chemistry* 41 1660-1684 (2020) (<https://doi.org/10.1002/jcc.26209>)

GW, MP2, RPA and double-hybrid functionals can be used with scalar relativistic effects within the ZORA, X2C, or RA-X2C formalism. GW should not be used in combination with solvent models, like COSMO, or other environments. In ADF2022 and later MP2 and double-hybrid functionals, GW and RPA can be used with spin-orbit coupling. Note that in case of spin-orbit coupling *approximate SS and OS contributions* (page 96) are calculated. In ADF2022 in case of ZORA by default the so-called scaled ZORA orbital energies are used in the MBPT expressions.

The Formalism used in the double-hybrid calculation can be changed using the Formalism key. By default, ADF selects the most appropriate algorithm for your system and functional.

The calculation of the independent-particle polarizability or Kohn-Sham density response function in imaginary time is the key step in SOS-MP2, opposite-spin only double-hybrid functionals, GW, and GW-BSE and RPA for larger systems. The equations are solved in the atomic orbital basis exploiting sparsity via advanced density fitting techniques (so-called pair-atomic resolution of the identity or pair-atomic density fitting)^{Page 384, 1}. In case of a SOS-MP2 or RPA calculation, the polarizability is then contracted with the Coulomb potential. For SOS-MP2, the correlation energy is then immediately evaluated in imaginary time while in a RPA calculation the product of Coulomb potential and polarizability is Fourier transformed to the imaginary frequency axis where the correlation energy is evaluated using a matrix logarithm. In a GW calculation, the polarizability is Fourier transformed to the imaginary frequency axis as well where the so-called screened interaction is calculated. The QP states are then evaluated along the real-frequency axis using analytical continuation techniques.

Recommended numerical settings

For all calculations using the MBPT scheme (which includes GW, GW-BSE, RPA, MP2, and double-hybrids), we recommend to consider the following points:

Basis set

Use a basis set of TZ quality or higher.

Dependency

One may improve stability of the results by removing linear dependencies in the basis set, by using the Dependency key. For example:

```
DEPENDENCY
  BAS 5e-04
END
```

- Augmented basis sets: A value of 5e-3 is recommended
- Non-augmented basis sets: Set the dependency key to values between 5e-4 and 5e-3
- quasiparticle self-consistent GW: A value of 5e-3 is recommended
- GW-BSE: A value of 5e-3 is recommended

In addition one can increase the value of RIHartreeFock%DependencyThreshold to improve numerical stability. Starting from AMS2022 ADF will use a Dependency bas=5e-3 and RIHartreeFock DependencyThreshold=5e-3 in case of (any variant of) GW and GW-BSE. One can override these values in the input. For RPA, MP2, and double-hybrids and non-augmented TZ basis sets, typically it is not needed to include this Dependency key.

Numerical Quality

- Augmented basis sets: Numerical quality should be VeryGood
- Non-augmented basis sets, TZ: Numerical quality should range from Normal to VeryGood
- Non-augmented basis sets, QZ: Numerical quality should range from Good to VeryGood

There is also the option to choose a different numerical quality for the MBPT and the preceding DFT calculation:


```

MBPT
    NumericalQuality Good
END

```

sets the numerical quality to Good only for the MBPT calculation. More information can be found in the [MBPT input block](#) (page 387) section.

The imaginary time and imaginary frequency grids

Not in all calculations that use the MBPT scheme the imaginary time and imaginary frequency grids are used. One can skip this part of the recommendations if they are not used.

- For SOS-MP2 and opposite-spin only double-hybrids the imaginary time grid is used (default MBPT%Formalism is LT), and only the remarks for nTime are relevant.
- For full MP2, SCS-MP2 and double-hybrids that depend not only on opposite-spin both grids are not used (default MBPT%Formalism is RI).
- For GW, GW-BSE, and RPA both imaginary time and imaginary frequency grids are used (default MBPT%Formalism is LT).
- For GW and GW-BSE, there is the option to use GW%analyticalintegration, see the [GW description](#) (page 255), in which case both grids are not used.
- If the MBPT%Formalism is set to RI the imaginary time grid is not used.

The imaginary time and imaginary frequency grids can be controlled with the nTime and nFrequency keys. For example:

```

MBPT
    nTime 32
    nFrequency 32
END

```

For an SOS-MP2 or opposite-spin only double-hybrid calculation (with default MBPT%Formalism is LT) the number of grid points for imaginary time (nTime) is automatically adjusted, and increases if the numerical quality is higher, and increases if heavier elements are part of the system. Note that the requirements for nTime are in general lower than for a GW, GW-BSE, or RPA calculation.

For GW, GW-BSE, and RPA the numerical quality automatically sets the number of grid points for imaginary time and frequency integration:

Numerical quality	Number of points
NORMAL	16
GOOD	20
VERYGOOD	24
EXCELLENT	32

Note the following: The number of points actually used in a calculation can differ. At runtime, the MBPT algorithm decides what is the maximum number of integration points which is reasonable to use. So the actual number of points which has been used will be equal or smaller. In case the number of points is set by hand, some info is printed in the output. In case of a GW calculation, the numbers of points can also be found in the `adf.rkf` file in the GW section under the names nTime and nFrequency.

Changing the defaults: the default settings for the size of the imaginary time and imaginary frequency integration grids are normally sufficient, unless the HOMO-LUMO gap of the system is very small. In that case, one should be careful and test if changing the grid size changes the results.

MBPT input block

```

MBPT
  Formalism [Auto | RI | LT | All]
  FrequencyGridType [LeastSquare | GaussLegendre]
  nTime integer
  nFrequency integer
  nLambda integer
  FitSetQuality [Auto | VeryBasic | Basic | Normal | Good | VeryGood]
  IntegrationQuality [VeryBasic | Basic | Normal | Good | VeryGood]
  ThresholdQuality [VeryBasic | Basic | Normal | Good | VeryGood | Excellent]
  Dependency Yes/No
  UseScaledZORA Yes/No
  SigmaFunctionalParametrization [W1 | W2 | S1 | S2 | S1re]
End

```

MBPT**Type**

Block

Description

Technical aspects of the MP2 algorithm.

Formalism**Type**

Multiple Choice

Default value

Auto

Options

[Auto, RI, LT, All]

Description

Specifies the formalism for the calculation of the MP2 correlation energy.

‘LT’ means Laplace Transformed MP2 (also referred to as AO-PARI-MP2),

‘RI’ means that a conventional RI-MP2 is carried out.

If ‘Auto’, LT will be used in case of DOD double hybrids and SOS MP2, and RI will be used in all other cases.

‘All’ means that both RI and LT formalisms are used in the calculation.

For a RPA or GW calculation, the formalism is always LT, irrespective of the formalism specified with this key.

FrequencyGridType**Type**

Multiple Choice

Default value

LeastSquare

Options

[LeastSquare, GaussLegendre]

Description

Use Gauss-legendre grid for imaginary frequency integration in RPA and GW calculations instead of the usually used Least-Square optimized ones. Has the advantage that it can be systematically converged and an arbitrary number of grid points can be used. Typically more grid points will be needed to get the same level of accuracy. However, the convergence of the results with the size of the grid can be more systematic. These grids can only be used when Formalism is set to RI.

nTime**Type**

Integer

GUI name

Number of time points

Description

Number of imaginary time points (only relevant in case the Laplace Transformed (LT) formalism is used).

In the many-body-perturbation theory module in ADF, the polarizability (or Kohn-Sham density response function) is evaluated in imaginary time to exploit sparsity in the AO basis. For MP2, this is often referred to as a Laplace transform. For MP2, 9 points are the default. This is a safe choice, guaranteeing accuracies higher than 1 Kj/mol for most systems (For many simple organic systems, 6 points are sufficient for good accuracy).

Only for systems with a very small HOMO-LUMO gap or low-lying core states (heavy elements starting from the 4th row of the periodic table) more points might be necessary.

In principle, the same considerations apply for RPA and GW as well, however, the accuracy requirements are somewhat higher and 12 point are the default for RPA. In a GW calculation, the number of points is adjusted according to the numerical quality. Using less than 9 points is strongly discouraged except for the simplest molecules.

In ADF2019, it can happen that the algorithm determining the imaginary time grid does not converge. In this case, the usual reason is that the number of points is too small and more points need to be specified. Starting from AMS2020, this does not happen any more. In case the imaginary time grid does not converge, the number of points is automatically adjusted until it does.

The computation time of AO-PARI-MP2, RPA, and GW scales linearly with the number of imaginary time points.

nFrequency**Type**

Integer

Default value

12

GUI name

N freq points

Description

Number of imaginary frequency points. This key is only relevant for RPA and GW and will be ignored if used in an AO-PARI-MP2 calculation. 12 Points is the default for a RPA calculation. It is technically possible to use a different number of imaginary frequency points than for imaginary time. The maximum number of points which can be requested for imaginary frequency integration is 42. Important note: The computation time and memory requirements roughly scale linearly with the number of imaginary frequency points. However, memory can be an

issue for RPA and GW when the number of imaginary frequency points is high. In case a job crashes, it is advised to increase the number of nodes since the necessary memory distributes over all nodes.

nLambda**Type**

Integer

Default value

1

GUI name

Number of lambda points

Description

Size of coupling constant integration grid for SOSEX variants in RPA. Default is 4 points

FitSetQuality**Type**

Multiple Choice

Default value

Auto

Options

[Auto, VeryBasic, Basic, Normal, Good, VeryGood]

Description

Specifies the fit set to be used in the MBPT calculation.

‘Normal’ quality is generally sufficient for basis sets up to and including TZ2P.

For larger basis sets (or for benchmarking purposes) a ‘VeryGood’ fit set is recommended. Note that the FitSetQuality heavily influences the computational cost of the calculation.

If not specified or ‘Auto’, the RIHartreeFock%FitSetQuality is used.

IntegrationQuality**Type**

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood]

Description

Specifies the integration quality to be used in the MBPT calculation. If not specified, the RIHartreeFock%IntegrationQuality is used.

ThresholdQuality**Type**

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Controls the distances between atomic centers for which the product of two basis functions is not fitted any more. Especially for spatially extended, large systems, ‘VERYBASIC’ and ‘BASIC’ can lead to large computational savings, but the fit is also more approximate. If not specified, the RIHartreeFock%ThresholdQuality is used.

Dependency**Type**

Bool

Default value

Yes

Description

If true, to improve numerical stability, almost linearly-dependent combination of basis functions are removed from the Green's function that are used in the MBPT equations. Disabling this key is strongly discouraged. Its value can however be changed. The key to adjust this value is `RiHartreeFock%DependencyThreshold`

UseScaledZORA**Type**

Bool

Default value

Yes

Description

If true, use the scaled ZORA orbital energies instead of the ZORA orbital energies in the MBPT equations.

SigmaFunctionalParametrization**Type**

Multiple Choice

Default value

S1re

Options

[W1, W2, S1, S2, S1re]

Description

Only relevant if a sigma-functional calculation is performed. Possible choices for the parametrization of the sigma-functional. Not all options are supported for all functionals.

10.1.6 Dependency (basis set, fit set)

Conceivably, the sizes of basis and/or fit sets may be so large that the function sets become almost linearly dependent. Numerical problems arise when this happens and results can be seriously affected (a strong indication that something is wrong is that the core orbital energies are shifted significantly from their values in normal basis sets). Although a few (incomplete) tests are carried out for the fit set, the program will generally not check such aspects and carry on without noticing that results may be unreliable.

A new feature has been implemented to take care of this. For reasons of compatibility with previous versions and also because our experience with it is limited so far, we have chosen not to make it the default.

You have to activate it explicitly. Our experience so far suggests that real problems only arise in case of large basis sets with very diffuse functions (i.e.: not with the normal basis sets provided in the standard package). Starting from ADF2022, it is automatically activated in case of (any variant of) GW.

The DEPENDENCY block turns internal checks on and invokes countermeasures by the program when the situation is suspect. A few technical (threshold-type) parameters can be set as well, but this is not necessary, assuming that the defaults are adequate.

```
DEPENDENCY
{bas tolbas}
{eig BigEig}
{fit tolfite}
End
```

tolbas

A criterion applied to the overlap matrix of unoccupied normalized SFOs. Eigenvectors corresponding to smaller eigenvalues are eliminated from the valence space. Default value: 1e-4. Note: if you choose a very coarse value, you'll remove too many degrees of freedom in the basis set, while if you choose it too strict, the numerical problems may not be countered adequately. Starting from AMS2022, ADF will use a rather large value 5e-3 in case of (any variant of) GW if it is not specified on input.

BigEig

Merely a technical parameter. When the DEPENDENCY key is activated, any rejected basis functions (i.e.: linear combinations that correspond with small eigenvalues in the virtual SFOs overlap matrix) are normally processed until diagonalization of the Fock matrix takes place. At that point, all matrix elements corresponding to rejected functions are set to zero (off-diagonal) and BigEig on the diagonal. Default: 1e8.

tolfit

Similar to tolbas. The criterion is now applied to the overlap matrix of fit functions. The fit *coefficients*, which give the approximate expansion of the charge density in terms of the fit functions (for the evaluation of the Coulomb potential) are set to zero for fit functions (i.e.: combinations of) corresponding to small-eigenvalue eigenvectors of the fit overlap matrix. Default: 1e-10.

Notes:

- Application/adjustment of tolfite is not recommended: it can seriously increase the CPU usage while the dependency problems with the fit set are usually not so serious anyway.
- Application of the dependency/tolbas feature should not be done in an automatic way: you should test and compare results obtained with different values; some systems look much more sensitive than others. We have, so far, not been able to understand an unambiguous pattern in these experiences. Of course, when things become clearer in this respect, we will implement corresponding logic into the program.
- When the dependency key is used, the number of functions that are effectively deleted is printed in the output file, in the SCF part (cycle 1) of the computation section.
- The `adf.rkf` (TAPE21) result file of a calculation that used the DEPENDENCY key contains information about the omitted functions and these will also be omitted from the fragment basis when the `adf.rkf` is used as a fragment file.

10.2 Basis Set Superposition Error (BSSE)

The *Ghost Atom* (page 51) feature enables the calculation of Basis Set Superposition Errors (BSSE). The idea is as follows. In a normal calculation of the bonding energy of a molecule *c*, composed of fragments *a* and *b*, one compares the total energies of *c* vs. those of isolated *a* and isolated *b* added together. In ADF this can be done in one stroke by running *c* from fragments *a* and *b*.

The BSSE is determined as the bonding energies of a pseudo-molecule *d* composed of (1) *a* plus a ghost *b* and (2) *b* plus a ghost *a*. The ghost atoms in the calculations are at their normal positions in the true molecule *c*, and they have their normal basis (and fit) functions. However, they do not have a nuclear charge and no electrons to contribute to the molecule. To set such a calculation up, one needs first to make the appropriate ghost basis set files: for each involved atom, copy the basis set file that was used for its creation and modify it to remove the frozen core. Next, create the ghosts with zero mass and zero nuclear charge. Apply these ghost fragments in the BSSE runs.

See also:

- *Example: Basis Set Superposition Error (BSSE): Cr(CO)₅ + CO* (page 1188)
- Tutorial: Basis set superposition error (BSSE)

10.3 Control of Program Flow

10.3.1 Limited execution

`STOPAFTER programpart`

programpart

Must be a predefined name associated with a (major) part of the program. With this key you tell ADF to terminate the job after the named program part has been executed.

A survey of the recognized names with a brief explanation follows below. The program parts are listed in order of execution: by taking a name further down the list you execute a larger part of the program.

init

Initialization procedure, input reading, and printing of the output header with the job identification.

input

Input-reading module.

geomet

Geometry section: organization of atoms in types of atoms and fragments, checks of the actual fragments against information on the attached fragment files.

config

Electronic configuration (if not determined only by the SCF procedure), printout of symmetry subspecies.

mainsy

Generation of symmetry information, representation matrices, etc.

symfit

Construction of symmetry-adapted fit functions.

cblock

Generation of integration points and their distribution in the blocks that control the internally used segmented vectorization loops.

engrad

Relevant only in an optimization calculation. Engrad calculates energy gradients. The geometry is not yet updated and no printing of convergence tests and new coordinates is carried out.

geopt

This routine evaluates energy gradients and updates the geometry accordingly; it also prints the convergence tests and the computed new coordinates. Compare 'stopafter engrad'.

forcematrix

In a frequencies run, terminate the calculation when all displacements have been done and before any further processing of the computed Hessian, such as the determination of normal modes, takes place.

10.3.2 Skipping

With the following key, you can restrict which parts of the program are actually executed:

```
SKIP argumentlist
```

argumentlist

A sequence of names, separated by blanks or commas. Skip may occur any number of times in input. The names in the argument list refer to various items that are associated with parts of the program. With this key you tell ADF to skip the named program part(s) and to continue execution thereafter. The program does not check consequences and may even crash when variables have not been initialized or have attained incorrect values due to the skipping.

Use of this key should be contemplated only in debugging and testing sessions, in which you may skip the computation of certain data when, before that data are needed, you'll halt the program to inspect something.

Recognized and operational arguments are, for instance (possibly not complete due to frequent extensions in this respect): atpair, ets, fitint, orthon, qmpot.

10.3.3 Ignore checks

ADF performs several checks during a calculation, and stops with an error message when intermediate results are suspicious, when input-specified instructions are incompatible, etc. These controlled aborts can in some cases be overridden. Of course, the checks have been inserted for good reasons and you should realize that ignoring them probably produces incorrect results and/or may lead to a program crash.

```
ALLOW argumentlist
```

argumentlist

A sequence of names, separated by blanks or commas. ALLOW may occur any number of times in input, see the list below for the names that can be used.

BadCoreInt

Numerical integration of the frozen core density should closely approximate the analytical value. If the deviation is large compared to the user-specified numerical integration precision the program aborts with an error message like 'BAD CORE INTEGRAL'. This control is overruled by using this ALLOW option.

BadIntegrals

Only applicable when the direct-SCF option is turned off for the basis functions. (This happens automatically for ZORA full-potential calculations). In that case, a sequence of elementary overlap integrals are evaluated with the numerical integration grid and the outcomes tested against the analytical value. If the deviation is too large a warning is issued. Above a certain threshold the program will abort, unless you override the exit with this ALLOW option.

BadSCF

If the SCF procedure has not converged, any geometry manipulations (optimization, linear transit...) will be aborted because the energy gradients are not reliably computed in a non-self-consistent field.

CloseAtoms

Atom-atom distances should not be less than 0.2 Bohr. This is checked in the program section where the numerical integration grid is generated.

RelGeo

Geometry manipulation (optimization, linear transit...) is not supported for all of the relativistic options. See [Relativistic effects](#) (page 106).

SmallBlocks

The list of numerical integration points is partitioned in blocks, so as to fit data arrays (for instance values of all

basis functions in the points of a block) in available memory. The program computes the maximum block length from available memory and size parameters such as numbers of basis functions. A small block size implies a severe reduction in CPU efficiency. Therefore, the program aborts (by default; override with this ALLOW option) if the block length turns out to be very small (less than 10).

XC

Certain combinations of the Density Functional options or application of them with some other features are not allowed. See XC.

10.4 Technical Settings

10.4.1 Memory usage

The amount of memory used by the program during a calculation is determined by three quantities:

- The size of the program itself (executable statements, static arrays). This quantity depends on the program version and is currently around 20 MB.
- Buffer space used by ADF for more efficient I/O handling. This quantity is set at installation. See the Installation Manual.
- Dynamically allocated arrays. The program allocates memory dynamically during the run according to the requirements of the actual calculation.

Starting from ADF2010, in case of parallel calculations some of the data arrays that are used within ADF will be shared by processes on the same node, provided the operating system allows shared memory. This will reduce the total amount of memory used by all ADF processes on each node because only one copy of certain large arrays per node will be present. Note that shared arrays are not the same as distributed arrays. To disable the use of shared memory one can specify the following keyword:

`NoSharedArrays`

10.4.2 Direct SCF: recalculation of data

The program's performance can be defined in terms of the amounts of time (CPU and I/O seconds) and disk space used in a calculation. Also important for the human user is the turn-around time. On multi-user machines CPU-cheap jobs may take a lot of real time to execute due to I/O scheduling. Therefore ADF recomputes some items, like basis functions and fit functions in the integration points, rather than store them on disk. This will increase the amount of CPU time but reduce disk access and it may also improve the turn-around.

The direct SCF method is default and cannot be changed. The keys DISK or DIRECTSCF are therefore obsolete and cannot be used.

10.4.3 Vector length

Numerical integration is applied in ADF to evaluate Fock matrix elements and many other quantities that are defined as integrals over basis functions, the charge density, the potential, etc. As a consequence a large part of the CPU time is spent in simple do loops over the integration points. The total number of points depends on the required precision and on the number of atoms, the geometry, and symmetry. All such numerical integration loops are segmented into loops over *blocks* of points, each block consisting of a certain number of points. This latter defines the most inner do loop and hence determines vectorization aspects.

Depending on the computer (cf. the compiler), vector operations may be executed more efficiently using longer vectors. Long vectors increase the demand on central memory, however, because the program may sometimes have to access large numbers of such vectors in combination (for instance all basis functions) so that they must be available in memory simultaneously. The optimum vector length depends therefore on the balance between vectorization efficiency and memory usage. The maximum vector length that you allow the program to use can be set via input.

```
VECTORLENGTH vectorlength
```

The default is set at the installation of ADF on your platform; see the Installation manual. For organizational reasons the true vector length actually used in the computation may be smaller than the value defined with this key, but will not exceed it (except in a Create run, but in that case performance and memory usage are no hot topics).

10.4.4 Tails and old gradients

The key TAILS is currently obsolescent because of the introduction of the LINEARSCALING block and may be removed in future versions.

Each block of points (see above) covers (more or less) a certain region in space and can hence be assigned a distance value with respect to a particular atom. These distances are used to control whether or not to evaluate functions centered on that atom in that particular block of points.

```
TAILS {bas=tailbas} {fit=tailfit}
```

tailbas, tailfit

Accuracy levels, similar to the integration parameter: a higher value implies higher precision. In this case, basis functions and fit functions respectively are assumed zero in blocks of points that are at a sufficiently large distance from the atom at which the function is centered. Sufficiently large is defined by comparing the integral of the (radial part of the) function beyond that distance with the total integral. By default tailbas and tailfit both depend on the numerical integration parameter.

Note: in contrast with some of the older versions, supplying only the keyword without parameters does not switch off the use of function cutoffs. To effectively switch off the distance effects in gradients evaluation one should specify large values for the BAS and FIT parameters. The value of 100 should be more than enough; thus, for example:

```
TAILS bas=100 fit=100
```

Improved performance in geometry optimizations and frequency runs is achieved by an implementation of the calculation of the gradients that uses linear scaling techniques.

The key TAILS is not used in geometry optimizations anymore. For controlling the use of distance effects in normal SCF calculations, and for calculations with the RESPONSE or EXCITATIONS keywords, please check the LINEARSCALING block.

10.4.5 Linear scaling

The LINEARSCALING block has a very similar function to the TAILS keyword described above. In addition to defining the precision of operations in the numerical integration grid, it also defines the precision for the calculation of the overlap matrix, the fit integrals, and the density fit procedure. Default values have been chosen which result in negligible differences in the results for our test calculations, so that these defaults can be considered safe. They have been chosen similarly to the defaults for the TAILS keyword.

However, it may be advisable to modify the settings for the linear scaling parameters in two cases. First, if a very accurate result is needed, and numerical noise is to be completely eliminated, strict values can be specified. Especially for small molecules, where timings are not so large anyway, this may be of interest. Second, for large molecules, in which the calculations are very time-consuming, one can experiment with less strict values for the LINEARSCALING block

keyword. In such a case one should be aware of the reduced accuracy and preferably test the influence of the changes on the results.

In the simplest application of the LINEARSCALING block, only one parameter is provided. All the subkeys described below will then be given this value. A very large value implies a calculation where no distance cut-offs are used. A normal value (almost default situation) would be 8 for linscal, 6 gives a faster but somewhat sloppier result. Whether this is acceptable is strongly case-dependent. A value of 10 or 12 is already quite strict and, unless there are some sort of numerical problems, there should not be much influence on the results by choosing a stricter value than that. A value of 99 for linscal virtually excludes the possibility that something will be neglected.

```
LINEARSCALING linscal
End
```

More refined control is possible by using the full block key

```
LINEARSCALING
  CUTOFF_FIT epsfit
  OVERLAP_INT ovint
  PROGCONV progconv
  CUTOFF_COULOMB epsvc
  CUTOFF_MULTIPOLES epsmp
END
```

CUTOFF_FIT

determines how many atom pairs are taken into account in the calculation of the fit integrals and the density fit procedure. If the value is too low, charge will not be conserved and the density fitting procedure will become unreliable. This parameter is relevant for the timings of the FITINT and RHOFIH routines of ADF.

OVERLAP_INT

determines the overlap criterion for pairs of AOs in the calculation of the Fock matrix in a block of points. Indirectly it determines what the cut-off radii for AOs should be. The value of ovint has a strong influence on the timing for the evaluation of the Fock matrix, which is very important for the overall timings. The default value for ovint is accint + 2 (typically 6). Again, a higher value implies a safer but slower calculation.

PROGCONV

determines how the overall accuracy changes during the SCF procedure ('progressive convergence'). The idea is that one might get away with a lower accuracy during the initial SCF cycles, as long as the last cycle(s) is/are sufficiently accurate. The current default is that progconv has the value 0, which means that the accuracy in the beginning of the SCF is the same as in the rest of the SCF. This keyword is currently still in the testing phase, so we do not recommend changing its default value. The value of progconv determines how much lower the other parameters in the LINEARSCALING input block are at the beginning of the SCF than at the end.

CUTOFF_COULOMB

determines the radii for the fit functions in the evaluation of the (short-range part of) the Coulomb potential. As the Coulomb potential may take a sizable amount of time, the value chosen for epsvc may influence the total ADF timing significantly as well. The default value for epsvc is accint + 4 (typically 8).

CUTOFF_MULTIPOLES

determines the cut-offs in the multipole (long-range) part of the Coulomb potential. This term scales quadratically with system size, but has a small prefactor. In most cases, change in the epsmp value will not affect the CPU time significantly. The default value for epsmp is accint + 4 (typically 8).

10.4.6 All Points

ADF makes use of symmetry in the numerical integrations. Points are generated for the *irreducible wedge*, a symmetry-unique subregion of space. Optionally the symmetry equivalent points are also used. This is achieved by setting the key

```
ALLPOINTS
```

The key has no argument. The CPU time increases roughly by a factor equal to the number of symmetry operators, and the results should be the same. This key is available only as a debugging feature, to check the correctness of certain symmetry related algorithms.

10.4.7 Full Fock

At every cycle in the SCF procedure the Fock operator is computed in all integration points. By default the *difference* with the values of the previous cycle are used to compute *changes* in the Fock matrix elements. This leads in general to better computational efficiency in two ways: 1) when all such difference values in a block of integration points are very small such a block is skipped in the calculation. 2) if the values are not negligible but still rather small, the contribution from such a block to matrix elements between basis functions with small overlaps are neglected.

With the key

```
FULLFOCK
```

this is turned off, so that the complete matrix elements are computed, no blocks are skipped and the neglect of matrix elements between functions with small overlaps (see also the key TAILS) is controlled solely by the function characteristics and precision requirements, not by the development of the SCF.

10.4.8 Save info

Several types of information, gathered during the run, are lost on exit. The SAVE key allows you to prevent the removal of such information.

```
SAVE info
```

info

A sequence of names separated by blanks or commas. SAVE may occur any number of times in the input file. SAVE turns save-info options on. Possible `info`:

TAPE10

File with numerical integration data: points and weights, values of functions (depends on direct-SCF options) and core densities and potentials.

TAPE13

Checkpoint file. This file is lost (by default) only upon normal program exit, i.e. a program-controlled termination (including a program-detected error condition leading to controlled exit). In all such cases all info on TAPE13 is also present on `adf.rkf`. TAPE13 exists when the program crashes into a core dump for instance, in which case it is uncertain what the contents of `adf.rkf` will be. The SAVE feature allows you to specify that TAPE13 is kept *also* upon normal exit.

TAPE14

Scratch file with numerical integration data, mainly pertaining to individual fragments.

TAPE15

Scratch file data related to matrices like the density matrix, the Fock matrix, and the overlap matrix.

RESTARTS

11.1 ADF Restart files

When an ADF calculation terminates abnormally - not controlled by the program itself, for instance after a core dump due to some bug - there will usually be a file TAPE13, which serves as a checkpoint file. TAPE13 can be used to restart the calculation at a point not too far before the fatal condition occurred. It contains only data for the restart, but none of the special analysis data on `adf.rkf` that would be useful for analysis, to serve as a fragment file, etc.

TAPE13 is updated during the calculation but discarded upon normal termination, namely when all relevant information has been saved on `adf.rkf`. At that point all info that would have been on TAPE13 is present on `adf.rkf`. If you wish to keep TAPE13 anyway - for instance because you plan a restart after normal termination and don't intend to keep the substantially bigger `adf.rkf` - you must use the SAVE key.

Upon normal (i.e. program-controlled) termination of a calculation, the `adf.rkf` result file can be used for restart purposes. When a crash occurs, however, chances are that `adf.rkf` has not correctly been closed and that its data structure is inconsistent: during the calculation large portions of `adf.rkf` are kept in memory rather than on file, and only at the point of final termination, all data is flushed to file.

During a running optimization the system's geometry is written out to the AMS driver's output file `ams.rkf` after every step.

General remarks

ADF restart files (`adf.rkf` or TAPE13) should be included using the key `EngineRestart` in the AMS part of the input. Other important keys in case of restarts in the AMS part of the input are `LoadEngine` (`adf.rkf` or TAPE13) and `LoadSystem` (`ams.rkf`). See the section on [restarting a geometry optimization in the AMS manual](#) on how to restart a (crashed) geometry optimization. Also for other tasks related to exploring the PES, for example, a Linear Transit, Transition State, IRC or IR Frequencies run, one should look in the [AMS manual](#).

If one uses the key `LoadSystem` (`ams.rkf`) one should not include the System block in the AMS part of the input, otherwise one would have two systems. However, if one does not include the key `LoadSystem` one has to include the System block in the AMS part of the input. Depending on the type of restart the coordinates in the System block may be different from those on the restart file. Obviously, if the system on the restart file is not the same as defined in the System block they cannot be completely unrelated. To let the restart data make sense the runs should correspond to the same molecule (i.e. its general definition in terms of fragment building blocks). The program does not check all aspects related to this and certain abuses will therefore survive the internal tests, but will surely lead to some error later on: it is the user's responsibility to ensure that the restart data match the calculation one has in mind.

If one uses the key `LoadEngine` one should not include the Engine ADF block in the AMS part of the input. If one does not include the key `LoadEngine` one has to include the Engine ADF block in the AMS part of the input, which can be useful if one wants or has to change ADF settings, for example SCF convergence settings. Note that in this case all ADF engine settings, (like fragments, basis set, XC) must be included, also those that did not change with respect to the restart file, ADF will not read these settings from the restart file. Again: it is the user's responsibility to ensure that the restart data match the calculation one has in mind.

A restart file supplies data from a previous run that might be useful in the current one. The applications are (combinations are possible):

- Get a better start in the (first) SCF procedure by providing the electronic charge density (in the form of fit coefficients or density matrix) from the preceding run (preferably `adf.rkf`)
- Continue an optimization by supplying the latest geometry (coordinates) from a previous run via the restart file (`ams.rkf`) using `LoadSystem` (rather than typing them in)

WARNING: The SCF and optimization procedures use *history* to improve convergence behavior. Most of such history information is not stored on a restart file. As a consequence, a restart may not continue exactly as the original run would have done if it hadn't terminated. In a SCF restart, for instance, the DIIS procedure has to rebuild the information. The same holds for geometry optimizations, although history plays usually not a very big role there.

11.2 The restart key

The name of the restart file must be provided via the `EngineRestart` key in the AMS driver part of the input (see below). A list of data items is read from the file (if present in the file and only as far as significant for the new run) and used unless their usage is explicitly suppressed by the user.

Simple usage:

```
$AMSBIN/ams << eor
...
EngineRestart restartfile
Engine ADF
...
EndEngine
eor
```

restartfile

The name of a file with restart data. The path (absolute or relative) to the file must be included if the file is not local to the directory where the calculation executes. In most cases it will be an `adf.rkf` file from an ADF calculation, but this is not necessary. It may be any file constructed by the user, for instance, provided it has the right structure. It must be a KF file and the data to be used must be stored in sections and under variable names, exactly how such data are generated by a normal ADF run in `adf.rkf` or in the checkpoint file TAPE13. Note: the filename must not be one of the standard filenames used internally by the program, such as `adf.rkf`, TAPE13, etc. Generally: don't use a name like TAPEnn where nn is a two-digit number.

One can also specify a list of restart options in the ADF part of the input:

```
Engine ADF
...
Restart
  optionlist
  optionlist
...
End
EndEngine
```

This is the list of possible options:

noSCF

Do not use any fit coefficients from the restart file as a first approximation to the (fitted) SCF density for the new

calculation. Instead, the sum-of-fragments density will be used, as in a non-restart run. Note, typically noSCF should be used in combination with noORB.

noORB

Do not use orbitals from the restart file.

SPINFLIP atomnumbers

See the separate [section about the spin-flip method](#) (page 69) for converging broken-symmetry systems.

Note: In ADF2020, AMS handles tasks related to exploring the PES. For restarts related to, for example, a Linear Transit, IRC, or IR Frequencies run, one should look in the [AMS manual](#).

11.3 Structure of the restart file

All data that may be retrieved from the restart file must be stored in a specific location on the restart file. If you are simply using an adf.rkf (TAPE21) result file or a TAPE13 checkpoint file you do not need to bother with this: ADF has put all data in the right place; the following discussion is primarily for those who want to manipulate the restart file or even construct one themselves.

Since the restart file must be a KF file, the location of the data is of the form Section%Variable, specifying the section and the variable name. The section and variable names are case-sensitive. For more information, see [the section on KF output files](#) (page 1391).

If the specified variable is not present in the specified section on the restart file - or if there is no such section at all - the data is not used, usually without an error message. In some cases a few global tests are carried out on the retrieved data; if they fail the tests the data are not used and a warning - in some cases an error abort - may be issued by the program.

KF files are binary files and so are the adf.rkf result file, the TAPE13 checkpoint file, and generally any restart files. If you wish to edit and modify the contents, or just inspect them, the standard KF utilities can be used. Use pkf to get a survey of the sections and variables on the file, dmpkf to get a complete ASCII version of the file, and udmpkf to transform an ASCII version - presumably edited and modified - back into binary format. Please consult the [the section on KF output files](#) (page 1391) for further information on accessing KF files.

AMS tasks

Starting with ADF2020, AMS handles tasks related to exploring the PES. For restarts related to, for example, a Geometry Optimization, a Linear Transit, Transition State, IRC, or IR Frequencies run, you should also look in the [AMS manual](#).

RECOMMENDATIONS AND TROUBLESHOOTING

12.1 Recommendations

12.1.1 Precision

The quality of the calculation, *given* the selected model Hamiltonian (density-functional, relativistic features, spin-restricted/unrestricted, ...) is determined to a large extent by several technical precision parameters.

The most significant ones are:

Basis set

Obviously, the quality of the basis set may have a large impact on the results. As a general rule, minimum and almost-minimum basis sets (types SZ and DZ) may be used for pilot calculations, but polarization functions should be included (DZP, TZP) for more reliable results.

SCF convergence

The self-consistent-field (SCF) and geometry optimization procedures terminate when convergence criteria are satisfied. If these are set too loosely the results may carry large *error bars*. The default SCF convergence tolerance is tight enough to trust the results from that aspect. However, when the SCF procedure encounters severe problems an earlier abort may occur, namely if a secondary (less stringent) criterion has been satisfied (see the key SCF). Although this still implies a reasonable convergence, one should be aware that, for instance, the energy may be off by a few milli-Hartree (order of magnitude; may depend quite a bit on the molecule). It is recommended that in such cases you try to overcome the SCF problems in a secondary calculation, by whatever methods and tricks you can come up with, rather than simply accept the first outcomes. Note: In a geometry optimization the SCF convergence criteria are relaxed as long as the geometry optimization has not yet converged. This should generally not affect the final results: the SCF density and hence the energy gradients may be somewhat inaccurate at the intermediate geometries, but since these are not a goal in themselves the only concern is whether this might inhibit convergence to the correct final geometry. Our experiences so far indicate that the implemented procedure is reliable in this aspect.

Geometry convergence

This is a far more troublesome issue. Three different types of convergence criteria are monitored: energy, gradients and coordinates. The energy does not play a critical role. Usually the energy has converged well in advance of the other items. The coordinates are usually what one is interested in. However, the program-estimated uncertainty in the coordinates depends on the Hessian, which is not computed exactly but estimated from the gradients that are computed in the various trial geometries. Although this estimated Hessian is usually good enough to guide the optimization to the minimum - or transition state, as the case may be - it is far from accurate enough to give a reasonable estimate of force constants, frequencies, and as a consequence, neither of the uncertainties in the coordinates. An aspect adding to the discrepancy between the Hessian-derived coordinate errors and the true deviations of the coordinates from the minimum-energy geometry is that the true energy surface is not purely quadratic and using the Hessian neglects all higher-order terms. The gradients provide a better criterion for convergence of the minimizer and therefore it is recommended to tighten the criterion on the gradients, rather than anything else, when stricter convergence than the default is required. The default convergence criteria, in particular for the gradients,

are usually more than adequate to get a fair estimate of the minimum energy. Tighter convergence should only be demanded to get more reliable coordinate values (and in particular, when the equilibrium geometry needs to be determined as a preliminary for a frequencies run).

Numerical integration accuracy

The BeckeGrid key block (or alternatively the old INTEGRATION key block) determines the numerical precision of integrals that are evaluated in ADF by numerical integration, primarily the Fock matrix elements and most of the terms in the gradients. In addition, the integration settings also determine several other computational parameters. The demands on numerical integration precision depend quite a bit on the type of application. The SCF convergence seems to suffer hardly from limited integration precision, but geometry convergence does, especially when tight convergence is required and also in transition state searches, which are generally more sensitive to the quality of the computed energy gradients. An extreme case is the computation of frequencies, since they depend on differences in gradients of almost-equal geometries. Frequency calculations on molecules with sloppy modes suggest that a BeckeGrid of “good” quality may be required. Note: A large integration value implies that a lot more points will be used in the numerical integrals, thereby increasing the computational effort (roughly linear in the number of points).

12.1.2 Electronic Configuration

Not specifying occupation numbers in the input will *not* automatically result in the computation of the ground state. It may even lead to non-convergence in the SCF and/or in the determination of minimum-energy geometries or transition states. Therefore: whenever possible, specify occupation numbers explicitly in the input (key OCCUPATIONS)!

Misunderstanding results of a calculation may easily result from a lack of awareness of how ADF treats the electronic configuration, which orbitals are occupied and which are empty. Unless you specify occupation numbers in the input they will be determined from the Aufbau principle but only during the first few SCF cycles. Thereafter the distribution of electrons over the different symmetry representations is frozen (see the key OCCUPATIONS, options AUFBAU and aufbau2). If at that point the potential has not yet sufficiently relaxed to self-consistency the *final* situation may be non-Aufbau.

A related aspect is that the *ground state* does not necessarily *have* an Aufbau occupation scheme. In principle, different competing electronic states have to be evaluated to determine which has the lowest total (strongest bonding) energy.

Check output always carefully as to which orbitals are occupied. In general, whenever possible, supply occupation numbers in the input. Be aware that the automatic choice by the program may, in a geometry optimization, result in different configurations in successive geometries: the automatic assessment by the program will be carried out anew in each SCF procedure. If competing configurations with comparable energies have different equilibrium geometries, the geometry optimization has a high failure probability. The gradients computed from the SCF solution of a particular configuration drive the atoms in a certain direction, but in the next geometry, when the program re-determines the occupations and finds a different configuration, the resulting gradients may drive the atoms in another direction.

See the keys CHARGE and OCCUPATIONS for user-control of occupation numbers.

Spin-unrestricted versus spin-restricted, Spin states

If your molecule has unpaired electrons, you should run an unrestricted calculation, in principle. However, if this exhibits convergence problems (or if you simply want to save time: an unrestricted calculation takes a factor of 2 more CPU time and data storage), you may consider doing it in two steps. First, run a *spin-restricted* calculation. Then perform a spin-unrestricted calculation using the restricted adf.rkf as a restart file. In the follow-up calculation you should specify the precise occupation numbers for the state you're interested in, *and* use the SCF input key to specify *only one* SCF cycle (iterations=1). This prohibits convergence (so you keep the converged *restricted* orbitals) and gives you a fairly adequate approximation to a converged unrestricted result. See also the H2 example run for a discussion in the Examples document.

An unrestricted calculation does not necessarily yield the multiplet configuration (triplet, doublet, ...). This is a rather complicated matter; see the discussion on multiplet states, key SLATERDETERMINANTS.

12.1.3 What basis set should I use in ADF?

This question is hard to answer in general, but a few broad suggestions can be made.

Note: This page discusses the basis set requirements for DFT calculations. For a discussion of this question for GW calculations, see also the discussion in the *GW page input block* (page 263).

ZORA or non-relativistic calculation?

By default, *scalar relativistic effects with ZORA* (page 106) are included.

If you are doing a ZORA calculation, you will need the ZORA basis sets, which can be found in \$AMSHOME/atomicdata/ADF/ZORA. You may also use the all-electron basis sets from the ET or AUG directory, but be aware that these were optimized for non-relativistic calculations. Currently the ZORA basis sets cover the entire periodic table and, besides all-electron basis sets, offer a choice of frozen cores. At present the ZORA directory does not contain basis sets with very diffuse functions, which may be required in calculations of hyperpolarizabilities or high-lying excitation energies, but for the lighter elements (H-Kr) you can certainly use the all-electron basis sets from the ET or AUG directory. Warning: in a ZORA calculation, use only the frozen core basis sets coming from the \$AMSHOME/atomicdata/ADF/ZORA directory, or use all-electron basis sets.

If you do not use ZORA, your basis sets should come from the directories SZ, DZ, DZP, TZP, TZ2P, or one of the ET or AUG basis sets. For many of the heavy elements only ZORA basis sets are available, but for such elements it would be inadvisable to do non-relativistic calculations anyway. For light elements the ZORA and normal basis sets should be identical except for the description of the frozen core. Usually the ZORA basis sets contain much steeper basis and fit functions to accurately describe the core region.

Large or small molecule?

For standard calculations (energies, geometries, etc.) we recommend the following hierarchy of basis sets: SZ < DZ < DZP < TZP < TZ2P < TZ2P+ < ET/ET-pVQZ < ZORA/QZ4P, where the largest and most accurate basis is on the right. Not all basis sets are available for all elements. For small negatively charged atoms or molecules, like F⁻ or OH⁻, basis sets with extra diffuse functions are needed, as available in the AUG or ET/QZ3P-nDIFFUSE directories. For example, the standard basis sets, or even the large ZORA/QZ4P basis set will often not be large enough for the accurate calculation of such anions.

In general it is advisable to use the best basis set that you can afford in terms of CPU time and memory. If you want to optimize the geometry or calculate the atomization energy of a diatomic molecule there is little reason not to use the very large ZORA/QZ4P basis, or (for light elements) a similarly large ET basis (we recommend the ET-pVQZ basis). If you are studying a molecule with 100 atoms or more, the use of such large basis sets not only becomes prohibitive because of the required CPU time and memory, but it also is much less needed than for smaller systems. In medium-sized or large molecules even the moderately large basis sets will prove to be quite adequate because of the effect of basis set sharing. Each atom benefits from the basis functions on its many neighbors. Additionally, if a large basis contains diffuse functions, linear dependency problems may occur. See also the input key DEPENDENCY. In many cases basis DZ or DZP will give acceptable accuracy for calculations on large systems. If you are inexperienced it may be prudent to test a few different basis sets to get a feel for the size of basis set effects. To get a rough idea for the size of various basis sets, we mention here the number of functions for all-electron basis sets from the directories ZORA/SZ up to ZORA/QZ4P. For carbon, the number of functions is 5 (basis ZORA/SZ), 10 (DZ), 15 (DZP), 19 (TZP), 26 (TZ2P), 43 (QZ4P). The same numbers for hydrogen are: 1 (SZ), 2 (DZ), 5 (DZP), 6 (TZP), 11 (TZ2P), 21 (QZ4P). These numbers arise because

ADF uses “pure” d and f functions. In other words, 5 instead of 6 d functions are used and 7 instead of 10 f functions. Note that especially the jump from TZ2P to QZ4P is quite steep.

In an overgeneralizing fashion we can state that the single zeta basis SZ is hardly ever sufficient to get more than a qualitative picture and should be used only when larger basis sets are not affordable. The double zeta basis DZ performs already much better and may give quite reasonable results, for example in geometry optimizations on large molecules. However, in more subtle situations, for example if hydrogen bonds are important, it is advisable to use at least one set of polarization functions. This is the double zeta polarized DZP basis set. Basis set TZP extends the valence space (but not the core space which remains double zeta) to triple zeta. In basis TZ2P an additional polarization function is added. For example, hydrogen gets a d polarization function in addition to its p polarization function and carbon gets an f polarization function on top of a d polarization function. Several tests have shown that often the second polarization function is of more use when it has an l value one higher than the first polarization function. This is reflected in the choice just described. If another polarization function is needed it is usually best to add another one of the lowest l value (2p+1d for hydrogen, 2d+1f for carbon). This choice has been made in the ET basis ET-QZ3P. There, sometimes even three d polarization functions were added, for example 3 p functions for Be, and 3 d functions for S. The reason for this is that S can occur in hypervalent species such as SF₆, which put special demands on the basis set. In the case of Be, the unoccupied p level is so close in energy to the occupied ones that it is sometimes called a valence level. Semantics aside, it is clear that a proper description of the p level of Be is very important and it is therefore not strange to add a third p function. In general, the unoccupied levels for the atoms on the left side of the periodic table are close to the occupied ones. This makes it necessary to add a few extra functions for the lowest unoccupied levels in order to get a description that corresponds to the general level of accuracy one expects from the hierarchical basis set names SZ-TZ2P. The basis set quality for a particular subdirectory is now rather uniform throughout the periodic system. At the same time we have attempted to increase the number of functions in a systematic fashion so that each element is described by at least as many functions of a particular l value as its predecessor.

The ZORA/QZ4P basis sets might be roughly described as core triple zeta, valence quadruple zeta, with 4 polarization functions (2 d and 2 f functions for C, 2 p and 2 d for H). The fit sets corresponding to these basis sets are also much larger than the fit sets found in basis sets SZ-TZ2P. If one has doubts about the adequacy of a fit set for a certain element, this can be tested by replacing its fit set by the large one from the QZ4P directory, see the subkey FitType of the key BASIS. In the ZORA/QZ4P basis sets, the choice for the exponents of the polarization functions was done in a systematic, but somewhat hand-waving manner. For this reason the exponents were always rounded to half integers. Also the geometric mean of the exponents usually does not coincide with the choices made in directories SZ-TZ2P and the ET basis sets. However, the fact that two polarization functions (with reasonable exponents) are present instead of a single one is far more important. A reasonable intermediate basis set, in size between TZ2P and QZ4P might be envisaged in which a single polarization function is added, as described above. This is roughly the choice for the polarization functions made in the ET directory ET-QZ3P.

Frozen core or all-electron?

In general we recommend the use of frozen core basis sets for LDA and GGA functionals if available. Especially for the heavier atoms the number of functions is much smaller than for their all-electron counterparts. Our tests indicate that the error made by invoking the frozen core approximation is usually clearly smaller than the difference with respect to slightly higher quality basis sets. For the ZORA/QZ4P basis sets, only all-electron basis sets are available as these are intended for near basis set limit calculations only in which the CPU time is not a major concern.

All-electron basis sets are required in case of SAOP, meta-GGA and meta-hybrid functionals, functionals that use LibXC, post-KS calculations like GW, RPA, MP2 or double hybrids. We recommend using all-electron basis sets in case of Hartree-Fock or (range-separated) hybrids. The X2C and RA-X2C relativistic method requires the use of all-electron basis sets.

Geometry optimizations involving atoms with a too large frozen core may give rise to numerical problems. In such cases it is recommendable to use a smaller frozen core. In previous occurrences we have removed such basis sets.

For accurate results on properties like nuclear magnetic dipole hyperfine interactions (ESR), nuclear quadrupole coupling constants, and chemical shifts (NMR), all-electron basis sets are needed on the atoms of interest. For such properties tight functions might be necessary for high accuracy, especially in a ZORA calculation.

Diffuse functions needed?

For small negatively charged atoms or molecules, like F^- or OH^- , basis sets with extra diffuse functions are needed, as available in the AUG or ET/QZ3P-nDIFFUSE directories. For example, the standard basis sets, or even the large ZORA/QZ4P basis set will often not be large enough for the accurate calculation of such anions.

For accurate results on properties like polarizabilities, hyperpolarizabilities, and high-lying excitation energies, also diffuse functions are needed. This is especially true for calculations on small molecules. In larger molecules the nature of the relevant virtuals is much more ‘molecular’, much less Rydberg-like, so that the normal basis sets may be sufficient. Basically all properties calculated through the RESPONSE keyword may require diffuse functions. If you use the EXCITATIONS keyword, the necessity of diffuse functions depends on the type of excitation you are interested in. The lowest excitations do not require diffuse functions, but Rydberg excitations do.

In case of diffuse basis functions the risk of linear dependency in the basis increases. This can be checked, and corrected for with the DEPENDENCY keyword. It is recommended to use this keyword for all calculations involving diffuse functions. A good default setting is

```
DEPENDENCY bas=1d-4
```

However, it may be advisable to experiment a bit with the parameter, especially if many linear dependent combinations of AOs are removed. Using too many diffuse functions on a large molecule will lead to insurmountable numerical problems. In such a case it is not only useless, but even harmful, to add many diffuse functions.

In the previous release only some basis sets were provided that contained diffuse functions. These were gathered in the directory Vdiff. Now several ET basis sets have been developed for the elements up to Ar containing some or many diffuse functions. We recommend using these instead of the Vdiff directory. Most of these basis sets are quite large and not very suitable for large molecules.

In ADF2005.01 augmented basis sets were added in the AUG directory, especially devised for use in TDDFT calculations, such that one can do a reasonably accurate calculation of excitation energies with a relatively small basis set, see D.P. Chong¹.

Normal or even-tempered basis?

For normal calculations (these form the vast majority) we recommend the use of the optimized basis sets in the directories SZ-TZ2P and, for ZORA calculations, ZORA/SZ-QZ4P. These should be sufficient in accuracy for even very demanding users and are available for the entire periodic system (in the case of the ZORA basis sets). They are also available with a frozen core variety, which saves much CPU time.

The ET basis sets, on the other hand, are available only in all-electron form at the moment. Furthermore, most are pretty large (larger, but also better than TZ2P). Additionally, relatively large basis set superposition errors were detected for molecules containing atoms in the row K-Kr. For this reason we only recommend ET basis sets for the elements H-Ar at the moment. There they have yielded quite nice, near basis set limit, results for the G2 test set. For these light elements the ET basis sets can be comparable in quality to the ZORA/QZ4P basis, even though it is smaller. The ET basis sets are considered to be especially useful when diffuse functions are required. In that case it is very easy to adapt the original ET basis and fit set. The utilities provided for this in ADF will be described below in an Appendix. The ET basis set utilities will also prove useful for users who want to experiment with making their own basis sets, or who have very special demands on the basis and fit. The provided utilities automate much of the work needed to make new atomic data files.

¹ D.P. Chong, *Augmenting basis set for time-dependent density functional theory calculation of excitation energies: Slater-type orbitals for hydrogen to krypton*, *Molecular Physics* 103, 749 (2005) (<https://doi.org/10.1080/00268970412331333618>)

Recommendations for Double-hybrids and MP2

Double-hybrid and MP2 calculations are correlated-electrons calculations and consequently they converge slower to the complete basis set limit than independent-electron methods. Also for large molecules, calculations with basis sets smaller than TZ2P are usually not very precise. We thus recommend TZ2P as a minimum requirement. The special, pseudo-correlation-consistent basis sets Corr/TZ3P and Corr/QZ6P usually give better results. They are similar to TZ2P and QZ4P, respectively, but they contain more polarization functions. They can also be used to extrapolate the **correlation energy** to the complete basis set limit according to

$$E_c^{CBS} = E_c^{QZ} - \frac{1}{N_{bas}^{QZ}} \frac{E_c^{QZ} - E_c^{TZ}}{\frac{1}{N_{bas}^{QZ}} - \frac{1}{N_{bas}^{TZ}}}.$$

where E_c^{QZ} and E_c^{TZ} are the values of the correlation energies calculated with Corr/TZ3P and Corr/QZ6P, respectively and N_{bas}^{QZ} and N_{bas}^{TZ} are the corresponding number of basis functions. In a double-hybrid calculation, one should only extrapolate the correlation contribution to the total energy and use the KS contribution from the calculation with the Corr/QZ6P basis set.

The dependency key should always be used, also when non-augmented basis sets are used (augmented basis sets should be avoided):

```
DEPENDENCY
  Bas 5e-4
END
```

is usually sufficient.

What accuracy do the basis sets give?

Tests on many diatomics were performed to assess the various basis sets. We now document the results of some of these tests, in order to give a feeling for the quality that can be obtained from the various basis sets. See also van Lenthe and Baerends².

Tests for non-relativistic calculations on 36 diatomics containing oxygen, namely the oxides of the first 36 elements (H-Kr). All-electron basis sets were used. The ZORA/QZ4P basis set was used to define the basis set limit result. The numbers in the table refer to bonding energies in eV. Differences were taken between the QZ4P results and the results in smaller basis sets. By construction, the errors in the QZ4P column are zero.

	QZ4P	DZ	DZP	TZP	TZ2P
Average error	0.0	1.33	0.39	0.18	0.06
Average absolute error	0.0	1.33	0.39	0.18	0.06
Maximum error	0.0	2.84	1.07	0.41	0.13
Worst case	all	SO	BeO	FO	O ₂

A few comments are in order to explain this table.

The oxides were used as a small test set because their equilibrium bond lengths are known in many cases. Also, they have a large influence on the electronic structure of the molecule, so that they also test the adequacy of the polarization functions.

The errors in the small basis sets are systematic, because the isolated atoms are described reasonably well, but the molecular energy is not deep enough. For this reason the average errors and average absolute errors are (nearly) always equal.

² E. van Lenthe and E.J. Baerends, *Optimized Slater-type basis sets for the elements 1-118*, Journal of Computational Chemistry 24, 1142 (2003) (<https://doi.org/10.1002/jcc.10255>)

Test calculations on 100 diatomics containing oxygen, using all-electron ZORA basis sets. Many basis sets for (very) heavy elements are included here, which could not be included in the table above. The numbers have the same interpretation as above and are again in eV.

	QZ4P	DZ	DZ	TZP	TZP	TZ2P	TZ2P
	ae	fc	ae	fc	ae	fc	ae
Average error	0.00	0.95	1.07	0.20	0.20	0.05	0.05
Average absolute error	0.00	0.98	1.07	0.20	0.21	0.05	0.05
Maximum error	0.00	2.86	2.83	0.74	0.74	0.19	0.17
Worst case	all	SO	SO	OgO	OgO	ThO	OgO

Again we place a few comments on these frozen core and all-electron results.

The trends are very similar to those in the previous table for the lighter elements.

The frozen core results are very satisfactory, as they are very close to the results with the corresponding all-electron basis sets. The error introduced by the frozen core approximation is typically much smaller than the one introduced by basis set incompleteness.

The average errors are quite comparable to those from the previous table. The heavier elements do not seem to be much more difficult than the lighter ones.

For heavy elements no reliable ET basis set is yet available for comparison.

More results, all-electron, non-relativistic on roughly 140 different diatomics at experimental or 'reasonable' equilibrium geometries.

	QZ4P	DZ	TZP
Average error	0.00	0.89	0.11
Average absolute error	0.00	0.89	0.11
Maximum error	0.00	2.84	0.32
Worst case	all	SO	O ₂

Only the non-relativistic basis sets DZ and TZP are fairly complete for heavier elements.

Also for these general diatomics (not just oxides) the average and maximum errors have decreased substantially, especially for basis TZP.

Same table, but now for frozen core basis sets. In all these tests the smallest frozen core files were employed (i.e. the largest basis).

	QZ4P	DZ	TZP
Average error	0.00	0.73	0.13
Average absolute error	0.00	0.75	0.16
Maximum error	0.00	2.87	1.80
Worst case	all	SO	ThO

The frozen core approximation has little influence on the accuracy for the basis DZ, but a somewhat larger effect on the basis TZP. This is especially due to certain worst cases, such as ThO.

ZORA, all-electron, over 240 diatomics

	QZ4P	DZ	TZP	TZ2P
Average error	0.00	0.70	0.11	0.02
Average absolute error	0.00	0.70	0.11	0.03
Maximum error	0.00	2.83	0.44	-0.16
Worst case	all	SO	I ₂	Cr ₂

The average error goes down very nicely from 0.70 to 0.11 to 0.03 eV when going from DZ to TZP to TZ2P. The average error in basis TZ2P is clearly below 1 kcal/mol (the famous chemical accuracy). Errors due to deficiencies in current XC functionals are still much larger than this. As a consequence, the ZORA/TZ2P basis will be more than adequate for all standard calculations.

It is to be expected that these conclusions will not dramatically change if larger test molecules are used. Also for geometry optimizations the improved basis sets SZ-TZ2P and ZORA/SZ-TZ2P should be more than sufficient for all standard cases. The ZORA/QZ4P can be considered a very safe (though expensive) option for basis set limit calculations.

12.1.4 Relativistic methods

The ZORA relativistic approach is often superior and in other cases at least similar to the older Pauli method. In particular, for all-electron calculations generally, and for very heavy elements even within the frozen core approach, the Pauli method may exhibit significant shortcomings. This is mostly due to the variational instability of the Pauli formalism in the deep-core region near the nucleus. The bigger the basis set and the smaller the frozen core, the more likely this will show up, while generally speaking you might be tempted to use smaller cores and bigger basis sets to *improve* your results. The ZORA approach does not suffer from these problems and is, therefore, highly recommended over the Pauli formalism.

12.2 Troubleshooting

This chapter contains hints to help you solve some problems and comments on frequently asked questions.

12.2.1 License file corrupt

You may find that, after having installed the license file, the program still doesn't run and prints a message like "your license file is corrupt." To explain how this may come about, and how to overcome this, a few words on license files.

Each license file consists of pairs of lines. The first of each pair is text that states, in a more or less readable format, typical aspects such as an expiration date, the version number of the software and so on. The second line contains the same information in encrypted format: a (long) string of characters that seem to make little sense. The program reads the license file and checks, with its internal encrypting formulas, that the two lines match. If not, it stops and prints the "corrupt" message. So, there are two common reasons why it may happen to you:

- You are using a license file for another version of the software than your executables correspond to. Newer (major) releases may contain a different encrypting formula, so that the match in old license files is not recognized anymore. So, please verify that your license file and executable belong to the same major release.
- More likely: the license file as it has been created has been modified in some way. Sometimes, people inspect it and "clean it up" a little bit, for instance by removing "redundant" spaces, or by making some other "improvements." Unfortunately, every such modification will destroy the encryption match and lead to the "corrupt" error. Most of the time, however, the reason lies in the mailing system by which the license file has been sent to you. If the encrypted line is rather long, the mailer may have cut it into two shorter lines. To verify (and correct) this, edit the license file and see if it consists of pairs of lines as described above. If not, reunify the broken lines and try again.

- Finally, the problem may lie in your OS, which may have inserted additional hidden CR characters (carriage returns) into the license file. You can remove them with our fix_license utility (in \$AMSHOME/Install); see the Installation manual.

12.2.2 Recover from Crash

A calculation may terminate in two ways: controlled or uncontrolled. Controlled termination includes cases where the program itself detects an error and decides that continuation of the calculation is impossible or pointless. In all such cases the standard exit routine is executed, resulting in an output section with some final information. This also ensures that the general result file adf.rkf is closed properly and all relevant information flushed to it.

Uncontrolled termination may occur, for instance when some bug causes the program to divide by zero, violate memory access restrictions, etc. Usually this leads to an immediate abort of the program by the operating system and hence loss of control by the program. In such situations the information on adf.rkf may be incomplete because some of the data are kept in memory until the final termination of the program is carried out. It would be a terrible nuisance to see all time spent so far being lost. To remedy this ADF supports a checkpoint file, named TAPE13, to help you recover at least some, if not most, of the results: not for analysis, but for continuation from a point not too long before the fatal condition occurred. TAPE13 can be used, just like adf.rkf, as a normal restart file in the ADF part of the input. See the RESTART key. For restarting, for example, a geometry optimization, one should use the file ams.rkf, which is produced by the AMS driver and should be used in the AMS part of the input.

12.2.3 Memory Management

***Problem*:** The program aborts with an error message “MEMORY ALLOCATION ERROR”. This message is issued both in the log file and in the output file.

***Cause*:** Memory allocation may fail due to:

- Insufficient virtual (i.e. total RAM + swap) memory
- On Unix: too low values for per-process memory limits
- Restrictions of the 32-bit architecture

***Cure*:** Problem 1: add more physical RAM or increase the size of the swap space (page file). Problem 2: add one or more ulimit commands to your run script, setting relevant limits to “unlimited.” Problem 3: Perform your calculations on a 64-bit system. ADF versions for the most common 64-bit operating systems are available, so use them.

All three problems above can be avoided by reducing the size of the calculation. The most important parameter defining the amount of used memory is the size of the basis set or, more precisely, the total number of Cartesian Slater functions, naos. The current value can always be found in the output file of the calculation, just search for the “naos” string. The amount of memory used by a particular calculation depends on the naos value and on the type of the calculation and, for large naos, it scales as naos^2 . For example, a non-relativistic calculation during SCF can use up to 40 naos^2 bytes of memory. Using spin-orbit coupling may double this amount and using a hybrid or a meta-GGA XC functional will add extra on top of it. Also TDDFT calculations require additional memory.

What can be done to reduce memory usage? First of all, reducing the basis set size for non-critical parts of the molecule will reduce the memory requirement without reducing the quality of the results. Secondly, performing a calculation with a pure GGA instead of B3LYP will not only reduce the amount of memory used but also make the calculation faster. The latter especially applies to geometry optimizations because B3LYP does not perform any better than some of the GGAs.

***Note*:** If workspace problems occur for relatively small calculations, there might be a bug. Notify your ADF contact: send us the output file so that we can have a look and check things out.

12.2.4 SCF Convergence Guidelines for ADF

The self-consistent field (SCF) method is the standard algorithm for finding electronic structure configurations within Hartree-Fock and density functional theory. SCF is an iterative procedure and can, depending on the situation at hand, sometimes be difficult to converge. Indeed, convergence problems occur in many different types of chemical systems. These problems are most frequently encountered when the electronic structure exhibits a very small HOMO-LUMO gap, in systems with d- and f-elements with localized open-shell configurations, and in transition state structures with dissociating bonds. Finally, many SCF convergence problems are rooted in nonphysical calculation setups, such as high-energy geometries or an inappropriate description of the electronic structure.

We advise you to check and test the following list of options and aspects when encountering SCF convergence issues, starting from the most common and trivial ones:

1. Ensure that the atomistic system under study is realistic. More specifically, check for the proper values of bond lengths, angles, and other internal degrees of freedom in the geometry. Unless specified otherwise, AMS expects atomic coordinates in Å. Also, when copying atomic structures into the graphical user interface, check that the imported structure is complete and that no atoms got lost during the process.
2. The initial electronic structure is typically initialized as linear combinations of atomic configurations. However, a moderately (but not fully) converged electronic structure from, say, an SCF iteration conducted previously, likely represents a better initial guess already. Indeed in the next step of a geometry optimization, this moderately converged electronic structure information is reused as initial guess. The SCF iterations of the following geometry steps then usually converge even if the first electronic structure calculation does not. In the case of single-point calculations, the electronic structure needs to be read in via a [manual restart](#) (page 399).
3. Assert that the correct spin multiplicity of the system is used. Open-shell configurations should be computed in a spin-unrestricted or, if necessary, a spin-orbit coupling formalism. You need to manually set the spin component (see the [tutorial on spin coupling within an iron complex](#) for more details). For non-converging open-shell systems, the evolution of the SCF errors during the iteration might also provide some insight into the problem. Strongly fluctuating errors may indicate an electronic configuration far away from any stationary point or an improper description of the electronic structure by the approximation used.
4. Change to a different SCF convergence acceleration method, like MESA, LISTi or EDIIS. To this end, examine the [documentation section](#) (page 368) for further details about the available SCF acceleration methods and the parameters controlling them. In the graphical user interface these options are available under **Details → SCF** and **Details → SCF Convergence Details**. The performance of these methods was tested for a variety of chemical systems that are difficult to converge. The corresponding results are depicted in Fig. 1 below and show that significant changes in the convergence behavior can be achieved with different accelerators.
5. The [Augmented Roothaan-Hall \(ARH\) method](#) (page 372) is another alternative, though computationally more expensive, convergence acceleration method. ARH directly minimizes the system's total energy as a function of the density matrix using a preconditioned conjugate-gradient method with a trust-radius approach. As shown in Fig. 2 below, ARH can in some situations be a viable alternative for difficult systems.
6. Some parameters of the DIIS algorithm may also be changed manually. Note that sometimes it is necessary to try multiple values and combinations of values until the desired outcome is achieved:
 - **Mixing** denotes the fraction of the computed Fock matrix that is added when constructing the next guess for this matrix. More specifically, the Fock matrix resulting from the current guess for the electron density is combined with the corresponding matrices from multiple previous SCF iteration steps by the DIIS algorithm in order to construct the next guess. The mixing parameter controls the proportion of the computed Fock matrix in this linear combination, whereas a value higher than the default value of 0.2 corresponds to a more aggressive acceleration, while a lower value will lead to a more stable iteration and should be used for problematic cases.
 - **Mixing1** corresponds to the mixing parameter used in the very first SCF cycle. Its default of 0.2 should mainly be altered only in situations where one attempts to slowly converge the electronic structure starting from a restart file (see above).

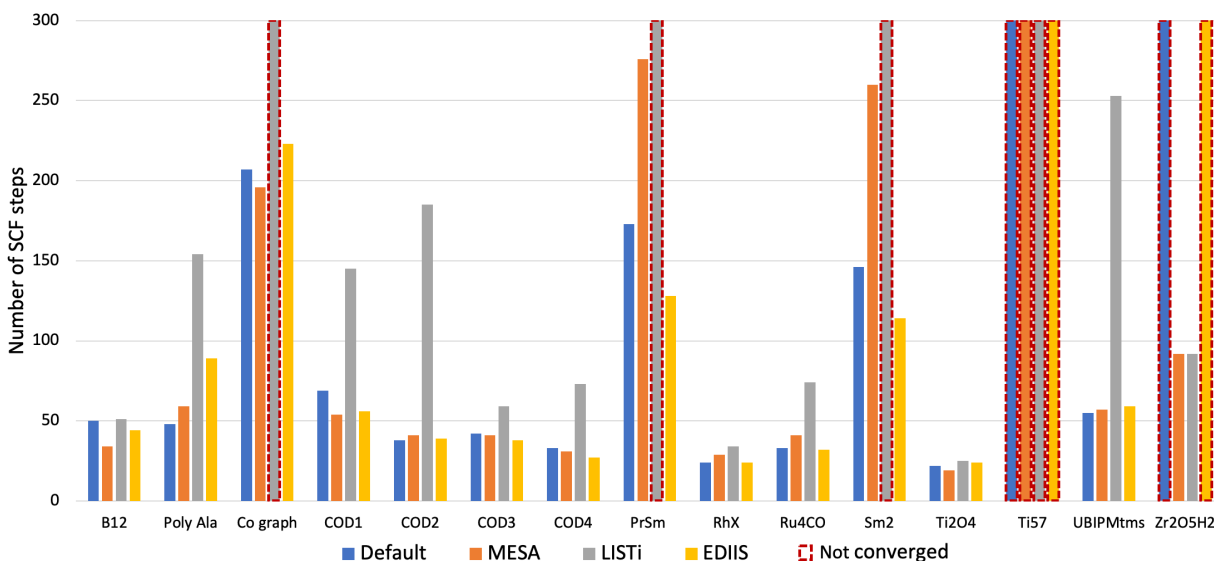


Fig. 12.1: Number of SCF iterations needed to converge a series of different types of chemical systems with the ADIIS+SDIIS (default), MESA, LISTi, and EDIIS accelerator methods. Non-converged SCF iterations are depicted by dashed borders.

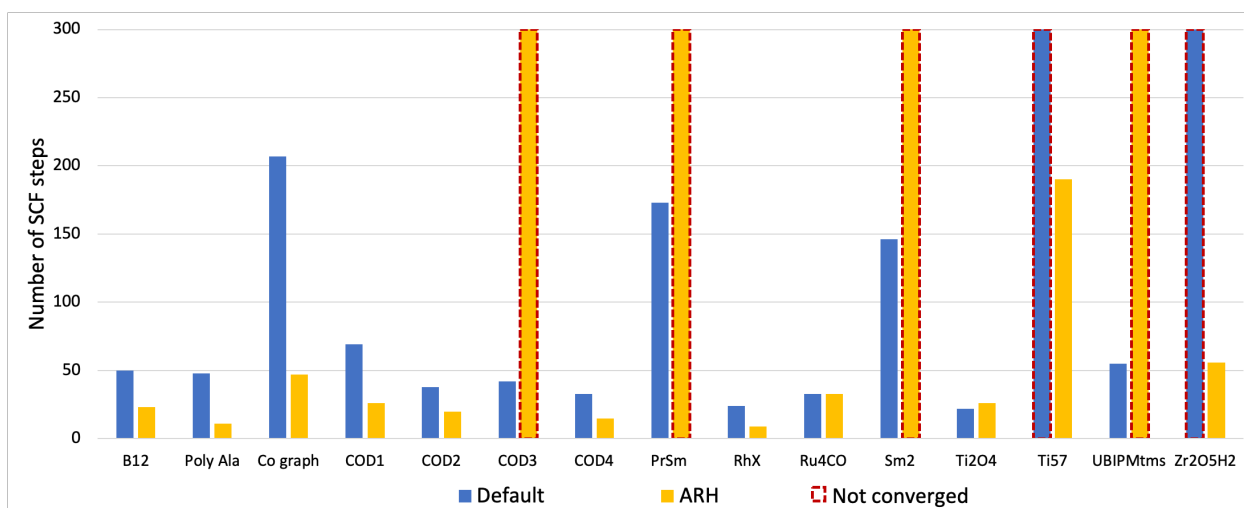


Fig. 12.2: Number of SCF iterations needed to converge a series of different types of chemical systems with the ADIIS+SDIIS (default) and ARH accelerators. Non-converged SCF iterations are depicted by dashed borders.

- **N** is the number of DIIS expansion vectors used for the SCF acceleration (default N=10). An input value smaller than 2 disables the DIIS. A higher number of expansion vectors (e.g. up to N=25) makes the SCF iteration more stable, while a smaller number makes it more aggressive.
- **Cyc** is the number of initial SCF iteration steps after which SDIIS will start (default Cyc=5). An initial equilibration will take place in the cycles before; a higher value of Cyc causes a more stable computation.
- As an example, the following parameter values can be used as a starting point for a slow but steady SCF iteration of a difficult system:

```
SCF
  DIIS
    N 25
    Cyc 30
  End
  Mixing 0.015
  Mixing1 0.09
End
```

Besides the methods discussed above, other algorithms and techniques can be used to converge a problematic SCF calculation. However, as opposed to the aforementioned options, the techniques listed below slightly alter the end result, which needs to be carefully tested:

7. *Electron smearing* (page 64) simulates a finite electron temperature by using fractional occupation numbers to distribute electrons over multiple electronic levels. This is particularly helpful to overcome convergence issues in larger systems exhibiting many near-degenerate levels. As electron smearing alters the system's total energy, the value of this parameter should be kept as low as possible, e.g. by using multiple restarts with successively smaller smearing values.
8. The *level shifting technique* (page 370) artificially raises the energy of unoccupied (virtual) electronic levels and can be used to overcome SCF convergence problems as well. It will, however, give incorrect values for properties involving virtual levels, such as excitation energies, response properties, and NMR shifts. Likewise, the electronic structure of metallic systems with a vanishing HOMO-LUMO gap might be inadequately described by this technique.

12.2.5 Geometry Optimization troubleshooting

See also the [section on geometry optimization in the AMS manual](#).

No convergence

First of all one should look at how the energy changed during the latest ten or so iterations. If the energy is changing more or less in one direction (increasing or decreasing), possibly with occasional jumps, then there is probably nothing wrong with the optimization. This behavior is typical in the cases when the starting geometry was far away from the minimum and the optimization has a long way to go. Just increase the allowed number of iterations, restart from the latest geometry, and see if the optimization converges.

If the **energy oscillates** around some value and the energy gradient hardly changes, then you may need to look at the calculation setup. We give some recommendations below.

The success of geometry optimization depends on the accuracy of the calculated forces. The default accuracy settings are sufficient in most cases. There are, however, cases when one has to increase the accuracy in order to get geometry optimization converged. First of all, this may be necessary if you tighten the optimization convergence criteria. In some cases it may be necessary to increase the accuracy also for the default criteria. Here's what you can do to increase the accuracy of gradients:

- Increase the numerical quality to "good"

- Add an ExactDensity keyword or select “Exact” in the “Density used in XC-potential” list in the Details:Accuracy panel. This will make the calculation 2 or 3 times slower.
- Tighten the SCF convergence criteria, for example, to 1e-8.

Example input with some of these stricter settings using a TZ2P basis set. ExactDensity is not included here since it will make the calculation much slower.

```
NumericalQuality Good
Basis
  Type TZ2P
  Core None
End
SCF
  converge 1e-8
End
```

Small HOMO-LUMO gap: check the HOMO-LUMO gap at the last SCF cycle at a recent geometry. Is it comparable with the changes in the MO energies between geometries? If yes, then it is possible that the electronic structure changes between optimization steps, which may lead to non-convergence. This may indicate a fundamental problem with the calculation setup. First of all, check that you obtain a ground state in a single-point calculation. Is the spin-polarization value correct? Try calculating some of the high-spin states if possible and see if they have lower energy. If the MO repopulation that is taking place is between MOs of different symmetry, then you can try freezing the number of electrons per symmetry using an OCCUPATIONS block.

Are there **constraints** imposed on the optimization? Note that using constraints may break the symmetry (by AMS), even if the starting geometry is symmetric and the constraints do not have to break symmetry.

Optimization in Cartesian coordinates usually needs more steps to converge compared to delocalized. If you haven't tried delocalized optimization for the system then you should do it. **Near 180-degree angles** with optimization in delocalized coordinates. ADF normally does not have a problem with a near-180-degree valence angle if the initial value of the angle was larger than 175 degrees or if it is a terminal bond angle. If the initial angle was larger than 175 degrees then it gets a special treatment. For example, any torsion angle that contains the three atoms is removed or replaced with a torsion angle involving only the two end atoms of the near-180-degree angle. If the angle defines a terminal bond then two angles in two coordinate planes are used to define the bond instead of a valence and a torsion angle. However, if the initial value of the angle was far from 180 degrees and has become close to it during optimization then optimization may become unstable, especially if this is an angle connecting large fragments. In this case, it may be useful to restart geometry optimization from the latest geometry. As a last resort, you may want to constrain the angle to a value close, but not equal, to 180 degrees.

Very short bonds

If the computed equilibrium geometry appears to exhibit unlikely values, typically significantly *too short* bond lengths, you may have run into a basis set problem, in particular (but not only) if the Pauli relativistic method is applied.

Problem: Optimized bond lengths are clearly too short. The energy may also look suspicious.

Possible cause 1: Basis set trouble: onset of Pauli variational collapse, if you have applied the Pauli relativistic option. Caused by small (or absent) frozen cores and/or relatively large basis sets, applied to heavy elements.

Possible cause 2: Basis set trouble also, but quite different from the previous potential cause: you have used relatively *large* frozen cores. When the atoms approach each other during the optimization and the frozen cores start to overlap, the energy computation and the computed energy gradients become more and more incorrect. This is a result of the inappropriateness of the frozen core approximation, which indeed assumes that frozen cores of neighboring atoms do not significantly overlap. Without going into a detailed explanation here, the net effect is that certain repulsive terms in the energy computation are missing and hence a spurious tendency to a “core collapse” arises, yielding too short bond lengths.

Cure: Best is to abandon the Pauli method and use the ZORA approach instead for any relativistic calculation. If for whatever reason you insist on using the Pauli formalism, apply bigger frozen cores and, if that doesn't help, reduce the basis set (not by deleting polarization functions, but by reducing the flexibility of the occupied-atomic-orbitals space, in particular *s*- and *p*-functions). Note, however, that large frozen cores can be a cause for trouble by themselves, irrespective of any relativistic feature. If you have reason to believe that your frozen cores might be too *large*, given the resulting bond lengths in your calculation, you have to pick smaller cores (and hence be very wary of using the Pauli formalism for any relativity).

12.2.6 Frequencies

Imaginary Frequencies

Problem: totally unexpected significant imaginary frequencies are obtained (in a frequencies run) where you are pretty convinced that all frequencies should be real.

Possible cause 1: problems with the electronic configuration. If there are competing configurations, the electronic *states* in the different displaced geometries may be different, resulting in energies and gradients belonging to different potential energy surfaces to be compared and combined into force constants (frequencies).

Check: orbital occupations and SCF convergence behavior: if the SCFs in the displaced geometries start with large errors and/or converge very slowly you are likely to have stumbled into different configurations, so that the results from the displaced geometries are incompatible.

Cure: This is a difficult situation that may require some experimenting and judicious manipulation of the various SCF options. The bottom line is that you should try anything you can to ensure that all involved geometries have the same electronic configuration. As long as you fail to achieve this, the results are meaningless.

Possible cause 2: flat potential energy surface (think about almost free rotation modes) coupled with relatively high noise level in gradients caused by numerical integration errors or not sufficiently converged geometry optimization.

Check: visualize the imaginary frequencies in AMSspectra and check that their respective normal modes correspond to movements that are expected to have a (nearly) flat energy profile.

Cure:

- restart geometry optimization with stricter convergence criteria. The default criterion on gradients of 0.001 Hartree/Angstrom may not be strict enough for some systems. In such cases a value of 0.0001 is recommended, and for accuracy reasons use “good” numerical quality and EXACTDENSITY (important for GGAs).

After AMSification, numerical frequencies or analytical frequencies can be computed immediately after a geometry optimization. Example input with strict settings using analytical frequencies, and a TZ2P basis set.

```
$ADFBIN/ams <<eor
  Task GeometryOptimization
  GeometryOptimization
    Convergence gradients=1e-4
  End
  Properties
    NormalModes True
  End
  NormalMode
    Hessian Analytical
  End

  Engine ADF
    NumericalQuality Good
    Basis
```

(continues on next page)

(continued from previous page)

```

      Type TZ2P
      Core None
    End
    ExactDensity
  EndEngine
eor

```

Geometry-displacement numbers in the logfile are not contiguous

Problem: successive displaced geometries in the log file are numbered, but in your case these numbers make sudden jumps, like “0, 1, 2, 5, 6, 13...”

Cause: you’re using Cartesian displacements in a system that has some symmetry in its equilibrium geometry. The program skips the displacements of symmetry-equivalent atomic coordinates to save time. The displacement counts in the logfile do not run over the actually performed displacements but over all atomic coordinates that could be displaced if no use were made of symmetry properties.

Cure: there is no error; don’t worry.

12.2.7 Input ignored

Problem: the program doesn’t get past the input and aborts with a message “EOF while reading (...)” Or the program seems to ignore some parts of the input and as a consequence goes wrong somewhere. Or it seems that part of the input has not been read correctly or not at all.

Cause 1. You have used tab characters in your input file. These are not normally visible when you edit your file, but they will affect the program’s scanning of the input. When you use tab characters in the input, it is very likely that the program will do something wrong somewhere. Tabs may be ignored by the program, so that items that you believed were separate (by a tab) are in fact read as contiguous.

Check: the input file for tab characters.

Cause 2: misuse of one of the block-type keys or general keys.

A case that relatively often shows up is typing a title as first line of the input file, *without preceding it by the keyword title*. The program does not understand this as the title, but rather tries to interpret the first word as a keyword. This leads to an error if the first word is recognized as one of the pre-defined block-type keys (possibly abbreviated).

Check: the input file for usage of block-type keys and proper usage of a title.

Cause 3: incorrect processing of expressions or unintended replacement of names by numerical values. Various kinds of mistyping or incorrect usage of variables may cause this.

Check: how the program sees input, *after parsing*. This can be done by rerunning the job, with as first line in input: `Print parser.`

This will cause the program to copy each input line *twice* to output, the second time after having parsed it. You may use `StopAfter Input` or `StopAfter Init` to let the program quit early so you can inspect what is going on with the input reading.

12.2.8 SFO Populations

In the section that prints the SFO populations of (selected) MOs you may occasionally find *negative* SFO contributions for some SFOs in some MOs. This may seem unphysical and hence suspicious, but it is only a result of the Mulliken-type analysis method that underlies the computation of the SFO contributions. See the section below that discusses the output file. Likewise for contributions larger than 100%: don't worry too much, these numbers may be correct (mathematically, given the Mulliken population formulas).

12.2.9 Error Aborts

The program performs a large number of checks during the calculation and may stop when it detects an error. It is close to impossible to show here a complete list of all possible error messages. In a large number of cases, additional information is printed in the output file to provide a clue as to the cause of the error. It is always useful to carefully inspect the printed information and try to understand the meaning of any error or warning messages. If you can't find your way out, try to get help from your ADF provider. If that fails, contact us directly at support@scm.com.

12.2.10 Warnings

The program attempts to detect bugs, instabilities, convergence problems, et cetera, and may issue warnings when something looks suspicious. This is not necessarily fatal to your results, but you should be cautious and try to understand what the messages are about. Most warnings are printed in the log file. Usually there is corresponding and more extensive information in the standard output file.

APPENDICES

13.1 Basis set file format

In `$AMSHOME/atomicdata/ADF` you can find standard basis sets (including fit sets and frozen core orbitals) for all chemical elements of the periodic table at different levels of accuracy. The database is partitioned in subdirectories. Some of these are special: for example, the subdirectory `Dirac` contains input files for the program *dirac* (computation of relativistic potentials and charge densities). Most subdirectories contain files for the create runs: for example, the subdirectories `SZ` through `TZ2P`. *The section about the STO basis sets* (page 40) describes all subdirectories in more details.

The names of the basis set files consist of two parts: the standard symbol for the chemical element and the level of frozen core approximation; e.g. `Mn.2p` is a basis set file for Manganese with a frozen core up to and including the 2p shell.

Many all-electron basis can be found in the data base, especially for the elements H-Kr. All electron basis sets for the heavier elements can be found in the `ZORA` subdirectory. Fit functions for the all-electron basis sets must include more, in particular more contracted functions than the standard fit sets that are provided in the frozen core basis set files. If you would combine a basis set with an inadequate fit set the results are unreliable and absolutely inadequate, in the same fashion as when you would have used a highly inadequate basis set.

13.1.1 Sections

The basis set file supplied to ADF in Create mode contains the following sections:

```
Title
Basis Functions
Core Expansion Functions
Core Description
Fit Functions
```

Each of these items is discussed below. The basis set file does *not* define the applied density functional, the electronic configuration, precision parameters (numerical integration, SCF convergence criterion...), etc etc. These items can be set in the normal input file if the default is not satisfactory.

Title

The title is the first record of the file. It may contain any text. Only the first 60 characters are actually used. This title is (by default) printed in the output; it is also used to stamp an identification on the result file (`adf.rkf`). The file stamp will be printed whenever you use it as a fragment file in another calculation.

Basis functions

A list of Slater type basis function characteristics. This part has the following format (example):

```

BASIS
  1s 5.4
  2s 1.24
  ...
  (etc.)
  ...
end

```

The words *basis* and *end* signal the beginning and the end of this section in the data file. The records in-between list the basis functions; each record contains the main quantum number, the angular quantum number, and the exponential decay factor for a *set* of Slater type basis functions.

The order of specification of the basis functions is not free. First must come the Core Functions used for core-orthogonalization. The CFs must be in order: s-functions first, then p-functions, then d-functions, and finally f-functions (as far as applicable). In the valence basis set there must be exactly one core-orthogonalization function for each frozen core shell (1s, 2s, 2p, ...).

Here as well as in all other function definitions below, the unit of length, implicit in the exponential decay factor, is bohr (atomic units), irrespective of the unit of length used in input for geometric items such as atomic positions (see units).

Core expansion functions

This part has the form

```

CORE ns, np, nd, nf
  1s 7.68
  ...
  (etc.)
  ...
end

```

It looks very much like the *basis functions*: a list of Slater type function descriptions, closed by *end*. The header record however (core...) contains in addition four integers ns, np, nd, nf. They are the numbers respectively of s-, p-, d-, and f- frozen core shells in the atom. If you create for instance a Ruthenium atom with a frozen core up to the 4p shell, these numbers would be 4 3 1 0 : four frozen s-shells (1s,2s,3s,4s), three frozen p-shells (2p,3p,4p), one frozen d-shell (3d), and no frozen f-shells.

The core expansion sets defined in this section are used to describe the frozen core orbitals; they are not included in the valence basis set. In the list of core expansion sets all s-type functions must come first, then the p-type functions, then the d-functions, and then the f-functions (as far as applicable).

Core description

Describes the frozen core shells as linear combinations of the core expansion functions. This section has the form

```

COREDESCRIPTION
  coefficients for the first frozen s-shell
  for the second s-shell
  for the n-th shell
  coefficients for the first frozen p-shell
  for the second p-shell
  for the d-shells
  for the f-shells
  pseudopotential parameters
end

```

For each of the angular momentum quantum numbers $l=s, p, d, f$ all n l frozen shells are described by giving expansion coefficients. There are as many coefficients as there are function *sets* with the pertaining l value in the

list of expansion functions. There are no separate coefficients for all m values: all m values are equivalent in a spherically symmetric model atom. See the Ca example below.

At the end of the (core) description section there is a record with pseudopotential parameters. The pseudopotential option, as an alternative to the frozen core approximation, is currently not supported, all values in this record must be zero, one for each frozen core shell. Equivalently you can put one zero, followed by a slash (/).

Fit functions

is again a list of Slater type functions. These are used for an expansion of the density. The Coulomb potential due to the electronic charge distribution is computed from this expansion.

The format of this section is similar to the *basis functions*:

```
FIT
 1s 10.8
...
(etc.)
...
end
```

The program cannot handle fit functions with l -value higher than 4, i.e. not higher than g -type functions. Bear this in mind if you construct alternative fit sets.

13.1.2 Example of a basis set file: Calcium

An example may serve to illustrate the format of a Create data file for DZ/Ca.2p (empty records inside and between the various sections are meaningless and ignored):

Calcium (DZ, 2p frozen)

BASIS

```
1S 15.8
2S 6.9
2P 8.1

3S 2.6
3S 3.9
3P 2.1
3P 3.4
4S 0.8
4S 1.35
4P 1.06
```

```
3D 2.000
```

END

CORE

```
2 1 0 0
1S 24.40
1S 18.25
2S 7.40
2S 4.85
3S 4.00
3S 2.55
4S 0.70
4S 1.05
4S 1.65
2P 10.85
```

(continues on next page)

(continued from previous page)

```

2P  6.45
3P  1.85
3P  2.70
3P  4.00
END

DESCRIPTION
  0.2076143E+00  0.7975138E+00 -0.7426673E-04  0.1302616E-03 -0.6095738E-04
  0.1508446E-04  0.1549420E-06 -0.2503155E-07 -0.1843317E-05
  0.8487466E-01 -0.4505954E+00  0.1009184E+01  0.9627952E-01 -0.3093986E-01
  0.1678301E-01 -0.2381843E-02  0.6270439E-02 -0.8899688E-02
  0.3454503E+00  0.6922138E+00 -0.1610756E-02  0.5640782E-02 -0.5674517E-02

0/
END

FIT
1S  31.80
2S  29.37
3S  25.15
4S  21.06
4S  13.99
5S  11.64
5S  8.05
6S  6.69
6S  4.76
6S  3.39
7S  2.82
7S  2.06
7S  1.50
2P  24.10
3P  14.78
4P  9.29
5P  5.98
6P  3.94
6P  2.24
7P  1.50
3D  16.20
4D  10.47
5D  6.91
6D  4.65
6D  2.70
7D  1.85
4F  7.00
5F  4.00
5G  3.50
END

```

13.1.3 Extending a basis set

Polarization functions are provided for most elements. We strongly recommend to use one of the default basis sets described [here](#) (page 40).

If you are considering making your own basis set by including one or more polarization functions, a good rule of thumb to choose the function characteristics is the following: take the next higher l -value that does not yet occur in the function set (however, do not go beyond f -functions: the program cannot (yet) handle g -type basis functions), select the minimum value for the main quantum number n that is compatible with the l -value (i.e.: 2p, 3d, 4f), and determine the exponential decay factor ζ , such that the function attains its maximum value at somewhere between 1/3 and 1/2 times the bond length. The functional maximum for a Slater-type function is at $R = (n - 1)/\zeta$. The maximum for r^2 times the square of a Slater-type function is at $R = n/\zeta$.

13.2 Elements of the Periodic Table

A few characteristics are predefined in ADF for all elements of the periodic table, as shown below.

The electronic configuration defines the default occupation numbers in Create mode. Basis sets for the elements Bk-Ubn ($Z=97$ -120) are only available in `$AMSHOME/atomicdata/ADF/ZORA/`.

Table 13.1: Nuclear charge Z , mass number of default isotope used for mass, and default electronic configuration used in Create mode.

Symbol	Z	mass number	electronic configuration
H	1	1	1s ¹
He	2	4	1s ²
Li	3	7	2s ¹
Be	4	9	2s ²
B	5	11	2s ² 2p ¹
C	6	12	2s ² 2p ²
N	7	14	2s ² 2p ³
O	8	16	2s ² 2p ⁴
F	9	19	2s ² 2p ⁵
Ne	10	20	2s ² 2p ⁶
Na	11	23	3s ¹
Mg	12	24	3s ²
Al	13	27	3s ² 3p ¹
Si	14	28	3s ² 3p ²
P	15	31	3s ² 3p ³
S	16	32	3s ² 3p ⁴
Cl	17	35	3s ² 3p ⁵
Ar	18	40	3s ² 3p ⁶
K	19	39	4s ¹
Ca	20	40	4s ²
Sc	21	45	3d ¹ 4s ²
Ti	22	48	3d ² 4s ²
V	23	51	3d ³ 4s ²
Cr	24	52	3d ⁵ 4s ¹
Mn	25	55	3d ⁵ 4s ²
Fe	26	56	3d ⁶ 4s ²
Co	27	59	3d ⁷ 4s ²
Ni	28	58	3d ⁹ 4s ¹ , 3d ⁸ 4s ²

continues on next page

Table 13.1 – continued from previous page

Symbol	Z	mass number	electronic configuration
Cu	29	63	$3d^{10} 4s^1$
Zn	30	64	$3d^{10} 4s^2$
Ga	31	69	$3d^{10} 4s^2 4p^1$
Ge	32	74	$3d^{10} 4s^2 4p^2$
As	33	75	$3d^{10} 4s^2 4p^3$
Se	34	80	$3d^{10} 4s^2 4p^4$
Br	35	79	$3d^{10} 4s^2 4p^5$
Kr	36	84	$3d^{10} 4s^2 4p^6$
Rb	37	85	$5s^1$
Sr	38	88	$5s^2$
Y	39	89	$4d^1 5s^2$
Zr	40	90	$4d^2 5s^2$
Nb	41	93	$4d^4 5s^1$
Mo	42	98	$4d^5 5s^1$
Tc	43	[98]	$4d^5 5s^2$
Ru	44	102	$4d^7 5s^1$
Rh	45	103	$4d^8 5s^1$
Pd	46	106	$4d^{10}$
Ag	47	107	$4d^{10} 5s^1$
Cd	48	114	$4d^{10} 5s^2$
In	49	115	$4d^{10} 5s^2 5p^1$
Sn	50	120	$4d^{10} 5s^2 5p^2$
Sb	51	121	$4d^{10} 5s^2 5p^3$
Te	52	130	$4d^{10} 5s^2 5p^4$
I	53	127	$4d^{10} 5s^2 5p^5$
Xe	54	132	$4d^{10} 5s^2 5p^6$
Cs	55	133	$6s^1$
Ba	56	138	$6s^2$
La	57	139	$5d^1 6s^2$
Ce	58	140	$4f^1 5d^1 6s^2$
Pr	59	141	$4f^3 6s^2$
Nd	60	142	$4f^4 6s^2$
Pm	61	[145]	$4f^5 6s^2$
Sm	62	152	$4f^6 6s^2$
Eu	63	153	$4f^7 6s^2$
Gd	64	158	$4f^7 5d^1 6s^2$
Tb	65	159	$4f^9 6s^2$
Dy	66	164	$4f^{10} 6s^2$
Ho	67	165	$4f^{11} 6s^2$
Er	68	166	$4f^{12} 6s^2$
Tm	69	169	$4f^{13} 6s^2$
Yb	70	174	$4f^{14} 6s^2$
Lu	71	175	$4f^{14} 5d^1 6s^2$
Hf	72	180	$4f^{14} 5d^2 6s^2$
Ta	73	181	$4f^{14} 5d^3 6s^2$
W	74	184	$4f^{14} 5d^4 6s^2$
Re	75	187	$4f^{14} 5d^5 6s^2$
Os	76	192	$4f^{14} 5d^6 6s^2$
Ir	77	193	$4f^{14} 5d^7 6s^2$
Pt	78	195	$4f^{14} 5d^9 6s^1$

continues on next page

Table 13.1 – continued from previous page

Symbol	Z	mass number	electronic configuration
Au	79	197	$4f^{14} 5d^{10} 6s^1$
Hg	80	202	$4f^{14} 5d^{10} 6s^2$
Tl	81	205	$4f^{14} 5d^{10} 6s^2 6p^1$
Pb	82	208	$4f^{14} 5d^{10} 6s^2 6p^2$
Bi	83	209	$4f^{14} 5d^{10} 6s^2 6p^3$
Po	84	[209]	$4f^{14} 5d^{10} 6s^2 6p^4$
At	85	[210]	$4f^{14} 5d^{10} 6s^2 6p^5$
Rn	86	[222]	$4f^{14} 5d^{10} 6s^2 6p^6$
Fr	87	[223]	$7s^1$
Ra	88	[226]	$7s^2$
Ac	89	[227]	$6d^1 7s^2$
Th	90	232	$6d^2 7s^2$
Pa	91	231	$5f^2 6d^1 7s^2$
U	92	238	$5f^3 6d^1 7s^2$
Np	93	[237]	$5f^4 6d^1 7s^2$
Pu	94	[244]	$5f^6 7s^2$
Am	95	[243]	$5f^7 7s^2$
Cm	96	[247]	$5f^7 6d^1 7s^2$
Bk	97	[247]	$5f^9 7s^2$
Cf	98	[251]	$5f^{10} 7s^2$
Es	99	[252]	$5f^{11} 7s^2$
Fm	100	[257]	$5f^{12} 7s^2$
Md	101	[258]	$5f^{13} 7s^2$
No	102	[259]	$5f^{14} 7s^2$
Lr	103	[266]	$5f^{14} 6d^1 7s^2$
Rf	104	[267]	$5f^{14} 6d^2 7s^2$
Db	105	[268]	$5f^{14} 6d^3 7s^2$
Sg	106	[269]	$5f^{14} 6d^4 7s^2$
Bh	107	[270]	$5f^{14} 6d^5 7s^2$
Hs	108	[269]	$5f^{14} 6d^6 7s^2$
Mt	109	[278]	$5f^{14} 6d^7 7s^2$
Ds	110	[281]	$5f^{14} 6d^8 7s^2$
Rg	111	[282]	$5f^{14} 6d^9 7s^2$
Cn	112	[285]	$5f^{14} 6d^{10} 7s^2$
Nh	113	[286]	$5f^{14} 6d^{10} 7s^2 7p^1$
Fl	114	[289]	$5f^{14} 6d^{10} 7s^2 7p^2$
Mc	115	[290]	$5f^{14} 6d^{10} 7s^2 7p^3$
Lv	116	[293]	$5f^{14} 6d^{10} 7s^2 7p^4$
Ts	117	[294]	$5f^{14} 6d^{10} 7s^2 7p^5$
Og	118	[294]	$5f^{14} 6d^{10} 7s^2 7p^6$
Uue	119	[315]	$5f^{14} 6d^{10} 7s^2 7p^6 8s^1$
Ubn	120	[299]	$5f^{14} 6d^{10} 7s^2 7p^6 8s^2$

Default (most abundant) isotope, used to set atomic mass (nr. of brackets gives mass directly). Default electronic configurations used in Create mode.

13.3 Multiplet States

Calculations with the ADF engine yield results for one-determinant electronic states, which are not always the ‘true’ states of the molecule. The evaluation of the correct multiplet energies is not trivial in this approach, see further below the section on multiplet energies. The point is to evaluate a specific multiplet state as a linear combination of selected one-determinant functions, each computed in the field of the so-called Average-of-Configuration (AOC). Typically, in an open shell system, the AOC is the spin-restricted system in which all orbitals in the open shell are degenerate and equally occupied. The AOC serves then as a fragment for the subsequent calculations, in which the different open shell orbitals are occupied differently by specifying the appropriate occupation numbers as explained below.

Important: in these follow-up calculations it is imperative that the results are obtained in the AOC field: no SCF convergence must be carried out, because we only want to assign the electrons differently, while keeping exactly the AOC orbitals. To achieve this, the follow-up calculations must use the keyword SCF, and the subkey iterations must be set to 0.

Since the ADF engine requires that the point-group symmetry matches not only to the nuclear frame but also to the electronic charge density and MO occupations, these calculations must run in a lower point group symmetry. Often you will also want to run the modified calculations spin-unrestricted. For an example, see the set of sample runs that come with the package and the discussion in the [Examples](#) (page 471).

The calculation of the one-determinant states based on the AOC reference state is controlled with the block SLATER-DETERMINANTS,

```
SLATERDETERMINANTS file
End
```

were the argument must be a file (including the path). The file must be an ASCII file containing data in the same format as you would supply in the data block, see below. All information on the file until the *eof* must be suitable for the data block, but no record ‘end’ on the file must be specified: only the *contents* of the data block.

Alternatively, you can use the SLATERDETERMINANTS block as follows

```
SLATERDETERMINANTS
  title1
    irrep occupies
    irrep occupies
    ...
  subend
  title2
    irrep occupies
    ...
  subend
  title3
    ...
  subend
  ...
end
```

Each ‘title’ functions as a subkey, but is otherwise an arbitrary string to label the resulting one-determinant calculation. Each such subkey block contains the occupation numbers for a single one-determinant calculation. It is necessary that the calculation uses the reference AOC run as its only fragment file. The occupations in the subkey blocks must be rearrangements of the AOC open-shell electrons. In the Slaterdeterminants calculation you must explicitly specify the point group symmetry in which you want to run; this must be a lower symmetry than the AOC one, otherwise you couldn’t rearrange the open shell electrons. See the sections below on multiplet energies. An sample run is included in [Examples](#) (page 471).

Each ‘irrep occupies’ record specifies the occupations for the indicated irrep in the usual way (see for instance the occupations key). The irrep labels must correspond to the (lower) point group symmetry used in the slaterdeterminants calculation.

Note that in an unrestricted calculations, occupations numbers must be given for both spins, using the double slash (//) to separate the occupations for spin- α and spin- β .

In this setup, the program will for each of the subkey blocks under the `slaterdeterminants` key execute an SCF calculation with only one cycle, i.e. no convergence, where the start-up field is the fragment field, i.e. the AOC field. So all one-determinant states in this calculation are evaluated in the AOC field. The resulting energies for the distinctly computed one-determinant states can then be combined to the desired multiplet values, corresponding to how the multiplet states are combinations of the one-determinant states.

13.3.1 Multiplet energies

The energies of atomic and molecular multiplet states that correspond to a given electron configuration can be calculated approximately with the method suggested in ref.¹. There it is indicated that it would not be justified to take an arbitrary configuration-state function (CSF), defined in general as a linear combination of determinants that has specific spin and space symmetry properties, and use the corresponding alpha and beta spin densities in a DFT energy expression. The same holds true for the densities corresponding to the average-of-configuration (see section 'DFT energy of a one-determinantal wave function', the 'procedure' notes).

Therefore, we restrict ourselves to just computing the DFT energies of single-determinant wavefunctions. Usually (but not always) this is sufficient information to obtain the multiplet energies. The procedure, which is explained in ^{Page 427, 1}, requires knowledge of the CSFs belonging to a given configuration. This means that a multiplet state with specific L, ML and S, MS values has to be written as a linear combination of the determinant wavefunctions that belong to the given configuration. In Ref.² Claude Daul exploited symmetry in order to simplify the relation between the multiplet energies and single-determinant energies.

It is often advantageous to search for CSFs that consist of one determinant only, since the energy of this determinant should correspond directly to the multiplet energy. Sometimes there is redundancy in the information and there may even be some inconsistency: two determinants may exist that both are CSFs belonging to the same multiplet state but yield somewhat different energies. We will illustrate this for the Carbon atom example treated below.

The discrepancies are a measure of 'error bars' associated with the theoretical multiplet energies. As a matter of fact, there are certain symmetry relations between the energies of the determinants of a configuration, calculated as the expectation value of the determinant for the full many-electron Hamiltonian. An example is the equal energy for the determinants of a p^1 configuration, whether the electron is placed in the p_0 ($= p_z$) orbital or in the p_{+1} ($= (p_x + ip_y)/\sqrt{2}$) orbital. This equality is not obtained with present-day density functionals, leaving an ambiguity ('error bar') in the determination of the energy. A more complete treatment of the symmetry relations between determinant energies is given in².

Warning: However, there have occasionally been found inconsistent results. A comparison to the results obtained by the procedure outlined in¹ may show significant differences and the latter seem more accurate and consistent.

DFT energy of a one-determinantal wave function

The determinant corresponds to a well defined ρ^α and ρ^β . Suppose we are dealing with a d^2 configuration and we wish to know the energy of

$$D_1 = |d_2^\alpha(1)d_1^\alpha(2)|$$

where d_m has the Y_{2m} angular part. This determinant is a CSF of the ^3F multiplet

$$D_1 = |^3F; M_L = 3; M_S = 1\rangle$$

We can easily transform to the real spherical harmonics that are used in the ADF engine:

$$Z_{lm}^C = \frac{1}{\sqrt{2}}(Y_l^{-m} + Y_l^{-m*}) = \frac{1}{\sqrt{2}}(Y_l^{-m} + (-1^m)Y_l^m)$$

¹ T. Ziegler, A. Rauk and E.J. Baerends, *On the calculation of Multiplet Energies by the Hartree Fock Slater method*, *Theoretica Chimica Acta* 43, 261 (1977) (<https://doi.org/10.1007/BF00551551>)

² C. Daul, *DFT applied to excited states*, *International Journal of Quantum Chemistry* 52, 867 (1994) (<https://doi.org/10.1002/qua.560520414>)

$$Z_{lm}^S = \frac{i}{\sqrt{2}}(Y_l^{-m} + Y_l^{-m*}) = \frac{i}{\sqrt{2}}(Y_l^{-m} + (-1^m)Y_l^m)$$

with back transformations:

$$Y_l^m = \frac{1}{\sqrt{2}}(-1)^m(Z_{lm}^C + iZ_{lm}^S)$$

$$Y_l^{-m} = \frac{1}{\sqrt{2}}(Z_{lm}^C - iZ_{lm}^S)$$

Here the superscripts c and s stand for the cosine, respectively sine type of combinations of $\exp(-im\phi)$ and $\exp(im\phi)$. This yields explicitly:

$$\begin{aligned}d_{z^2} &= d_0 \\d_{xz} &= 1/\sqrt{2}(d_{-1} - d_1) \\d_{yz} &= i/\sqrt{2}(d_{-1} + d_1) \\d_{x^2-y^2} &= 1/\sqrt{2}(d_{-2} + d_2) \\d_{xy} &= i/\sqrt{2}(d_{-2} - d_2) \\d_0 &= d_{z^2} \\d_1 &= -1/\sqrt{2}(d_{xz} + id_{yz}) \\d_{-1} &= 1/\sqrt{2}(d_{xz} - id_{yz}) \\d_2 &= 1/\sqrt{2}(d_{x^2-y^2} + id_{xy}) \\d_{-2} &= 1/\sqrt{2}(d_{x^2-y^2} - id_{xy})\end{aligned}$$

For D_1 we obtain:

$$\begin{aligned}\rho_\alpha &= |d_2|^2 + |d_1|^2 = 1/2|d_{x^2-y^2}|^2 + 1/2|d_{xy}|^2 + 1/2|d_{xz}|^2 + 1/2|d_{yz}|^2 \\ \rho_\beta &= 0\end{aligned}$$

The fractional occupations have to be used in order to generate the densities ρ_α and ρ_β and the corresponding density matrices ρ_α and ρ_β . The density matrices can be used to calculate the energy of D_1 (and ${}^3F$) with respect to the energy of the ‘master fragment’, which should be the restricted atom with d^2 occupation. Other determinants of this configuration can be treated similarly to obtain more multiplet energies of the d^2 configuration.

Below is an example of how you can obtain determinant energies ‘by hand’, i.e. by carrying out a specific sequence of ADF calculations. The ADF engine supports an automatic procedure to do this, using the input key SLATERDETERMINANTS, see the ADF User’s Guide, the [Examples](#) (page 471), and below.

Procedure

1. Determine a set of orbitals belonging to the given configuration. These orbitals are generated in what we call the average-of-configuration (AOC) calculation. This is a spin-restricted SCF calculation where the electrons of the configuration are distributed equally over the subspecies of the open shell irreps in order to retain the A1 symmetry of the total density in the symmetry group of the molecule. For instance, in case of an atomic d^2 configuration, the AOC calculation can be done in symmetry atom with occupation 2 in the d irrep. In case of an $t_{2g}^5 e_g^1$ configuration of an octahedral complex, the AOC calculation requires an occupation of 5 electrons in the t_{2g} , and 1 electron in the e_g . The result file adf.rkf of the AOC calculation has to be saved, to be used as a fragment file in the subsequent calculations.
2. The AOC is used as a fragment in all subsequent calculations that are performed to obtain single determinant energies. This means that those single determinant energies are always with respect to the AOC energy. This is a case where there is only one “fragment”, which is actually the complete system, but in a different electronic configuration and in possibly a different symmetry group.

Suppose that a single determinant corresponds to spin-up and spin-down densities ρ^α and ρ^β , i.e. to specific spin-unrestricted occupations of the AOC orbitals. These densities ρ^α and ρ^β correspond to a symmetry group that will in

general be a subgroup of the symmetry group of the molecule. For instance, the occupation $(p_{+1} \alpha)^1$ in the case of an atomic p^1 configuration corresponds to

$$\rho^\alpha = 1/2p_x^2 + 1/2p_y^2$$

with $D_{\infty h}$ symmetry.

To obtain the energy of the determinant wave function we must now perform *one* cycle (iterations= 0 in the block key SCF) of a spin-unrestricted calculation, with AOC as (the only) fragment with alpha and beta occupation numbers (using the input key occupations) such that ρ^α and ρ^β result. Note that the appropriate (lower) symmetry point group must be specified in the input file.

Occasionally, the single determinant corresponds to a closed shell configuration in the appropriate lower symmetry, for instance determinant $D_{10} = |0^+ 0^-|$ of the p^2 configuration of Carbon, with density $r=p_z^2$. In that case the one-cycle calculation can of course be spin-restricted.

N.B.1. One cycle will regenerate the SCF orbitals of AOC, if the same field is used as the converged AOC field. This will actually be the case because the starting potential is taken from the fragment adf.rkf file. The key `modifstartpotential` must not be used (the density should be distributed equally over the spins).

N.B.2. After diagonalization in the one-cycle run, the AOC orbitals have been obtained again and are occupied as specified. The ('bonding') energy is calculated from the resulting charge density.

Remarks:

- If one does not perform just one cycle, but instead converges the unrestricted calculation, the energy will be lowered by 'polarization' of the orbitals. It is theoretically not so clear what the status of such converged energies is. Usually the energy lowering is in the order of 0.1 eV, but it may be quite a bit larger.
- It is not necessary to use AOC as fragment in the single-determinant runs. It is also perfectly allowed to run all calculations (ground state, AOC, determinants) from one set of fragments, for instance the standard atomic fragments. Since we must arrange that the one-cycle determinant calculations use the AOC field, so as to reproduce the AOC orbitals, we must then supply the result file adf.rkf of the AOC run as a restart file, using the key `restart`; see the adf User's Guide. Of course, in such an approach the computed energies are with respect to another reference, for instance the restricted atoms.

Results for first period atoms

In one of the next sections tables are given for the energy lowering in going from the converged spherically symmetric spin-restricted atom (the 'master' fragment) to specific one-determinant wavefunctions with the orbital occupations as specified. Note that the p_x and p_y populations are always equal; only their sum is given. In many cases the determinant corresponds to a specific state, which is then given in the last column. For each atom, the first calculation is for the spherically symmetric spin-unrestricted atom. These tables are now obsolete, all information needed to obtain the atomic reference energies, i.e. the ground state multiplet energy with respect to the AOC, can be found in ref.³.

Examples worked out for all first period atoms:

H: Configuration $(1s)^1$. Only one determinant: $|1s \alpha (1)|$

He: Configuration $(1s)^2$. Closed shell.

Li: Configuration $(2s)^1$. Only one determinant: $|2s \alpha (1)|$

Be: Configuration $(2s)^2$. Closed shell.

B: Configuration $(2p)^1$.
Ground multiplet ^2P .

$$D_1 = |p_1 \alpha (1)| = |^2P; M_L = 1; M_S = 1/2\rangle$$

$$\rho^\alpha = 1/2(p_x - ip_y)(p_x + ip_y) = 1/2(p_x^2 + p_y^2)$$

³ E.J. Baerends, V. Branchadell and M. Sodupe, *Atomic reference-energies for density functional calculations*, *Chemical Physics Letters* 265, 481 (1997) ([https://doi.org/10.1016/S0009-2614\(96\)01449-2](https://doi.org/10.1016/S0009-2614(96)01449-2))

The occupation numbers for D_1 are

$$p_x^\alpha = p_y^\alpha = 1/2$$

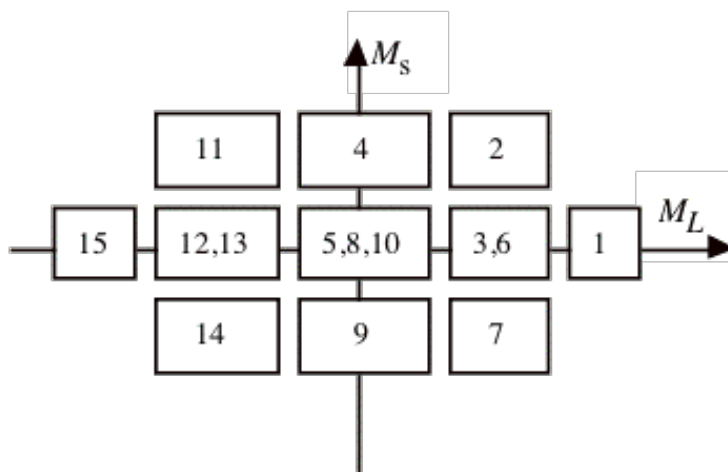
$$p_z^\alpha = p_x^\beta = p_y^\beta = p_z^\beta = 0$$

Another determinant belonging to ^2P is $D_2 = |..p_0 \alpha(1)|$ with occupations $p_z^\alpha = 1$ and all other p-occupations zero. This determinant is 0.04 eV lower in energy than D_1 for LDA, but 0.15 eV for BP.

C: Configuration p^2 .

Multiplet states are ^3P , ^1S and ^1D . We use this atom as an example of the general procedure. First write down all determinants belonging to p^2 and group them according to M_S and M_L ($1^+ \equiv p_1 \alpha, \dots$)

Determinant	M_S	M_L
$D_1 = 1^+ 1^- $	0	2
$D_2 = 1^+ 0^+ $	1	1
$D_3 = 1^+ 0^- $	0	1
$D_4 = 1^+ -1^+ $	1	0
$D_5 = 1^+ -1^- $	0	0
$D_6 = 1^- 0^+ $	0	1
$D_7 = 1^- 0^- $	-1	1
$D_8 = 1^- -1^+ $	0	0
$D_9 = 1^- -1^- $	-1	0
$D_{10} = 0^+ 0^- $	0	0
$D_{11} = 0^+ -1^+ $	1	-1
$D_{12} = 0^+ -1^- $	0	-1
$D_{13} = 0^- -1^+ $	0	-1
$D_{14} = 0^- -1^- $	-1	-1
$D_{15} = -1^+ -1^- $	0	-2



The presence of a determinant with $M_L = 2$, $M_S = 0$ and no $M_L = 2$, $M_S = 0$ determinant indicates the presence of a ^1D multiplet, and $E(^1D) = E(D_1)$. There is also a ^3P , the determinant with $M_S = 1$, $M_L = 1$. We should have $E(^3P) = E(D_2) = E(D_4)$. The two determinants D_3 and D_6 in the $M_S = 0$, $M_L = 1$ box will mix, and the solutions of the 2 by 2 secular problem will be $E(^1D)$ and $E(^3P)$. Since the sum of the eigenvalues is equal to the sum of the initial diagonal elements, we have $E(^1D) + E(^3P) = E(D_3) + E(D_6)$. We should also have $E(D_3) + E(D_6) = E(D_1) + E(D_2)$. Such a relation provides a test on the consistency of the results. Finally we have the $M_S = 0$, $M_L = 0$ block. The sum of the energies of D_5 , D_8 and D_{10} should be the sum of the energies of ^1S , ^3P and ^1D . Since $E(^3P)$ and $E(^1D)$ are already known, $E(^1S)$ can be calculated.

In the appendix we first locate for C the spherical unrestricted atom. Next we have $E(D_4)$, yielding $E(^3P) = -1.345$ eV (LDA + Becke). Next $E(D_2) = E(^3P) = -1.189$ (always LDA + Becke). The difference is substantial: ~ 0.15 . Next we have $E(D_3) = -0.812$. Since $E(D_6) = E(D_3)$, because $\rho^\alpha(D_6) = \rho^\beta(D_3)$ and $\rho^\beta(D_6) = \rho^\alpha(D_3)$, we should have $2E(D_3) = -1.624 = E(^1D) + E(^3P)$. Therefore $E(^1D) = -1.624 - (-1.345) = -0.279$ or $E(^1D) = -1.624 - (-1.189) = -0.435$. These numbers can be checked against $E(D_1)$ which also should be $E(^1D)$: $E(D_1) = +0.044$. The discrepancy is large! Finally, ^1S can be obtained: $E(D_{10}) = +0.319$ (D_8) = $E(D_1) = +0.044$ $E(D_5) = E(D_1) = +0.044$. So $0.407 = E(^1S) + E(^3P) + E(^1D)$. Different results for $E(^1S)$ are obtained depending on the $E(^3P)$ and $E(^1D)$ we choose: e.g. $E(^1S) = 0.407 - (-1.345) - (-0.279) = 2.031$ or $E(^1S) = 0.407 - (-1.189) - (0.044) = 1.552$. Comparing to experiment we might calculate the excitation energies w.r.t. $E(^3P)$:

	calculated	experimental	HF
$^3P \rightarrow ^1D$:	1.066 to 1.389	1.26	1.55
$^3P \rightarrow ^1S$:	2.741 to 3.376	2.684	3.78

N: Configuration p^3 .

Ground multiplet ^4S , corresponds to the spherical unrestricted atom, energy -2.943 eV. Other multiplets: ^2P , ^2D . According to the printed output for configuration p^3 we have $|^2D; M_L=2; M_S=1/2\rangle = |p_1^\alpha p_1^\beta p_0^\alpha\rangle = D_2 \rho^\alpha = 1/2 p_x^2 + 1/2 p_y^2 + p_z^2 \rho^\beta = 1/2 p_x^2 + 1/2 p_y^2$ $E(D_2) = -0.745$ according to the table in the Appendix (LDA + Becke). The energy of D_1 , with $\rho^\alpha = p_x^2 + p_y^2$, $\rho^\beta = p_z^2$, is $E(|1A\ 2B\ 3A\rangle) = -1.9702$. The energy of D_3 , with $\rho^\alpha = 1/2 p_x^2 + 1/2 p_y^2 + p_z^2$, $\rho^\beta = p_z^2$ corresponding to $|1A\ 2A\ 2B\rangle$ or $|2A\ 2B\ 3A\rangle$, is $E(D_3) = -0.158$. Finally, D_4 has $\rho^\alpha = p_x^2 + p_y^2$, $\rho^\beta = 1/2 p_x^2 + 1/2 p_y^2$, corresponding to $|1A\ 1B\ 3A\rangle$ and $|1A\ 3A\ 3B\rangle$, and $E(D_4) = -0.109$. The $M_L = 1$, $M_S = 1/2$ determinants are $|1A\ 1B\ 3A\rangle$ and $|1A\ 2A\ 2B\rangle$. Therefore $E(^2D) + E(^2P) = E(D_4) + E(D_3)$, so $E(^2P) = -0.109 - 0.158 - (-0.745) = +0.478$. We can use D_1 in the $M_L=0$, $M_S=1/2$ block, from which we find $E(^4S) + E(^2D) + E(^2P) = 2E(D_2) = +E(D_1)$. Hence $E(^2P) = -1.490 - 1.9702 - (-0.745) - (-2.943) = +0.2278$.

O: Configuration p^4 .

Multiplet states ^3P , ^1S , ^1D . D_1 , with $\rho^\alpha = p_x^2 + p_y^2 + p_z^2$, $\rho^\beta = p_z^2$ corresponds to $|1A\ 2A\ 2B\ 3A\rangle$, the $M_L=1$, $M_S=1$ determinant of ^3P : $E(^3P) = -1.836$ D_2 with $\rho^\alpha = p_x^2 + p_y^2 + p_z^2$, $\rho^\beta = 1/2 p_x^2 + 1/2 p_y^2$, corresponds to $|1A\ 1B\ 2A\ 3A\rangle$, the determinant of ^3P : $E(^3P) = -1.568$ D_3 , with $\rho^\alpha = 1/2 p_x^2 + 1/2 p_y^2 + p_z^2$, $\rho^\beta = p_x^2 + p_y^2$, corresponds to $|1A\ 1B\ 2A\ 3B\rangle$, and $M_L=1$, $M_S=0$ belonging to ^3P as well as ^1D .

F: Configuration p^5 .

Ground multiplet ^2P . As in B, we have two determinants with different energies belonging to this state: $D_1 = |\dots(p_0^\alpha)^\dagger (p_0^\beta)^0\rangle \rightarrow E(D_1) = -0.715$. $D_2 = |(p_{-1})^2 (p_0)^2 (p_1^\alpha)^\dagger (p_1^\beta)^0\rangle \rightarrow E(D_2) = -0.467$.

Ne: Configuration p^6 . Closed shell.

Ground and Excited State Multiplets

The computation of multiplets can be carried out with adf, using the input block SLATERDETERMINANTS.

The method described in¹ for the calculation of the energies of proper spin and spatial symmetry adapted Configuration State Functions is based on the calculation of the energies of single determinantal wavefunctions. The densities corresponding to those Slater determinants are inserted in the approximation used for the exchange-correlation energy.

The procedure as detailed above is somewhat involved. Moreover, one would like to have an easy procedure to calculate many determinants. This is particularly desirable if one wishes to calculate the energies of all Slater determinants of a given configuration, for instance if one wishes to calculate certain averages in view of the inconsistencies of the method.

We have implemented a semi-automatic procedure, using the block SLATERDETERMINANTS.

The general idea of this method is to first perform a restricted calculation in the symmetry that is appropriate for the molecule. This is called the average-of-configuration (AOC) calculation. This AOC calculation generates the orbitals which will be used in all the Slater determinants.

The AOC is the fragment that *must* be used in all subsequent calculations. The subsequent calculations are characterized by having the AOC as the (only) fragment, and by specifying the keyword SLATERDETERMINANTS. If an argument is

given this must be a file name. The named file should contain the occupations for the determinants (see below). If no file name is specified, the occupations should be specified in the data block.

The required information, on file or in the data block, is the specification of the determinant or determinants that are to be calculated in the form of orbital occupation numbers for the AOC orbitals, using the irrep labels of the point group of the AOC calculation, see below for format. All specified determinants will be calculated, and the obtained energy will always be the energy difference with respect to the AOC. Default occupations for all subspecies of the AOC fragment are the occupations of the AOC itself. Therefore, only the open (modified) subspecies have to be specified.

One has to be careful with respect to the point group symmetry to use in the `SLATERDETERMINANTS` calculation. The density belonging to a specific determinant is usually lower than the AOC symmetry (which is the full symmetry group of the system). In that case this lower point group symmetry has to be specified in the `SLATERDETERMINANTS` calculation. Everything will always work fine if one just does not use any symmetry at all (nosym). However, if for reasons of computational efficiency one does want to use a subgroup of the system that corresponds to the determinant density or densities, this is perfectly possible. However, all the densities of the determinants specified *must* then have this (or a higher) symmetry. The program does not check on this, it is the user's responsibility to make sure that this condition is satisfied for all the determinants. The only check that is performed is that occupations of equivalent representations (subspecies of one irrep) in the lower point group of the `SLATERDETERMINANTS` run, that result from the specified occupations of the subspecies of the AOC symmetry, are equal.

Format of the input.

Important: in the SlaterDeterminants calculations it is imperative that the results are obtained in the AOC field: no SCF convergence must be carried out, because we only want to assign the electrons differently, while keeping the AOC orbitals exactly as they are. To achieve this, the calculations should use the keyword SCF, and the subkey iterations has to be set to 0 in the SCF data block.

Since adf requires that the point-group symmetry conforms not only to the nuclear frame but also to the electronic charge density and mo occupations, these calculations must run in a lower point group symmetry. Often you will also want to run the modified calculations spin-unrestricted.

For an example, see the set of sample runs that come with the package and the comments in the examples.

See: *SLATERDETERMINANTS block* (page 426). Each 'title' functions as a subkey, but is otherwise an arbitrary string to label the resulting one-determinant calculation. Each such subkey block contains the occupation numbers for a single one-determinant calculation. It is necessary that the calculation uses the reference AOC run as its only fragment file. The occupations in the subkey blocks must be re-arrangements of the AOC open-shell electrons. In the `SLATERDETERMINANTS` calculation you must explicitly specify the point group symmetry in which you want to run. The ρ^α and ρ^β densities of all determinants to be calculated must have this point group symmetry, or a higher symmetry.

Each 'irrep occurs' record specifies the occupations for the indicated irrep in the usual way (see for instance the occupations key). The irrep labels must correspond to the AOC point group symmetry used in the AOC calculation, *not the point group symmetry used in the "SLATERDETERMINANTS" calculation!*. Note that in an unrestricted calculations, occupations numbers must be given for both spins, using the double slash (//) to separate the occupations for spin-alpha and spin-beta.

In this setup, the program will for each of the subkey blocks under the `SLATERDETERMINANTS` key execute an SCF calculation with only one cycle, i.e. no convergence, where the start-up field is the fragment field, i.e. the AOC field. So all one-determinant states in this calculation are evaluated in the AOC field. The resulting energies for the distinctly computed one-determinant states can then be combined to the desired multiplet values.

Example: Carbon p^2

```
SlaterDeterminants
C(p2) ALFA: s=1, px=py=2/3, pz=2/3; BETA: s=1, p=0 ! title
  S 1 // 1 ! irrep name and occupations
  P:x 0.6666666666666666 // 0 ! another irrep, et cetera
  P:y 0.6666666666666666 // 0
  P:z 0.6666666666666666 // 0
  D:z2 0 // 0
```

(continues on next page)

(continued from previous page)

```

D:x2-y2 0 // 0
D:xy 0 // 0
D:xz 0 // 0
D:yz 0 // 0
SUBEND
C(p2) ALFA: S=1, px=py=1, pz=0; BETA: s=1 !next (Sl.Determinant) title
S 1 // 1
P:x 1 // 0
P:y 1 // 0
P:z 0 // 0
D:z2 0 // 0
D:x2-y2 0 // 0
D:xy 0 // 0
D:xz 0 // 0
D:yz 0 // 0
SUBEND
C(p2) ALFA: s=1, px=py=0.5, pz=1; BETA: s=1
S 1 // 1
P:x 0.5 // 0
P:y 0.5 // 0
P:z 1 // 0
D:z2 0 // 0
D:x2-y2 0 // 0
D:xy 0 // 0
D:xz 0 // 0
D:yz 0 // 0
SUBEND
C(p2) ALFA: s=1, px=py=0.5, pz=0; BETA: s=1, px=py=0, pz=1
S 1 // 1
P:x 0.5 // 0
P:y 0.5 // 0
P:z 0 // 1
D:z2 0 // 0
D:x2-y2 0 // 0
D:xy 0 // 0
D:xz 0 // 0
D:yz 0 // 0
SUBEND
C(p2) ALFA: s=1, px=py=0.5, pz=0; BETA: s=1, px=py=0.5, pz=0
S 1 // 1
P:x 0.5 // 0.5
P:y 0.5 // 0.5
P:z 0 // 0
D:z2 0 // 0
D:x2-y2 0 // 0
D:xy 0 // 0
D:xz 0 // 0
D:yz 0 // 0
SUBEND
C(p2) ALFA: s= 1, px=py=0, pz=1; BETA: s=1, px=py=0, pz=1
S 1 // 1
P:x 0 // 0
P:y 0 // 0
P:z 1 // 1
D:z2 0 // 0
D:x2-y2 0 // 0
D:xy 0 // 0

```

(continues on next page)

(continued from previous page)

```
D:xz 0 // 0
D:yz 0 // 0
SUBEND
```

In the example the AOC calculation is the Carbon atom in spherical symmetry (symmetry name atom).

Several spin states can be generated from this AOC set of orbitals, but they all have a lower symmetry than the AOC. In the example the point group $D_{\infty h}$ (DLIN) could be used in the SLATERDETERMINANTS calculation. In $D_{\infty h}$ the p orbitals split into two sets, p_x^* and p_y^* occur in π_x and π_y respectively, so their occupations must be identical, and p_z^* is a Σ_u orbital.

In the block SLATERDETERMINANTS (or in the file) we now specify the occupations for the subspecies of the atom irreps of a specific Slater determinant and the program will sort out the corresponding occupations in the d(lin) symmetry.

In all cases the orbitals used for the energy calculation(s) will be the self-consistent AOC orbitals.

In the given example, the first set of occupations does not correspond to a Slater determinant, but is the spin-polarized spherical case with the p electrons evenly distributed over all components.

LDA results, with and without GGA (Becke-Perdew)

Energy changes (eV) for atoms going from restricted to (one-cycle) unrestricted. Results between parentheses are for converged unrestricted calculations)

All calculations have been performed in $D_{\infty h}$ symmetry, since p_x and p_y always had equal occupations and therefore could occur as π_u -x and π_u -y partners of the Π_u irrep.

El.	Occupations alpha-spin			beta-spin			LDA	LDA+Becke	BP
	s	px+py	pz	s	px+py	pz			
H	1	0	0	0	0	0	-0.868 (-0.898)	-0.758 (-0.837)	-0.889 (-0.948)
Li	1	0	0	0	0	0	-0.231 (-0.235)	-0.195 (-0.207)	-0.249 (-0.256)
Be	1	0	0	1	0	0	0.000 (0.000)	0.000 (0.000)	0.000 (0.000)
B	1	2/3	1/3	1	0	0	-0.247 (-0.255)	-0.231 (-0.242)	-0.276 (-0.281)
	1	0	1	1	0	0	-0.295 (-0.321)	-0.436 (-0.474)	-0.448 (-0.485)
	1	1	0	1	0	0	-0.266 (-0.279)	-0.296 (-0.316)	-0.333 (-0.348)
C	1	4/3	2/3	1	0	0	-1.163 (-1.203)	-1.109 (-1.158)	-1.252 (-1.285)
	1	2	0	1	0	0	-1.152 (-1.211)	-1.271 (-1.345)	-1.372 (-1.436)
	1	1	1	1	0	0	-1.152 (-1.197)	-1.134 (-1.189)	-1.267 (-1.307)
	1	1	0	1	0	1	-0.462 (-0.506)	-0.726 (-0.812)	-0.778 (-0.868)
	1	1	0	1	1	0	0.159 (0.150)	0.039 (0.044)	0.087 (0.086)
	1	0	1	1	0	1	0.730 (0.668)	0.322 (0.319)	0.480 (0.450)
N	1	2	1	1	0	0	-2.936 (-3.032)	-2.827 (-2.943)	-3.101 (-3.190)
	1	2	0	1	0	1	-1.362 (-1.454)	-1.811 (-1.972)	-1.943 (-2.108)
	1	1	1	1	1	0	-0.581 (-0.618)	-0.688 (-0.745)	-0.746 (-0.801)
	1	1	1	1	0	1	0.178 (0.088)	-0.104 (-0.158)	-0.069 (-0.140)
	1	2	0	1	1	0	0.197 (0.135)	-0.077 (-0.109)	-0.011 (-0.053)
O	1	2	1	1	2/3	1/3	-1.400 (-1.477)	-1.361 (-1.447)	-1.480 (-1.552)
	1	2	1	1	0	1	-1.442 (-1.583)	-1.698 (-1.836)	-1.816 (-1.957)
	1	2	1	1	1	0	-1.422 (-1.515)	-1.470 (-1.568)	-1.590 (-1.678)
	1	1	1	1	2	0	-0.564 (-0.623)	-0.866 (-0.960)	-0.913 (-1.013)
	1	1	1	1	1	1	0.358 (0.321)	0.255 (0.237)	0.292 (0.266)
F	1	2	0	1	2	0	1.323 (1.220)	0.825 (0.789)	0.992 (0.932)
	1	2	1	1	4/3	2/3	-0.374 (-0.398)	-0.366 (-0.391)	-0.394 (-0.416)
	1	2	1	1	2	0	-0.323 (-0.409)	-0.605 (-0.686)	-0.627 (-0.715)
	1	2	1	1	1	1	-0.349 (-0.389)	-0.401 (-0.441)	-0.427 (-0.467)

13.4 Dirac program: relativistic core potentials

In all relativistic calculations - scalar as well as spin-orbit - the relativistic atomic core densities and the relativistic atomic potentials *must* be made available to ADF on a file specified with the key COREPOTENTIALS. This is necessary only in the 'create' run of the atoms. In the molecular calculation this key is not required anymore. If supplied then the file must contain data for *all* atom types in the molecule, even for those atoms where relativistic aspects are expected to be negligible or that may not have a frozen core at all (such as Hydrogen). Excepted are any Ghost atoms (for instance for a BSSE calculation): these can not have any core potentials. This is tested by the program, internally, by looking at the nuclear charge and at the number of electrons belonging to an atom: if both numbers are zero, no (relativistic or other) core potential is allowed. Also the potential used in the ZORA kinetic energy operator in the MAPA (the Minimum of neutral Atomic potential Approximation) method should be present on this file (which will be the case if the program DIRAC is used to generate this file).

Relativistic potentials can and should be generated with the auxiliary program `dirac`, see the next section, and the examples (in particular *Example: Gold electrodes* (page 1089)).

The recommended way to generate atomic fragments and relativistic potentials is by using the *BASIS* (page 44) keyword.

The auxiliary program DIRAC, which is installed in the Amsterdam Modeling Suite, serves to compute relativistic frozen core potentials (and densities), necessary to apply the (scalar) relativistic option in ADF. `$AMSHOME/atomicdata` has a subdirectory `Dirac`, which contains input files for DIRAC for all atoms of the periodic table of elements. The *names* of the input files indicate the frozen core level: *Ag.3d* for instance is the input file for a calculation on a Silver atom with a frozen core up to and including the 3d shell (i.e.: 1s, 2s, 2p, 3s, 3p, and 3d). The frozen core level used in the DIRAC calculation defines the core data computed and should therefore match the frozen core level in the ADF Create run for the atom that it will be used for.

A DIRAC run with the inputs provided in the `$AMSHOME/atomicdata/Dirac/` involves a fully relativistic calculation on the atom (spin-orbit coupling, double group symmetries). It generates a file TAPE12 with the corresponding core potential and density (a table of values for a sequence of radial distance values). Other files produced by DIRAC should be removed after the DIRAC run; they are needed for other applications of the program but play no role here.

If you run DIRAC while a file TAPE12 already exists the computed core data will be written at the end of it, after the existing data. The program will assume, however, that the existing data on the file are also core-data from DIRAC runs, and may abort otherwise.

Starting from ADF2006.01 it is not necessary anymore to make one big TAPE12 which contains data for all atoms involved in the molecular calculation. Instead only in the ADF Create run for each atom one needs a TAPE12 which contains data for the atom that is created. The corresponding core data is written to the `adf.rkf` of this atomic fragment. In the molecular ADF run one then should not include the CorePotentials key, such that ADF will read core data on the `adf.rkf`'s of the atomic fragments. One can still use the CorePotentials key, but then one should proceed as in previous releases.

Implied options

The DIRAC calculations imply the *local* Density Functional in its simple X-alpha approximation without any gradient corrections. Not the *scalar* relativistic but the *fully* relativistic Hamiltonian is used, including spin-orbit coupling. In ADF you may use the *scalar* relativistic Hamiltonian and most users will employ a more sophisticated *lda* than X-alpha, such as the default *vwn* (Vosko, Wilk, Nusair) formulas, and may in addition routinely apply gradient corrections. The core potential may not exactly match the Fock operator applied in the molecular calculation. The effect is very small and one can neglect the discrepancy.

Input

The ASCII input files for DIRAC, as available in the directory `$AMSHOME/atomicdata/Dirac` (point nucleus) and `$AMSHOME/atomicdata/Dirac.gaussian` (finite nucleus), have a structure as described below. With this information you should be able to construct alternative input files, with other frozen cores for instance.

1. Title (60 characters at most). Plays no role

2. Ngrid, Nshell, rmin, rmax, Z, Xion, Anuc Ngrid=number of radial grid points, in which the core potentials are computed. Nshell=number of atomic orbital shells rmin, rmax=minimum and maximum radial grid values Z=nuclear charge Xion=net charge of the 'atom' Anuc=atomic weight
3. Pinit, Pfinal, eps, del, delrv Pinit, Pfinal= initial and final density iteration averaging factors. Each iteration cycle changes the actual averaging factor by taking the average of the previous and the final one, starting with the 'initial' one. eps=Exp(-sqrt(eps)) is set to zero, so eps determines the exponential underflow control. del=absolute convergence criterion for orbital eigenenergies. delrv=convergence criterion on the potential (multiplied by the radial distance r).
4. Idirc, Nmax, Ndebu, Nprin, Ipun, Ircor, Iwcor Idirc=zero for non-relativistic, otherwise one. Nmax=maximum number of iterations allowed to reach convergence. Ndebu=non-zero for additional output (for debugging purposes mainly) Nprin=print parameter. Use 2 or larger to get the orbitals printed. Ipun=punched output is produced if Ipun is non-zero. (out-of-date) Ircor=number of core orbitals from the fully relativistic run, to be kept frozen in the subsequent (if any) first-order perturbation calculation. Iwcor=number of core orbitals used to construct the core density and core potential, that are output on TAPE12. So, here you specify the relativistic core.
5. Xalph, Xlatt, Rnuc Xalph= Exchange parameter in the Xalpha formalism. Xlatt=Coulomb tail parameter Rnuc=size of nuclear radius, in bohr. If set to 1.0 or larger, it is recomputed as $0.0000208 \cdot \text{Anuc}^{1/3}$
6. For each orbital shell: N, L, J, E, Z, D N, L, J = The usual orbital quantum numbers. J is used only for relativistic runs. E = Initial estimate of orbital energy, in atomic units. Z = Number of electrons on the shell D = Initial estimate of the error in the orbital energy
7. Icorp, Npcl, Demp, Peps Icorp = If 1 (one): Do a first order perturbation calculation after the fully relativistic run. This option plays no role in the current application for ADF. Npcl = Maximum number of cycles in the perturbation calculation. Demp = Damping factor in the perturbation iterations Peps = Convergence criterion in the perturbation iterations.

13.5 Symmetry

Note: Starting from the 2020 release, ADF does not automatically symmetrize and re-orient the molecule. If your molecule is symmetric and you want to make sure that the highest possible symmetry is used, you should either

- Symmetrize your molecule in AMSinput using the symmetrize button 
- Use the **System%Symmetrize** option in the [AMS driver](#)

13.5.1 Schönflies symbols and symmetry labels

A survey of all point groups that are recognized by ADF is given below. The table contains the Schönflies symbols together with the names of the subspecies of the irreducible representations as they are used internally by ADF. The subspecies names depend on whether single-group or double-group symmetry is used. Double-group symmetry is used only in relativistic spin-orbit calculations.

Note that for some input of TDDFT (Response) calculations, other conventions apply for the subspecies, see below.

Table 13.2: Schönflies symbols and the labels of the irreducible representations.

Point Group	Schönflies Symbol in ADF	Irreducible representations in single-group symmetry	Irreducible representations in double-group symmetry
C ₁	NOSYM	A	A1/2
R ³	ATOM	s p d f	s1/2 p1/2 p3/2 d3/2 d5/2 f5/2 f7/2
T _d	T(D)	A1 A2 E T1 T2	E1/2 U3/2 E5/2
O _h	O(H)	A1.g A2.g E.g T1.g T2.g A1.u A2.u E.u T1.u T2.u	E1/2.g U3/2.g E5/2.g E1/2.u U3/2.u E5/2.u
C _{∞v}	C(LIN)	Sigma Pi Delta Phi	J1/2 J3/2 J5/2 J7/2
D _{∞h}	D(LIN)	Sigma.g Sigma.u Pi.g Pi.u Delta.g Delta.u Phi.g Phi.u	J1/2.g J1/2.u J3/2.g J3/2.u J5/2.g J5/2.u J7/2.g J7/2.u
C _i	C(I)	A.g A.u	A1/2.g A1/2.u
C _s	C(S)	AA AAA	A1/2 A1/2*
C _n	C(N), n must be 2	A B	A1/2 A1/2*
C _{nh}	C(NH), n must be 2	A.g B.g A.u B.u	A1/2.g A1/2.g* A1/2.u A1/2.u*
C _{nv}	C(NV), n<9	A1 A2 B1 B2 E1 E2 E3 ... odd n: without B1 and B2	E1/2 E3/2 E5/2 ... odd n also: An/2 An/2*
D _n	D(N), n<9	n=2: A B1 B2 B3 other: A1 A2 B1 B2 E1 E2 E3 ... odd n: without B1 B2	E1/2 E3/2 ... odd n also: An/2 An/2*
D _{nh}	D(NH), n<9	n=2: A.g B1.g B2.g B3.g A.u B1.u B2.u B3.u other: A1.g A2.g B1.g B2.g E1.g E2.g E3.g ... A1.u A2.u B1.u ... odd n: AA1 AA2 EE1 EE2 ... AAA1 AAA2 EEE1 EEE2	E3/2.g E3/2.u ... odd n: E1/2 E3/2 E5/2 ...
D _{nd}	D(ND), n<9	even n: A1 A2 B1 B2 E1 ... odd n: A1.g A2.g E1.g E2.g ... E(n-1)/2.g A1.u A2.u E1.u E2.u ... E(n-1)/2.u	even n: E1/2 E3/2 ... odd n: E1/2.g E1/2.u E3/2.g E3/2.u ... An/2.g An/2.u An/2.g* An/2.u*

Most labels are easily associated with the notation usually encountered in literature. Exceptions are AA, AAA, EE1, EEE1, EE2, EEE2, etcetera. They stand for A', A'', E1', E1'', and so on. The AA, etc. notation is used in ADF to avoid using quotes in input files in case the subspecies names must be referred to.

The symmetry labeling of orbitals may depend on the choice of coordinate system. For instance, B1 and B2 representations in C_{nv} are interchanged when you rotate the system by 90 degrees around the z-axis so that x-axis becomes y-axis and vice-versa (apart from sign).

Labels of the symmetry subspecies are easily derived from those for the irreps. For one-dimensional representations they are identical, for more-dimensional representations a suffix is added, separated by a colon: For the two- and three-dimensional E and T representations the subspecies labels are obtained by adding simply a counting index (1, 2, 3) to the name, with a colon in between; for instance, the EE1 irrep in the D_{nh} pointgroup has EE1:1 and EE1:2 subspecies. The same holds for the two-dimensional representations of C_{∞v} and D_{∞h}. For the R3 (atom) point group symmetry the subspecies are p:x, p:y, p:z, d:z2, d:x2-y2, etc.

All subspecies labels are listed in the Symmetry section, very early in the ADF output. To get this, perform a quick run of the molecule using the STOPAFTER key (for instance: stopafter config).

TDDFT irrep labels

The printed symmetry in the output in TDDFT calculations is actually the symmetry of transition density. For closed-shell systems, the symmetry of the excited state is the same as the symmetry of the transition density, while for open-shell systems, the symmetry of the excited states is the direct product between the symmetry of the transition density and the ground state symmetry. Note that the ground state symmetry of an open shell molecule is not necessarily A1.

The TDDFT module uses a different notation for some irrep names, for example, A' is used instead of AA, A'' (A two apostrophes) instead of AAA, A1' instead of AA1, A2'' instead of AAA2. In case of atoms, one should use a subgroup. In case of linear systems, if one does not specify the symmetry ADF will lower the symmetry automatically. For C(LIN) ADF will use internally C(7V), however, the names of the irreps in the TDDFT output will be S+, S-, Pi, De, Phi, instead of A1, A2, E1, E2, E3, respectively. For D(LIN) ADF will use internally D(7D), however, the names of the irreps in the TDDFT output will be S+.g, S-.g, Pi.g, De.g, Ph.g, S-.u, S+.u, Pi.u, De.u, Ph.u, instead of A1.g, A2.g, E1.g, E2.g, E3.g, A1.u, A2.u, E1.u, E2.u, E3.u, respectively.

Table 13.3: Schönfliess symbols and the labels of the irreducible representations for TDDFT.

Point Group	Schönfliess Symbol in ADF	Irreducible representations
C ₁	NOSYM	A
T _d	T(D)	A1 A2 E T1 T2
O _h	O(H)	A1.g A1.u A2.g A2.u E.g E.u T1.g T1.u T2.g T2.u
C _{∞v}	C(LIN)	S+ S- Pi De Ph
D _{∞h}	D(LIN)	S+.g S-.g Pi.g De.g Ph.g S-.u S+.u Pi.u De.u Ph.u
C _i	C(I)	A.g A.u
C _s	C(S)	A' A''
C _n	C(N), n must be 2	A B
C _{nh}	C(NH), n must be 2	A.g B.g A.u B.u
C _{nv}	C(NV), n<9	n=2: A1 A2 B1 B2 n=3: A1 A2 E n=4: A1 A2 B1 B2 E even n: A1 A2 B1 B2 E1 E2 ... odd n: A1 A2 E1 E2 ...
D _n	D(N), n<9	n=2: A B1 B2 B3 n=3: A1 A2 E n=4: A1 A2 B1 B2 E even n: A1 A2 B1 B2 E1 E2 ... odd n: A1 A2 E1 E2 ...
D _{nh}	D(NH), n<9	n=2: A.g A.u B1.g B1.u B2.g B2.u B3.g B3.u n=4: A1.g A1.u A2.g A2.u B1.g B1.u B2.g B2.u B3.g B3.u E.g E.u even n: A1.g A1.u A2.g A2.u B1.g B1.u B2.g B2.u B3.g B3.u E1.g E1.u E2.g E2.u ... n=3: A1' A1'' A2' A2'' E' E'' odd n: A1' A1'' A2' A2'' E1' E1'' E2' E2'' ...
D _{nd}	D(ND), n<9	n=2: A1 A2 B1 B2 E even n: A1 A2 B1 B2 E1 E2 ... n=3: A1.g A1.u A2.g A2.u E.g E.u odd n: A1.g A1.u A2.g A2.u E1.g E1.u E2.g E2.u ...

13.5.2 Molecular orientation requirements

ADF requires that the molecule has a specific orientation in space, as follows:

- The origin is a fixed point of the symmetry group.
- The z-axis is the main rotation axis, xy is the σ_h -plane (axial groups, $C(s)$).
- The x-axis is a C_2 axis (D symmetries).
- The xz-plane is a σ_v -plane (C_{nv} symmetries).
- In T_d and O_h the z-axis is a fourfold axis (S_4 and C_4 , respectively) and the (111)-direction is a threefold axis.

If the user-specified symmetry equals the true symmetry of the nuclear frame (including electric field and point charges) the program will adapt the input coordinates to the above requirements, if necessary. If no symmetry has been specified at all ADF assumes you have specified the symmetry of the nuclear frame, accounting for any fields. If a subgroup has been specified for the molecular symmetry the input coordinates will be used as specified by the user. If a Z-matrix input is given this implies for the Cartesian coordinates: first atom in the origin, second atom on the positive x-axis, third atom in the xy-plane with positive y value.

Molecular orientation conventions

The molecular requirements for ADF may not fully determine the orientation of the molecule, like for D_{2h} molecules. See Mulliken¹ for standard conventions on the molecular orientation and notation. A few of these conventions are listed below:

- in planar C_{2v} molecules the x axis is perpendicular to the plane of the molecule.
- in planar D_{2h} molecules the x axis is perpendicular to the plane of the molecule and the z-axis passes through the greatest number of atoms. If the last condition is not decisive, the z-axis should pass through the greatest number of bonds.
- in planar D_{4h} and D_{6h} molecules the C_2 -axis passes through the greatest number of atoms. If the last condition is not decisive, the C_2 -axis should pass through the greatest number of bonds.

13.6 Binary result files

13.6.1 ams.rkf

The main ams.rkf file is written by the AMS driver. It contains high level information about the trajectory that the AMS driver took over the potential energy surface. Part of what used to be on TAPE21 is since the AMSification of ADF in ams.rkf.

This file contains information on geometry optimization, transition state search, linear transit, PES scan, NEB, or IRC, if that was requested in the calculation. For a geometry optimization or transition state search, for example, it contains the history of how the systems geometry changed during the optimization as well as the final optimized geometry. The format in which this information is written is independent from which engine was used for a calculation.

If a property, like vibrational modes, is tied to a special point on the potential energy surface, it is stored in the engine main output file adf.rkf.

- [AMS manual](#)
 - [Section and variables on ams.rkf](#)

¹ R.S Mulliken, *Report on Notation for the Spectra of Polyatomic Molecules*, Journal of Chemical Physics 23, 1997 (1955) (<https://doi.org/10.1063/1.1740655>)

13.6.2 adf.rkf (TAPE21)

adf.rkf is the general result file of an ADF calculation. In ADF<=2019 it was known as TAPE21. It is a KF file: Direct-Access, binary, and keyword driven. It contains information about the calculation. You can use it as a fragment file in a subsequent calculation on a bigger molecule, where the current one may be a part, or in an analysis program. Part of what used to be on TAPE21 is since the AMSification of ADF in ams.rkf.

A description of the various utilities that can be used to process adf.rkf can be found in other parts of this ADF manual.

- *Sections and variables on adf.rkf* (page 1392)

adf.rkf: Added notes

Section Multipole matrix elements

Information about a response calculation

dipole elements

The matrix elements of the 3 dipole operator components between occupied and virtual orbitals: outer loop over the operators (in order: y, z, x), loop over virtual MOs, inner loop over occupied MOs

quadrupole elements

Similar as for dipole. Order of operators: $\sqrt{3} * xy \sqrt{3} * yz z^2 - (x^2 + y^2)/2 \sqrt{3} * xz \sqrt{3} * (x^2 - y^2)/2$

octupole elements

Similar as for dipole and quadrupole. Order of operators: $\sqrt{10} * y * (3 * x^2 - y^2)/4 \sqrt{15} * xyz \sqrt{6} * y * (4 * z^2 - x^2 - y^2)/4 z * (z^2 - 3 * (x^2 - y^2)/2) \sqrt{6} * x * (4 * z^2 - x^2 - y^2)/4 \sqrt{15} * z * (x^2 - y^2)/2 \sqrt{10} * x * (x^2 - 3 * y^2)/4$

hexadecapole elements

Similar as for dipole and quadrupole. Order of operators: $\sqrt{35} * xy * (x^2 - y^2)/2 \sqrt{70} * z * (3 * x^2 * y - y^3)/4 \sqrt{5} * xy * (6 * z^2 - x^2 - y^2)/2 \sqrt{10} * (4 * yz^3 - 3 * yz * (x^2 + y^2))/4 (8 * z^4 - 24 * z^2 * (x^2 + y^2) + 3 * (x^4 + 2 * x^2 * y^2 + y^4))/8 \sqrt{10} * (4 * xz^3 - 3 * xz * (x^2 + y^2))/4 \sqrt{5} * (x^2 - y^2) * (6 * z^2 - x^2 - y^2)/4 \sqrt{70} * z * (x^3 - 3 * xy^2)/4 \sqrt{35} * (x^4 - 6 * x^2 * y^2 + y^4)/8$

Representation of functions and frozen cores

ADF uses the cartesian representation for the spherical harmonics part in functions:

$$f(x, y, z) = x^a y^b z^c r^d e^{-\alpha r}$$

The angular momentum quantum number l is then given by $l = a + b + c$, and the main quantum number $n = l + d + 1$.

There are $(l + 1)(l + 2)/2$ different combinations of (a, b, c) for a given l - value, rather than $(2l + 1)$. The excess is caused by the presence of spurious non- l Functions in the set; a Cartesian d-set for instance consists of six functions, five of which are true d-functions while one linear combination is in fact an s-type function ($x^2 + y^2 + z^2$). Only the five true d-combinations are actually used as degrees of freedom in the basis set, but lists of primitive basis functions (bas) for instance run over all Cartesian functions including the improper ones.

A function *set* in ADF is characterized by the quantum numbers l and n , and by the exponential decay factor a . A set thus represents $(l + 1)(l + 2)/2$ Cartesian functions and $(2l + 1)$ degrees of freedom.

The atomic frozen core orbitals are described as expansions in Slater-type functions; these are not the functions of the normal basis set but another set of functions, defined on the data files you use in Create mode.

Orthogonality of the valence space to the frozen core states is enforced as follows: for each frozen core shell (characterized by the quantum numbers l and n : all orbitals with $m = -l \dots +l$ are identical apart from rotation in space) the set of valence basis functions is augmented with a so-called core orthogonalization function set. You may conceptually interpret the core orthogonalization functions as single zeta expansions of the true frozen core states. Each of the normal valence basis

functions is now transformed into a linear combination of that valence function with all core orthogonalization functions, where the coefficients are uniquely defined by the requirement that the resulting function is orthogonal to all true core functions.

So the list of all Cartesian basis functions is much larger than the degree of freedom of the basis: it contains the spurious *non-l* combinations and it contains also the core orthogonalization functions.

Evaluation of the charge density and molecular orbitals

adf.rkf contains all the information you need to evaluate the charge density or a Molecular Orbital (MO) in any point in space. Most of the information is located in section Basis:

A list of function characteristics (kx,ky,kz,kr,alf), including the core orthogonalization functions. This list does *not* run over *all* bas functions used in the molecule: if a particular function is used on the atoms of a given atomtype, the function occurs only once in the list, but in the molecule it occurs as many times as there are atoms of that type.

With array nbptr you locate the subsections in the function list that correspond to the different types of atoms: for atom type *i* the functions nbptr(*i*)...nbptr(*i*+1)-1. The distinct atom types are listed in an early section of the standard output file.

Array nqptr gives the number of atoms for type *i*: nqptr(*i*+1)-nqptr(*i*). With this information you construct the complete list of all functions. Repeat the subsection of type *i* as many times as there are atoms of that type: the complete list can be considered to be constructed as a double loop, the outer being over the atom types, the inner over the atoms that belong to that type. The total 'overall' list of functions you obtain in this way contains naos functions. Note that in this way we have implicitly also defined a list of all atoms, where all atoms that belong to a particular atom type are contiguous. This list is the so-called 'internal' atom ordering, which may not be identical to the order in which atoms were specified in input, under atoms.

For a given symmetry representation (Sections S) the array npart gives the indices of the basis functions in the overall list that are used to describe orbitals in this representation. In case of an unrestricted run the array npart applies for either spin: the same basis functions are used; the expansion coefficients for the molecular orbitals are different of course.

In the symmetry-representation sections Eigen_bas gives the expansion coefficients that describe the MOs. The expansion refer to the functions indicated by npart, and the function characteristics are given by the arrays kx,ky,kz,kr,alf, *and* bnorm, i.e. the expansion is in* normalized*functions.

The value of an MO is now obtained as a summation of values of primitive basis functions. For the evaluation of any such basis function you have to take into account that its characteristics are defined in the local coordinate system of its atom.

To obtain the charge density you sum all MOs, squared and multiplied by the respective occupation numbers (array froc in the appropriate irrep section).

Note that the auxiliary program densf, which is provided with the ADF package, generates orbital and density values on a user-specified grid.

13.6.3 TAPE10

TAPE10 is a binary KF file. By default TAPE10 is a scratch file. TAPE10 contains data related to the numerical integration: points and weights, values of functions (depends on direct-SCF options) and core densities and potentials.

Use the keywords 'SAVE TAPE10' in the ADF calculation such that TAPE10 is saved. NMR requires a TAPE10 file, see also documentation on *NMR chemical shifts* (page 232) and *NMR spin-spin couplings* (page 240).

13.6.4 TAPE13

TAPE13 is a binary KF file. TAPE13 is the checkpoint file for restarts after a crash. It is a concise version of `adf.rkf`, containing only the data the program uses for restarting the calculation. See the restart keyword. Note that since the AMSification of ADF in most case this TAPE13 has lost its usefulness. Instead one should use the file `ams.rkf`, which is produced by the AMS driver, for restarting a geometry optimization, for example.

Like `adf.rkf`, TAPE13 is a binary, keyword driven KF file.

The calculation that produces TAPE13 determines which sections are written on it. The actual values of the variables should be identical to the corresponding variables on `adf.rkf`. Also they should have the same names and be located in the same sections. In some cases, TAPE13 contains the complete corresponding section of `adf.rkf`.

13.6.5 TAPE15

TAPE15 is a binary KF file. By default TAPE15 is a scratch file. TAPE15 contains data related to matrices like the density matrix, the Fock matrix, and the overlap matrix.

Use the keywords 'SAVE TAPE15' in the ADF calculation such that TAPE15 is saved. Some external programs may need data that is stored on TAPE15. See, for example, the documentation on [adf2nbo to produce an input for NBO](#) (page 309) and [adf2damqt to produce an input for DAMQT](#) (page 323).

13.6.6 TAPE41

TAPE41 is a binary KF file. It is produced by the *densf* program to generate values of molecular orbitals, charge densities and potentials in a user-specified grid, to be used typically for plotting or graphical display, see the documentation on *densf* (page 342).

13.6.7 Other binary files

In the [results directory](#) that *ams* creates one may find other binary KF files. There may be binary `adf.rkf`-like output files for some points on the potential energy surface that was visited during the calculation. One may find `t21.*.elementname` files which are atomic `adf.rkf`-like files, that were created during an ADF calculation. One may find the binary `t12.rel` file that is not a KF file, which is an auxiliary binary file for relativistic calculations. Depending on the kind of ADF calculation more binary KF (scratch) files may be used.

13.7 Error messages

ERROR: STOP GEOMETRY ITERATIONS

The SCF procedure did not converge, which caused the geometry optimization to be aborted. See WARNING: SCF NOT COMPLETELY CONVERGED below.

ERROR: imo is not occupied PT1W

ERROR: imo is occupied PT1W

The electronic structure is not auf-bau, that is the LUMO is lower in energy than the HOMO. Disable the KeepOrbitals option by setting it to a large number and try different SCF version until you get the SCF properly converged. See the SCF Troubleshooting section for details.

ERROR: More cycles needed. Geometry NOT CONVERGED**ERROR: GEOMETRY DID NOT CONVERGE****ERROR: GEOMETRY NOT CONVERGED****ERROR: TRANSIT FAILED**

The geometry optimization did not converge in the allowed number of steps. See the Geometry Optimization Troubleshooting section for recommendations on how to proceed.

ERROR: TAPE12 NOT SUPPLIED with TAPE10**ERROR: Relativistic option is used but no file with core potentials was found**

Before running a relativistic calculation you need to run the dirac program to create a TAPE12 file. This can be done automatically by adding a Basis block to the input and executing ADF as \$AMSBIN/adf instead of adf.exe.

ERROR: calculating FDE interactions for the same fragment

It's a program bug. Send your input file to SCM

ERROR: Abort because one processor has no integration points

Repeat the calculation with fewer processors in the MPI job.

ERROR: Davidson method not converged

The Davidson method did not converge that is used in the calculation of excitation energies. Increase the number of ITERATIONS in the EXCITATIONS block key, or use a larger TOLERANCE.

ERROR: EMPTY FIELD FOUND AT END OF ...**ERROR: Cannot read ... even as a string**

Check the QMMM block in the input. Every simple key in the block (as opposed to a block key) must be followed by a value. See the QMMM Manual for the correct syntax.

ERROR: LenRecUnits: reflen units not determined

This error is most likely caused by compiler problems or by incorrect compilation flags. See <https://www.scm.com/support/downloads/platform-specific-information/> for supported compiler versions and contact SCM for an advice on compilation flags. Do not forget to include the \$AMSHOME/buildinfo file in your request.

13.8 Warnings

WARNING: (slightly) inaccurate ETA integral(s)**WARNING: SUSPICIOUS ETA INTEGRALS**

Eta's are symmetry adapted STO's. This error is usually caused by numerical stability problems in the symmetric matrix eigensolver. On the x86(-64) platforms you can try using a different version of the Intel MKL library (newer is not always better).

WARNING: 1-character identifier(s) in DEFINE

The Define input block does not allow single-character identifiers.

WARNING: activating keyword SDFTEnergy for the calculation of subsystem DFT energy.

For more than two frozen subsystems the sDFT energy needs the corresponding logical switch, which is normally activated via the SDFTEnergy key in the FDE input block.

WARNING: AMAT not far from singularity**WARNING: Bmatrix not far from singular**

Amat and Bmatrix are used in COSMO solvation model. This warning could be printed when the distance between two COSMO surface points is shorter than 0.01 Bohr. You may want to try different COSMO accuracy parameters.

WARNING: Atom (...) exceeded the max allowed bonds in DimQMHybridization

The number of bonds per atom is exceeded in DimQM. Check your input geometry for correctness (coordinate units, etc.). The bond limit per atom type is currently hardcoded in the program and cannot be increased with recompiling the program.

WARNING: inaccurate integration of Core Density**WARNING: BAD CORE INTEGRAL ...**

The core density must integrate to number of core electrons very accurately. If this is not the case then something is wrong either with the integration grid, with the input geometry or with the core orbitals. In any case, check your input geometry (Angstrom vs. Bohr vs. the Units input block, check bond lengths). Try using a smaller core and/or better grid.

WARNING: BAD FIT**WARNING: CANNOT NORMALIZE THE FIT****WARNING: LOSS OF CHARGE**

These warnings are printed when the accuracy of the STO fit is not high enough. This might, for example, happen for negatively charged molecules for which the electron density cannot be adequately represented by the fit functions. This can be solved by using a larger fit type (e.g. FitType QZ4P in the Basis input block) or using the AddDiffuseFit keyword, or by using the ZlmFit instead of STOfit.

WARNING: The use of the SOLVATION option with non-basic fragments is not supported**WARNING: Bond energies are incorrect**

Do not use the energy decomposition analysis if the fragments are calculated with COSMO solvation.

WARNING: C(lin) or D(lin) not supported in Freq runs

When performing numerical frequency calculation for a linear molecule you should not set the symmetry explicitly to C(lin) or D(lin). Use something like C(8v) or D(8h) instead.

WARNING: CD spectrum for triplex excit. NOT SUPPORTED**WARNING: CD spectrum for triplet excitations is NOT SUPPORTED**

A CD spectrum calculation has been requested for triplet-only excitations, which is not supported by the program. The excitation rotary strengths will not be calculated.

WARNING: In ReadEpsilon: HOMO energy is positive**WARNING: Check if basis or fit sets are dependent**

The HOMO energy is positive where it should usually be negative. The positive HOMO energy means the solution is not stable and the following TDDFT calculation may produce incorrect results.

WARNING: Combination of unrestricted and MODEL potential not extensively tested

Using the model XC functionals for spin-unrestricted calculations is not officially supported. Read the literature on the functional used to make sure you do not obtain nonsense results.

WARNING: Virtuals almost lin. dependent

WARNING: Consider using keyword DEPENDENCY

This warning is printed is when the smallest eigenvalue of the virtual SFO overlap matrix is smaller than 1e-5. You may want to add a Dependency keyword to your input.

WARNING: convMCD very small. Achieving convergence is unlikely

This warning is printed when the MCD convergence criterion is smaller than 1e-4. You may want to set the CONVMCD parameter in the MCD input block to a larger value if the CG solver does not converge.

WARNING: Core orb. en. with MODEL xc pot not implemented

Calculation of the core orbital energies in combination with model XC potentials (e.g. LB94) is not implemented.

WARNING: Could not find vecdimension excitations on SUBTAPE

WARNING: Trying to find vecdimension in ResponsePmats section ...

When performing a Subsystem DFT excitations calculation the excitations must be calculated for each sub-system (fragment).

WARNING: Density fitting may not be accurate enough!

WARNING: H12 and Electronic Coupling possibly INACCURATE

WARNING: Diagonal energies and overlap(s) should be accurate

These messages are printed together and already contain a hint. To avoid the problem you may want to increase the quality of the fit using one or more of the following options: FitType QZ4P, AddDiffuseFit, NumericalQuality {Good|VeryGood|Excellent}.

WARNING: diagonalization error in dvdrvrhf. Results will be incomplete.

WARNING: diagonalization error in dvdrvrhfso. Results will be incomplete.

The LAPACK subroutine dsygv (dzhegv in case of dvdrvrhfso) returned a non-zero status for the (A-B)(A+B) matrix. Analysis of the obtained solution will not be done.

WARNING: dihedral jumps 180 degrees

This warning is printed by the old optimizer branch. Check the optimization results and switch to the new branch if you encounter any problems.

WARNING: DIM dipoles not converged upon SCF convergence

Use more tight SCF convergence criteria.

WARNING: No default parameters for classical Hirshfeld partitioning

WARNING: Dispersion added with factor 1.0

You may want to set the steepness factor ATT0 and the scaling factor BTT0 for the SCBR empirical dispersion.

WARNING: doing final FDE cycle - FDE NOT converged

The FDE freeze-and-thaw procedure has not converged. You may want to increase the number of the FDE freeze-and-thaw cycles.

WARNING: DPERTURB calculation, no CI-type couplings calculated

Since the CI-coupling does not make much sense in combination with DPERTURB, the former is disabled.

WARNING: ERROR OPENING ONE OF THE NBO DATA FILES. SEE OUTPUT

Check the output to see which NBO file is missing and look for clues in the NBO output preceding the calculation.

WARNING: Euclidian distance between NEB images is too short. NEB may have problems

The total Euclidian distance between two NEB images should be large compared to the Cartesian optimization step size. Otherwise the NEB optimization may result in a zig-zag path and may eventually fail. One way to increase the distance is by reducing the number of images.

WARNING: Extra DFT term related to g_xc suspiciously large

This warning is printed when the $\text{abs}(\text{beta}(\text{diff}))$ value is larger than $1\text{e-}3$ and is larger than $\text{abs}(\text{beta}(\text{total}))$ in a hyperpolarizability calculation. This may be an indication of a numerical instability.

WARNING: FDE in combination with ZlmFit not thoroughly tested. Consider using STOFIT

[[[Mirko??]]]

WARNING: FILE POSSIBLY TOO BIG IN AORUN

This warning is printed when the AORUN input keyword is specified in certain types of TDDFT calculations (e.g. polarizability). In such a case the writing of the orbital values on the grid is disabled because otherwise it would result in a huge TAPE10 file. Note: the AORUN keyword serves no other purpose but to disable writing of the orbitals to TAPE10, so it should be used with care.

WARNING: Geometry optimization did not converge - frequencies are not calculated

This warning is printed when ADF is instructed to compute the vibrational spectrum of a molecule after geometry optimization but the optimization did not converge. In this case the frequencies are not computed.

WARNING: GRADIENT ILL-DEFINED FOR BOND ANGLE 180 OR 0

This warning is generated by the old geometry optimization branch when a valence angle gets close to 0 or 180 degrees. Such angles cannot be treated properly by the optimizer so one should avoid them, for example by adding dummy atoms.

WARNING: Hessian is incomplete

This warning just informs the user that only a fraction of the Hessian matrix has been done, as specified by the NUC keyword of the AnalyticalFreq input block. The missing matrix elements are calculated from an empirical MM forcefield and the combined Hessian matrix is analyzed.

WARNING: inaccurate elimination of XX motions, recover

This warning is generated by the old geometry optimization branch. Add PRINT FREEMV to your input to get more information.

WARNING: Inconsistent relativistic options used

This warning is printed when inconsistent relativistic options are used for the fragments and the final calculation and the RELOPTINCONS keyword is used to prevent ADF from stopping the calculation. If you add RELOPTINCONS then you probably know what you're doing.

WARNING: Infrared Intensities are wrong

WARNING: Infrared Intensities wrong

These warnings are issued when the computed dipole moment derivative is larger than 0.1 a.u. for a normal modes for which it must be zero by symmetry.

WARNING: Inter-node communication is slow! You may want to run on fewer nodes (or even one).

WARNING: Intra-node communication is VERY slow! Check CPU affinity, hyperthreading and over-subscription

The program tests the latency of the MPI communication at the beginning of each parallel calculation. The overall (i.e. the whole MPI "world" including all processes from all nodes) and the intra-node (i.e. including only the processes within one node) latency are measured separately. The first warning is printed if the overall latency is higher than 1 ms. This usually occurs when running on multiple nodes with a slow interconnect (e.g. 1 Gbps Ethernet), or when running on too many nodes. In this case it is recommended to run on fewer nodes. It is **not** recommended to run multi-node jobs at all if the cluster does not have a fast interconnect. The second warning is printed when the intra-node latency is higher than 1 ms, which should **never** happen. If the intra-node communication is slow the user is advised to stop running further MPI calculations until the issue is resolved. Possible reasons for this are: incorrect CPU affinity settings enforced by the batch scheduler (e.g. more than one process is bound to the same core), host is oversubscribed (i.e. other jobs are running on the same machines and ADF has to compete with them for resources). When two or more MPI jobs have to compete for the same resources both jobs will have a low performance because the MPI synchronization calls also consume CPU cycles.

WARNING: INVALID SPRING PARAMETER. DEFAULTS ARE ENFORCED.

The valid values for the first NEBSRING parameter are 1 through 6. If a value outside this range is specified it is set to 1 and this warning is printed.

WARNING: IRC START REQUEST IMPOSSIBLE: ADJUSTED

This warning is printed when the IRC eigenvector index specified by the IRC HESS parameter is larger than the number of free coordinates.

WARNING: KeepOrbitals on

This warning is printed when the MO populations become non-aufbau due to the KeepOrbitals feature. The KeepOrbitals usually kicks in after N/2 SCF iterations, where N is the max number of SCF iterations allowed. See the Occupations keyword for details.

WARNING: LB94 XC FUNCTIONAL USED FOR ENERGY GRADIENTS

The LB94 XC functional is supposed to be used to calculate spectroscopic properties such as optical excitation spectra and is not intended for the bonding energy (and gradients thereof) calculations.

WARNING: LMO beta analysis has nonzero B-field frequency. Check output.

This warning is printed when the magnetic perturbation field in the dynamic beta tensor (optical rotation) calculation has a finite frequency. Use the DEBUG keyword of the LOCORB input block to get more information.

WARNING: localized MOs: unknown symmetry key ...

This warning is printed when there is an unrecognized keyword is found in the LOCORB input block. Check that your input conforms the documentation of the LOCORB input block.

WARNING: Low value for “numvec” detected in AllocDavidson

WARNING: Using numvec = [number of excitations] + 5 instead

WARNING: Specify larger value for VECTORS in EXCITATION input block

These warnings are printed together and are self-explanatory.

WARNING: GIAOS ARE NOT IMPLEMENTED WITH LIFETIME. SWITCHING OFF GIAOS

WARNING: MAGOPTROT AND QUADRUPOLE OPTIONS ARE MUTUALLY EXCLUSIVE.

SWITCHING OFF QUADRUPOLE

WARNING: MAGPERT AND QUADRUPOLE OPTIONS ARE MUTUALLY EXCLUSIVE. SWITCHING OFF QUADRUPOLE

WARNING: MAGPERT AND VROA OPTIONS ARE MUTUALLY EXCLUSIVE. SWITCHING OFF MAGPERT

WARNING: OPTICALROT AND VROA OPTIONS ARE MUTUALLY EXCLUSIVE. SWITCHING OFF OPTICALROT

WARNING: OPTROT AND GIAO AND NBO OPTIONS WITHOUT MAGPERT ARE NOT IMPLEMENTED. SWITCHING OFF NBO

WARNING: OPTROT AND QUADPERT OPTIONS ARE MUTUALLY EXCLUSIVE. SWITCHING OFF QUADPERT

WARNING: VROA OPTION MUST BE USED WITH QUADRUPOLE. SWITCHING ON QUADRUPOLE

WARNING: VELOCITYORD DOES NOT WORK WITH GIAO. SWITCHING OFF GIAO

WARNING: ZLMFIT AND FITAODERIV ARE NOT IMPLEMENTED. SWITCHING OFF FITAODERIV

These warnings are results of the AOResponse internal checks.

WARNING: max no. of iterations reached

This warning is printed when the CPKS procedure did not converge in the given number of steps. This may indicate a numerical stability issue or some other problem. In any case, you should check if the SCF has converged, if the electronic configuration is correct. Increasing the numerical accuracy might also help. Finally, you can try increasing the number of CPKS cycles for the feature in question (TD-DFT, analytical frequencies, etc.).

WARNING: maxBlockSize does not divide (maxBasisSize - minRestartSize). Suboptimal performance expected!

This warning is printed by the Davidson method using the PRIMME library. The fact that (maxBasisSize - minRestartSize) is not divisible by maxBlockSize does not affect the results so there is no reason to worry. [[[Robert is

there any way to influence this?]]]

WARNING: MIXED OCCUPATIONS in locmo (localized MO)

This warning is printed when occupation numbers of the localized MOs after 2x2 rotations do not match the original ones, which essentially means that the occupied and virtual orbitals have been mixed together.

WARNING: mo levels nearly degenerate

This warning is usually issued by the CPKS driver routine when the energy difference between an occupied and a virtual orbital is less than 1e-3 a.u.. This usually means that the HOMO-LUMO gap is very small which may lead to problems in the CPKS procedure.

WARNING: MODTRC refers to non-existing free variable

WARNING: ... selecting the first mode instead

This warning is printed by the old optimization branch in response to an invalid setting for the transition state search vector. In this case the TS procedure will use the eigenvector corresponding to the lowest eigenvalue of the Hessian matrix.

WARNING: More iterations needed. MODERATELY CONVERGED

WARNING: More iterations needed. NOT CONVERGED

WARNING: SCF did not converge - frequencies are not calculated

WARNING: SCF NOT COMPLETELY CONVERGED

One of these warnings is issued when the SCF procedure did not (completely) converge. See the SCF Troubleshooting section for recommendation on how to improve the SCF convergence.

WARNING: More nodes than energies on the contour: this is inefficient

This warning is printed by the NEGF code when the number of energies on the contour is smaller than the number of MPI tasks. This means that you can probably perform the calculation in the same time using fewer processors.

WARNING: multiple small orbital energy differences found

This warning is printed when the undocumented ASYMPCOR keyword is specified and more than one occupied-virtual orbital pair is found for which the energy difference is less than 1e-3 a.u..

WARNING: Negative root found. AllocDavidson

WARNING: Negative root found. AllocDavidsonso

These warnings are issued when the Davidson procedure finds a negative eigenvalue. This usually indicates a triplet instability.

WARNING: negative sqrt in the CI-type coupling parameters

WARNING: the results might be not trustworthy!!!!

This warning is printed by the subsystem TDDFT module when checking requirements for the CI coupling calculation. The latter will not be done if any element of the CI_omega matrix is imaginary.

WARNING: no convergence in svdcmp

This is a generic warning from a singular value decomposition routine. When this occurs the SVD procedure will be aborted, which may lead to incorrect results in the module that called the routine.

WARNING: No DIM points found for projection matrix.

This warning is printed when projecting rigid rotations/translations from the DIM/QM energy gradients in the case there are no DIM points found within the cutoff radius specified by the PROJECTIONMATRIXPOINTS CUTOFF keyword.

WARNING: no optimization done in DVDSON: using guess vector results

This warning is printed to remind the user that he/she has specified SFGUESS or TRUSTSFGUESS in the input.

WARNING: root must be bracketed in rtsafe

The rtsafe function finds a root of the given callback-function in the given interval. The requirement is that the function has the opposite signs at the ends of the interval. This warning is printed when the requirement is not fulfilled.

WARNING: rtsafe exceeding maximum iterations

This warning is printed when the rtsafe function fails to find a root within the allowed number of iterations, currently 100.

WARNING: Non Aufbau energies used

This warning is printed by the Response code (excitations, polarizabilities, etc.) when the HOMO lies higher than LUMO in energy or when these are degenerate.

WARNING: Non-standard use of LAP functional**WARNING: Non-standard use of LYP functional**

The LAP and LYP functionals already contain a term for correlation at the LDA level. This warning is printed when an LDA functional is specified in addition to LAP or LYP.

WARNING: NONRELATIVISTIC RUN WITH RELATIVISTIC COREPOTENTIALS**WARNING: RELATIVISTIC RUN WITHOUT RELATIVISTIC COREPOTENTIALS**

This warning is printed when the CorePotentials keyword is used (or not used) inconsistently with the Relativistic option. Before running a relativistic calculation you need to run the dirac program to create a TAPE12 file, which then needs to be specified in the CorePotentials keyword. This can be done automatically by adding a Basis block to the input and executing ADF as \$AMSBIN/adf instead of adf.exe.

WARNING: not all AIM bond paths converged

This warning is printed by the AIM bond path search module when some of the paths failed to converge to an attractor (a nucleus).

WARNING: not all scratch files were closed

This warning probably indicates a programmer error. Send the output to support@scm.com.

WARNING: not enough initial estimates

WARNING: Too many initial estimates.?

One of these warnings is issued when the number of initial vectors in the Davidson procedure is either too high or too low.

WARNING: Number of states in energy window changed

This warning is printed when the number of molecular orbitals in the energy window given with the ELTHRES/EUTHRES sub-keys of the VIBRON input block changes during calculation.

WARNING: occupations may be NOT AUFBAU

This warning is printed during a single-point calculation or the last iteration of a geometry optimization if the HOMO has a higher energy than the LUMO. For fractionally occupied orbitals, the HOMO is the highest MO that is populated by at least 1e-6 electrons and the LUMO is the lowest MO that misses at least 1e-6 electron to be fully occupied.

WARNING: omega and d(omega) incompatible in Verdet run

This warning is printed during calculation of the Verdet's constant when the value of the frequency ω is lower than the half-width of the interval used for numerical differentiation $\Delta\omega$.

WARNING: Out of parameterized Coulomb radii limits

The Coulomb radius parameters used to determine the COSMO sphere radii are currently available for elements up to 105. For heavier elements this warning is printed and the calculation stops.

WARNING: partially occupied orbitals

This warning is printed at the end of the SCF process if it results in partially occupied orbitals. The user should examine the resulting electronic structure carefully to see if this is the result they expected. One way to avoid fractional occupations is to repeat the calculation as spin-unrestricted with a non-zero total spin.

WARNING: Patchkovskii routines for PBE used. Check output

This warning is printed when USESPCODE is specified in the input together with the PBE functional. The bonding energy and other fragment analysis data may be incorrect.

WARNING: potential problem with dependency in AOResponse. Check output**WARNING: potential problem with dependency in LOCMO. Check output**

When using the Dependency keyword, the linearly-dependent orbitals are not removed completely but are effectively excluded from variation by setting the corresponding diagonal matrix element to a large positive value. One of these warnings is issued when the any of the molecular orbitals included in the variation have the energy close to that large value, which probably means there is some bug in the SCF bookkeeping.

WARNING: Pressure must be positive, adjusted

This warning is printed when the pressure specified in the Thermo keyword is smaller than 1e-4 atmosphere.

WARNING: PRIMITIVE FIT COEFFICIENTS A BIT LARGE**WARNING: PRIMITIVE FIT COEFFICIENTS LARGE****WARNING: PRIMITIVE FIT COEFFICIENTS TOO LARGE**

One or more of these warnings are printed when the number of electrons due to a single STO fit-function exceeds certain limits (20, 200, and 2000 times the largest number of valence electrons on a single atom in the molecule, respectively). This may indicate a linear dependence (over-fitting) problem in the fit or the basis set.

WARNING: problem with NEB optimisation. Re-initializing Hessian

This warning is printed during an NEB calculation if the Euclidian angle between three images becomes less than 30 degrees. This may indicate that there are too many NEB images for such a short reaction path.

WARNING: ReadExSym: found large energy differences

This warning is printed in a Vibron calculation when the excitation energy difference between two geometries is larger than 0.2 eV. You should check the results carefully.

WARNING: Restricted Open-Shell calculation, Unrestricted setup may be needed

This warning is printed when a molecule with an odd number of electrons (a radical) is calculated spin-restricted. This often indicates an error in the input (either wrong geometry or a missing Charge keyword). This warning may safely be ignored if the result of this calculation is to be used as a fragment.

WARNING: SchmidtOrth keeps finding noise

This warning is printed by the Schmidt orthogonalization procedure when it fails to orthogonalize the input vector to the reference set within 4 attempts. Two normalized vectors are considered orthogonal when their dot product is smaller than $1e-8$ in the absolute value.

WARNING: sDFT energies should be used together with the FULLGRID option! Results might not be reliable!

Enable the FULLGRID option.

WARNING: SLOW SCF**WARNING: ... apply ElectronSmearing**

In case of really problematic SCF a finite electron temperature (smearing of electrons around the Fermi level) is applied automatically if the user a) has not specified smearing via input and b) has not defined the occupation numbers explicitly. Furthermore, smearing is not automatically turned on in single-point calculations and in the final geometry. That is, it is only allowed during geometry optimization in the intermediate geometries. To disable automatic smearing specify Occupations Smeaq=0 in the input.

WARNING: small delta epsilon found

This warning is printed when the energy difference in an occupied-virtual MO pair is smaller than 0.001 a.u., which means the HOMO and LUMO are nearly degenerate.

WARNING: SOLVATION block: DISC is not compatible with C-Mat POT

This warning is printed when the DISC option in the Solvation input block is set for the C-Matrix POT (which is the default), where it does not make sense. The user should check their input and either remove the DISC option or set C-Matrix to EXACT or FIT.

WARNING: SOMCD indicated but closed-shell calculation

The SOMCD feature (used to calculate the C terms of the magnetic circular dichroism spectra) is available only in spin-unrestricted calculation. If SOMCD is specified in a spin-restricted calculation then it is ignored and this warning is printed.

WARNING: SSB-D XC FUNCTIONAL USED FOR ENERGY GRADIENTS

The use of “GGA SSB-D” in a geometry optimization may lead to numerical issues for some systems. Check carefully that the energy goes down smoothly and continuously. Also compare with a calculation performed with the “METAGGA SSB-D” specified in the XC input block.

WARNING: Strange column number EXCITATIONS

The second (undocumented) argument of the irrep sub-keys of the Davidson and Exact sub-blocks can optionally specify that the 2nd or 3rd projection of a multi-dimensional irrep should be used to calculate intensities. This warning is printed when the number specified is larger than the dimensionality of the irrep.

WARNING: Suspicious delocalized coordinates. Change GEigenvalueThreshold or optimize in Cartesian coords

This warning is printed when the number of generated delocalized coordinates is not equal to $3N-6$ for a system of 5 atoms and more. This may indicate some problems in generation of internal coordinates for the input geometry, for example because of isolated molecules (which should normally not be a problem). This warning may also be caused by the presence of a block constraint, in which case it may be safely ignored. Otherwise, one should check the number of the generated delocalized coordinates in the output file. If it is larger than $3N-6$ then it is advised to look at the “G-matrix eigenvalues” table in the output and set the GEigenvalueThreshold parameter in the Geometry block to an average of the eigenvalues number $3N-6$ and $3N-5$.

WARNING: Symmetry is not yet supported in VCD

The vibrational circular dichroism (VCD) intensities are not calculated if the symmetry used in the calculation is other than C:sub:1 (i.e. NOSYM)

WARNING: TDA in FDEc also requires TDA excitations as input

Use TDA consistently in coupled frozen density embedding (FDEc).

WARNING: Temperature must be positive, adjusted

The temperature value specified in the Thermo keyword must be larger than 0.1 K.

WARNING: The full TDDFT kernel icw symmetry may give incorrect results.

WARNING: Results can be checked with symmetry NOSYM

As this warning already suggest, you can check the results with SYMMETRY NOSYM.

WARNING: thin plane error. HULL33

WARNING: thin planes inconsist 1. HULL33

These warnings can appear when the Te Velde integration grid is used. Use the Becke grid in this case.

WARNING: Unknown GGA functional for UFF dispersion.’

The UFF dispersion parameters depend on the XC functional used. Currently the parameters are defined for the PBE, B3LYP, PW91 and B3PW91 functionals. For any other functional the PBE parameters are used and this warning is printed.

WARNING: Unknown GGA functional for MBD dispersion.'

The MBD dispersion parameters depend on the XC functional used. Currently the parameters are defined for the PBE, PBE0, HSE03 and HSE06 functionals. For any other functional no short-range damping is applied and this warning is printed.

WARNING: Unknown GGA used. Dispersion added with factor 1.0

The Grimme dispersion corrections are defined per XC functional. For any unknown functional the dispersion is, by default, added with a factor 1.0, which can be changed from input.

WARNING: Unknown global optimization type requested. Using Quasi-Newton

WARNING: Unknown NEB optimization type specified. Using default

WARNING: Unknown optimization type requested. Using Quasi-Newton

One of these warnings is printed when the NEBOPT sub-key of the Geometry block contains an invalid argument.

WARNING: Unknown XC functional for DFT-D3

This warning is printed when an unknown XC functional is specified together with "Dispersion Grimme3" keyword in the XC input block. In such a case the PBE parameters are used for the dispersion correction.

WARNING: Untested MBD dispersion parameters are used. Check results.

WARNING: Untested dispersion parameters are used. Check results.

This warning is printed when the system under study contains atoms with an element index greater than the maximum defined for the given correction. Currently, the limits are set as follows: 54 for Grimme, 86 for MBD, 94 for Grimme3, 102 for sCBR, and 103 for the UFF dispersion type.

WARNING: Unrecognized key for Irrep

This warning is printed when an unrecognized irreducible representation name is given in the Davidson or Exact sub-blocks of the Excitations block.

WARNING: use of multiple fragments not yet allowed !!!

WARNING: Use results from parallel runs with caution!

These self-explanatory informative warnings are printed by the (relatively new) SubsystemResponse module.

WARNING: USING >ADIABS< scheme in vibron.

WARNING: DO YOU REALLY KNOW WHAT YOU ARE DOING?

The ADIABS scheme in the Vibron module can only be used for totally symmetric modes. Add ONLYSYM to the Vibron block key.

WARNING: using LDA-only response. Please check your output

This warning is printed by the AOResponse code in cases when the use of the GGA is disabled automatically, usually in open-shell calculations.

WARNING: VERY HIGH VALUE FOR FRANGE IN RANG2

WARNING: VERY HIGH VALUE FOR QPNEAR IN RANGQP

This warning is printed by the grid generation routine when a basis or an STO fit function has a very long range ($>10,000$ a.u.). This may occur for an extremely diffuse function when a very high integration accuracy is requested.

WARNING: VERY SMALL A(0) IN LOCORB1. Check output!

This warning is printed by the routines performing the Pipek-Mezey (PM) and Boys localization on first-order perturbed molecular orbitals when the absolute value of the A(0) denominator becomes smaller than $1e-10$.

WARNING: VROA OPTION MUST BE USED WITH QUADRUPOLE

The AOResponse Quadrupole options is switched on and this warning is printed when the vibrational Raman optical activity (VROA) is to be calculated.

WARNING: WRONG COORDINATES

This warning is printed by QUILD in the same situations where ADF exits with the same "WRONG COORDINATES" message: the input geometry does not satisfy the point group specified by the Symmetry keyword. This usually happens when the molecule's orientation does not match the symmetry operations. Note that when the point group is set from input, the program does not re-orient the input geometry to match the symmetry.

WARNING: wrong nr of functions deleted. ORTNRM

Internal ADF error message. Related to STO fit. Send your input file to SCM. Alternative is to use ZlmFit.

WARNING: zero number of filtered transitions found, try larger demax

This warning is printed by the approximate TD-DFT module (TD-DFTB, sTDDFT, sTDA, KSSPECTRUM) when there are no transitions found for the given energy range. This should not happen if there is at least one occupied and one virtual orbital present because in ADF the range is by default very large ($\sim 1e308$ a.u.)

REQUIRED CITATIONS

When you publish results in the scientific literature that were obtained with programs of the ADF package, you are required to include references to the program package with the appropriate release number, and a few key publications.

In addition to these general references, references to special features are mandatory if you have used them.

14.1 General References

For calculations with the molecular ADF program, version 2026.1:

E.J. Baerends, N.F. Aguirre, N.D. Austin, J. Autschbach, F.M. Bickelhaupt, R. Bulo, C. Cappelli, A.C.T. van Duin, F. Egidi, C. Fonseca Guerra, A. Förster, M. Franchini, T.P.M. Goumans, T. Heine, M. Hellström, C.R. Jacob, L. Jensen, M.V. Krykunov, E. van Lenthe, A. Michalak, M. Mitoraj, J. Neugebauer, V.P. Nicu, P.H.T. Philipsen, H. Ramanantoanina, R. Rüger, G. Schreckenbach, M. Stener, M. Swart, J.M. Thijssen, T. Trnka, L. Visscher, A.L. Yakovlev, S.J.A. van Gisbergen, *The Amsterdam Modeling Suite*, *Journal of Chemical Physics* 162, 162501 (2025) (<https://doi.org/10.1063/5.0258496>) (bibtex)

ADF 2026.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <https://www.scm.com>. Optionally, you may add the following list of authors and contributors: E.J. Baerends, T. Ziegler, A.J. Atkins, J. Autschbach, O. Baseggio, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, C. Cappelli, L. Cavallo, C. Daul, D.P. Chong, D.V. Chulhai, L. Deng, R.M. Dickson, J.M. Dieterich, F. Egidi, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, A. Förster, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A. Goetz, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, Z. Hu, C.R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J.W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M.V. Krykunov, P. LaFiosca, E. van Lenthe, D.A. McCormack, M. Medves, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, M. Pavanello, C.A. Peeples, P.H.T. Philipsen, D. Post, C.C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, M. Reimann, J.I. Rodríguez, P. Ros, R. Rüger, P.R.T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Stener, M. Swart, D. Swerhone, V. Tognetti, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev

Note: if you have used a modified (by yourself, for instance) version of the code, you should mention in the citation that a modified version has been used.

14.2 Feature References

When you have used special features, you should include one (or more, as the case may be) lead reference(s) to the implementation. Additional references to related publications are suggested.

14.2.1 Coordinates, basis sets, fragments

Basis Sets

E. van Lenthe and E.J. Baerends, *Optimized Slater-type basis sets for the elements 1-118*, *Journal of Computational Chemistry* 24, 1142 (2003) (<https://doi.org/10.1002/jcc.10255>)

Correlation-consistent basis sets

Arno Förster, Lucas Visscher, *GW100: A Slater-Type Orbital Perspective*, *Journal of Chemical Theory and Computation* 17 (8), 5080–5097 (2021) (<https://doi.org/10.1021/acs.jctc.1c00308>)

Spherical Gaussian nuclear charge distribution model

J. Autschbach, *Magnitude of Finite-Nucleus-Size Effects in Relativistic Density Functional Computations of Indirect NMR Nuclear Spin-Spin Coupling Constants*, *ChemPhysChem* 10, 2274 (2009) (<https://doi.org/10.1002/cphc.200900271>)

14.2.2 Geometry optimizations, transition states, and reaction paths

Transition State search

L. Versluis and T. Ziegler, *The determination of Molecular Structure by Density Functional Theory*, *Journal of Chemical Physics* 88, 322 (1988) (<https://doi.org/10.1063/1.454603>)

L. Fan and T. Ziegler, *Nonlocal density functional theory as a practical tool in calculations on transition states and activation energies*, *Journal of the American Chemical Society* 114, 10890 (1992) (<https://doi.org/10.1021/ja00053a027>)

IRC

L. Deng, T. Ziegler and L. Fan, *A combined density functional and intrinsic reaction coordinate study on the ground state energy surface of H₂ CO*, *Journal of Chemical Physics* 99, 3823 (1993) (<https://doi.org/10.1063/1.466129>)

L. Deng and T. Ziegler, *The determination of Intrinsic Reaction Coordinates by density functional theory*, *International Journal of Quantum Chemistry* 52, 731 (1994) (<https://doi.org/10.1002/qua.560520406>)

Nudged Elastic Band

G. Henkelman, B.P. Uberuaga and H. Jónsson, *A climbing image nudged elastic band method for finding saddle points and minimum energy paths*, *Journal of Chemical Physics* 113, 9901 (2000) (<https://doi.org/10.1063/1.1329672>)

14.2.3 Model Hamiltonians

Range Separated Functionals

M. Seth and T. Ziegler, *Range-Separated Exchange Functionals with Slater-Type Functions*, *Journal of Chemical Theory and Computation* 8, 901 (2012) (<https://doi.org/10.1021/ct300006h>)

MP2, double hybrids

A. Förster, M. Franchini, E. van Lenthe, L. Visscher, *A Quadratic Pair Atomic Resolution of the Identity Based SOS-AO-MP2 Algorithm Using Slater Type Orbitals*, *Journal of Chemical Theory and Computation* 16, 875 (2020) (<https://doi.org/10.1021/acs.jctc.9b00854>)

double hybrids

A. Förster, L. Visscher, *Double hybrid DFT calculations with Slater type orbitals*, *Journal of Computational Chemistry* 41 1660–1684 (2020) (<https://doi.org/10.1002/jcc.26209>)

RPA+SOSSX

A. Förster, L. Visscher, *Exploring the statically screened G3W2 correction to the GW self-energy : Charged excitations and total energies of finite systems*, *Physical Review B* 105, 125121 (2022) (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.105.125121>)

RPA, RPA+SOSEX, RPA+SOSSX

A. Förster, *Assessment of the Second-Order Statically Screened Exchange Correction to the Random Phase Approximation for Correlation Energies*, *Journal of Chemical Theory and Computation* 18, 5948 (2022) (<https://doi.org/10.1021/acs.jctc.2c00366>)

Sigma-functionals

S.Fauser, A. Förster, L. Redeker, C. Neiss, J. Erhard, E. Trushin, A. Görling, *Basis Set Requirements of σ -Functionals for Gaussian-and Slater-Type Basis Functions and Comparison with Range-Separated Hybrid and Double Hybrid Functionals*, *Journal of Chemical Theory and Computation* 20 (6), 2404–2422 (2024) (<https://doi.org/10.1021/acs.jctc.3c01132>)

14.2.4 Relativistic Effects**ZORA**

E. van Lenthe, E.J. Baerends and J.G. Snijders, *Relativistic regular two-component Hamiltonians*, *Journal of Chemical Physics* 99, 4597 (1993) (<https://doi.org/10.1063/1.466059>)

E. van Lenthe, E.J. Baerends and J.G. Snijders, *Relativistic total energy using regular approximations*, *Journal of Chemical Physics* 101, 9783 (1994) (<https://doi.org/10.1063/1.467943>)

E. van Lenthe, A.E. Ehlers and E.J. Baerends, *Geometry optimization in the Zero Order Regular Approximation for relativistic effects*, *Journal of Chemical Physics* 110, 8943 (1999) (<https://doi.org/10.1063/1.478813>)

ZORA suggested

E. van Lenthe, J.G. Snijders and E.J. Baerends, *The zero-order regular approximation for relativistic effects: The effect of spin-orbit coupling in closed shell molecules*, *Journal of Chemical Physics* 105, 6505 (1996) (<https://doi.org/10.1063/1.472460>)

E. van Lenthe, R. van Leeuwen, E.J. Baerends and J.G. Snijders, *Relativistic regular two-component Hamiltonians*, *International Journal of Quantum Chemistry* 57, 281 (1996) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1996\)57:3%3C281::AID-QUA2%3E3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-461X(1996)57:3%3C281::AID-QUA2%3E3.0.CO;2-U))

Pauli

J.G. Snijders, E.J. Baerends and P. Ros, *A perturbation theory approach to relativistic calculations. II. Molecules*, *Molecular Physics* 38, 1909 (1979) (<https://doi.org/10.1080/00268977900102941>)

P.M. Boerrigter, E.J. Baerends and J.G. Snijders, *A relativistic LCAO Hartree-Fock-Slater investigation of the electronic structure of the actinocenes $M(COT)_2$, $M=Th, Pa, U, Np$ and Pu* , *Chemical Physics* 122, 357 (1988) ([https://doi.org/10.1016/0301-0104\(88\)80018-1](https://doi.org/10.1016/0301-0104(88)80018-1))

T. Ziegler, V. Tschinke, E.J. Baerends, J.G. Snijders and W. Ravenek, *Calculation of bond energies in compounds of heavy elements by a quasi-relativistic approach*, *Journal of Physical Chemistry* 93, 3050 (1989) (<https://doi.org/10.1021/j100345a036>)

14.2.5 Solvents and other environments

COSMO: Conductor like Screening Model

C.C. Pye and T. Ziegler, *An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package*, *Theoretical Chemistry Accounts* 101, 396 (1999) (<https://doi.org/10.1007/s002140050457>)

SM12: Solvation Model 12

C.A. Peeples and G. Schreckenbach, *Implementation of the SM12 Solvation Model into ADF and Comparison with COSMO*, *Journal of Chemical Theory and Computation* 12, 4033 (2016) (<https://doi.org/10.1021/acs.jctc.6b00410>)

QM/MM: Quantum mechanical and Molecular Mechanics model

T. K. Woo, L. Cavallo and T. Ziegler, *Implementation of the IMOMM methodology for performing combined QM/MM molecular dynamics simulations and frequency calculations*, *Theoretical Chemistry Accounts* 100, 307 (1998) (<https://doi.org/10.1007/s002140050391>)

QM/MM suggested

T. K. Woo, S. Patchkovskii, and T. Ziegler, *Atomic Scale Modeling of Polymerization Catalysts*, *Computing in Science & Engineering*, 2, 28-37 (2000) (<https://doi.org/10.1109/5992.881705>)

QM/MM AddRemove model

M. Swart, *AddRemove: A new link model for use in QM/MM studies*, *International Journal of Quantum Chemistry* 91, 177 (2003) (<https://doi.org/10.1002/qua.10463>)

FDE: Frozen Density Embedding

T.A. Wesolowski and A. Warshel, *Frozen Density Functional Approach for ab-initio Calculations of Solvated Molecules*, *Journal of Physical Chemistry* 97, 8050 (1993) (<https://doi.org/10.1021/j100132a040>)

J. Neugebauer, C.R. Jacob, T.A. Wesolowski and E.J. Baerends, *An Explicit Quantum Chemical Method for Modeling Large Solvation Shells Applied to Aminocoumarin C151* *Journal of Physical Chemistry A* 109, 7805 (2005) (<https://doi.org/10.1021/jp0528764>)

C.R. Jacob, J. Neugebauer and L. Visscher, *A flexible implementation of frozen-density embedding for use in multilevel simulations*, *Journal of Computational Chemistry* 29, 1011 (2008) (<https://doi.org/10.1002/jcc.20861>)

DIM/QM: Discrete Interaction Model/Quantum Mechanics

J.L. Payton, S.M. Morton, Justin E. Moore, and Lasse Jensen, *A discrete interaction model/quantum mechanical method for simulating surface-enhanced Raman spectroscopy*, *Journal of Chemical Physics* 136, 214103 (2012) (<https://doi.org/10.1063/1.4722755>)

DRF: Discrete Solvent Reaction Field model

L. Jensen, P.T. van Duijnen and J.G. Snijders, *A discrete solvent reaction field model within density functional theory* *Journal of Chemical Physics* 118, 514 (2003) (<https://doi.org/10.1063/1.1527010>)

QM/FQ: Quantum Mechanics/Fluctuating Charges

T. Giovannini, F. Egidi and C. Cappelli, *Molecular spectroscopy of aqueous solutions: a theoretical perspective*, *Chemical Society Reviews*, 49, 5664 (2020) (<https://doi.org/10.1039/C9CS00464E>)

3D-RISM: Three-Dimensional Reference Interaction Site Model

S. Gusarov, T. Ziegler, and A. Kovalenko, *Self-Consistent Combination of the Three-Dimensional RISM Theory of Molecular Solvation with Analytical Gradients and the Amsterdam Density Functional Package*, *Journal of Physical Chemistry A* 110, 6083 (2006) (<https://doi.org/10.1021/jp054344t>)

3D-RISM suggested

A. Kovalenko and F. Hirata, *Self-consistent description of a metal-water interface by the Kohn-Sham density functional theory and the three-dimensional reference interaction site model*, *Journal of Chemical Physics* 110, 10095 (1999) (<https://doi.org/10.1063/1.478883>)

A. Kovalenko, *Three-dimensional RISM theory for molecular liquids and solid-liquid interfaces*, In *Molecular Theory of Solvation*; Hirata, Fumio, Ed.; Understanding Chemical Reactivity (series); Mezey, Paul G., Series Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; Vol. 24, pp 169-275.

14.2.6 Frequencies, IR Intensities, Raman, VCD

Numerical Differentiation of Gradients

L. Fan and T. Ziegler, *Application of density functional theory to infrared absorption intensity calculations on main group molecules*, *Journal of Chemical Physics* 96, 9005 (1992) (<https://doi.org/10.1063/1.462258>)

L. Fan and T. Ziegler, *Application of density functional theory to infrared absorption intensity calculations on transition-metal carbonyls*, *Journal of Physical Chemistry* 96, 6937 (1992) (<https://doi.org/10.1021/j100196a016>)

Analytical Second Derivatives

A. Bérces, R. M. Dickson, L. Fan, H. Jacobsen, D. Swerhone and T. Ziegler, *An implementation of the coupled perturbed Kohn-Sham equations: perturbation due to nuclear displacements*, *Computer Physics Communications* 100, 247 (1997) ([https://doi.org/10.1016/S0010-4655\(96\)00120-8](https://doi.org/10.1016/S0010-4655(96)00120-8))

H. Jacobsen, A. Bérces, D. Swerhone and T. Ziegler, *Analytic second derivatives of molecular energies: a density functional implementation*, *Computer Physics Communications* 100, 263 (1997) ([https://doi.org/10.1016/S0010-4655\(96\)00119-1](https://doi.org/10.1016/S0010-4655(96)00119-1))

S. K. Wolff, *Analytical second derivatives in the Amsterdam density functional package*, *International Journal of Quantum Chemistry* 104, 645 (2005) (<https://doi.org/10.1002/qua.20653>)

Mobile Block Hessian (MBH)

A. Ghysels, D. Van Neck, V. Van Speybroeck, T. Verstraelen and M. Waroquier, *Vibrational Modes in partially optimized molecular systems* *Journal of Chemical Physics* 126, 224102 (2007) (<https://doi.org/10.1063/1.2737444>)

MBH suggested

A. Ghysels, D. Van Neck and M. Waroquier, *Cartesian formulation of the Mobile Block Hessian Approach to vibrational analysis in partially optimized systems* *Journal of Chemical Physics* 127, 164108 (2007) (<https://doi.org/10.1063/1.2789429>)

Raman scattering

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Application of time-dependent density functional response theory to Raman scattering*, *Chemical Physics Letters* 259, 599 (1996) ([https://doi.org/10.1016/0009-2614\(96\)00858-5](https://doi.org/10.1016/0009-2614(96)00858-5))

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Implementation of time-dependent density functional response equations*, *Computer Physics Communications* 118, 119 (1999) ([https://doi.org/10.1016/S0010-4655\(99\)00187-3](https://doi.org/10.1016/S0010-4655(99)00187-3))

Resonance Raman: excited-state finite lifetime

L. Jensen, L. Zhao, J. Autschbach and G.C. Schatz, *Theory and method for calculating resonance Raman scattering from resonance polarizability derivatives*, *Journal of Chemical Physics* 123, 174110 (2005) (<https://doi.org/10.1063/1.2046670>)

Resonance Raman: excited-state gradient

J. Neugebauer, E.J. Baerends, E. Efremov, F. Ariese and C. Gooijer, *Combined Theoretical and Experimental Deep-UV Resonance Raman Studies of Substituted Pyrenes*, *Journal of Physical Chemistry A* 109, 2100 (2005) (<https://doi.org/10.1021/jp045360d>)

VROA: (Resonance) vibrational Raman optical activity

L. Jensen, J. Autschbach, M. Krykunov, and G.C. Schatz, *Resonance vibrational Raman optical activity: A time-dependent density functional theory approach*, *Journal of Chemical Physics* 127, 134101 (2007) (<https://doi.org/10.1063/1.2768533>)

Vibrational Circular Dichroism (VCD)

V.P. Nicu, J. Neugebauer, S.K. Wolff and E.J. Baerends, *A vibrational circular dichroism implementation within a Slater-type-orbital based density functional framework and its application to hexa- and hepta-helices*, *Theoretical Chemical Accounts* 119, 245 (2008) (<https://doi.org/10.1007/s00214-006-0234-x>)

VCD analysis: VCDtools

V.P. Nicu, J. Neugebauer and E.J. Baerends, *Effects of Complex Formation on Vibrational Circular Dichroism Spectra*, *Journal of Physical Chemistry A* 112, 6978 (2008) (<https://doi.org/10.1021/jp710201q>)

M.A.J. Koenis, O. Visser, L. Visscher, W.J. Buma, V.P. Nicu, *GUI Implementation of VCDtools, A Program to Analyze Computed Vibrational Circular Dichroism Spectra*, *J. Chem. Inf. Model* 60, 259 (2020) (<https://pubs.acs.org/doi/abs/10.1021/acs.jcim.9b00956>)

V.P. Nicu, *Revisiting an old concept: the coupled oscillator model for VCD. Part 1: the generalised coupled oscillator mechanism and its intrinsic connection to the strength of VCD signals*, *Physical Chemistry Chemical Physics* 18, 21202 (2016) (<https://doi.org/10.1039/C6CP01282E>).

Franck-Condon factors

J.S. Seldenthuis, H.S.J. van der Zant, M.A. Ratner and J.M. Thijssen, *Vibrational Excitations in Weakly Coupled Single-Molecule Junctions: A Computational Analysis*, *ACS Nano* 2, 1445 (2008) (<https://doi.org/10.1021/nn800170h>)

14.2.7 Time-Dependent DFT**For all Time-Dependent DFT features (Excitation Energies, (Hyper) Polarizabilities, Dispersion Coefficients, Raman Scattering, include:**

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Implementation of time-dependent density functional response equations*, *Computer Physics Communications* 118, 119 (1999) ([https://doi.org/10.1016/S0010-4655\(99\)00187-3](https://doi.org/10.1016/S0010-4655(99)00187-3))

Excitation Energies and Oscillator Strengths**Lead reference**

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Implementation of time-dependent density functional response equations*, *Computer Physics Communications* 118, 119 (1999) ([https://doi.org/10.1016/S0010-4655\(99\)00187-3](https://doi.org/10.1016/S0010-4655(99)00187-3))

Suggested (when ZORA relativistic results are used)

A. Rosa, E.J. Baerends, S.J.A. van Gisbergen, E. van Lenthe, J.A. Groeneveld and J. G. Snijders, *Article Electronic Spectra of $M(CO)_6$ ($M = Cr, Mo, W$) Revisited by a Relativistic TDDFT Approach*, *Journal of the American Chemical Society* 121, 10356 (1999) (<https://doi.org/10.1021/ja990747t>)

Open Shell ground state

F. Wang and T. Ziegler, *Mol. Phys.* 102, 2585 (2004)

Spin-flip transitions

F. Wang and T. Ziegler, *Time-dependent density functional theory based on a noncollinear formulation of the exchange-correlation potential*, *Journal of Chemical Physics* 121, 12191 (2004) (<https://doi.org/10.1063/1.1821494>)

F. Wang and T. Ziegler, *The performance of time-dependent density functional theory based on a noncollinear exchange-correlation potential in the calculations of excitation energies*, *Journal of Chemical Physics* 122, 74109 (2005) (<https://doi.org/10.1063/1.1844299>)

Core excitations

M. Stener, G. Fronzoni and M. de Simone, *Time dependent density functional theory of core electrons excitations*, *Chemical Physics Letters* 373, 115 (2003) ([https://doi.org/10.1016/S0009-2614\(03\)00543-8](https://doi.org/10.1016/S0009-2614(03)00543-8))

Quadrupole intensities

S. Bernadotte, A.J. Atkins, Ch.R. Jacob, *Origin-independent calculation of quadrupole intensities in X-ray spectroscopy*, *Journal of Chemical Physics* 137, 204106 (2012) (<https://doi.org/10.1063/1.4766359>)

XES: X-ray emission spectroscopy

A.J. Atkins, M. Bauer, and Ch.R. Jacob, *The chemical sensitivity of X-ray spectroscopy: high energy resolution XANES versus X-ray emission spectroscopy of substituted ferrocenes*, *Physical Chemistry Chemical Physics* 15, 8095 (2013) (<https://doi.org/10.1039/C3CP50999K>)

Excitations including spin-orbit coupling

F. Wang, T. Ziegler, E. van Lenthe, S.J.A. van Gisbergen and E.J. Baerends, *The calculation of excitation energies based on the relativistic two-component zeroth-order regular approximation and time-dependent density-functional with full use of symmetry*, *Journal of Chemical Physics* 122, 204103 (2005) (<https://doi.org/10.1063/1.1899143>)

Perturbative approach to include spin-orbit coupling

F. Wang and T. Ziegler, *A simplified relativistic time-dependent density-functional theory formalism for the calculations of excitation energies including spin-orbit coupling effect*, *Journal of Chemical Physics* 123, 154102 (2005) (<https://doi.org/10.1063/1.2061187>)

CV(n)-DFT: Constricted Variational DFT

J. Cullen, M. Krykunov, and T. Ziegler, *The formulation of a self-consistent constricted variational density functional theory for the description of excited states*, *Chemical Physics* 391, 11 (2011) (<https://doi.org/10.1016/j.chemphys.2011.05.021>)

M. Krykunov and T. Ziegler, *Self-consistent Formulation of Constricted Variational Density Functional Theory with Orbital Relaxation. Implementation and Applications*, *Journal of Chemical Theory and Computation* 9, 2761 (2013) (<https://doi.org/10.1021/ct300891k>)

CV(n)-DFT: triplet states

Y.C. Park, F. Senn, M. Krykunov, and T. Ziegler, *Self-Consistent Constricted Variational Theory RSCF-CV(∞)-DFT and Its Restrictions To Obtain a Numerically Stable Δ SCF-DFT-like Method: Theory and Calculations for Triplet States*, *Journal of Chemical Theory and Computation* 12, 5438 (2016) (<https://doi.org/10.1021/acs.jctc.6b00333>)

TD-DFT+TB: Tight-Binding approximations to time-dependent Density Functional Theory

R. Rüger, E. van Lenthe, T. Heine, L. Visscher, *Tight-Binding Approximations to Time-Dependent Density Functional Theory - a fast approach for the calculation of electronically excited states*, *Journal of Chemical Physics* 144, 184103 (2016) (<https://doi.org/10.1063/1.4948647>)

GW-BSE: GW-Bethe-Salpeter Equation

Arno Förster, Lucas Visscher, *Quasiparticle Self-Consistent GW-Bethe-Salpeter equation calculations for large chromophoric systems*, *Journal of Chemical Theory and Computation* 18 (11) 6779–6793 (2022) (<https://doi.org/10.1021/acs.jctc.2c00531>)

Excited state gradients**General**

M. Seth, G. Mazur, and T. Ziegler, *Time-dependent density functional theory gradients in the Amsterdam density functional package: geometry optimizations of spin-flip excitations*, *Theoretical Chemistry Accounts* 129, 331 (2011) (<https://doi.org/10.1007/s00214-010-0819-2>)

TD-DFT+TB excited state gradients

S. Havenridge, R. Rüger, C.M. Aikens, *Analytical excited state gradients for time-dependent density functional theory plus tight binding (TDDFT + TB)* *The Journal of Chemical Physics* 158, 224103 (2023) (<https://doi.org/10.1063/5.0142240>).

Polarizabilities

General

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *A Density Functional Theory study of frequency-dependent polarizabilities and van der Waals dispersion coefficients for polyatomic molecules*, *Journal of Chemical Physics* 103, 9347 (1995) (<https://doi.org/10.1063/1.469994>)

Suggested

V.P. Osinga, S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Density functional results for isotropic and anisotropic multipole polarizabilities and C6, C7, and C8 Van der Waals dispersion coefficients for molecules*, *Journal of Chemical Physics* 106, 5091 (1997) (<https://doi.org/10.1063/1.473555>)

Polarizabilities including spin-orbit coupling

A. Devarajan, A. Gaenko, and J. Autschbach, *Two-component relativistic density functional method for computing nonsingular complex linear response of molecules based on the zeroth order regular approximation*, *Journal of Chemical Physics* 130, 194102 (2009) (<https://doi.org/10.1063/1.3123765>)

PolTDDFT: Damped complex polarizabilities

O. Baseggio, G. Fronzoni, and M. Stener, *A new time dependent density functional algorithm for large systems and plasmons in metal clusters*, *Journal of Chemical Physics* 143, 024106 (2015) (<https://doi.org/10.1063/1.4923368>)

Hyperpolarizabilities

Hyperpolarizabilities with RESPONSE

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory*, *Journal of Chemical Physics* 109, 10644 (1998) (<https://doi.org/10.1063/1.477762>)

Suggested:

S.J.A. van Gisbergen, J.G. Snijders, and E.J. Baerends, *Time-dependent Density Functional Results for the Dynamic Hyperpolarizability of C60*, *Physical Review Letters* 78, 3097 (1997) (<https://doi.org/10.1103/PhysRevLett.78.3097>)

First hyperpolarizabilities with AORESPONSE

Z. Hu, J. Autschbach, and L. Jensen, *Simulation of resonance hyper-Rayleigh scattering of molecules and metal clusters using a time-dependent density functional theory approach*, *Journal of Chemical Physics* 141, 124305 (2014) (<https://doi.org/10.1063/1.4895971>)

Second hyperpolarizabilities with AORESPONSE

Z. Hu, J. Autschbach, and L. Jensen, *Simulating Third-Order Nonlinear Optical Properties Using Damped Cubic Response Theory within Time-Dependent Density Functional Theory*, *Journal of Chemical Theory and Computation* 12, 1294 (2016) (<https://doi.org/10.1021/acs.jctc.5b01060>)

CD, ORD, magnetizability, MCD, Verdet constants

Circular Dichroism (CD)

J. Autschbach and T. Ziegler, *Calculating molecular electric and magnetic properties from time-dependent density functional response theory*, *Journal of Chemical Physics* 116, 891 (2002) (<https://doi.org/10.1063/1.1420401>)

J. Autschbach, T. Ziegler, S.J.A. van Gisbergen and E.J. Baerends, *Chiroptical properties from time-dependent density functional theory. I. Circular dichroism spectra of organic molecules*, *Journal of Chemical Physics* 116, 6930 (2002) (<https://doi.org/10.1063/1.1436466>)

Optical Rotation (OR), Optical Rotation Dispersion (ORD)

J. Autschbach and T. Ziegler, *Calculating molecular electric and magnetic properties from time-dependent density functional response theory*, *Journal of Chemical Physics* 116, 891 (2002) (<https://doi.org/10.1063/1.1420401>)

J. Autschbach, S. Patchkovskii, T. Ziegler, S.J.A. van Gisbergen and E.J. Baerends, *Chiroptical properties from time-dependent density functional theory. II. Optical rotations of small to medium sized organic molecules*, *Journal of Chemical Physics* 117, 581 (2002) (<https://doi.org/10.1063/1.1477925>)

Magnetizability

M. Krykunov and J. Autschbach, *Calculation of static and dynamic linear magnetic response in approximate time-dependent density functional theory*, *Journal of Chemical Physics* 126, 24101 (2007) (<https://doi.org/10.1063/1.2423007>)

Magnetic Circular Dichroism (MCD)

M. Seth, M. Krykunov, T. Ziegler, J. Autschbach and A. Banerjee, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism: Calculation of B terms*, *Journal of Chemical Physics* 128, 144105 (2008) (<https://doi.org/10.1063/1.2901967>)

M. Seth, M. Krykunov, T. Ziegler and J. Autschbach, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism. II. Calculation of A terms*, *Journal of Chemical Physics* 128, 234102 (2008) (<https://doi.org/10.1063/1.2933550>)

M. Seth, T. Ziegler and J. Autschbach, *Application of magnetically perturbed time-dependent density functional theory to magnetic circular dichroism. III. Temperature-dependent magnetic circular dichroism induced by spin-orbit coupling*, *Journal of Chemical Physics* 129, 104105 (2008) (<https://doi.org/10.1063/1.2976568>)

Verdet constant and Faraday term

M. Krykunov, A. Banerjee, T. Ziegler and J. Autschbach, *Calculation of Verdet constants with time-dependent density functional theory. Implementation and results for small molecules*, *Journal of Chemical Physics* 122, 074105 (2005) (<https://doi.org/10.1063/1.1850919>)

M. Krykunov, M. Seth, T. Ziegler and J. Autschbach, *Calculation of the magnetic circular dichroism B term from the imaginary part of the Verdet constant using damped time-dependent density functional theory*, *Journal of Chemical Physics* 127, 244102 (2007) (<https://doi.org/10.1063/1.2806990>)

Dispersion Coefficients

Lead reference

V.P. Osinga, S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Density functional results for isotropic and anisotropic multipole polarizabilities and C6, C7, and C8 Van der Waals dispersion coefficients for molecules*, *Journal of Chemical Physics* 106, 5091 (1997) (<https://doi.org/10.1063/1.473555>)

Suggested

S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *A Density Functional Theory study of frequency-dependent polarizabilities and van der Waals dispersion coefficients for polyatomic molecules*, *Journal of Chemical Physics* 103, 9347 (1995) (<https://doi.org/10.1063/1.469994>)

14.2.8 LFDFT

Lead reference

M. Atanasov, C.A. Daul, C. Rauzy, *A DFT Based Ligand Field Theory*, *Structure & Bonding* 106, 97 (2004) (<https://doi.org/10.1007/b11308>)

LFDFT for two-open-shell configuration

H. Ramanantoanina, W. Urland, F. Cimpoesu, and C. Daul, *Ligand field density functional theory calculation of the $4f^2 \rightarrow 4f^1 5d^1$ transitions in the quantum cutter $\text{Cs}_2 \text{KYF}_6 \text{Pr}^{3+}$* , *Physical Chemistry Chemical Physics* 15, 13902 (2013) (<https://doi.org/10.1039/C3CP51344K>).

14.2.9 NMR

NMR Chemical Shifts

Lead reference

G. Schreckenbach and T. Ziegler, *The calculation of NMR shielding tensors using GIAO's and modern density functional theory*, *Journal of Physical Chemistry* 99, 606 (1995) (<https://doi.org/10.1021/j100002a024>)

NMR chemical shifts with hybrid functionals

M. Krykunov, T. Ziegler and E. van Lenthe, *Hybrid density functional calculations of nuclear magnetic shieldings using Slater-type orbitals and the zeroth-order regular approximation*, *International Journal of Quantum Chemistry* 109, 1676 (2009) (<https://doi.org/10.1002/qua.21985>)

NMR chemical shifts with NBO analysis

J. Autschbach and S. Zheng, *Analyzing Pt chemical shifts calculated from relativistic density functional theory using localized orbitals: The role of Pt 5d lone pairs*, *Magnetic Resonance in Chemistry* 46, S45 (2008) (<https://doi.org/10.1002/mrc.2289>)

J. Autschbach, *Analyzing NMR shielding tensors calculated with two-component relativistic methods using spin-free localized molecular orbitals*, *Journal of Chemical Physics* 128, 164112 (2008) (<https://doi.org/10.1063/1.2905235>)

Paramagnetic NMR chemical shifts

J. Autschbach, S. Patchkovskii, and B. Pritchard, *Calculation of Hyperfine Tensors and Paramagnetic NMR Shifts Using the Relativistic Zeroth-Order Regular Approximation and Density Functional Theory*, *Journal of Chemical Theory and Computation* 7, 2175 (2011) (<https://doi.org/10.1021/ct200143w>)

Suggested

G. Schreckenbach and T. Ziegler, *The calculation of NMR shielding tensors based on density functional theory and the frozen-core approximation*, *International Journal of Quantum Chemistry* 60, 753 (1996) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1996\)60:3%3C753::AID-QUA4%3E3.0.CO;2-W](https://doi.org/10.1002/(SICI)1097-461X(1996)60:3%3C753::AID-QUA4%3E3.0.CO;2-W))

G. Schreckenbach and T. Ziegler, *Calculation of NMR shielding tensors based on density functional theory and a scalar relativistic Pauli-type Hamiltonian. The application to transition metal complexes*, *International Journal of Quantum Chemistry* 61, 899 (1997) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1997\)61:6%3C899::AID-QUA3%3E3.0.CO;2-R](https://doi.org/10.1002/(SICI)1097-461X(1997)61:6%3C899::AID-QUA3%3E3.0.CO;2-R))

S.K. Wolff and T. Ziegler, *Calculation of DFT-GIAO NMR shifts with inclusion of spin-orbit coupling*, *Journal of Chemical Physics* 109, 895 (1998) (<https://doi.org/10.1063/1.476630>)

S.K. Wolff, T. Ziegler, E. van Lenthe and E.J. Baerends, *Density functional calculations of nuclear magnetic shieldings using the zeroth-order regular approximation (ZORA) for relativistic effects: ZORA nuclear magnetic resonance*, *Journal of Chemical Physics* 110, 7689 (1999) (<https://doi.org/10.1063/1.478680>)

NMR spin-spin coupling

Lead reference

J. Autschbach and T. Ziegler, *Nuclear spin-spin coupling constants from regular approximate density functional calculations. I. Formalism and scalar relativistic results for heavy metal compounds*, *Journal of Chemical Physics* 113, 936 (2000) (<https://doi.org/10.1063/1.481874>)

J. Autschbach, and T. Ziegler, *Nuclear spin-spin coupling constants from regular approximate relativistic density functional calculations. II. Spin-orbit coupling effects and anisotropies*, *Journal of Chemical Physics* 113, 9410 (2000) (<https://doi.org/10.1063/1.1321310>)

NMR spin-spin couplings with PBE0

J. Autschbach, *Two-component relativistic hybrid density functional computations of nuclear spin-spin coupling tensors using Slater-type basis sets and density-fitting techniques*, *Journal of Chemical Physics* 129,

094105 (2008) (<https://doi.org/10.1063/1.2969100>), Erratum: *Journal of Chemical Physics* 130, 209901 (2009) (<https://doi.org/10.1063/1.3131724>)

NMR spin-spin couplings with NBO analysis

J. Autschbach, *Analyzing molecular properties calculated with two-component relativistic methods using spin-free Natural Bond Orbitals: NMR spin-spin coupling constants* *Journal of Chemical Physics* 127, 124106 (2007) (<https://doi.org/10.1063/1.2768363>)

Suggested

R.M. Dickson and T. Ziegler, *NMR Spin-Spin Coupling Constants from Density Functional Theory with Slater-Type Basis Functions*, *Journal of Physical Chemistry* 100, 5286 (1996) (<https://doi.org/10.1021/jp951930l>)

J. Khandogin and T. Ziegler, *A density functional study of nuclear magnetic resonance spin-spin coupling constants in transition-metal systems*, *Spectrochimica Acta* 55, 607 (1999) ([https://doi.org/10.1016/S1386-1425\(98\)00265-0](https://doi.org/10.1016/S1386-1425(98)00265-0))

J. Autschbach and T. Ziegler, *Solvent Effects on Heavy Atom Nuclear Spin-Spin Coupling Constants: A Theoretical Study of Hg.C and Pt.P Couplings*, *Journal of the American Chemical Society* 123, 3341 (2001) (<https://doi.org/10.1021/ja003481v>)

J. Autschbach and T. Ziegler, *A Theoretical Investigation of the Remarkable Nuclear Spin-Spin Coupling Pattern in [(NC)₅ Pt-Tl(CN)]⁻*, *Journal of the American Chemical Society* 123, 5320 (2001) (<https://doi.org/10.1021/ja003866d>)

Suggested book reference

J. Autschbach, T. Ziegler, in *Encyclopedia of Nuclear Magnetic Resonance*, Eds. D.M. Grant, R. K. Harris, John Wiley and Sons, Chichester, 2002, Vol. 9 *Advances in NMR*.

14.2.10 ESR/EPR

G-tensor: Zeeman interaction

G-tensor: self-consistent spin-orbit coupling

E. van Lenthe, A. van der Avoird and P.E.S. Wormer, *Density functional calculations of molecular g-tensors in the zero order regular approximation for relativistic effects*, *Journal of Chemical Physics* 107, 2488 (1997) (<https://doi.org/10.1063/1.474590>)

G-tensor: perturbative inclusion spin-orbit coupling

J. Autschbach and B. Pritchard, *Calculation of molecular g-tensors using the zeroth-order regular approximation and density functional theory: expectation value versus linear response approaches*, *Theoretical Chemistry Accounts* 129, 453 (2011) (<https://doi.org/10.1007/s00214-010-0880-x>)

G-tensor: perturbative inclusion spin-orbit coupling with EPR/NMR program

G. Schreckenbach and T. Ziegler, *Calculation of the G-tensor of electron paramagnetic resonance spectroscopy using Gauge-Including Atomic Orbitals and Density Functional Theory*, *Journal of Physical Chemistry A* 101, 3388 (1997) (<https://doi.org/10.1021/jp963060t>) (for ESR/EPR g-tensor)

S. Patchkovskii and T. Ziegler, *Calculation of the EPR g-Tensors of High-Spin Radicals with Density Functional Theory*, *Journal of Physical Chemistry A* 105, 5490 (2001) (<https://doi.org/10.1021/jp010457a>) (for high-spin ESR/EPR g-tensor)

A-tensor: Nuclear magnetic dipole hyperfine interaction**A-tensor**

E. van Lenthe, A. van der Avoird and P.E.S. Wormer, *Density functional calculations of molecular hyperfine interactions in the zero order regular approximation for relativistic effects*, *Journal of Chemical Physics* 108, 4783 (1998) (<https://doi.org/10.1063/1.475889>)

A-tensor: perturbative inclusion spin-orbit coupling

J. Autschbach, S. Patchkovskii, and B. Pritchard, *Calculation of Hyperfine Tensors and Paramagnetic NMR Shifts Using the Relativistic Zeroth-Order Regular Approximation and Density Functional Theory*, *Journal of Chemical Theory and Computation* 7, 2175 (2011) (<https://doi.org/10.1021/ct200143w>)

14.2.11 Nuclear Quadrupole Interaction (EFG)**EFG, NQCC (in ESR called Q-tensor: Nuclear electric quadrupole hyperfine interaction)**

E. van Lenthe and E.J. Baerends, *Density functional calculations of nuclear quadrupole coupling constants in the zero-order regular approximation for relativistic effects*, *Journal of Chemical Physics* 112, 8279 (2000) (<https://doi.org/10.1063/1.481433>)

EFG with NBO analysis

A.J. Rossini, R.W. Mills, G.A. Briscoe, E.L. Norton, S.J. Geier, I. Hung, S. Zheng, J. Autschbach, and R.W. Schurko, *Solid-State Chlorine NMR of Group IV Transition Metal Organometallic Complexes*, *Journal of the American Chemical Society* 131, 3317 (2009) (<https://doi.org/10.1021/ja808390a>)

J. Autschbach, S. Zheng, and R.W. Schurko, *Analysis of Electric Field Gradient Tensors at Quadrupolar Nuclei in Common Structural Motifs*, *Concepts in Magnetic Resonance Part A* 36A, 84 (2010) (<https://doi.org/10.1002/cmr.a.20155>)

14.2.12 GW**Lead reference**

Arno Förster, Lucas Visscher, *Low-order scaling G0W0 by pair atomic density fitting*, *Journal of Chemical Theory and Computation* 16 (12), 7381–7399 (2020) (<https://doi.org/10.1021/acs.jctc.0c00693>)

Suggested

Arno Förster, Lucas Visscher, *GW100: A Slater-Type Orbital Perspective*, *Journal of Chemical Theory and Computation* 17 (8), 5080–5097 (2021) (<https://doi.org/10.1021/acs.jctc.1c00308>)

Quasiparticle self-consistent GW

Arno Förster, Lucas Visscher, *Low-Order Scaling Quasiparticle Self-Consistent GW for Molecules*, *Frontiers in Chemistry* 9, 736591 (2021) (<https://doi.org/10.3389/fchem.2021.736591>)

Vertex-corrected GW

Arno Förster, Lucas Visscher, *Exploring the statically screened G3W2 correction to the GW self-energy: Charged excitations and total energies of finite systems*, *Physical Review B* 105, 125121 (2022) (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.105.125121>)

F.Bruneval, A. Förster, *Fully Dynamic G3W2 Self-Energy for Finite Systems: Formulas and Benchmark*, *Journal of Chemical Theory and Computation* 20 (8), 3218–3230 (2024) (<https://doi.org/10.1021/acs.jctc.4c00090>)

A. Förster, F.Bruneval, *Why Does the GW Approximation Give Accurate Quasiparticle Energies? The Cancellation of Vertex Corrections Quantified*, *The Journal of Physical Chemistry Letters* 15, 12526–12534 (2024) (<https://doi.org/10.1021/acs.jpcllett.4c03126>)

A. Förster, *Beyond quasi-particle self-consistent GW for molecules with vertex corrections*, *arXiv:2412.01581* (2024) (<https://arxiv.org/abs/2412.01581>)

14.2.13 Transport properties: Non-self-consistent Green's function

Lead reference

Chapter 2 and appendix C of J.S. Seldenthuis, *Electrical and mechanical effects in single-molecule junctions* (<https://downloads.scm.com/Doc/Seldenthuis2011.pdf>), PhD thesis, Delft University of Technology, 2011

Wide-band limit

C.J.O. Verzijsl, J.S. Seldenthuis, and J.M. Thijssen, *Applicability of the wide-band limit in DFT-based molecular transport calculations*, *Journal of Chemical Physics* **138**, 094102 (2013) (<https://doi.org/10.1063/1.4793259>)

14.2.14 Analysis

Bond Energy Analysis

T. Ziegler and A. Rauk, *A theoretical study of the ethylene-metal bond in complexes between Cu⁺, Ag⁺, Au⁺, Pt⁰ or Pt²⁺ and ethylene, based on the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* **18**, 1558 (1979) (<https://doi.org/10.1021/ic50196a034>)

T. Ziegler and A. Rauk, *Carbon monoxide, carbon monosulfide, molecular nitrogen, phosphorus trifluoride, and methyl isocyanide as sigma donors and pi acceptors. A theoretical study by the Hartree-Fock-Slater transition-state method*, *Inorganic Chemistry* **18**, 1755 (1979) (<https://doi.org/10.1021/ic50197a006>)

F.M. Bickelhaupt and E.J. Baerends, In: *Rev. Comput. Chem.*; K.B. Lipkowitz and D.B. Boyd, Eds.; Wiley, New York, 2000, Vol. 15, p.1-86

ETS-NOCV

M. Mitoraj, A. Michalak and T. Ziegler, *A Combined Charge and Energy Decomposition Scheme for Bond Analysis*, *Journal of Chemical Theory and Computation* **5**, 962 (2009) (<https://doi.org/10.1021/ct800503d>)

QTAIM, Bader analysis, grid-based algorithm

J.I. Rodríguez, R.F.W. Bader, P.W. Ayers, C. Michel, A.W. Götz and C. Bo, *A high performance grid-based algorithm for computing QTAIM properties*, *Chemical Physics Letters* **472**, 149 (2009) (<https://doi.org/10.1016/j.cplett.2009.02.081>)

J.I. Rodríguez, *An Efficient Method for Computing the QTAIM Topology of a Scalar Field: The Electron Density Case*, *Journal of Computational Chemistry* **34**, 681 (2013) (<https://doi.org/10.1002/jcc.23180>)

Localized molecular orbitals

J. Autschbach and H.F. King, *Analyzing molecular static linear response properties with perturbed localized orbitals*, *Journal of Chemical Physics* **133**, 044109 (2010) (<https://doi.org/10.1063/1.3455709>)

14.2.15 Accuracy and efficiency

Linear scaling methods

C. Fonseca Guerra, J.G. Snijders, G. te Velde and E.J. Baerends, *Towards an order-N DFT method*, *Theoretical Chemistry Accounts* **99**, 391 (1998) (<https://doi.org/10.1007/s002140050353>)

Numerical integration

M. Franchini, P.H.T. Philipsen, L. Visscher, *The Becke Fuzzy Cells Integration Scheme in the Amsterdam Density Functional Program Suite*, *Journal of Computational Chemistry* **34**, 1818 (2013) (<https://doi.org/10.1002/jcc.23323>).

Density fitting

M. Franchini, P.H.T. Philipsen, E. van Lenthe, L. Visscher, *Accurate Coulomb Potentials for Periodic and Molecular Systems through Density Fitting*, *Journal of Chemical Theory and Computation* **10**, 1994 (2014) (<https://doi.org/10.1021/ct500172n>)

14.3 External programs and Libraries

Third party software used in the 2026.1 version of the Amsterdam Modeling Suite can be found in the file titled “third-party-software.txt” in the root of your AMS installation.

EXAMPLES

15.1 Introduction

The AMS package contains a series of sample runs. They consist of UNIX scripts (to run the calculations) and the resulting output files.

The examples serve:

- To demonstrate how to do calculations. The number of options available in AMS is substantial and the sample runs do not cover all of them. They should be sufficient, however, to get a feeling for how to explore the possibilities.
- To work out special applications that do not fit well in the User's Guide.

Note: Most of the provided samples have been devised to be short and simple, at the expense of physical or chemical relevance and precision or general quality of results. They serve primarily to illustrate the use of input, necessary files, and type of results. The descriptions have been kept brief. Extensive information about using keywords in input and their implications is given in the User's Manual.

Where references are made to the operating system (OS) and to the file system on your computer, the terminology of a UNIX type OS is used.

All sample files are stored in subdirectories under `$AMSHOME/examples/`, where `$AMSHOME` is the main directory of the AMS package. There are many subdirectories in `$AMSHOME/examples/`: the examples presented in this section are located in `$AMSHOME/examples/adf/`. Each sample run has its own directory. For instance, `$AMSHOME/examples/adf/HCN/` contains an ADF calculation on the HCN molecule.

Each sample subdirectory contains:

- A file `TestName.run`: the UNIX script to execute the calculation(s). A sample may involve several calculations, for instance a molecular AMS calculation (using ADF engine) followed by NMR calculation (using the NMR program) to compute chemical shifts.
- A file `TestName_orig.out.gz`: the resulting output(s) against which you can compare the outcome of your own calculation. Note: the files are compressed using [gzip](https://en.wikipedia.org/wiki/Gzip) (<https://en.wikipedia.org/wiki/Gzip>).
- Zero or more files with a `.ams` extension. These files, if present, are intended for AMSinput and demonstrate the same functionality as the two files above. However, there are also differences between the `.ams` and the `TestName.run` files so the results obtained with the `.ams` files **cannot be compared directly** with `TestName_orig.out`. Also, the `TestName.run` file usually contains more than one calculation, for which more than one `.ams` file is required. That's why in some directories you may find more than one `.ams` file.

Technical notes:

- Running the examples on Windows: You can run an example calculation by double-clicking on the appropriate `.run` file. After the calculation has finished, you can compare the `TestName.out` file with the reference `TestName_orig.out` file. See remarks about comparing output files below.

- The UNIX scripts make use of the *rm* (remove) command. Some UNIX users may have aliased the *rm* command. They should accordingly adapt these commands in the sample scripts so as to make sure that the scripts will remove the files. New users may get stuck initially because of files that are lingering around after an earlier attempt to run one of the examples. In a subsequent run, when the program tries to open a similar (temporary or result) file again, an error may occur if such a file already exists. Always make sure that no files are left in the run-directory except those that are required specifically.
- It is a good idea to run each example in a separate directory that contains no other important files.
- The run-scripts use the environment variables `AMSBIN` and `AMSRESOURCES`. They stand respectively for the directory that contains the program executables and the main directory of the basis set files. To use the scripts as they are you must have defined the variables `AMSBIN` and `AMSRESOURCES` in your environment. If a parallel version has been installed, it is preferable to have also the environment variable `NSCM`. This defines the default number of parallel processes that the program will try to use. Consult the Installation Manual for details.
- As you will note the sample run scripts refer to the programs by names like 'ams', 'nmr', and so on. When you inspect your `$AMSBIN` directory, however, you may find that the program executables have names 'ams.exe', 'nmr.exe'. There are also files in `$AMSBIN` with names 'ams', 'nmr', but these are in fact scripts to execute the binaries. We strongly recommend that you use these scripts in your calculations, in particular when running parallel jobs: the scripts take care of some aspects that you have to do otherwise yourself in each calculation.
- You need a license file to run any calculations successfully. If you have troubles with your license file, consult the Installation manual. If that doesn't help contact us at support@scm.com

When you compare your own results with the sample outputs, you should check in particular (as far as applicable):

- Occupation numbers and energies of the one-electron orbitals;
- The optimized geometry;
- Vibrational frequencies;
- The bonding energy and the various terms in which it has been decomposed;
- The dipole moment;
- The logfile. At the end of a calculation the logfile is automatically appended (by the program itself) to the standard output.

General remarks about comparisons:

- For technical reasons, the discussion of which is beyond the scope of this document, differences between results obtained on different machines (or with different numbers of parallel processes) may be much larger than you would expect. They may significantly exceed the machine precision. What you should check is that they fall well (by at least an order of magnitude) within the *numerical integration* precision used in the calculation.
- For similar reasons the orientation of the molecule used by the program may be different on different machines, even when the same input is supplied. In such cases the different orientations should be related and only differ in some trivial way, such as by a simple rotation of all coordinates by 90 degrees around the z-axis. When in doubt, contact an SCM representative.

15.2 Model Hamiltonians

15.2.1 Special exchange-correlation functionals

Example: r2SCAN-3c

Download `r2SCAN-3c.run`

```
#!/bin/sh

# r2SCAN-3c example

# To use r2SCAN-3c in ADF one needs the r2SCAN functional icw a predefined basis set
↪ (mTZ2P),
# D4-dispersion and a geometrical counterpoise (gCP) correction.
# r2SCAN-3c also needs relativistic effects to be included,
# which are included by default in ADF, and (at least) a numericalquality GOOD.

# The usage of metagga r2scan-3c in the XC block automatically includes the correct
# D4 dispersion and gCP correction. It is in fact the same as using
# XC
#   gcp stor2scan3c
#   libxc r2scan
#   Dispersion Grimme4 s6=1.0 s8=0.0 s9=1.53 a1=0.42 a2=5.65 g_a=2.0 g_c=1.0
# end
# Note that LibXC is used to calculate the r2SCAN part of r2SCAN-3c.

$AMSBIN/ams << eor
System
  GeometryFile $AMSHOME/examples/adf/r2SCAN-3c/struc.xyz
end

Task SinglePoint

Engine ADF
  basis
    core None
    type mTZ2P
  end
  xc
    metagga r2scan-3c
  end
  numericalquality good
EndEngine
eor
```

Example: Asymptotically correct XC potentials: CO

Download CO_model.run

```
#!/bin/sh

# For property calculations, XC potentials with asymptotically correct (-1/r)
# behavior outside the molecule, the results tend to be superior to regular LDA
# or GGA calculations. This is especially true for small molecules and for
# properties that depend heavily on the proper description of the outer region
# of the molecule. In the example, all-electron basis sets are used. This is
# mandatory for the SAOP potential.

# In the first example, excitation energies are calculated with the GRACLB
# potential. This potential requires one number as argument: the experimental
# ionization potential in atomic units. This number can be either based on an
# experimental value, or on previous GGA total energy calculations.

AMS_JOBNAME=GRACLB $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    O 0 0 0
    C 1.128205364 0 0
  end
end

Task SinglePoint

Engine ADF
  title CO excitations grac potential
  beckegrid
    quality good
  end
  excitations
    lowest 10
    onlising
  end
  basis
    core None
    type TZ2P
  end
  xc
    model GRACLB 0.515
  end
EndEngine

eor

# The same calculation with the SAOP XC potential would differ in the XC block
# only:

AMS_JOBNAME=SAOP $AMSBIN/ams <<eor
System
```

(continues on next page)

(continued from previous page)

```

symmetrize
atoms
  O  0          0  0
  C  1.128205364  0  0
end
end

Task SinglePoint

Engine ADF
  title CO excitations SAOP
  beckegrid
    quality good
  end
  excitations
    lowest 10
    onlising
  end
  basis
    core None
    type TZ2P
  end
  xc
    model SAOP
  end
EndEngine

eor

# SAOP depends on the orbitals which makes it more expensive to evaluate than
# GRAC for large molecules, but is much easier to use, since it does not require
# an ionization potential parameter as input.

```

Example: Meta-GGA energy functionals: OH

Download OH_MetaGGA.run

```

#!/bin/sh

AMS_JOBNAME=TPSSh $AMSBIN/ams <<eor
System
  atoms
    O    0.000000    0.000000    0.108786
    H    0.000000    0.000000   -0.870284
  end
end

Task SinglePoint

Engine ADF
  title OH radical, C*v symm. MP2(full)/6-31G* Geom. MP2=-75.5232063
  dependency
    bas 1.0e-4

```

(continues on next page)

(continued from previous page)

```

end
irrepopulations
  A1 3 // 3
  A2 0 // 0
  B1 1 // 1
  B2 1 // 0
end
metagga
basis
  type ET/ET-QZ3P
end
noprnt BAS FIT FUNCTIONS SFO
numericalquality VeryGood
spinpolarization 1
symmetry C(2V)
unrestricted
xc
  metahybrid TPSSh
end
EndEngine
eor

AMS_JOBNAME=TPSS $AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000    0.108786
    H      0.000000    0.000000   -0.870284
  end
end

Task SinglePoint

Engine ADF
  title OH radical, C*v symm. MP2(full)/6-31G* Geom. MP2=-75.5232063
  dependency
    bas 1.0e-4
  end
  hartreefock
  irrepopulations
    A1 3 // 3
    A2 0 // 0
    B1 1 // 1
    B2 1 // 0
  end
  metagga
  basis
    type ET/ET-QZ3P
  end
  noprnt BAS FIT FUNCTIONS SFO
  numericalquality VeryGood
  spinpolarization 1
  symmetry C(2V)
  unrestricted
  xc
    metagga SCF TPSS
  end

```

(continues on next page)

(continued from previous page)

```

EndEngine
eor

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/H
mv TAPE12 t12.rel

AMS_JOBNAME=H_HF $AMSBIN/ams <<eor
System
  Atoms
    H 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create H file=$AMSRESOURCES/ADF/ET/ET-QZ3P/H
  hartreefock
  xc
    gga PBE
  end
  corepotentials t12.rel
    H 1
  end
EndEngine
eor

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/O
mv TAPE12 t12.rel

AMS_JOBNAME=O_HF $AMSBIN/ams <<eor
System
  Atoms
    O 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create O file=$AMSRESOURCES/ADF/ET/ET-QZ3P/O
  hartreefock
  xc
    gga PBE
  end
  corepotentials t12.rel
    O 1
  end
EndEngine
eor

AMS_JOBNAME=H_HF_unr $AMSBIN/ams <<eor
System
  atoms
    H      0.0      0.0      0.0
  End
End
Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title H unrestricted correction
  fragments
    H H_HF.results/adf.rkf
  end
  hartreefock
  metagga
  numericalquality VeryGood
  spinpolarization 1
  unrestricted
  xc
    gga PBE
  end
EndEngine
eor

```

```
AMS_JOBNAME=O_HF_unr $AMSBIN/ams <<eor
```

```

System
  atoms
    O      0.0    0.0    0.0
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title O unrestricted correction
  fragments
    O O_HF.results/adf.rkf
  end
  hartreefock
  irreproccupations
    sigma 3 // 3
    pi    2 // 0
  end
  metagga
  numericalquality VeryGood
  spinpolarization 2
  symmetry C(lin)
  unrestricted
  xc
    gga PBE
  end
EndEngine
eor

```

```
AMS_JOBNAME=OH_HF $AMSBIN/ams <<eor
```

```

System
  atoms
    O      0.000000    0.000000    0.108786
    H      0.000000    0.000000   -0.870284
  end
end
Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title OH radical, C*v symm. MP2(full)/6-31G* Geom. MP2=-75.5232063
  dependency
    bas 1.0e-4
  end
  energyfrag
    O O_HF_unr.results/adf.rkf
    H H_HF_unr.results/adf.rkf
  end
  fragments
    O O_HF.results/adf.rkf
    H H_HF.results/adf.rkf
  end
  hartreefock
  irreppoccupations
    A1 3 // 3
    A2 0 // 0
    B1 1 // 1
    B2 1 // 0
  end
  metagga
  noprint BAS FIT FUNCTIONS SFO
  numericalquality VeryGood
  spinpolarization 1
  symmetry C(2V)
  unrestricted
  xc
    gga PBE
  end
EndEngine
eor

```

```

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/H
mv TAPE12 t12.rel

```

```

AMS_JOBNAME=H_OLYP $AMSBIN/ams <<eor
System
  atoms
    H      0.0      0.0      0.0
  End
End
Task SinglePoint
Engine ADF
  create H file=$AMSRESOURCES/ADF/ET/ET-QZ3P/H
  hartreefock
  xc
    gga OLYP
  end
  corepotentials t12.rel
    H 1
  end
EndEngine
eor

```

```

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/O

```

(continues on next page)

(continued from previous page)

```

mv TAPE12 t12.rel

AMS_JOBNAME=O_OLYP $AMSBIN/ams <<eor
System
  atoms
    O      0.0    0.0    0.0
  End
End
Task SinglePoint
Engine ADF
  create 0 file=$AMSRESOURCES/ADF/ET/ET-QZ3P/O
  hartreefock
  xc
    gga OLYP
  end
  corepotentials t12.rel
    O 1
  end
EndEngine
eor

AMS_JOBNAME=H_OLYP_unr $AMSBIN/ams <<eor
System
  atoms
    H      0.0    0.0    0.0
  end
end

Task SinglePoint

Engine ADF
  title H unrestricted correction
  fragments
    H H_OLYP.results/adf.rkf
  end
  hartreefock
  metagga
  numericalquality VeryGood
  spinpolarization 1
  unrestricted
  xc
    gga OLYP
  end
EndEngine
eor

AMS_JOBNAME=O_OLYP_unr $AMSBIN/ams <<eor
System
  atoms
    O      0.0    0.0    0.0
  end
end

Task SinglePoint

Engine ADF

```

(continues on next page)

(continued from previous page)

```

title 0 unrestricted correction
fragments
  O O_OLYP.results/adf.rkf
end
hartreefock
irrepoccupations
  sigma 3 // 3
  pi 2 // 0
end
metagga
numericalquality VeryGood
spinpolarization 2
symmetry C(lin)
unrestricted
xc
  gga OLYP
end
EndEngine
eor

AMS_JOBNAME=OH_OLYP $AMSBIN/ams <<eor
System
  atoms
    O 0.000000 0.000000 0.108786
    H 0.000000 0.000000 -0.870284
  end
end

Task SinglePoint

Engine ADF
  title OH radical, C*v symm. MP2(full)/6-31G* Geom. MP2=-75.5232063
  dependency
    bas 1.0e-4
  end
  energyfrag
    O O_OLYP_unr.results/adf.rkf
    H H_OLYP_unr.results/adf.rkf
  end
  fragments
    O O_OLYP.results/adf.rkf
    H H_OLYP.results/adf.rkf
  end
  hartreefock
  irrepoccupations
    A1 3 // 3
    A2 0 // 0
    B1 1 // 1
    B2 1 // 0
  end
  metagga
  noprint BAS FIT FUNCTIONS SFO
  numericalquality VeryGood
  spinpolarization 1
  symmetry C(2V)
  unrestricted

```

(continues on next page)

(continued from previous page)

```

xc
  gga OLYP
end
EndEngine
eor

```

Example: Hartree-Fock: HI

Download HI_EFG.run

```

#!/bin/sh

# Example shows a Hartree-Fock calculation with a non-relativistic, scalar-
↪relativistic ZORA,
# and a spin-orbit coupled ZORA Hamiltonian. In this case ADF also calculates
# the electric field gradient (EFG) at the H and I nuclei (keyword QTENS).

# First the non-relativistic calculation.
# Note that in this case the all-electron basis sets are obtained from the
↪$AMSRESOURCES/ADF/ZORA directory

# == non-relativistic ==

AMS_JOBNAME=NR $AMSBIN/ams <<eor
System
  atoms
    H 0 0 0
    I 0 0 1.609
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type ZORA/TZ2P
    CreateOutput Yes
  end
  qtens
  xc
    hartreefock
  end
EndEngine
eor

# == scalar relativistic ZORA ==

# Next the scalar relativistic ZORA calculation. Note that in this case the all-

```

(continues on next page)

(continued from previous page)

```

↪electron basis sets are
# also obtained from the $AMSRESOURCES/ADF/ZORA directory, but this is default place↪
↪where the key BASIS will
# search for basis sets in case of ZORA. ADF will also calculate the EFG including↪
↪the small component density,
# also called SR ZORA-4.

AMS_JOBNAME=SR $AMSBIN/ams <<eor
System
  atoms
    H 0 0 0
    I 0 0 1.609
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  xc
    hartreefock
  end
EndEngine
eor

# == Relativistic Spinorbit ZORA ==

# Next the spin-orbit coupled relativistic ZORA calculation. Note that in this case↪
↪the all-electron basis sets are
# also obtained from the $AMSRESOURCES/ADF/ZORA directory, but again this is default↪
↪place where the key BASIS will search
# for basis sets in case of ZORA. ADF will calculate the EFG including the small↪
↪component density, also called ZORA-4.

AMS_JOBNAME=SO $AMSBIN/ams <<eor
System
  atoms
    H 0 0 0
    I 0 0 1.609
  end
end

Task SinglePoint

```

(continues on next page)

(continued from previous page)

```
Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  qtens
  relativity
    level spin-orbit
    formalism ZORA
  end
  xc
    hartreefock
  end
EndEngine
eor

# == Relativistic Spinorbit ZORA with no symmetry ==
# Should give the same results as with symmetry.

AMS_JOBNAME=SO_nosym $AMSBIN/ams <<eor
System
  atoms
    H 0 0 0
    I 0 0 1.609
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  qtens
  relativity
    level spin-orbit
    formalism ZORA
  end
  symmetry nosym
  xc
    hartreefock
  end
EndEngine
eor
```

Example: B3LYP: H2PO

Download H2PO_B3LYP.run

```

#!/bin/sh

# Example shows an unrestricted B3LYP calculation. In this case ADF also
# calculates the hyperfine interactions at H, P, and O nuclei (keyword ESR).

# The 'RIHartreeFock%DependencyThreshold' key is set to 1E-4.
# One should check that the results remain reliable if one uses a smaller value
# for the DependencyThreshold key.

AMS_JOBNAME=TZ2P $AMSBIN/ams <<eor
System
  atoms
    O   1.492  0.000  0.000
    P   0.000  0.000  0.000
    H  -0.600 -0.650  1.100
    H  -0.600 -0.650 -1.100
  end
end

Task SinglePoint

Engine ADF
  title hfs H2PO B3LYP TZ2P
  esr
  end
  basis
    core None
    type TZ2P
  end
  numericalquality good
  rihartreefock
    dependencythreshold 1E-4
    quality Normal
  end
  spinpolarization 1
  unrestricted
  xc
    hybrid B3LYP
  end
EndEngine
eor

# For the hyperfine interactions it is important to use all-electron basis sets
# on the interesting nuclei. One can get more accurate results if one uses a
# larger basis set, like the QZ4P basis set, which is present in the
# $AMSRESOURCES/ADF/ZORA directory.

AMS_JOBNAME=QZ4P $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  O   1.492   0.000   0.000
  P   0.000   0.000   0.000
  H  -0.600  -0.650   1.100
  H  -0.600  -0.650  -1.100
end
end

Task SinglePoint

Engine ADF
  title hfs H2PO B3LYP QZ4P
  esr
  end
  basis
    core None
    type ZORA/QZ4P
  end
  numericalquality good
  rihartreefock
    dependencythreshold 1E-4
    quality Normal
  end
  spinpolarization 1
  unrestricted
  xc
    hybrid B3LYP
  end
EndEngine
eor

# The QZ4P results for the isotropic value of the A-tensor are approximately:
# -24.61 MHz for 17O, 957.33 MHz for 31P, and 110.83 MHz for 1H.

# You may want to compare the results with previous B3LYP results by N. R.
# Brinkmann and I. Carmichael, J. Phys. Chem. A (2004), 108, 9390-9399, which
# give for the Isotropic Fermi Contact Couplings (MHz) for the 2 A' State of H2
# PO using B3LYP, with an aug-cc-pCVQZ basis set: -24.24 MHz for 17O, 963.33
# MHz for 31P, and 111.51 MHz for 1H.

```

Example: Long-range corrected GGA functional LCY-BP: H2O

Download LCY-BP_H2O.run

```

#!/bin/sh

# Example for the range separated functional LCY-BP for a geometry optimization
# of water.

$AMSBIN/ams <<eor
System
atoms
  O  -0.00000000   0.00000000   0.46983780
  H   0.00000000   0.63395481  -0.23491890

```

(continues on next page)

(continued from previous page)

```

      H    0.00000000  -0.63395481  -0.23491890
    end
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    Gradients 0.0001
  End
End

Engine ADF
  title H2O geometry with LCY-BP functional
  basis
    type DZP
  end
  noprint BAS FIT FUNCTIONS SFO
  numericalquality Good
  xc
    gga Becke Perdew
    rangesep GAMMA=0.75
    xcfun
  end
EndEngine
eor

```

Example: Range-separated functional CAMY-B3LYP: H2O

Download CAMY-B3LYP_H2O.run

```

#!/bin/sh

# Example for the range separated functional CAMY-B3LYP for a geometry
# optimization of water. Note that CAMY-B3LYP is not the same as CAM-B3LYP.

$AMSBIN/ams <<eor
  Task GeometryOptimization
  System
    ATOMS
      O    0.000000    0.000000    0.000000
      H    0.000000    0.500000   -0.6
      H    0.000000   -0.500000   -0.6
    End
  End
  GeometryOptimization
    Convergence Gradients=1.0E-4
  End
  Engine ADF
    TITLE  H2O geometry with LC-BP functional
    NOPRINT BAS FIT FUNCTIONS SFO
    XC
      HYBRID CAMYB3LYP
      xcfun
    End
  EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

        RANGESEP GAMMA=0.34
    End
    BeckeGrid
        Quality good
    End
    RIHartreeFock
        UseMe False
    End
    basis
        Type DZP
    End
    EndEngine
eor

```

Example: Single point MP2

Download Water_MP2_AO.run

```

#!/bin/sh

# spin-restricted calculation on water, SOS-MP2
# AO-based algorithm, 6 imaginary time points

$AMSBIN/ams <<eor
System
    symmetrize
    atoms
        O   -0.702196054  -0.056060256   0.009942262
        H   -1.022193224   0.846775782  -0.011488714
        H    0.257521062   0.042121496   0.005218999
    End
End
Symmetry
    SymmetrizeTolerance 0.001
End

Task SinglePoint

Engine ADF
    Basis
        core None
        type TZP
    End

    XC
        MP2
        EmpiricalScaling SOS
    End

    MBPT nTime=6
EndEngine
eor

```

Example: Water Dimer SOS-AO-PARI-MP2

Download WaterDimer_SOS-MP2_AO.run

```

#!/bin/sh

# calculation on water, SOS-MP2
# AO-based algorithm, 8 imaginary time points

$AMSBIN/ams <<eor
System
  atoms
    O   -0.702196054  -0.056060256   0.009942262
    H   -1.022193224   0.846775782  -0.011488714
    H    0.257521062   0.042121496   0.005218999
    O    2.220871067   0.026716792   0.000620476
    H    2.597492682  -0.411663274   0.766744858
    H    2.593135384  -0.449496183  -0.744782026
  End
End

Task SinglePoint

Engine ADF
  Basis
    core None
    type TZ2P
  End

  XC
    empiricalscaling SOS
    MP2
  End

  MBPT
    formalism LT
    nTime 8
  End
EndEngine

eor

```

Example: Single point B2GPPLYP

Download Water_MeOH_B2GPPLYP.run

```

#!/bin/sh

# Dispersion corrected double hybrid calculation on
# a Water-Methanol complex using the double hybrid
# B2GPPLYP and standard settings
#
# First the fragments Water and MeOH are calculated.
# Next the bond energy of the Water-Methanol complex
# is calculated wrt to these fragments.
#

```

(continues on next page)

(continued from previous page)

```
# Note that for the calculation of the Pauli repulsion
# term the MP2 part of the double hybrid is not included.
#
# Next the BSSE is calculated for Water and MeOH.
# If one uses a TZ2P instead of a DZP basis set,
# the BSSE corrections will be smaller.
```

```
AMS_JOBNAME=Water $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    O      -0.525330      -0.050971      -0.314517
    H      -0.942007       0.747902       0.011253
    H       0.403697       0.059786      -0.073568
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  basis
    core None
    type DZP
  end
  xc
    dispersion GRIMME3 BJDAMP
    doublehybrid B2GPPLYP
  end
EndEngine
```

```
eor
```

```
AMS_JOBNAME=MeOH $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    O      2.316633       0.045501       0.071858
    H      2.684616      -0.526577       0.749387
    C      2.781638      -0.426129      -1.190301
    H      2.350821       0.224965      -1.943415
    H      3.867602      -0.375336      -1.264613
    H      2.453296      -1.445999      -1.389381
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  basis
    core None
    type DZP
  end
  xc
    dispersion GRIMME3 BJDAMP
    doublehybrid B2GPPLYP
  end
EndEngine
```

```
eor
```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=Water_MeOH $AMSBIN/ams <<eor
System
  atoms
    O      -0.525330      -0.050971      -0.314517 adf.f=Water
    H      -0.942007       0.747902       0.011253 adf.f=Water
    H       0.403697       0.059786      -0.073568 adf.f=Water
    O       2.316633       0.045501       0.071858 adf.f=MeOH
    H       2.684616      -0.526577       0.749387 adf.f=MeOH
    C       2.781638      -0.426129      -1.190301 adf.f=MeOH
    H       2.350821       0.224965      -1.943415 adf.f=MeOH
    H       3.867602      -0.375336      -1.264613 adf.f=MeOH
    H       2.453296      -1.445999      -1.389381 adf.f=MeOH
  end
end

Task SinglePoint

Engine ADF
  fragments
    Water Water.results/adf.rkf
    MeOH MeOH.results/adf.rkf
  end
  xc
    dispersion GRIMME3 BJDAMP
    doublehybrid B2GPPLYP
  end
EndEngine

eor

# =====
# BSSE for Water
# =====

AMS_JOBNAME=Water_BSSE $AMSBIN/ams <<eor
System
  atoms
    O      -0.525330      -0.050971      -0.314517 adf.f=Water
    H      -0.942007       0.747902       0.011253 adf.f=Water
    H       0.403697       0.059786      -0.073568 adf.f=Water
    Gh.O    2.316633       0.045501       0.071858
    Gh.H    2.684616      -0.526577       0.749387
    Gh.C    2.781638      -0.426129      -1.190301
    Gh.H    2.350821       0.224965      -1.943415
    Gh.H    3.867602      -0.375336      -1.264613
    Gh.H    2.453296      -1.445999      -1.389381
  end
end

Task SinglePoint

Engine ADF
  fragments
    Water Water.results/adf.rkf
  end
  basis

```

(continues on next page)

(continued from previous page)

```

    core None
    type DZP
end
xc
    dispersion GRIMME3 BJDAMP
    doublehybrid B2GPPLYP
end
EndEngine

eor

# =====
# BSSE for MeOH
# =====

AMS_JOBNAME=MeOH_BSSE $AMSBIN/ams <<eor
System
    atoms
        Gh.O  -0.525330      -0.050971      -0.314517
        Gh.H  -0.942007       0.747902       0.011253
        Gh.H   0.403697       0.059786      -0.073568
        O      2.316633       0.045501       0.071858 adf.f=MeOH
        H      2.684616      -0.526577       0.749387 adf.f=MeOH
        C      2.781638      -0.426129      -1.190301 adf.f=MeOH
        H      2.350821       0.224965      -1.943415 adf.f=MeOH
        H      3.867602      -0.375336      -1.264613 adf.f=MeOH
        H      2.453296      -1.445999      -1.389381 adf.f=MeOH
    end
end

Task SinglePoint

Engine ADF
    fragments
        MeOH MeOH.results/adf.rkf
    end
    basis
        core None
        type DZP
    end
    xc
        dispersion GRIMME3 BJDAMP
        doublehybrid B2GPPLYP
    end
EndEngine

eor

```

Example: Water-MeOH - DODSCAN

Download Water_MeOH_DODSCAN.run

```

#!/bin/sh

# Calculation on the bonding energy of the Water-methanol dimer using
# the meta-hybrid based, dispersion corrected double-hybrid functional DOD-SCAN.

# the AO-based algorithm is employed here by default, 8 numerical quadrature points
# are used for the numerical Laplace transform (as opposed to 9, which is the
↪default).
# For the MP2 calculation only, the Normal fitset is used, while during the SCF
# default numerical settings are used together with the VeryGood fitset.

$AMSBIN/ams <<eor
System
  atoms
    O      -0.525330      -0.050971      -0.314517
    H      -0.942007      0.747902      0.011253
    H      0.403697      0.059786      -0.073568
    O      2.316633      0.045501      0.071858
    H      2.684616      -0.526577      0.749387
    C      2.781638      -0.426129      -1.190301
    H      2.350821      0.224965      -1.943415
    H      3.867602      -0.375336      -1.264613
    H      2.453296      -1.445999      -1.389381
  End
End

Task SinglePoint

Engine ADF
  basis
    core None
    type DZP
  End

  XC
    DoubleHybrid DODSCAN
  End

  MBPT
    nTime 8
    FitSetQuality Normal
  END
  RIHartreeFock
    FitSetQuality VeryGood
  End
EndEngine
eor

```

Example: unrestricted MP2: Li

Download MP2_Li.run

```

#!/bin/sh

# unrestricted MP2 calculation for Li

$AMSBIN/ams << eor
System
  Atoms
    Li      0.0000000000    0.0000000000    0.0000000000
  End
End

task SinglePoint

Engine adf
  SpinPolarization 1
  Unrestricted Yes
  basis
    Core None
    Type DZP
  End
  xc
    mp2
  End
EndEngine
eor

```

Example: RPA@PBE calculation: H2O

Download RPA_H2O.run

```

#!/bin/sh

# RPA@PBE calculation for Water.
# We use an all-electron basis set since core-correlation effects are important

# For H2O, PBE will be a suitable reference since it is only weakly correlated and
→ the
# KS HOMO-LUMO gap will be reasonably large.

# RECOMMENDED: Good numerical quality

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    O      2.220871067    0.026716792    0.000620476
    H      2.597492682   -0.411663274    0.766744858
    H      2.593135384   -0.449496183   -0.744782026
  End

```

(continues on next page)

(continued from previous page)

```

    Symmetrize Yes
End

task SinglePoint

Engine adf

    Basis
      Core None
      Type TZ2P
    end

    NumericalQuality GOOD
    RIHartreeFock fitsetQuality=Normal

    Relativity
      Level None
    End

    XC
      GGA PBE
      RPA Direct
    end
EndEngine
eor

```

Example: RPASOX@PBE0 calculation: H2O

Download RPA-SOSSX_H2O.run

```

#!/bin/sh

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    O   2.220871067   0.026716792   0.000620476
    H   2.597492682  -0.411663274   0.766744858
    H   2.593135384  -0.449496183  -0.744782026
  End
  Symmetrize Yes
End

task SinglePoint

Engine adf
  symmetry nosym
  Basis
    Core None
    Type TZ2P
  end
  NumericalQuality GOOD

```

(continues on next page)

(continued from previous page)

```

Relativity
  Level None
End
XC
  hybrid pbe0
  RPA SOSSX
end
EndEngine
eor

```

Example: Grimme Molecular Mechanics dispersion-corrected functionals (DFT-D3-BJ)

Download MM_Dispersion.run

```

#!/bin/sh

# In this example a structure with 2 benzene molecules and a hydrogen molecule
# is optimized with the Grimme dispersion corrected PBE, in this case the (so
# far) latest variant the DFT-D family, which is DFT-D3-BJ. Needed is the subkey
# DISPERSION in the key XC, and the arguments Grime3 and BJDAMP. If one starts
# with atomic fragments the part of the bond energy that is due to the Grimme
# dispersion corrected functional is both inter-molecular as well as intra-
# molecular.

AMS_JOBNAME=Grimme_dispersion $AMSBIN/ams <<eor
System
atoms
  C  0.0          1.39730802 -3.09
  H  0.0          2.48914064 -3.09
  C  1.21010424   0.69865401 -3.09
  H  2.15565903   1.24457032 -3.09
  C  1.21010424  -0.69865401 -3.09
  H  2.15565903  -1.24457032 -3.09
  C  0.0          -1.39730802 -3.09
  H  0.0          -2.48914064 -3.09
  C -1.21010424  -0.69865401 -3.09
  H -2.15565903  -1.24457032 -3.09
  C -1.21010424   0.69865401 -3.09
  H -2.15565903   1.24457032 -3.09
  C -1.21010424  -0.69865401  3.09
  H -2.15565903  -1.24457032  3.09
  C  0.0          -1.39730802  3.09
  H  0.0          -2.48914064  3.09
  C  1.21010424  -0.69865401  3.09
  H  2.15565903  -1.24457032  3.09
  C  1.21010424   0.69865401  3.09
  H  2.15565903   1.24457032  3.09
  C  0.0          1.39730802  3.09
  H  0.0          2.48914064  3.09
  C -1.21010424   0.69865401  3.09
  H -2.15565903   1.24457032  3.09
  H  0.0          0.0          -0.37
  H  0.0          0.0          0.37

```

(continues on next page)

(continued from previous page)

```

    end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    Gradients 1E-4
  End
End

Engine ADF
  title Geometry optimization with Grimme3-BJ dispersion correction for GGA
  basis
    type TZP
    core small
  end
  noprint sfo
  xc
    dispersion Grimme3 BJDAMP
    gga PBE
  end
EndEngine
eor

# The next calculations in this example demonstrate dispersion corrections when
# using non-atomic fragments. First three molecules (2 benzene molecules and a
# hydrogen molecule) are calculated . Needed again is the subkey DISPERSION in
# the key XC.

AMS_JOBNAME=benzene1 $AMSBIN/ams <<eor
System
  atoms
    C      0.000000    1.398973   -3.054539
    H      0.000000    2.490908   -3.049828
    C      1.211546    0.699486   -3.054539
    H      2.157190    1.245454   -3.049828
    C      1.211546   -0.699486   -3.054539
    H      2.157190   -1.245454   -3.049828
    C      0.000000   -1.398973   -3.054539
    H      0.000000   -2.490908   -3.049828
    C     -1.211546   -0.699486   -3.054539
    H     -2.157190   -1.245454   -3.049828
    C     -1.211546    0.699486   -3.054539
    H     -2.157190    1.245454   -3.049828
  end
end

Task SinglePoint

Engine ADF
  title Grimme3-BJ dispersion-corrected GGA
  basis
    core small
    type TZP

```

(continues on next page)

(continued from previous page)

```

end
noprnt sfo
scf
  converge 1.0E-06 1.0E-6
  iterations 60
end
xc
  dispersion Grimme3 BJDAMP
  gga PBE
end
EndEngine
eor

AMS_JOBNAME=benzene2 $AMSBIN/ams <<eor
System
  atoms
    C      -1.211546   -0.699486    3.054539
    H      -2.157190   -1.245454    3.049828
    C       0.000000   -1.398973    3.054539
    H       0.000000   -2.490908    3.049828
    C       1.211546   -0.699486    3.054539
    H       2.157190   -1.245454    3.049828
    C       1.211546    0.699486    3.054539
    H       2.157190    1.245454    3.049828
    C       0.000000    1.398973    3.054539
    H       0.000000    2.490908    3.049828
    C      -1.211546    0.699486    3.054539
    H      -2.157190    1.245454    3.049828
  end
end

Task SinglePoint

Engine ADF
  title Grimme3-BJ dispersion-corrected GGA
  basis
    core small
    type TZP
  end
  noprnt sfo
  xc
    dispersion Grimme3 BJDAMP
    gga PBE
  end
EndEngine
eor

AMS_JOBNAME=h2 $AMSBIN/ams <<eor
System
  atoms
    H      0.000000    0.000000   -0.377906
    H      0.000000    0.000000    0.377906
  end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  title Grimme3-BJ dispersion-corrected GGA
  basis
    core small
    type TZP
  end
  noprint sfo
  xc
    dispersion Grimme3 BJDAMP
    gga PBE
  end
EndEngine
eor

```

```

AMS_JOBNAME=fragments $AMSBIN/ams <<eor

```

```

System
  atoms
    C      0.000000    1.398973   -3.054539   adf.f=b1
    H      0.000000    2.490908   -3.049828   adf.f=b1
    C      1.211546    0.699486   -3.054539   adf.f=b1
    H      2.157190    1.245454   -3.049828   adf.f=b1
    C      1.211546   -0.699486   -3.054539   adf.f=b1
    H      2.157190   -1.245454   -3.049828   adf.f=b1
    C      0.000000   -1.398973   -3.054539   adf.f=b1
    H      0.000000   -2.490908   -3.049828   adf.f=b1
    C     -1.211546   -0.699486   -3.054539   adf.f=b1
    H     -2.157190   -1.245454   -3.049828   adf.f=b1
    C     -1.211546    0.699486   -3.054539   adf.f=b1
    H     -2.157190    1.245454   -3.049828   adf.f=b1
    C     -1.211546   -0.699486    3.054539   adf.f=b2
    H     -2.157190   -1.245454    3.049828   adf.f=b2
    C      0.000000   -1.398973    3.054539   adf.f=b2
    H      0.000000   -2.490908    3.049828   adf.f=b2
    C      1.211546   -0.699486    3.054539   adf.f=b2
    H      2.157190   -1.245454    3.049828   adf.f=b2
    C      1.211546    0.699486    3.054539   adf.f=b2
    H      2.157190    1.245454    3.049828   adf.f=b2
    C      0.000000    1.398973    3.054539   adf.f=b2
    H      0.000000    2.490908    3.049828   adf.f=b2
    C     -1.211546    0.699486    3.054539   adf.f=b2
    H     -2.157190    1.245454    3.049828   adf.f=b2
    H      0.000000    0.000000   -0.377906   adf.f=h2
    H      0.000000    0.000000    0.377906   adf.f=h2
  end
end

```

```

Task SinglePoint

Engine ADF
  title Grimme3-BJ dispersion-corrected GGA
  fragments
    b1 benzene1.results/adf.rkf
    b2 benzene2.results/adf.rkf
    h2 h2.results/adf.rkf

```

(continues on next page)

(continued from previous page)

```

end
noprnt sfo
xc
  dispersion Grimme3 BJDAMP
  gga PBE
end
EndEngine

eor

```

Example: Density-Dependent Dispersion Correction (dDsC): CH₄-dimer

Download `methane_dimer_dispersion.run`

```

#!/bin/sh

# The density-dependent dispersion energy correction, dDsC, by S.N. Steinmann
# and C. Corminboeuf, is used to calculate interactions between non-overlapping
# densities, which standard density functional approximations cannot accurately
# describe. The example is for the methane dimer.

# The 'debug dispersion' is included such that in the output one can find more
# details on the exact parameters that are used.

$AMSBIN/ams <<eor
System
atoms
  C -0.000959    0.000775    1.853082
  H -0.747186    0.712608    1.489389
  H  0.987865    0.294742    1.490258
  H -0.241511   -0.998876    1.480724
  H -0.002970   -0.005330    2.946903
  C  0.000962   -0.000776   -1.853082
  H  0.004264    0.004684   -2.946903
  H -0.989749   -0.289559   -1.491241
  H  0.743184   -0.716138   -1.488107
  H  0.246099    0.997870   -1.481022
end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    Gradients 1E-3
    Energy    0.1
    Step      0.1
  End
End

Engine ADF
  title methane-dimer
  debug dispersion

```

(continues on next page)

(continued from previous page)

```

basis
  type TZP
end
numericalquality good
symmetry nosym
xc
  dispersion DDsC
  gga Becke LYP
end
EndEngine
eor

```

Example: DFT-ulg Dispersion Correction: Benzene dimer T-shaped

Download `Benzene_dimer_tshaped.run`

```

#!/bin/sh

# The universal correction of density functional theory to include London
# dispersion (DFT-ulg) is used, which is related to UFF. This is yet another MM
# dispersion correction. The example is for the T-shaped benzene dimer.

$AMSBIN/ams <<eor
Task SinglePoint
System
  Atoms
    C 0.000000 0.000000 1.059035
    C 0.000000 -1.206008 1.757674
    C 0.000000 -1.207177 3.151591
    C 0.000000 0.000000 3.848575
    C 0.000000 1.207177 3.151591
    C 0.000000 1.206008 1.757674
    H 0.000000 0.000000 -0.021580
    H 0.000000 -2.141639 1.214422
    H 0.000000 -2.143566 3.692995
    H 0.000000 0.000000 4.930150
    H 0.000000 2.143566 3.692995
    H 0.000000 2.141639 1.214422
    C -1.394063 0.000000 -2.454152
    C -0.697047 1.207238 -2.454628
    C 0.697047 1.207238 -2.454628
    C 1.394063 0.000000 -2.454152
    C 0.697047 -1.207238 -2.454628
    C -0.697047 -1.207238 -2.454628
    H -2.475399 0.000000 -2.450322
    H -1.238232 2.143565 -2.453676
    H 1.238232 2.143565 -2.453676
    H 2.475399 0.000000 -2.450322
    H 1.238232 -2.143565 -2.453676
    H -1.238232 -2.143565 -2.453676
  end
end
Engine ADF
  Title Calculate the optimum structure of a dibenzene molecule and dispersion

```

(continues on next page)

(continued from previous page)

```

    basis
      type TZP
      CreateOutput Yes
    End
    XC
      GGA PBE
      dispersion uff
    End
  EndEngine
End
eor

$AMSBIN/densf <<eor
adffile ams.results/adf.rkf
Grid Medium
End
NCI BOTH
eor

```

15.2.2 Relativistic effects: ZORA, X2C, spin-orbit coupling

Example: ZORA Relativistic Effects: Au2

Download `Au2_ZORA.run`

```

#!/bin/sh

# A relativistic geometry optimization with the ZORA formalism. Both a scalar
# relativistic geometry optimization, as well as a spin-orbit coupled
# relativistic geometry optimization are performed. Spin-orbit effects on the
# geometry are often not so large for closed shell molecules, but takes
# typically a factor 4 times as much as a scalar relativistic calculation.

AMS_JOBNAME=Au2_GO_scalar $AMSBIN/ams <<eor
System
  atoms
    Au  0.0  0.0 -1.250
    Au  0.0  0.0  1.250
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence Gradients=1E-4
End

Engine ADF
  basis
    type TZ2P
    core Small
    CreateOutput Yes
  end
  relativity

```

(continues on next page)

(continued from previous page)

```

    level scalar
    formalism ZORA
end
xc
    gga Becke Perdew
end
EndEngine

eor

AMS_JOBNAME=Au2_GO_spinorbit $AMSBIN/ams <<eor
System
    atoms
        Au  0.0  0.0 -1.250
        Au  0.0  0.0  1.250
    end
end

Task GeometryOptimization

GeometryOptimization
    Convergence Gradients=1E-4
End

Engine ADF
    basis
        type TZ2P
        core Small
        CreateOutput Yes
    end
    relativity
        level spin-orbit
        formalism ZORA
    end
EndEngine

eor

```

Example: Spin-Orbit coupling: Bi and Bi2

Download SO_ZORA_Bi2.run

```

#!/bin/sh

# Application of the Spin-Orbit relativistic option (using double-group
# symmetry) to Bismuth (atom and dimer).

# For comparison with the full double-group calculation, the 'standard'
# unrestricted calculation on Bismuth is carried out, using the scalar
# relativistic option.

# A net spin polarization of 3 electrons is applied (key charge).

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=Bi_SR $AMSBIN/ams <<eor
System
  atoms
    Bi   0.000000      0.000000      0.00000000
  end
end

Task SinglePoint

Engine ADF
  title Bi unrestricted
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 3
  unrestricted
  xc
    gga becke perdew
  end
EndEngine
eor

# The CHARGE key, in conjunction with the UNRESTRICTED key is used to specify
# that 3 electrons must be unpaired (second value of the CHARGE key), while the
# system is neutral (first value of the CHARGE key).

# Next we do a Spin-Orbit calculation on the Bismuth atom.

# Note that it is a 'unrestricted' run using the noncollinear approximation, and
# SYMMETRY NOSYM. The electronic charge density is spin-polarized.

AMS_JOBNAME=Bi_SO $AMSBIN/ams <<eor
System
  atoms
    Bi   0.000000      0.000000      0.00000000
  end
end

Task SinglePoint

Engine ADF
  title Bi spinorbit unrestricted noncollinear
  beckegrid
    quality good
  end
  basis
    core None

```

(continues on next page)

(continued from previous page)

```

    type TZ2P
    CreateOutput Yes
end
relativity
  level spin-orbit
  formalism ZORA
  spinorbitmagnetization noncollinear
end
symmetry nosym
unrestricted
xc
  gga becke perdew
end
EndEngine
eor

# Because an all electron basis set is used, the bond energy is huge, due to the
# very large higher order spin-orbit effect on the 2p orbitals.

# == Bi2 dimer ==

# Now we turn to the dimer Bi2: a series of Single Point calculations, all with
# the same inter atomic distance.

# First the scalar relativistic run.

AMS_JOBNAME=Bi2_SR $AMSBIN/ams <<eor
System
  atoms
    Bi      0.0      0.0      1.33
    Bi      0.0      0.0     -1.33
  end
end

Task SinglePoint

Engine ADF
  title Bi2, scalar relativistic
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

# The calculated scalar relativistic atomization energy will be close to 2.74
# eV. This is the bond energy of the dimer minus 2 times the bond energy of the
# unrestricted scalar relativistic atom.

# The result file tape21 is used as reference in subsequent calculations: run
# the spin-orbit case starting from the just completed dimer calculation as a
# fragment. The resulting 'bonding energy', ie the energy w.r.t. the scalar
# relativistic ZORA dimer, gives directly the effect of the full-relativistic
# ZORA versus the scalar relativistic ZORA option: the energy is lowered by huge
# amount, again mainly due to the large spin-orbit effect on the 2p orbitals.

AMS_JOBNAME=Bi2_SO_frag $AMSBIN/ams <<eor
System
  atoms
    Bi    0.0    0.0    1.33  adf.f=Bi2
    Bi    0.0    0.0   -1.33  adf.f=Bi2
  end
end

Task SinglePoint

Engine ADF
  title Bi2 from fragment Bi2,  with SpinOrbit coupling
  beckegrid
    quality good
  end
  fragments
    Bi2      Bi2_SR.results/adf.rkf
  end
  print SpinOrbit
  relativity
    level spin-orbit
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine
eor

```

```

# If one looks at the SFO analysis in the output of this calculation, one can
# observe that a first-order spin-orbit splitting of the scalar relativistic
# fragment orbitals is a good approximation to many of the calculated valence
# spinors.

```

```

# A final consistency check: run the spin-orbit dimer from single-atom
# fragments. The bonding energy should equal the sum of the bonding energies of
# the previous two runs: scalar relativistic dimer w.r.t. single atom fragments
# plus spin-orbit dimer w.r.t. the scalar relativistic dimer.

```

```

AMS_JOBNAME=Bi2_SO $AMSBIN/ams <<eor
System
  atoms
    Bi    0.0    0.0    1.33
    Bi    0.0    0.0   -1.33
  end

```

(continues on next page)

(continued from previous page)

```

end

Task SinglePoint

Engine ADF
  title Bi2 from atomic fragments, SpinOrbit coupling
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  print SpinOrbit
  relativity
    level spin-orbit
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine
eor

# The calculated spin-orbit coupled relativistic atomization energy will be
# close to 2.18 eV. This is the bond energy of the dimer minus 2 times the bond
# energy of the unrestricted non-collinear spin-orbit coupled relativistic atom.
# Note that one has to subtract huge numbers.

```

Example: Spin-Orbit unrestricted non-collinear: Tl

Download Tl_noncollinear.run

```

#!/bin/sh

# Application of the Spin-Orbit relativistic option (using double-group
# symmetry, in this case NOSYM) to Tl using the collinear and non-collinear
# approximation for unrestricted Spin-Orbit calculations

# Note: For the collinear and the non-collinear approximation one should use
# symmetry NOSYM and use the key UNRESTRICTED.

# == Tl scalar restricted ==

AMS_JOBNAME=Scalar $AMSBIN/ams <<eor
System
  atoms
    Tl 0 0 0
  end
end

Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title Tl scalar restricted
  beckegrid
    quality good
  end
  basis
    PerAtomType Symbol=Tl File=ZORA/TZ2P/Tl.4f
    CreateOutput Yes
  end
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga Becke Perdew
  end
EndEngine

eor

# == Tl spinorbit restricted ==

AMS_JOBNAME=SpinOrbit_Restricted $AMSBIN/ams <<eor
System
  atoms
    Tl 0 0 0
  end
end

Task SinglePoint

Engine ADF
  title Tl spinorbit restricted
  beckegrid
    quality good
  end
  eprint
    sfo eig
  end
  fragments
    Tl Scalar.results/adf.rkf
  end
  relativity
    level spin-orbit
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine

eor

# == Tl spinorbit collinear z-axis ==

AMS_JOBNAME=SpinOrbit_Collinear $AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Tl 0 0 0
  end
end

Task SinglePoint

Engine ADF
  title Tl spinorbit collinear z-axis
  beckegrid
    quality good
  end
  eprint
    sfo eig
  end
  fragments
    Tl Scalar.results/adf.rkf
  end
  relativity
    level spin-orbit
    formalism ZORA
    spinorbitmagnetization collinear
  end
  symmetry nosym
  unrestricted
  xc
    gga becke perdew
  end
EndEngine

eor

# == Tl spinorbit noncollinear ==

AMS_JOBNAME=SpinOrbit_NonCollinear $AMSBIN/ams <<eor
System
  atoms
    Tl 0 0 0
  end
end

Task SinglePoint

Engine ADF
  title Tl spinorbit noncollinear
  beckegrid
    quality good
  end
  eprint
    sfo eig
  end
  fragments
    Tl Scalar.results/adf.rkf
  end
  relativity
    level spin-orbit

```

(continues on next page)

(continued from previous page)

```
    formalism ZORA
    spinorbitmagnetization noncollinear
end
symmetry nosym
unrestricted
xc
    gga becke perdew
end
EndEngine

eor

# == T1 spinorbit noncollinear ==

AMS_JOBNAME=SpinOrbit_SOUEXACT $AMSBIN/ams <<eor
System
    atoms
        T1 0 0 0
    end
end

Task SinglePoint

Engine ADF
    title T1 spinorbit noncollinear
    beckegrid
    quality good
end
eprint
    sfo eig
end
fragments
    T1 Scalar.results/adf.rkf
end
relativity
    level spin-orbit
    formalism ZORA
    spinorbitmagnetization noncollinear
    souexact
end
symmetry nosym
unrestricted
xc
    gga becke perdew
end
EndEngine

eor
```

Example: Excitation energies including spin-orbit coupling: AuH

Download AuH_analyse_exciso.run

```

#!/bin/sh

# Calculation of the excitation energies of AuH including spin-orbit coupling.

# ADF can not handle ATOM and linear symmetries in excitation calculations.
# In case of linear symmetries ADF will automatically use a
# a subsymmetry, in this case symmetry C(7v).
# In the excitation part of the output the symmetry labels are those of C(LIN) in
↳ this case.

# A relatively small TZ2P basis set is used, which is not sufficient for
# excitations to Rydberg-like orbitals, one needs more diffuse functions.

# The key STCONTRIB is used, which will give a composition of the spin-orbit
# coupled excitation in terms of singlet-singlet and singlet-triplet scalar
# relativistic excitations. In order to use the key STCONTRIB the scalar
# relativistic fragment should be the complete molecule.

# For precision reasons the Beckegrid quality is set to good. One might also
# increase the ZlmFit quality for better accuracy

# One needs to include the subkey SFO of the key EPRINT with arguments eig and
# ovl in order to get the SFO MO coefficients and SFO overlap matrix printed on
# standard output.

AMS_JOBNAME=scalar $AMSBIN/ams <<eor
System
  atoms
    Au 0.0000  0.0000  1.5238
    H  0.0000  0.0000  0.0000
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  eprint
    sfo eig ovl
  end
  excitations
    descriptors
      lowest 40
    nto
    sfoanalysis
    esestdm
  end
  print SOMATRIX
  sopert
end

```

(continues on next page)

(continued from previous page)

```

basis
  type TZ2P
  core None
  CreateOutput Yes
end
EndEngine
eor

AMS_JOBNAME=spinorbit $AMSBIN/ams <<eor
System
  atoms
    Au 0.0000 0.0000 1.5238 adf.f=Frag
    H 0.0000 0.0000 0.0000 adf.f=Frag
  end
end

Task SinglePoint

Engine ADF
  beckegrid
  quality good
end
eprint
  sfo eig ovl
end
excitations
  descriptors
  lowest 40
  nto
  sfoanalysis
  esestdm
end
fragments
  Frag scalar.results/adf.rkf
end
relativity
  level spin-orbit
end
stcontrib
EndEngine
eor

```

Example: ZORA, X2C and RA-X2C: HgI2 = Hg + I2

Download HgI2.run

```

#!/bin/sh

# The scalar relativistic ZORA, scalar relativistic X2C, and scalar relativistic
# RA-X2C are compared in this example for the bond dissociation energy of HgI2
# in Hg and I2. The division between scalar and spin-orbit relativistic effects
# is somewhat arbitrary and depends on the method of separation. Thus the scalar

```

(continues on next page)

(continued from previous page)

```
# relativistic results of X2C and RA-X2C will be different even in the basis set
# limit. However, the differences for bond energies are not so large. The
# results for scalar relativistic ZORA are often closer to scalar relativistic
# RA-X2C, than to scalar relativistic X2C.
```

```
for f in "ZORA" "X2C" "RA-X2C"
do
```

```
AMS_JOBNAME=HgI2_ $f $AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

```
  Hg 0 0 0
```

```
  I 0 0 2.554
```

```
  I 0 0 -2.554
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
basis
```

```
  core None
```

```
  type ZORA/DZ
```

```
end
```

```
numericalquality good
```

```
relativity
```

```
  level scalar
```

```
  formalism $f
```

```
end
```

```
xc
```

```
  gga bp86
```

```
end
```

```
EndEngine
```

```
eor
```

```
AMS_JOBNAME=I2_ $f $AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

```
  I 0 0 1.333
```

```
  I 0 0 -1.333
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
basis
```

```
  core None
```

```
  type ZORA/DZ
```

```
end
```

```
numericalquality good
```

```
relativity
```

```
  level scalar
```

```
  formalism $f
```

```
end
```

```
xc
```

```
  gga bp86
```

(continues on next page)

(continued from previous page)

```

    end
EndEngine
eor
done

```

Example: spin-orbit coupled MP2: atomization energy I2

Download I2_SO_MP2.run

```

#!/bin/sh

# MP2 results are calculated for I2 and the open shell atom I, such
# that the atomization energy of I2 can be calculated.
# The relativistic RA-X2C method is used and spin-orbit coupling is included.

# Remark: the atomization energy will be almost the same if one would compare
# the results for the relativistic methods ZORA, X2C, and RA-X2C in case
# spin-orbit coupling is included.

AMS_JOBNAME=I2 $AMSBIN/ams <<eor
System
  atoms
    I  0 0  1.333
    I  0 0 -1.333
  end
end

Task SinglePoint

engine ADF
  Basis
    Type TZ2P
    Core None
  End
  relativity
    level spin-orbit
    formalism RA-X2C
  end
  xc
    mp2
  end
endengine
eor

AMS_JOBNAME=I_SO $AMSBIN/ams <<eor
System
  atoms
    I 0.0 0.0 0.0
  end
end

Task SinglePoint

engine ADF

```

(continues on next page)

(continued from previous page)

```

Basis
  Type TZ2P
  Core None
End
relativity
  level spin-orbit
  formalism RA-X2C
  SpinOrbitMagnetization NonCollinear
end
unrestricted
occupations integeraufbau
symmetry nosym
xc
  mp2
end
endengine
eor

```

Example: Spin-Orbit spin-polarized start-up: Cr3

Download Cr3_noncollinear.run

```

#!/bin/sh

# Application of the non-collinear approach in spin-orbit coupled
# calculations on Cr3 using a spin-polarized start-up potential
# that has a different magnetization direction in each region.

# In the non-collinear approach by default ADF uses in the first SCF
# cycle an artificial magnetic field in the z-direction that only
# affects spin (spin-Zeeman term).
# In this example a different artificial magnetic field is included
# that can have a different orientation in different regions.
# This is similar as using a spin-polarized start-up potential, however,
# with the key SpinOrbitMagnetization one can also choose an arbitrary
# magnetization direction.

# Remark: keys MODIFYSTARTPOTENTIAL and RESTART%spinflip can not be used
# in spin-orbit coupled calculations. The key SpinOrbitMagnetization
# should be used instead.

$AMSBIN/ams <<eor
System
  atoms
    Cr      -0.76594   -1.292    0.0    region=r1
    Cr      -0.76594    1.292    0.0    region=r2
    Cr       1.49188    0.000    0.0    region=r3
  End
End

Task SinglePoint

Engine ADF
  relativity
    Level spin-orbit

```

(continues on next page)

(continued from previous page)

```

    SpinOrbitMagnetization NonCollinear
end
Basis
  type TZP
  core none
End
symmetry nosym
SpinOrbitMagnetization
  PerRegion
    region r1
    direction -0.76594 -1.292 0.0
  End
  PerRegion
    region r2
    direction -0.76594 1.292 0.0
  End
  PerRegion
    region r3
    direction 1.49188 0.000 0.0
  End
End
unrestricted
EndEngine
eor

```

15.2.3 Solvents, other environments

Example: COSMO: HCl

Download Solv_HCl.run

```

#!/bin/sh

# Computing solvent effects, with the COSMO model, is illustrated in the HCl
# example.

# After a non-solvent (reference) calculation, which is omitted here, two
# solvent runs are presented, with somewhat different settings for a few input
# parameters. The block key Solvation controls all solvent-related input.

# All subkeys in the SOLVATION block are discussed in the User's Guide. Most of
# them are rather technical and should not severely affect the outcome.
# Physically relevant is the specification of the solute properties, by the
# SOLVENT subkey: the dielectric constant and the effective radius of the
# solvent molecule.

# Note that a non-electrostatic terms as a function of surface area is included
# in the COSMO calculation, by setting the values for CAV0 and CAV1 in the
# subkey SOLVENT of the key SOLVATION. In ADF2010 one should explicitly include
# such values for CAV0 and CAV1, otherwise this non-electrostatic term will be
# taken to be zero, since the defaults have changed in ADF2010.

# A rather strong impact on the computation times has the method of treating the

```

(continues on next page)

(continued from previous page)

```
# 'C-matrix'. There are 3 options (see the User's Guide): EXACT is the most
# expensive, but presumably most accurate. POTENTIAL is the cheapest alternative
# and is usually quite adequate. EXACT uses the exact charge density for the
# Coulomb interaction between the molecular charge distribution and the point
# charges (on the Van der Waals type molecular surface) which model the effects
# of the solvent. The alternatives, notably 'POTENTIAL', use the fitted charge
# density instead. Assuming that the fit is a fairly accurate approximation to
# the exact charge density, the difference in outcome should be marginal.
```

```
AMS_JOBNAME=Gas $AMSBIN/ams <<eor
```

```
System
```

```
  symmetrize
  atoms
    H      0.000000      0.000000      0.000000
    Cl     1.304188      0.000000      0.000000
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title HCl(0) reference run (gas phase)
  eprint
    scf NoEigvec
  end
  basis
    type DZP
    CreateOutput Yes
  end
  noprint Bas EigSFO EKin SFO, frag, functions
```

```
EndEngine
```

```
eor
```

```
AMS_JOBNAME=Exact $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    H      0.000000      0.000000      0.000000      adf.R=1.18
    Cl     1.304188      0.000000      0.000000      adf.R=1.75
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title HCl(1) Solv-excl surface; Gauss-Seidel (old std options)
  eprint
    scf NoEigvec
  end
  noprint Bas EigSFO EKin SFO, frag, functions
  basis
    type DZP
  end
  solvation
    c-mat Exact
```

(continues on next page)

(continued from previous page)

```

    charged Method=Gauss-Seidel
    disc SScale=0.01 LEGendre=10 TOLerance=1.0e-2
    div ND=4 min=0.5 Ofac=0.8
    scf Variational
    solv epsilon=78.8 radius=1.4 cav0=1.321 cav1=0.0067639
    surf delley
  end
  symmetry NOSYM
EndEngine
eor

# In the second solvent run, another (technical) method is used for determining
# the charge distribution on the cavity surface (conjugate-gradient versus
# Gauss-Seidel in the previous calculation), and the POTENTIAL variety is used
# for the C-matrix handling. The results show that it makes little difference in
# outcome, but quite a bit in computation times.

AMS_JOBNAME=Potential $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    H    0.000000    0.000000    0.000000    adf.R=1.18
    Cl   1.304188    0.000000    0.000000    adf.R=1.75
  end
end

Task SinglePoint

Engine ADF
  title HCl(9) NoDisk and Cmatrix potential
  eprint
    scf NoEigvec
  end
  noprint Bas EigSFO EKin SFO, frag, functions
  basis
    type DZP
  end
  solvation
    c-mat POTENTIAL
    charged Method=conjugate-gradient
    div ND=4 min=0.5 Ofac=0.8
    scf Variational
    solv epsilon=78.8 radius=1.4 cav0=1.321 cav1=0.0067639
    surf delley
  end
EndEngine
eor

```

Example: solvation model SM12: Acetamide

Download Acetamide_SM12.run

```

#!/bin/sh

# In this example solvent effects are calculated with the solvation model SM12
# with CM5 charges for Acetamide.

# After a non-solvent (reference gas phase) calculation, the same geometry is
# used in the solvated case. At the moment it is not possible to do a geometry
# optimization with the SM12 model with CM5 charges in ADF.
# The default SM12 parameters are used, which means a solvation in Water is simulated.

AMS_JOBNAME=Acetamide $AMSBIN/ams <<eor
System
  atoms
    O      -0.08557000      1.83373000      0.00836000
    C      0.09782000      0.61787000     -0.01303000
    C     -1.04418000     -0.38854000     -0.01026000
    N      1.35837000      0.07376000     -0.01671000
    H     -0.79705000     -1.31834000     -0.54107000
    H     -1.92168000      0.07841000     -0.46849000
    H     -1.29425000     -0.64220000      1.03061000
    H      1.51930000     -0.92568000     -0.01800000
    H      2.15296000      0.70225000      0.03378000
  end
end

Task SinglePoint

Engine ADF
  basis
    core None
    type TZ2P
  end
  xc
    hybrid B3LYP
  end
EndEngine
eor

$AMSBIN/ams <<eor
System
  atoms
    O      -0.08557000      1.83373000      0.00836000 adf.f=Acetamide
    C      0.09782000      0.61787000     -0.01303000 adf.f=Acetamide
    C     -1.04418000     -0.38854000     -0.01026000 adf.f=Acetamide
    N      1.35837000      0.07376000     -0.01671000 adf.f=Acetamide
    H     -0.79705000     -1.31834000     -0.54107000 adf.f=Acetamide
    H     -1.92168000      0.07841000     -0.46849000 adf.f=Acetamide
    H     -1.29425000     -0.64220000      1.03061000 adf.f=Acetamide
    H      1.51930000     -0.92568000     -0.01800000 adf.f=Acetamide
    H      2.15296000      0.70225000      0.03378000 adf.f=Acetamide
  end

```

(continues on next page)

(continued from previous page)

```

end

Task SinglePoint

Engine ADF
  fragments
    Acetamide Acetamide.results/adf.rkf
  end
  solvation SM12
    SM12SolvationPotential cm5 #CM5 charges for now
  end
  xc
    hybrid B3LYP
  end
EndEngine
eor

```

Example: geometry optimization with SM12 using RESP charges

Download Ethanol_SM12_resp.run

```

#!/bin/sh

# Example that does a geometry optimization on Ethanol with SM12 using RESP charges.
# SM12 analytical gradients are implemented for CHELPG or RESP charges.
# NumericalQuality good is recommended.

"$AMSBIN/ams" << eor
Task GeometryOptimization
System
  Atoms
    C      0.01247000    0.02254000    1.08262000
    C     -0.00894000   -0.01624000   -0.43421000
    H     -0.49334000    0.93505000    1.44716000
    H      1.05522000    0.04512000    1.44808000
    H     -0.64695000   -1.12346000    2.54219000
    H      0.50112000   -0.91640000   -0.80440000
    H      0.49999000    0.86726000   -0.84481000
    H     -1.04310000   -0.02739000   -0.80544000
    O     -0.66442000   -1.15471000    1.56909000
  End
End

Engine ADF
  Basis
    Type DZP
    Core None
  End
  XC
    GGA PBE
  End
  SOLVATION SM12
    SOLV NAME=WATER
    SM12SolvationPotential RESP
    SM12espgridspacing 0.3

```

(continues on next page)

(continued from previous page)

```
End
  NumericalQuality Good
EndEngine
eor
```

Example: Electric Field: PtCO

Download `Field_PtCO.run`

```
#!/bin/sh

$AMSBIN/ams <<eor
System
  Atoms
    Pt 0 0 0
    C 0 0 1.70
    O 0 0 2.85
  End

  ElectrostaticEmbedding
    ElectricField 0 0 0.01 [a.u.]
  End
end

Task SinglePoint

Engine ADF
  title Pt-CO in electric field
  beckegrid
    quality good
  end
  basis
    Core None
    Type DZ
    PerAtomType Symbol=Pt File=DZ/Pt.4d
  end
  symmetry C(LIN)
  scf
    converge 1.0E-10
  end
EndEngine
eor
```

Example: Electric Field, Point Charge: N2

Download Efield.PntQ_N2.run

```

#!/bin/sh

# For N2, three calculations are provided: 1) a normal N2 run as a reference
# 2) with a homogeneous electric field, 3) with a point charge.

AMS_JOBNAME=reference $AMSBIN/ams <<eor
System
  atoms
    N  0 0 -0.55
    N  0 0  0.55
  end
end

Task SinglePoint

Engine ADF
  title N2 reference for comparison with E-Field runs
  basis
    type DZP
    core Small
    CreateOutput Yes
  end
EndEngine

eor

AMS_JOBNAME=efield $AMSBIN/ams <<eor
System
  atoms
    N  0 0 -0.55
    N  0 0  0.55
  end
  ElectrostaticEmbedding
    ElectricField 0.0 0.0 0.01 [a.u.]
  End
end

Task SinglePoint

Engine ADF
  title N2 in a homogeneous electric field
  Symmetry NoSym
  basis
    type DZP
    core Small
  end
EndEngine

eor

AMS_JOBNAME=point_charge $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  N 0 0 -0.55
  N 0 0 0.55
end
  ElectrostaticEmbedding
    MultipolePotential
      # Format of each entry in the Coordinates block: x y z q (length units:↵
↵angstrom)
      Coordinates
        0 0 3.0 1.0
      End
    End
  End
end

Task SinglePoint

Engine ADF
  title N2 polarized by a point charge on the axis
  Symmetry NoSym
  basis
    type DZP
    core Small
  end
EndEngine

eor

```

Example: 3D-RISM: Glycine

Download 3DRISM-Glycine.run

```

#!/bin/sh

# == Expert option ==

# Computing solvent effects with the 3D-RISM model is illustrated on the glycine
# example.

# All subkeys in the RISM block are discussed in the User's Guide. The things to
# pay attention to here are adf.SigU and EpsUadf. parameters for each atom in the↵
↵ATOMS
# block, the solvent parameters in the SOLVENT sub-block and the FFT box
# parameters in the SOLUTE sub-block. Both adf.SigU and EpsUadf. values as well as the
# solvent parameters may be obtained from force field parameter lists.
# Parameters for some common solvents are available in the ADF User's Guide.

# One should take into account the following when choosing FFT box parameters in
# the SOLUTE block:

# - the box should be at least twice as large as your model in each dimension,
# - the number of grid points in each dimension must be a power of 2, and
# - accuracy of the results and the memory usage depend on the number of grid-
# points

```

(continues on next page)

(continued from previous page)

```

# In this example only the gradients are calculated, no geometry optimization is
↳ performed.

# == Remarks for different solvent than water ==

# The default values for the RISM1D subblock key are only applicable if the
# solvent is water. You must change the FLUIDPARAM subkey of the subblock key
# RISM1D when modeling a different solvent, at least the dielectric constant and
# the density. In that case you may also have to change other subkeys of the
# subblock key RISM1D. For a different solvent than water, of course, you also
# have to change the description of the subblock SOLVENT. You may have to change
# the boxsize.

$AMSBIN/ams <<eor
System
  atoms
    C 0.0 0.0 0.0 adf.SigU=3.50 ↳
↳ adf.EpsU=0.066
    O 1.208031058311462 0.0 0.0 adf.SigU=2.96 ↳
↳ adf.EpsU=0.200
    O -0.741720974445343 1.118348836898804 0.0 adf.SigU=2.96 ↳
↳ adf.EpsU=0.200
    C -0.8529478907585144 -1.228639006614685 0.0 adf.SigU=3.50 ↳
↳ adf.EpsU=0.066
    N -0.1451586186885834 -2.467742681503296 0.0 adf.SigU=3.25 ↳
↳ adf.EpsU=0.170
    H -0.09300804138183594 1.869869947433472 0.0 adf.SigU=1.00 ↳
↳ adf.EpsU=0.046
    H -1.528575420379639 -1.167157530784607 0.8756611347198486 adf.SigU=1.00 ↳
↳ adf.EpsU=0.046
    H -1.528575420379639 -1.167157530784607 -0.8756611347198486 adf.SigU=1.00 ↳
↳ adf.EpsU=0.046
    H 0.4767249822616577 -2.513782262802124 0.8179888725280762 adf.SigU=1.00 ↳
↳ adf.EpsU=0.046
    H 0.4767249822616577 -2.513782262802124 -0.8179888725280762 adf.SigU=1.00 ↳
↳ adf.EpsU=0.046
  end
end

Task SinglePoint

Properties
  Gradients Yes
End

Engine ADF
  title 3D-RISM test
  basis
    core small
    type DZP
  end
  nobeckegrid
  Relativity Level=None
  rism glycine 1N

```

(continues on next page)

(continued from previous page)

```

RISM1D
SUBEND
SOLVENT1 water
  UNITS      uWeight=g/mol  ULJsize=A  ULJenergy=kcal/mol  Ucoord=A  Udens=1/A3
  Parameters Weight=18.015  nAtoms=2
  1    -0.8476   3.166    0.1554      0.000000   0.00000   0.000000
  2     0.4238   1.000    0.0460     -0.816490   0.00000   0.577359
                                     0.816490   0.00000   0.577359

  DenSpe=0.03333
SUBEND
SOLUTE CO
  BOXSIZe 32.0 32.0 32.0
  BOXGRID 64 64 64
SUBEND
end
symmetry C(s)
xc
  lda
end
EndEngine
eor

# The densf utility can be used to convert the 3D-RISM grid data stored in the adf.
# →rkf file to
# the TAPE41 format suitable for visualization by AMSview. The following fields are
# →created
# for each solvent site: Huv (solvent total correlation function), Uuv (solvent
# →potential in RT),
# Guv (solvent pair distribution function), Cuv (solvent direct correlation),
# and PMF (potentials of mean force in kcal/mol)

$AMSBIN/densf << eor
adffile ams.results/adf.rkf
RISM
eor

```

Example: 3D-RISM: Entropy

Download 3DRISM-Entropy.run

```

#!/bin/sh

# == Expert option ==

# Computing entropy contributions from the solvent with the 3D-RISM model is
# →illustrated
# on a water molecule with a constant point charge electrostatic potential

# All subkeys in the RISM block are discussed in the User's Guide.
# See also the 3DRISM-Glycine example

# density, dielectric constant as well as all DOEPS keys need to be taken from

```

(continues on next page)

(continued from previous page)

```

↪experiment!

$AMSBIN/ams <<eor
System
  ATOMS
    O      0.000000    0.000000   -0.079297  adf.SigU=3.1660 adf.EpsU=0.1554 adf.
↪ChgU=-0.8476
    H      0.000000    0.768138    0.520093  adf.SigU=1.0000 adf.EpsU=0.0560 adf.
↪ChgU=+0.4238
    H      0.000000   -0.768138    0.520093  adf.SigU=1.0000 adf.EpsU=0.0560 adf.
↪ChgU=+0.4238
  End
End

Task SinglePoint

Properties
  Gradients Yes
End

Engine ADF
  title 3D-RISM Entropy test

  ZLMfit
    Quality verygood
  End

  basis
    core small
    type DZP
  end

  Relativity Level=None

  XC
    GGA PBE
  End

  RISM Water in Water
    RISM1D theory=DRISM closure=HNC
    FLUIDPARAM temper=298.15 DielConst=78.46 UTotDens=G/CM3 0.9971
    DODEPS alpha=0.257e-3 kappa=0.457e-9 dedtp=-0.360 dedpt=0.037e-6
  SUBEND

  SOLVENT1 water (SPC/E)
    UNITS      uWeight=g/mol  ULJsize=A  ULJenergy=kcal/mol  Ucoord=A  Udens=MOL
    Parameters Weight=18.015  nAtoms=2
      1   -0.847600   3.16600   0.1554    0.00000000    0.00000000    0.06461505
      2    +0.423800   1.00000   0.0560    0.81649029    0.00000000   -0.51274392
                                -0.81649029    0.00000000   -0.51274392
    DenSpe=1.00000
  SUBEND

  SOLUTE  Water
    BOXSIZE 32.0 32.0 32.0
    BOXGRID 64 64 64

```

(continues on next page)

(continued from previous page)

```

    CHRGLVL=MM DERIV
  SUBEND
end
EndEngine
eor

```

15.2.4 FDE: Frozen Density Embedding

Example: FDE: H2O in water

Download FDE_H2O_128.run

```

#!/bin/sh

# This example demonstrates how to use FDE in combination with a large
# environment, that is modeled as a superposition of the densities of isolated
# molecules. Here, the excitation energies of a water molecule surrounded by an
# environment of 127 water molecules. For details, see also: C.R. Jacob, J.
# Neugebauer, L. Jensen and L. Visscher, Comparison of frozen-density embedding
# and discrete reaction field solvent models for molecular properties, Physical
# Chemistry Chemical Physics 8, 2349 (2006)

# This calculation consists of two steps:
# - First a prototype water molecule is calculated.
# - Next the embedding calculation of water in water is performed.

# To reduce the amount of output the next lines are included in the adf
# calculations:
#   EPRINT
#   SFO NOEIG NOOVL NOORBPOP
#   SCF NOPOP
#   END
#   NOPRINT BAS FUNCTIONS

# create atomic fragment files

AMS_JOBNAME=O $AMSBIN/ams <<eor
System
  Atoms
    O 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create 0 file=$AMSRESOURCES/ADF/DZP/O
  Relativity Level=None
EndEngine
eor
mv O.results/adf.rkf t21.DZP.O

AMS_JOBNAME=H $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

Atoms
  H 0.0 0.0 0.0
End
End
Task SinglePoint
Engine ADF
  create H file=$AMSRESOURCES/ADF/DZP/H
  Relativity Level=None
EndEngine
eor
mv H.results/adf.rkf t21.DZP.H

# First, a prototype water molecule is calculated. The density of this isolated
# water molecules will afterwards be used to model the environment.

AMS_JOBNAME=H2O $AMSBIN/ams <<eor
System
  atoms [bohr]
    O      -11.380487000000000    -11.810553000000000    -4.515226000000000
    H      -13.10476265095705    -11.83766918322447    -3.96954531282721
    H      -10.51089289290947    -12.85330720999229    -3.32020577897331
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fragments
    O t21.DZP.O
    H t21.DZP.H
  end
  noprint BAS FUNCTIONS
  numericalquality good
  scf
    converge 1.0e-6 1.0e-6
    diis
      cx 5.0
      cxx 10.0
      cyc 5
      n 10
      ok 0.5
    end
    iterations 50
    lshift 0.0
    mixing 0.2
  end
  symmetry NOSYM
  title Input generated by modco
  xc
    lda
  end

```

(continues on next page)

(continued from previous page)

```

    Relativity Level=None
EndEngine
eor

mv H2O.results/adf.rkf t21.mol_1

# Afterwards, the FDE calculation is performed. In this FDE calculation, there
# is one nonfrozen water molecule and the previously prepared water molecule is
# included as a frozen fragment that is duplicated 127 times. For this frozen
# fragment, the more efficient fitted density is used.

AMS_JOBNAME=FDE $AMSBIN/ams <<eor
System
  atoms [Bohr]
    O      0.000000000000000    0.000000000000000    0.000000000000000
    H     -1.430143000000000    0.000000000000000    1.107393000000000
    H      1.430143000000000    0.000000000000000    1.107393000000000
    O     -11.380487000000000   -11.810553000000000   -4.515226000000000   adf.
↪f=frag1|1
    H     -13.10476265095705   -11.83766918322447   -3.96954531282721   adf.
↪f=frag1|1
    H     -10.51089289290947   -12.85330720999229   -3.32020577897331   adf.
↪f=frag1|1
    O     -1.116350000000000     9.119186000000000   -3.230948000000000   adf.
↪f=frag1|2
    H     -2.82271357869859     9.71703285239153   -3.18063201242303   adf.
↪f=frag1|2
    H     -0.12378551814273    10.53819303003839   -2.70860866559857   adf.
↪f=frag1|2
    O     -16.969012000000000   -3.658353000000000  -10.785713000000000   adf.
↪f=frag1|3
    H     -15.70823656958949   -4.23996689198245   -9.62648920152293   adf.
↪f=frag1|3
    H     -16.47814038897754   -4.36080868684451  -12.37857352487904   adf.
↪f=frag1|3
    O     -10.765608000000000   -4.163577000000000     0.518032000000000   adf.
↪f=frag1|4
    H     -9.16115845895954   -3.98623150326079   -0.29800688710696   adf.
↪f=frag1|4
    H     -11.97483852095230   -3.79636551545084   -0.77600078745886   adf.
↪f=frag1|4
    O     -6.554233000000000   -9.202975000000000  -11.231254000000000   adf.
↪f=frag1|5
    H     -8.15301944239612   -9.65354271558258  -10.51536304076499   adf.
↪f=frag1|5
    H     -6.90715220963067   -7.74998343249339  -12.24902957370683   adf.
↪f=frag1|5
    O     -14.167136000000000   -6.558132000000000   -6.629574000000000   adf.
↪f=frag1|6
    H     -13.74689800192609   -8.31204468643143   -6.76675830514850   adf.
↪f=frag1|6
    H     -15.43294077464585   -6.49537593456625   -5.33906885435316   adf.
↪f=frag1|6
    O     -1.012338000000000   -6.537375000000000  -20.632283000000000   adf.

```

(continues on next page)

(continued from previous page)

→f=frag1 7					
H	0.51358895613388	-7.01674081354516	-19.78766204266023	adf.	
→f=frag1 7					
H	-2.25846754637793	-6.48721751306148	-19.32222614537351	adf.	
→f=frag1 7					
O	-7.97372300000000	4.33381600000000	8.85869700000000	adf.	
→f=frag1 8					
H	-7.39209897744333	2.71703281820261	9.42381190837837	adf.	
→f=frag1 8					
H	-7.34133495205587	4.47772485325760	7.17021271491547	adf.	
→f=frag1 8					
O	1.68768000000000	-11.29316300000000	-2.87636700000000	adf.	
→f=frag1 9					
H	1.52000307205134	-11.65999321781241	-4.63958827351129	adf.	
→f=frag1 9					
H	0.92563970293820	-9.66478590395236	-2.67815953059656	adf.	
→f=frag1 9					
O	1.09184600000000	-1.69811700000000	-18.81717100000000	adf.	
→f=frag1 10					
H	2.07215988260319	-2.34326255514507	-20.19354345122146	adf.	
→f=frag1 10					
H	0.13398919688371	-3.11903886392137	-18.23829710737747	adf.	
→f=frag1 10					
O	-13.85258700000000	-1.51317200000000	-3.42847700000000	adf.	
→f=frag1 11					
H	-13.34561409429037	-1.90947670800034	-5.11890601995987	adf.	
→f=frag1 11					
H	-15.31887324674441	-2.53345289474331	-3.14451376182312	adf.	
→f=frag1 11					
O	5.28960400000000	-6.81266800000000	-13.10585800000000	adf.	
→f=frag1 12					
H	7.01709448187639	-6.62178372023976	-12.60488989024026	adf.	
→f=frag1 12					
H	4.34671789396407	-5.97791594280375	-11.80749041866683	adf.	
→f=frag1 12					
O	-11.47407200000000	-10.90708300000000	-9.44085000000000	adf.	
→f=frag1 13					
H	-11.21611173248622	-12.45441460630369	-10.34132244308043	adf.	
→f=frag1 13					
H	-11.17634020521638	-11.33593027595366	-7.70907363612158	adf.	
→f=frag1 13					
O	-1.64592100000000	-11.43523300000000	1.48098000000000	adf.	
→f=frag1 14					
H	-0.30557034252542	-10.47362907146570	0.73908565451392	adf.	
→f=frag1 14					
H	-1.72993170289473	-12.94068698496448	0.48190338473989	adf.	
→f=frag1 14					
O	-7.32468400000000	-5.01818100000000	4.38774900000000	adf.	
→f=frag1 15					
H	-8.81838077448469	-4.73028985072788	3.40916949260461	adf.	
→f=frag1 15					
H	-7.75923926090726	-6.38911120628163	5.48470646359115	adf.	
→f=frag1 15					
O	5.20879700000000	-6.83850600000000	3.69146100000000	adf.	
→f=frag1 16					
H	5.26579130261858	-6.68511818556767	1.89011343551333	adf.	
→f=frag1 16					

(continues on next page)

(continued from previous page)

H	6.39162739624924	-5.60718291987245	4.28841938067655	adf.
↪f=frag1 16				
O	6.73749100000000	-0.26065600000000	-6.58850100000000	adf.
↪f=frag1 17				
H	6.56301678911955	-2.04681439624047	-6.81394756463717	adf.
↪f=frag1 17				
H	8.29925639010887	0.14828805200118	-7.40413401232653	adf.
↪f=frag1 17				
O	5.30624300000000	-5.54309500000000	-6.43599300000000	adf.
↪f=frag1 18				
H	3.81279050995479	-6.09072594663625	-7.29699777727678	adf.
↪f=frag1 18				
H	6.65189674819999	-6.43527789528092	-7.25136362341575	adf.
↪f=frag1 18				
O	-5.72214300000000	-7.59376400000000	-5.60989200000000	adf.
↪f=frag1 19				
H	-5.63766272358672	-7.49959469188493	-7.41422690365166	adf.
↪f=frag1 19				
H	-3.99734274429106	-7.51425600722341	-5.07105423295232	adf.
↪f=frag1 19				
O	-4.96412100000000	4.32334900000000	-3.25899700000000	adf.
↪f=frag1 20				
H	-6.26920382212011	5.55951483151335	-3.05829302735551	adf.
↪f=frag1 20				
H	-3.43114054713299	5.22630232648312	-2.93303718111639	adf.
↪f=frag1 20				
O	-10.94232600000000	0.55437900000000	-13.18244900000000	adf.
↪f=frag1 21				
H	-9.99364526446256	2.08335246724114	-13.36649850073860	adf.
↪f=frag1 21				
H	-12.25798450895047	0.68645755108753	-14.41662950801929	adf.
↪f=frag1 21				
O	-9.29636700000000	5.39923600000000	-12.62463400000000	adf.
↪f=frag1 22				
H	-7.78716246923940	5.39969899801535	-11.62767327349474	adf.
↪f=frag1 22				
H	-8.71366631604628	5.57073538127912	-14.32835095341294	adf.
↪f=frag1 22				
O	2.97641300000000	-12.44506100000000	3.62605000000000	adf.
↪f=frag1 23				
H	3.66110125710447	-10.77090992621746	3.63307801290360	adf.
↪f=frag1 23				
H	1.22148596207982	-12.21500271544869	3.25334655288432	adf.
↪f=frag1 23				
O	-7.52033800000000	-2.70960600000000	-16.43185500000000	adf.
↪f=frag1 24				
H	-8.54144292463491	-2.01657808726233	-15.10947598274278	adf.
↪f=frag1 24				
H	-8.12619297191493	-1.91113986970532	-17.93750940057940	adf.
↪f=frag1 24				
O	-1.69701700000000	-2.04382200000000	-8.20675700000000	adf.
↪f=frag1 25				
H	-1.16935910005967	-0.43265303835196	-8.83710685355905	adf.
↪f=frag1 25				
H	-0.63663168422293	-2.33781858979711	-6.77122484449879	adf.
↪f=frag1 25				
O	5.30132200000000	-9.56047300000000	8.45223600000000	adf.

(continues on next page)

(continued from previous page)

→f=frag1 26				
H	5.27386189469879	-8.61762538446407	6.90889108173823	adf.
→f=frag1 26				
H	4.55017557362690	-8.45544294990206	9.67137143822390	adf.
→f=frag1 26				
O	5.99489300000000	-5.84398700000000	-1.27866800000000	adf.
→f=frag1 27				
H	6.10499825242707	-5.94881824033588	-3.08103213209623	adf.
→f=frag1 27				
H	7.02298278120587	-4.42064928461433	-0.84422038296580	adf.
→f=frag1 27				
O	-8.49933400000000	6.30730300000000	1.26206900000000	adf.
→f=frag1 28				
H	-9.26414421853983	5.21634012956926	0.03875605345364	adf.
→f=frag1 28				
H	-9.84131776823032	6.72028388514297	2.40230140460829	adf.
→f=frag1 28				
O	1.42265800000000	7.15100500000000	-6.70245700000000	adf.
→f=frag1 29				
H	0.49123529007929	7.74531228135872	-5.27036768330312	adf.
→f=frag1 29				
H	2.87243479479048	6.33486591183760	-5.99276142000362	adf.
→f=frag1 29				
O	1.16572300000000	-15.86327300000000	-8.03011700000000	adf.
→f=frag1 30				
H	-0.43980652899404	-16.56646285956896	-8.47669081602252	adf.
→f=frag1 30				
H	1.27023658519214	-14.33069688850776	-8.98504681689730	adf.
→f=frag1 30				
O	-1.89194800000000	-10.63552100000000	-8.58469800000000	adf.
→f=frag1 31				
H	-2.78816305171149	-10.71751973024788	-10.15367983850320	adf.
→f=frag1 31				
H	-2.90779524204234	-11.59056143861734	-7.43250195607063	adf.
→f=frag1 31				
O	1.30322100000000	-6.54666700000000	-9.29066800000000	adf.
→f=frag1 32				
H	0.04144584195376	-7.80383112457906	-8.97588071525340	adf.
→f=frag1 32				
H	0.43997569188912	-4.97291783823648	-9.06767765025571	adf.
→f=frag1 32				
O	-4.10800400000000	-6.59387200000000	-16.43397700000000	adf.
→f=frag1 33				
H	-4.90090013771901	-8.11414568563407	-17.00992218470793	adf.
→f=frag1 33				
H	-5.44796070593591	-5.38061594011036	-16.36971704696261	adf.
→f=frag1 33				
O	-5.19983400000000	-12.82687600000000	-4.96878500000000	adf.
→f=frag1 34				
H	-6.70471369416354	-13.43327229448220	-5.76831602526536	adf.
→f=frag1 34				
H	-5.42955949756766	-11.03545071340780	-4.87067679172327	adf.
→f=frag1 34				
O	-4.89786700000000	5.50178800000000	-16.51771100000000	adf.
→f=frag1 35				
H	-4.96675000682788	7.30587317882606	-16.40743398906903	adf.
→f=frag1 35				

(continues on next page)

(continued from previous page)

H	-3.22762417250174	5.07795982200470	-15.96792726530632	adf.
→f=frag1 35				
O	-17.57898700000000	-4.99346700000000	-2.97681500000000	adf.
→f=frag1 36				
H	-18.76387465651032	-3.84193458717524	-2.24085062321750	adf.
→f=frag1 36				
H	-17.39866900954461	-6.30611916234463	-1.74554195748830	adf.
→f=frag1 36				
O	-3.50776800000000	-17.32380200000000	-10.10442500000000	adf.
→f=frag1 37				
H	-4.40193812130934	-18.63309464188228	-10.97496609167801	adf.
→f=frag1 37				
H	-4.53952158473348	-16.94953791159138	-8.66671344522861	adf.
→f=frag1 37				
O	-10.81911600000000	-4.66640800000000	-11.14487100000000	adf.
→f=frag1 38				
H	-11.62185710527301	-4.88296610749300	-9.53852778505075	adf.
→f=frag1 38				
H	-10.60915967583231	-2.87735761828481	-11.30864113107593	adf.
→f=frag1 38				
O	-6.39205500000000	0.01793500000000	-6.73248500000000	adf.
→f=frag1 39				
H	-5.82125006722311	1.22625909145182	-5.51356587267281	adf.
→f=frag1 39				
H	-4.87489255123650	-0.72801711445480	-7.37542911048570	adf.
→f=frag1 39				
O	-11.30505500000000	0.46379700000000	-8.25065700000000	adf.
→f=frag1 40				
H	-9.64226007733910	0.80674572776125	-7.62685540050746	adf.
→f=frag1 40				
H	-11.19896085378185	0.79109534466454	-10.02638879504226	adf.
→f=frag1 40				
O	9.00392400000000	1.26046800000000	-13.97805200000000	adf.
→f=frag1 41				
H	8.87294935217592	1.02947962110145	-12.18888481086687	adf.
→f=frag1 41				
H	7.29424845398649	1.45338312957695	-14.53608144577292	adf.
→f=frag1 41				
O	-10.89041700000000	3.43422700000000	-2.58901500000000	adf.
→f=frag1 42				
H	-11.04828427051772	1.96350979597573	-3.63002318964871	adf.
→f=frag1 42				
H	-12.48348293054753	3.56267021936991	-1.74211071819919	adf.
→f=frag1 42				
O	-5.77532000000000	11.85364600000000	-3.10184700000000	adf.
→f=frag1 43				
H	-7.42098370181530	11.26896732951829	-2.63113365512790	adf.
→f=frag1 43				
H	-5.59494422717391	13.43644886209393	-2.24522382582680	adf.
→f=frag1 43				
O	-1.56797700000000	3.41013100000000	-9.46461500000000	adf.
→f=frag1 44				
H	-0.62647981010343	4.69229425860768	-8.60364482634544	adf.
→f=frag1 44				
H	-1.22975840621731	3.70013224540235	-11.21764410491830	adf.
→f=frag1 44				
O	-5.85114500000000	5.94789900000000	-8.75297600000000	adf.

(continues on next page)

(continued from previous page)

→f=frag1 45				
H	-4.36435430864595	4.93739949116572	-8.95290949638818	adf.
→f=frag1 45				
H	-5.23356351746774	7.64390869587085	-8.63572496098009	adf.
→f=frag1 45				
O	-5.55413300000000	-7.92360000000000	0.25554800000000	adf.
→f=frag1 46				
H	-4.38326585687764	-9.28844448621082	0.45022435153192	adf.
→f=frag1 46				
H	-6.01769107687214	-7.47995835111906	1.94667176216252	adf.
→f=frag1 46				
O	-10.80147900000000	4.92460700000000	-18.42825600000000	adf.
→f=frag1 47				
H	-9.46772203676955	4.11444445205056	-19.34278223208070	adf.
→f=frag1 47				
H	-12.08285494971162	3.65684979597704	-18.27835293347214	adf.
→f=frag1 47				
O	11.84765600000000	6.04652000000000	-5.60335700000000	adf.
→f=frag1 48				
H	12.23822731048506	7.54282902057004	-4.66519785219186	adf.
→f=frag1 48				
H	10.14515882225660	6.29374114330687	-6.16191644024222	adf.
→f=frag1 48				
O	9.40177200000000	-2.16451100000000	0.06593400000000	adf.
→f=frag1 49				
H	9.99192042697073	-0.60334687050214	-0.63128950443925	adf.
→f=frag1 49				
H	10.90850263662718	-3.09972302317630	0.42194641911128	adf.
→f=frag1 49				
O	-3.83766900000000	11.00009100000000	-8.55948700000000	adf.
→f=frag1 50				
H	-3.74373964993300	10.83305937748681	-6.76090229682198	adf.
→f=frag1 50				
H	-4.87440105609424	12.45821519867243	-8.82531410042130	adf.
→f=frag1 50				
O	-8.92277200000000	7.51515500000000	-5.13005000000000	adf.
→f=frag1 51				
H	-7.64240242456374	6.79630036125453	-6.18623699995818	adf.
→f=frag1 51				
H	-9.98750814060132	6.11915279273326	-4.69517258001857	adf.
→f=frag1 51				
O	-0.32879900000000	4.85643700000000	-14.28493900000000	adf.
→f=frag1 52				
H	-0.20121901190276	6.61816864447670	-13.89551098390984	adf.
→f=frag1 52				
H	1.10559652418602	4.51955612567933	-15.33404544784882	adf.
→f=frag1 52				
O	-2.88119200000000	-21.16143900000000	-13.73773700000000	adf.
→f=frag1 53				
H	-1.09646919425263	-20.88154858029820	-13.82748709656689	adf.
→f=frag1 53				
H	-3.12787937393977	-22.76872743498338	-14.52980568926457	adf.
→f=frag1 53				
O	4.08430100000000	-17.32350200000000	4.72137100000000	adf.
→f=frag1 54				
H	4.02413151632988	-15.51826748869058	4.62578223161330	adf.
→f=frag1 54				

(continues on next page)

(continued from previous page)

H	2.36935484299032	-17.81891859379031	5.01313401917970	adf.
→f=frag1 54				
O	-12.71856600000000	7.20558900000000	4.46079500000000	adf.
→f=frag1 55				
H	-14.45999505747860	7.69416069947355	4.47955006523861	adf.
→f=frag1 55				
H	-11.90975612966972	8.36888327939108	5.58515108034031	adf.
→f=frag1 55				
O	3.64630900000000	-5.77729500000000	11.93616900000000	adf.
→f=frag1 56				
H	4.69770672445712	-5.28069451760816	13.32165808553043	adf.
→f=frag1 56				
H	1.98018929821852	-5.85215747794930	12.63620066423870	adf.
→f=frag1 56				
O	-11.58290200000000	-8.00977000000000	-14.71744100000000	adf.
→f=frag1 57				
H	-11.15452934215944	-6.96177583707747	-13.30682612671804	adf.
→f=frag1 57				
H	-13.31014912674778	-7.60719902330076	-15.07262764680259	adf.
→f=frag1 57				
O	-22.69131900000000	-4.60206700000000	-11.33851100000000	adf.
→f=frag1 58				
H	-22.22272486043639	-6.12263420792208	-12.19869942051499	adf.
→f=frag1 58				
H	-21.13544211851963	-3.70468130859725	-11.12508740068061	adf.
→f=frag1 58				
O	4.56872600000000	15.36672100000000	-5.27290200000000	adf.
→f=frag1 59				
H	6.23209824653603	14.72493681821289	-5.57775451137379	adf.
→f=frag1 59				
H	4.56888064677390	17.00621625499974	-6.03687769799284	adf.
→f=frag1 59				
O	-19.42024500000000	0.10101200000000	-13.92810800000000	adf.
→f=frag1 60				
H	-18.31405236374814	-1.07169409540655	-13.10790833801040	adf.
→f=frag1 60				
H	-20.71321177209865	0.43336205711680	-12.70770480925147	adf.
→f=frag1 60				
O	4.02837000000000	-8.18071600000000	-24.03669300000000	adf.
→f=frag1 61				
H	5.65512609076238	-8.96585900909256	-24.13073712086871	adf.
→f=frag1 61				
H	3.08016870759219	-9.23647651818391	-22.91513710771192	adf.
→f=frag1 61				
O	-16.59841600000000	-12.07983100000000	-3.02725000000000	adf.
→f=frag1 62				
H	-16.86792190502099	-10.47849662259938	-2.23055432463633	adf.
→f=frag1 62				
H	-17.75928521418718	-12.09663441135308	-4.41422653012776	adf.
→f=frag1 62				
O	-7.26966600000000	11.01317800000000	-13.83432500000000	adf.
→f=frag1 63				
H	-8.50533384743054	11.78916627619676	-12.76540199703817	adf.
→f=frag1 63				
H	-5.99921818801193	12.28193782381027	-14.05299015201462	adf.
→f=frag1 63				
O	14.92607800000000	0.72989200000000	-0.88069200000000	adf.

(continues on next page)

(continued from previous page)

→f=frag1 64				
H	14.68468379195669	0.44423157042895	0.88898485624517	adf.
→f=frag1 64				
H	13.43262120167169	1.60465761841764	-1.40602569068362	adf.
→f=frag1 64				
O	-10.24993000000000	-15.51193700000000	-12.56703500000000	adf.
→f=frag1 65				
H	-10.81569785539303	-16.80205979146874	-11.43252226892721	adf.
→f=frag1 65				
H	-8.81118264459048	-16.23360868276287	-13.39214081855071	adf.
→f=frag1 65				
O	6.15377400000000	-6.81034900000000	-18.37876400000000	adf.
→f=frag1 66				
H	5.66882347580422	-7.60131711703521	-16.82608191819916	adf.
→f=frag1 66				
H	7.80239299356986	-6.14232206320171	-18.05104612139325	adf.
→f=frag1 66				
O	3.76793000000000	-11.87319400000000	-12.00003600000000	adf.
→f=frag1 67				
H	5.53017998300823	-12.15041382890993	-12.29878904864723	adf.
→f=frag1 67				
H	3.52066686277755	-10.11552847274610	-12.34799636768586	adf.
→f=frag1 67				
O	4.23865500000000	2.16969600000000	-16.37654900000000	adf.
→f=frag1 68				
H	3.03592238765764	0.92692640056214	-16.90625382926868	adf.
→f=frag1 68				
H	5.02860305993563	2.71732123822040	-17.90876707954152	adf.
→f=frag1 68				
O	-14.68271000000000	0.72381400000000	-16.71344500000000	adf.
→f=frag1 69				
H	-15.14615918038738	-0.55817879758533	-17.90228415832504	adf.
→f=frag1 69				
H	-16.24034166467332	1.19193697588290	-15.92208663689043	adf.
→f=frag1 69				
O	-8.56171900000000	-1.14046300000000	-21.11237400000000	adf.
→f=frag1 70				
H	-7.24726382704255	0.10164744794682	-21.14397231666602	adf.
→f=frag1 70				
H	-7.96722618972135	-2.45668030593841	-22.20129726831652	adf.
→f=frag1 70				
O	3.09803900000000	-19.30437100000000	-4.72950400000000	adf.
→f=frag1 71				
H	4.47592822929893	-18.53926720940844	-3.84199812304267	adf.
→f=frag1 71				
H	2.31606384558652	-17.93639511851180	-5.61762585411266	adf.
→f=frag1 71				
O	-11.48197100000000	-2.62773000000000	8.98577000000000	adf.
→f=frag1 72				
H	-12.10181120734499	-1.96357292082485	7.42169752349214	adf.
→f=frag1 72				
H	-12.53715834883977	-4.05824316030399	9.32015800703900	adf.
→f=frag1 72				
O	-15.32683200000000	4.99378800000000	0.71520300000000	adf.
→f=frag1 73				
H	-16.28231903578986	3.62492951609735	1.41155075487152	adf.
→f=frag1 73				

(continues on next page)

(continued from previous page)

H	-14.24707811603547	5.52532871717421	2.06546208560370	adf.
→f=frag1 73				
O	4.69924600000000	-3.09331300000000	-22.21218100000000	adf.
→f=frag1 74				
H	4.44004838777616	-3.02721933390031	-24.00105702850179	adf.
→f=frag1 74				
H	4.90782404353437	-4.85303119199437	-21.84956458183150	adf.
→f=frag1 74				
O	5.48125400000000	-14.87156900000000	-2.30008800000000	adf.
→f=frag1 75				
H	6.04793062228805	-15.53700673074120	-0.71651626102270	adf.
→f=frag1 75				
H	4.08123415431168	-13.81006617390298	-1.87025109596218	adf.
→f=frag1 75				
O	7.71692700000000	7.49170500000000	-0.28146900000000	adf.
→f=frag1 76				
H	7.15009959892487	7.47463483734514	1.43610036604224	adf.
→f=frag1 76				
H	6.70446411622425	6.23931957052779	-1.10490887468917	adf.
→f=frag1 76				
O	-0.09971700000000	10.17858400000000	-12.50337600000000	adf.
→f=frag1 77				
H	1.43320771620038	10.52645688573944	-11.60852657687974	adf.
→f=frag1 77				
H	-1.38648439654237	10.22688417289634	-11.23313966659599	adf.
→f=frag1 77				
O	0.17403100000000	-13.35840700000000	-17.21967600000000	adf.
→f=frag1 78				
H	-1.53885665094696	-13.32910704018195	-16.63934279586859	adf.
→f=frag1 78				
H	1.16036533522916	-13.51667655796879	-15.71179705645900	adf.
→f=frag1 78				
O	-12.87620000000000	-6.35854400000000	5.05140600000000	adf.
→f=frag1 79				
H	-11.96560105641672	-7.83983990822539	5.54960396913384	adf.
→f=frag1 79				
H	-12.07232354985510	-5.82614364999607	3.52106744189462	adf.
→f=frag1 79				
O	10.37496800000000	3.01364200000000	-1.65565900000000	adf.
→f=frag1 80				
H	10.56060903951036	4.59152033506358	-0.79109750165770	adf.
→f=frag1 80				
H	10.50573068374942	3.43968959450338	-3.40865305303111	adf.
→f=frag1 80				
O	-10.54672300000000	11.48736100000000	-1.14189100000000	adf.
→f=frag1 81				
H	-10.87795175377343	9.85135127695166	-1.83858958546889	adf.
→f=frag1 81				
H	-11.17355773718848	12.64365945215504	-2.38352527948959	adf.
→f=frag1 81				
O	16.77188300000000	5.46660900000000	-7.08505700000000	adf.
→f=frag1 82				
H	15.05944999981585	5.87188178668200	-6.66677909180415	adf.
→f=frag1 82				
H	17.62236540790539	5.39342341222859	-5.49040119833247	adf.
→f=frag1 82				
O	3.75457600000000	11.31207900000000	-9.30406600000000	adf.

(continues on next page)

(continued from previous page)

→f=frag1 83				
H	3.86003631554596	12.75207030857270	-8.21460174023312	adf.
→f=frag1 83				
H	3.06160535139532	10.00588129699877	-8.26231611492555	adf.
→f=frag1 83				
O	-12.29225900000000	3.56799200000000	15.55877400000000	adf.
→f=frag1 84				
H	-11.55132238527440	2.03988079459175	14.93626432369441	adf.
→f=frag1 84				
H	-13.88471345817920	3.05255666747083	16.24435317034552	adf.
→f=frag1 84				
O	-6.10108600000000	-22.91748700000000	-8.30037600000000	adf.
→f=frag1 85				
H	-4.39703335260680	-23.51961699551631	-8.22775875933953	adf.
→f=frag1 85				
H	-6.81851364400339	-23.76013175020010	-9.73105799918286	adf.
→f=frag1 85				
O	-16.47411100000000	-10.06716200000000	-10.99026800000000	adf.
→f=frag1 86				
H	-16.57824909007337	-8.41061556718373	-11.70904362169910	adf.
→f=frag1 86				
H	-14.81816261652035	-10.64777696598199	-11.42881650898706	adf.
→f=frag1 86				
O	-19.79746500000000	-9.66763600000000	-6.29115500000000	adf.
→f=frag1 87				
H	-19.30039040153150	-9.92412834081941	-8.01125899188181	adf.
→f=frag1 87				
H	-20.69151106695596	-8.09537391433191	-6.30780271266956	adf.
→f=frag1 87				
O	-5.17342500000000	-12.71280800000000	-15.39516900000000	adf.
→f=frag1 88				
H	-6.29838943798551	-11.96053470711536	-16.59523946722675	adf.
→f=frag1 88				
H	-5.88688186704289	-12.30005902553624	-13.78513137150979	adf.
→f=frag1 88				
O	-0.98586800000000	2.69855900000000	-21.38983900000000	adf.
→f=frag1 89				
H	-2.77204881462932	2.96779943896921	-21.48309619116062	adf.
→f=frag1 89				
H	-0.80499110215822	1.20344697675802	-20.38807696838254	adf.
→f=frag1 89				
O	-6.03694100000000	3.69212200000000	-20.94210000000000	adf.
→f=frag1 90				
H	-6.14071267530565	5.16732160002454	-21.98356377744071	adf.
→f=frag1 90				
H	-5.38953086150776	4.29598484602752	-19.36481963241442	adf.
→f=frag1 90				
O	8.56921900000000	-3.79464900000000	6.33985500000000	adf.
→f=frag1 91				
H	9.50635468663971	-2.25984004884893	6.53419338664101	adf.
→f=frag1 91				
H	9.73243046417235	-5.09792887162821	6.80890110437856	adf.
→f=frag1 91				
O	1.62911600000000	13.17414900000000	-1.60348400000000	adf.
→f=frag1 92				
H	2.66594110342472	13.03446639023091	-0.12798012211089	adf.
→f=frag1 92				

(continues on next page)

(continued from previous page)

H	2.66565709768483	14.04258475743428	-2.80473562652369	adf.
→f=frag1 92				
O	-1.79383000000000	17.03966900000000	-2.19674400000000	adf.
→f=frag1 93				
H	-0.53200588641356	15.75727680306069	-2.00993024293071	adf.
→f=frag1 93				
H	-1.42725302708876	17.80645974200545	-3.79338324012655	adf.
→f=frag1 93				
O	-7.66877400000000	-18.37494100000000	-6.40129600000000	adf.
→f=frag1 94				
H	-8.48426657117146	-18.61293045852318	-4.80443592340425	adf.
→f=frag1 94				
H	-7.09966518295817	-20.02669116913405	-6.86974035671357	adf.
→f=frag1 94				
O	10.40397100000000	-3.09718200000000	-22.16627000000000	adf.
→f=frag1 95				
H	8.72972380889992	-2.49326115967796	-21.84408188422351	adf.
→f=frag1 95				
H	11.11812043738098	-1.87363862919898	-23.29078579938355	adf.
→f=frag1 95				
O	-15.30392700000000	1.38087600000000	7.30094900000000	adf.
→f=frag1 96				
H	-14.62180203945480	2.68484739436449	8.35261118963587	adf.
→f=frag1 96				
H	-16.43220546537447	0.47060667386509	8.38261486369176	adf.
→f=frag1 96				
O	8.58612500000000	-8.60056200000000	-9.05727500000000	adf.
→f=frag1 97				
H	8.70489512259771	-9.81319946167069	-10.39407463523348	adf.
→f=frag1 97				
H	8.62856020038021	-9.58970781613463	-7.54354008582316	adf.
→f=frag1 97				
O	16.03912900000000	1.51573000000000	-10.24266300000000	adf.
→f=frag1 98				
H	15.15629413827772	2.19658252062845	-11.66697745696204	adf.
→f=frag1 98				
H	16.44244740848228	2.95789688018386	-9.22822101876796	adf.
→f=frag1 98				
O	-15.02490500000000	4.61696500000000	-7.22941300000000	adf.
→f=frag1 99				
H	-13.96280647503120	5.31092864978721	-8.51859506482347	adf.
→f=frag1 99				
H	-14.28853929511416	3.00824288473906	-6.85340464006069	adf.
→f=frag1 99				
O	-3.38051600000000	-15.91202400000000	-1.00061000000000	adf.
→f=frag1 100				
H	-4.22410184376431	-15.04185487754888	-2.34329307606914	adf.
→f=frag1 100				
H	-1.90382516434679	-16.61447063748981	-1.77362777442889	adf.
→f=frag1 100				
O	-15.26048000000000	6.49459500000000	-20.09531600000000	adf.
→f=frag1 101				
H	-13.52897204979343	6.24438887420643	-19.63607060457812	adf.
→f=frag1 101				
H	-15.47768447407662	5.50940621247909	-21.59659174135803	adf.
→f=frag1 101				
O	-18.03907100000000	-8.43103500000000	0.81066000000000	adf.

(continues on next page)

(continued from previous page)

→f=frag1 102				
H	-19.83364526460744	-8.64920488317246	0.75120975933977	adf.
→f=frag1 102				
H	-17.60426054198021	-8.72510837516712	2.54157429534231	adf.
→f=frag1 102				
O	-1.66133700000000	-24.85433900000000	-7.59562300000000	adf.
→f=frag1 103				
H	-0.93912195987639	-26.25608107787563	-6.70953395077215	adf.
→f=frag1 103				
H	-2.16378824805376	-25.53854670810930	-9.19280994513164	adf.
→f=frag1 103				
O	-13.11411600000000	4.62406100000000	10.65633500000000	adf.
→f=frag1 104				
H	-12.77074621481150	4.11089532103550	12.35644893641187	adf.
→f=frag1 104				
H	-11.48603903104276	4.71705763077764	9.87382583582304	adf.
→f=frag1 104				
O	-12.41558900000000	11.84804700000000	-6.99447300000000	adf.
→f=frag1 105				
H	-11.30168153595745	10.44978337527290	-6.71933990939709	adf.
→f=frag1 105				
H	-12.47123642287374	12.03565896451106	-8.79261334416275	adf.
→f=frag1 105				
O	-6.99029300000000	15.09813200000000	-9.14840700000000	adf.
→f=frag1 106				
H	-8.45117315114006	15.70172502049625	-10.02768731357616	adf.
→f=frag1 106				
H	-7.14889401470228	15.78429001622505	-7.48238284738053	adf.
→f=frag1 106				
O	-12.34625400000000	10.56150500000000	-12.23873500000000	adf.
→f=frag1 107				
H	-11.44958979728050	8.99509889893791	-12.35703315867646	adf.
→f=frag1 107				
H	-12.49821882155289	11.12665028131793	-13.95020252415008	adf.
→f=frag1 107				
O	11.40803400000000	-1.03651800000000	-9.30311700000000	adf.
→f=frag1 108				
H	13.12420580954423	-0.46728539979694	-9.35167405119891	adf.
→f=frag1 108				
H	11.31625950576437	-2.30813269496276	-10.58615133000387	adf.
→f=frag1 108				
O	-5.11896700000000	-0.12253200000000	11.02394500000000	adf.
→f=frag1 109				
H	-3.92681627947473	1.22947829217064	10.87403152613883	adf.
→f=frag1 109				
H	-4.37657440580777	-1.48587544764282	10.09563930570322	adf.
→f=frag1 109				
O	-9.99475100000000	-0.33650000000000	13.26488800000000	adf.
→f=frag1 110				
H	-8.34486345702615	0.24573595608403	12.80608345859702	adf.
→f=frag1 110				
H	-10.59609456116402	-1.19896273277279	11.79310420533769	adf.
→f=frag1 110				
O	-2.30216800000000	10.69499300000000	2.99722800000000	adf.
→f=frag1 111				
H	-1.93606116560115	10.01830345774807	1.36025326914961	adf.
→f=frag1 111				

(continues on next page)

(continued from previous page)

H	-4.04923519757226	11.15628108452666	2.91615338962990	adf.
→f=frag1 111				
O	13.02295800000000	-5.27441800000000	1.23847500000000	adf.
→f=frag1 112				
H	14.31033554297163	-4.63482922705865	0.14065238973499	adf.
→f=frag1 112				
H	13.91152105495786	-5.78567177035616	2.72866923628817	adf.
→f=frag1 112				
O	7.56659100000000	6.94211200000000	-9.52506900000000	adf.
→f=frag1 113				
H	8.22168391057836	5.87923316520027	-10.83379780356249	adf.
→f=frag1 113				
H	6.67225115956347	8.24497386381330	-10.40501831435555	adf.
→f=frag1 113				
O	-2.17755000000000	7.03555800000000	6.40129900000000	adf.
→f=frag1 114				
H	-2.96551413318437	5.65850851485069	5.53269295552737	adf.
→f=frag1 114				
H	-2.21627359256819	8.40062348976667	5.21525504034563	adf.
→f=frag1 114				
O	9.00788300000000	12.60897400000000	-5.62029800000000	adf.
→f=frag1 115				
H	10.26246081511818	11.86068291737544	-4.55365645678727	adf.
→f=frag1 115				
H	7.97453521284851	11.22086747860001	-6.14656429973985	adf.
→f=frag1 115				
O	-1.44785500000000	-3.72480700000000	-24.99109500000000	adf.
→f=frag1 116				
H	0.23683814213660	-4.37145767071870	-25.11471193705296	adf.
→f=frag1 116				
H	-1.92063360111663	-4.01890345598422	-23.27016756076567	adf.
→f=frag1 116				
O	-7.64825200000000	12.61552300000000	3.06517700000000	adf.
→f=frag1 117				
H	-7.81167293245439	14.38063407144895	3.42476805177055	adf.
→f=frag1 117				
H	-8.83689943470846	12.31223844466806	1.73598952764555	adf.
→f=frag1 117				
O	4.46933200000000	-0.50378800000000	2.21087700000000	adf.
→f=frag1 118				
H	4.27357465941304	-2.08510082915893	3.06688986215400	adf.
→f=frag1 118				
H	5.91907845739645	-0.73702803715971	1.15473407570514	adf.
→f=frag1 118				
O	-1.24895400000000	-6.97750900000000	-2.93109400000000	adf.
→f=frag1 119				
H	-2.37833578618925	-6.59579569242172	-1.57079221286929	adf.
→f=frag1 119				
H	-0.21288275291882	-5.50308282339477	-3.08674554325879	adf.
→f=frag1 119				
O	-5.92082900000000	-3.03107100000000	-2.51072800000000	adf.
→f=frag1 120				
H	-5.78071219226800	-4.56089081895937	-3.46553050415439	adf.
→f=frag1 120				
H	-6.21267678923423	-1.74791100910179	-3.75166671237991	adf.
→f=frag1 120				
O	1.14317500000000	-2.76826300000000	-3.93086600000000	adf.

(continues on next page)

(continued from previous page)

```

→f=frag1|121
  H      2.94971664531870      -2.78102101161944      -3.84213191918490      adf.
→f=frag1|121
  H      0.62850650734009      -1.73939210305163      -2.53510649267729      adf.
→f=frag1|121
  O     -5.21546600000000      -0.71679400000000      1.97558900000000      adf.
→f=frag1|122
  H     -5.88193806317475      -1.35755002215181      0.42095852001025      adf.
→f=frag1|122
  H     -5.82594782496319      -1.86151827602300      3.23595476257813      adf.
→f=frag1|122
  O     -5.42031600000000      3.66296900000000      4.47881900000000      adf.
→f=frag1|123
  H     -6.47734991529745      4.75371897638942      3.49669222043088      adf.
→f=frag1|123
  H     -5.28387721038046      2.15431400285173      3.49041213110813      adf.
→f=frag1|123
  O      4.64978600000000      3.67542600000000      -3.78351700000000      adf.
→f=frag1|124
  H      5.30464821970122      2.16136749204504      -4.52541424890080      adf.
→f=frag1|124
  H      3.40016650933066      3.10039840282737      -2.60903925511290      adf.
→f=frag1|124
  O      1.38687600000000      -3.56100200000000      5.14710300000000      adf.
→f=frag1|125
  H      2.35586583709350      -2.84555947523344      6.49648430622687      adf.
→f=frag1|125
  H      2.25995224007779      -5.08706726956497      4.72228980076397      adf.
→f=frag1|125
  O     -3.30635200000000      -3.51075400000000      7.52143300000000      adf.
→f=frag1|126
  H     -1.82144215646564      -3.75776796826252      6.51860894948698      adf.
→f=frag1|126
  H     -4.64977283415043      -4.18421132786886      6.51481526117547      adf.
→f=frag1|126
  O      5.96480100000000      4.51370300000000      3.70332800000000      adf.
→f=frag1|127
  H      5.24291272273548      3.06620845434369      2.89384293177905      adf.
→f=frag1|127
  H      4.73614594944492      5.00201400735317      4.93765482424434      adf.
→f=frag1|127
  end
end

```

Task SinglePoint

```

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  excitations
    lowest 5
    onlysing
  end
  fde
    pw91k

```

(continues on next page)

(continued from previous page)

```

end
fragments
  O      t21.DZP.O
  H      t21.DZP.H
  frag1  t21.mol_1
end
fdefragments
  frag1  type=fde &
         fdedenstype SCFfitted
  SubEnd
end
noprnt BAS FUNCTIONS
numericalquality Good
scf
  converge 1.0e-6 1.0e-6
  diis
    cx 5.0
    cxx 10.0
    cyc 5
    n 10
    ok 0.5
  end
  iterations 50
  lshift 0.0
  mixing 0.2
end
symmetry NOSYM
title Input generated by modco
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

```

Example: FDE freeze-and-thaw: HeCO2

Download FDE_HeCO2_freezeandthaw.run

```

#!/bin/sh

# This example demonstrates how a freeze-and-thaw FDE calculation can be
# performed. As test system, a He-CO2 van der Waals complex is used. It will
# further be shown how different exchange-correlation potential can be used for
# different subsystems, and how different basis set expansions can be employed.
# For details, see C.R. Jacob, T.A. Wesolowski, L. Visscher, J. Chem. Phys. 123
# (2005), 174104. It should be stressed that the basis set and integration grid
# used in this example are too small to obtain good results.

# Summary:
# - PW91 everywhere
# - SAOP for He; PW91 for CO2
# - FDE(s) calculation with PW91 everywhere

# Important, this kind of FDE geometry optimization only works with the non-

```

(continues on next page)

(continued from previous page)

```

# default STO pair fitting method. This means that one has to include the key
# STOFIT in the input for ADF. If one does not use the BASIS key, like in this
# example, one should also include the key STOFIT in all fragment calculations
# (also in the create runs).

# Create atom

AMS_JOBNAME=C $AMSBIN/ams <<eor
System
  Atoms
    C 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create C $AMSRESOURCES/ADF/TZ2P/C
  stofit
  Relativity Level=None
EndEngine
eor
mv C.results/adf.rkf t21.C

AMS_JOBNAME=O $AMSBIN/ams <<eor
System
  Atoms
    O 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create O $AMSRESOURCES/ADF/TZ2P/O
  stofit
  Relativity Level=None
EndEngine
eor
mv O.results/adf.rkf t21.O

AMS_JOBNAME=He $AMSBIN/ams <<eor
System
  Atoms
    He 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create He $AMSRESOURCES/ADF/TZ2P/He
  stofit
  Relativity Level=None
EndEngine
eor
mv He.results/adf.rkf t21.He

# == PW91 everywhere ==

```

(continues on next page)

(continued from previous page)

```
# In the first part, the PW91 functional will be used for both the He and the
# CO2 subsystems. In this part, the FDE(m) basis set expansion is used, i.e.,
# basis functions of the frozen subsystem are not included in the calculation of
# the nonfrozen subsystem.
```

```
# First, the CO2 molecule is prepared. In this calculation, the C2v symmetry of
# the final complex is used, and the NOSYMFIT option has to be included because
# this molecule will be rotated as a frozen fragment.
```

```
#####
# Preparation of frozen CO2
#####
```

```
AMS_JOBNAME=CO2 $AMSBIN/ams <<eor
```

```
System
```

```
atoms [Bohr]
```

```
  C      0.000000  0.000000  0.000000
  O     -2.192000  0.000000  0.000000
  O      2.192000  0.000000  0.000000
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
eprint
```

```
scf NOPOP
```

```
sfo NOEIG NOOVL NOORBPOP
```

```
end
```

```
fragments
```

```
  C t21.C
```

```
  O t21.O
```

```
end
```

```
noprint BAS FUNCTIONS
```

```
nosymfit
```

```
numericalquality Good
```

```
stofit
```

```
symmetry C(2V)
```

```
title TEST 1 -- Preparation of frozen CO2
```

```
xc
```

```
gga pw91
```

```
end
```

```
Relativity Level=None
```

```
EndEngine
```

```
eor
```

```
mv CO2.results/adf.rkf t21.co2.0
```

```
# Afterwards, the FDE calculation is performed. In this calculation, the He atom
# is the nonfrozen system, and the previously prepared CO2 molecule is used as
# frozen fragment. For this frozen fragment the RELAX option is specified, so
# that the density of this fragment is updated in freeze-and-thaw iteration (a
# maximum number of three iteration is specified).
```

```
#####
```

(continues on next page)

(continued from previous page)

```

# Embedding calculation
#####

AMS_JOBNAME=FDE $AMSBIN/ams <<eor
System
  atoms [Bohr]
    He   0.000000  0.000000  6.019000  adf.f=He
    C    0.000000  0.000000  0.000000  adf.f=co2
    O    -2.192000  0.000000  0.000000  adf.f=co2
    O     2.192000  0.000000  0.000000  adf.f=co2
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    fullgrid
    pw91k
    relaxcycles 3
  end
  fragments
    He   t21.He
    co2  t21.co2.0
  end
  fdefragments
    co2 type=fde &
        fdeoptions RELAX
  SubEnd
end
noprnt BAS FUNCTIONS
nosymfit
numericalquality Good
stofit
title TEST 1 -- Embedding calculation: He with frozen CO2 density -- freeze-and-thaw
xc
  gga pw91
end
Relativity Level=None
EndEngine
eor

# == SAOP for He; PW91 for CO2 ==

# In this second part, the above example is modified such that PW91 is employed
# for the CO2 subsystem, while the SAOP potential is used for He. This can be
# achieved by choosing SAOP in the XC key (this sets the functional that will be
# used for the nonfrozen subsystem). Additionally, for the frozen fragment the
# XC option is used to chose the PW91 functional for relaxing this fragment.
# Furthermore, the PW91 functional is chosen for the nonadditive exchange-
# correlation functional that is used in the embedding potential with the
# GGAPOTXFD and GGAPOTCFD options in the FDE key.

```

(continues on next page)

(continued from previous page)

```
#####
# Embedding calculation
#####

AMS_JOBNAME=FDE1 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    He  0.000000  0.000000  6.019000  adf.f=He
    C   0.000000  0.000000  0.000000  adf.f=co2
    O   -2.192000  0.000000  0.000000  adf.f=co2
    O    2.192000  0.000000  0.000000  adf.f=co2
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    fullgrid
    pw91k
    relaxcycles 3
    xcnadd PW91
  end
  fragments
    He  t21.He
    co2 t21.co2.0
  end
  fdefragments
    co2 type=fde &
      fdeoptions RELAX
      XC          GGA PW91
    SubEnd
  end
  noprint BAS FUNCTIONS
  nosymfit
  numericalquality Good
  stofit
  title TEST 2 -- Embedding calculation: He with frozen CO2 density -- freeze-and-thaw
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

rm t21.co2.0

# == FDE(s) calculation with PW91 everywhere ==

# In this third part, the PW91 functional is applied for both subsystems again,
```

(continues on next page)

(continued from previous page)

```
# but in contrast to part 1, now the FDE(s) basis set expansion is used, i.e.,
# the basis functions of the frozen subsystem are included in the calculation of
# the nonfrozen subsystem. This can be achieved by employing the USEBASIS
# option. This option can be combined with the RELAX option.
```

```
#####
# Preparation of frozen CO2
#####
```

```
AMS_JOBNAME=CO2_PW91 $AMSBIN/ams <<eor
```

```
System
```

```
  atoms [Bohr]
    C      0.000000  0.000000  0.000000
    O     -2.192000  0.000000  0.000000
    O      2.192000  0.000000  0.000000
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fragments
    C  t21.C
    O  t21.O
  end
  noprint BAS FUNCTIONS
  nosymfit
  numericalquality Good
  stofit
  symmetry C(2V)
  title TEST 3 -- Preparation of frozen CO2
  xc
    gga pw91
  end
  Relativity Level=None
```

```
EndEngine
```

```
eor
```

```
mv CO2_PW91.results/adf.rkf t21.co2.0
```

```
#####
# Embedding calculation
#####
```

```
AMS_JOBNAME=FDE_PW91 $AMSBIN/ams <<eor
```

```
System
```

```
  atoms [Bohr]
    He  0.000000  0.000000  6.019000 adf.f=He
    C   0.000000  0.000000  0.000000 adf.f=co2
    O  -2.192000  0.000000  0.000000 adf.f=co2
    O   2.192000  0.000000  0.000000 adf.f=co2
```

(continues on next page)

(continued from previous page)

```

    end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    fullgrid
    pw91k
    relaxcycles 3
  end
  fragments
    He    t21.He
    co2   t21.co2.0
  end
  fdefragments
    co2 type=fde &
        fdeoptions RELAX USEBASIS
  SubEnd
end
noprnt BAS FUNCTIONS
nosymfit
numericalquality Good
stofit
title TEST 3 -- Embedding calculation: He with frozen CO2 density -- freeze-and-thaw
xc
  gga pw91
end
Relativity Level=None
EndEngine
eor

```

Example: FDE energy: NH3-H2O

Download FDE_Energy_NH3-H2O.run

```

#!/bin/sh

# This is example for a calculation of FDE interaction energies in ADF in case
# of closed shell fragments#

# It performs single point runs for H2O and NH3
# with LDA/DZ (all-electron) and uses these fragments in
# A) an FDE energy embedding calculation calculation in which the energy of
#   water in presence of a frozen ammonia is computed
#   This requires a supermolecular integration grid
# B) a fully variational FDE energy calculation (with freeze-and-thaw)
#
# NumericalQuality is good which should give total energies for the
# fragments accurate at least up to 10**(-4) atomic units

```

(continues on next page)

(continued from previous page)

```

# NH3 LDA/DZ

AMS_JOBNAME=NH3 $AMSBIN/ams <<eor
System
  atoms
    N      -1.51248      -0.03714      -0.00081
    H      -1.71021       0.95994      -0.11003
    H      -1.96356      -0.53831      -0.76844
    H      -1.92899      -0.35123       0.87792
  end
end

Task SinglePoint

Engine ADF
  title H2O LDA/DZ single point
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZ
  end
  noprint BAS FUNCTIONS
  nosymfit
  numericalquality Good
  symmetrytolerance 1e-2
  Relativity
    Level None
  End
EndEngine
eor

mv NH3.results/adf.rkf t21.ammonia

# H2O LDA/DZ

AMS_JOBNAME=H2O $AMSBIN/ams <<eor
System
  atoms
    O      1.45838       0.10183       0.00276
    H      0.48989      -0.04206       0.00012
    H      1.84938      -0.78409      -0.00279
  end
end

Task SinglePoint

Engine ADF
  title H2O LDA/DZ single point
  eprint

```

(continues on next page)

(continued from previous page)

```

    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
end
exactdensity
basis
  core None
  type DZ
end
noprnt BAS FUNCTIONS
nosymfit
numericalquality Good
symmetrytolerance 1e-2
Relativity
  Level None
End
EndEngine
eor
mv H2O.results/adf.rkf t21.water

# NH3-H2O: FDE energy of H2O in presence of frozen NH3

AMS_JOBNAME=FDE $AMSBIN/ams <<eor
System
  atoms
    O      1.45838      0.10183      0.00276      adf.f=frag1
    H      0.48989     -0.04206      0.00012      adf.f=frag1
    H      1.84938     -0.78409     -0.00279      adf.f=frag1
    N     -1.51248     -0.03714     -0.00081      adf.f=frag2
    H     -1.71021      0.95994     -0.11003      adf.f=frag2
    H     -1.96356     -0.53831     -0.76844      adf.f=frag2
    H     -1.92899     -0.35123      0.87792      adf.f=frag2
  end
end

Task SinglePoint

Engine ADF
  title NH3-H2O LDA/Thomas-Fermi/DZ FDE single point with interaction energy
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    energy
    fullgrid
    thomasfermi
  end
  fragments
    frag1 t21.water
    frag2 t21.ammonia
  end
  fdefragments
    frag2 type=FDE
  end

```

(continues on next page)

(continued from previous page)

```

noprnt BAS FUNCTIONS
numericalquality Good
symmetrytolerance 1e-2
Relativity
  Level None
End
EndEngine
eor

# NH3-H2O FDE interaction energy

AMS_JOBNAME=FDE1 $AMSBIN/ams <<eor
System
  atoms
    O      1.45838      0.10183      0.00276      adf.f=frag1
    H      0.48989     -0.04206      0.00012      adf.f=frag1
    H      1.84938     -0.78409     -0.00279      adf.f=frag1
    N     -1.51248     -0.03714     -0.00081      adf.f=frag2
    H     -1.71021      0.95994     -0.11003      adf.f=frag2
    H     -1.96356     -0.53831     -0.76844      adf.f=frag2
    H     -1.92899     -0.35123      0.87792      adf.f=frag2
  end
end

Task SinglePoint

Engine ADF
  title NH3-H2O LDA/Thomas-Fermi/DZ FDE single point with interaction energy
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    energy
    relaxcycles 3
    thomasfermi
  end
  fragments
    frag1 t21.water
    frag2 t21.ammonia
  end
  fdefragments
    frag2 type=FDE &
    fdeoptions RELAX
  SubEnd
end
noprnt BAS FUNCTIONS
numericalquality Good
symmetrytolerance 1e-2
Relativity
  Level None
End
EndEngine
eor

```

Example: FDE energy: unrestricted fragments: Ne-H2O

Download FDE_Energy_H2O-Ne_unrestricted.run

```

#!/bin/sh

# This is example for a calculation of FDE interaction energies in ADF for an
# open-shell frozen fragment.

# It performs single point runs for H2O and Ne, the latter unrestricted
# with LDA/DZ (all-electron) and uses these fragments in an FDE energy
# embedding calculation in which the energy of water in presence of a frozen
# (open-shell) neon atom is computed
# This is a bit of an artificial test but it serves its purpose
#
# No freeze-thaw is done, this is at present not possible with unrestricted
# (open shell) fragments, but has to be done manually, see the example in
# $AMSHOME/examples/Test/FDE_Spin.run
#
# NumericalQuality is good which should give total energies for the
# fragments accurate at least up to 10**(-4) atomic units
#
# This test has been checked to yield the same energy as a run with a closed-
# shell (restricted) Ne atom (just comment UNRESTRICTED in the input below)
#

# Ne LDA/DZ (unrestricted)

AMS_JOBNAME=Ne $AMSBIN/ams <<eor
System
  atoms
    Ne      -1.51248      -0.03714      -0.00081
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZ
  end
  noprint BAS FUNCTIONS
  nosymfit
  numericalquality Good
  scf
    converge 1.0e-06 1.0e-06
    iterations 100
  end
  spinpolarization 0
  symmetrytolerance 1e-2
  title Ne LDA/DZ single point, unrestricted
  unrestricted

```

(continues on next page)

(continued from previous page)

```

xc
  lda
end
Relativity Level=None
EndEngine
eor

mv Ne.results/adf.rkf t21.ne

# H2O LDA/DZ

AMS_JOBNAME=H2O $AMSBIN/ams <<eor
System
  atoms
    O      1.45838      0.10183      0.00276
    H      0.48989     -0.04206      0.00012
    H      1.84938     -0.78409     -0.00279
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZ
  end
  noprint BAS FUNCTIONS
  nosymfit
  numericalquality Good
  spinpolarization 0
  symmetrytolerance 1e-2
  title H2O LDA/DZ single point
  xc
    lda
  end
  Relativity Level=None
EndEngine
eor
mv H2O.results/adf.rkf t21.water

# NH3-H2O: FDE energy of H2O in presence of frozen (unrestricted) Ne

AMS_JOBNAME=FDE $AMSBIN/ams <<eor
System
  atoms
    O      1.45838      0.10183      0.00276      adf.f=frag1
    H      0.48989     -0.04206      0.00012      adf.f=frag1

```

(continues on next page)

(continued from previous page)

```

      H      1.84938      -0.78409      -0.00279      adf.f=frag1
      Ne     -1.51248      -0.03714      -0.00081      adf.f=frag2
    end
  end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    energy
    fullgrid
    thomasfermi
  end
  fragments
    frag1 t21.water
    frag2 t21.ne
  end
  fdefragments
    frag2 type=FDE
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  spinpolarization 0
  symmetrytolerance 1e-2
  title Ne-H2O LDA/Thomas-Fermi/DZ FDE single point with interaction energy
  xc
    lda
  end
  Relativity Level=None
EndEngine
eor

```

Example: FDE geometry optimization: H2O-Li(+)

Download GO_FDE_H2O-Li.run

```

#!/bin/sh

# This example demonstrates how to perform a geometry optimization of an active
# subsystem (a lithium atom) in the presence of a frozen FDE fragment (the water
# molecule).

# Notes:
#
# a) Only the geometry of the active fragment will be relaxed (in this case, the
#    Li atom). The geometry of the FDE fragment (the water molecule) will not
#    change during the optimization.
#
# b) When performing geometry optimization ICW FDE one must:
#    - Disable symmetry ('Symmetry NoSym')

```

(continues on next page)

(continued from previous page)

```

#   - It is advised to use the FullGrid option ('FDE => FullGrid')

# Prepare the water molecule fragment:
# =====

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000    0.0000000   -1.53403200
    H     -0.7782160    0.0000000   -2.13596600
    H      0.7782160    0.0000000   -2.13596600
  end
end

Task SinglePoint

Engine ADF
  basis
    core None
    type DZP
  end
  numericalquality Good
  symmetry NOSYM
  totalenergy
  xc
    lda
  end
  Relativity
    Level None
  End
EndEngine
eor

mv Iso2.results/adf.rkf t21.iso.rho2

# H2O-Li(+) Geometry optimization
# (Li optimization in the presence of a 'frozen' water molecule)
# =====

AMS_JOBNAME=GO_FDE $AMSBIN/ams <<eor
System
  atoms
    Li      0.0000000    0.0000000    0.4529560
    O      0.0000000    0.0000000   -1.5340320  adf.f=rho2 region=frozen
    H     -0.7782160    0.0000000   -2.1359660  adf.f=rho2 region=frozen
    H      0.7782160    0.0000000   -2.1359660  adf.f=rho2 region=frozen
  end
  charge 1
end

Task GeometryOptimization

GeometryOptimization
  Convergence Step=1.0e-3

```

(continues on next page)

(continued from previous page)

```

End

Properties
  Gradients Yes
End

Constraints
  Block frozen
End

Engine ADF
  fde
    fullgrid
    sdftenergy
    thomasfermi
  end
  fragments
    rho2 t21.iso.rho2
  end
  fdefragments
    rho2 type=fde
  end
  basis
    core None
    type DZP
  end
  numericalquality Good
  symmetry NOSYM
  totalenergy
  xc
    lda
  end
  Relativity
    Level None
  End
EndEngine
eor

echo "Final Geometry"
echo ""
echo "Final Geometry after FDE optimization"

$AMSBIN/amsreport GO_FDE.results/adf.rkf 'distances#labels'

```

Example: FDE NMR shielding: Acetonitrile in water

Download FDE_NMR_relax.run

```

#!/bin/sh

# This examples demonstrates both the calculation of NMR shieldings using FDE,
# and how the approximate environment density can be improved by partial
# relaxation of individual solvent molecules. The test system is a cluster of
# acetonitrile and 12 solvent water molecules, of which for two the densities

```

(continues on next page)

(continued from previous page)

```
# are relaxed, while for the remaining 10 the frozen density of the isolated
# water is used. For details, see Refs. C. R. Jacob, J. Neugebauer, and L.
# Visscher, A flexible implementation of frozendensity embedding for use in
# multilevel simulation, submitted, 2007. R. E. Bulo, Ch. R. Jacob, and L.
# Visscher, NMR Solvent Shifts of Acetonitrile from Frozen-Density Embedding
# Calculation

# First, the isolated solvent water molecule is prepared. Again, because this
# will be rotated and translated afterwards, the option NOSYMFIT has to be
# included.

# create atomic fragment files

AMS_JOBNAME=O $AMSBIN/ams <<eor
System
  Atoms
    O 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create O file=$AMSRESOURCES/ADF/DZP/O
  Relativity Level=None
EndEngine
eor
mv O.results/adf.rkf t21.O.DZP

AMS_JOBNAME=H $AMSBIN/ams <<eor
System
  Atoms
    H 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create H file=$AMSRESOURCES/ADF/DZP/H
  Relativity Level=None
EndEngine
eor
mv H.results/adf.rkf t21.H.DZP

AMS_JOBNAME=C $AMSBIN/ams <<eor
System
  Atoms
    C 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create C file=$AMSRESOURCES/ADF/DZP/C
  Relativity Level=None
EndEngine
eor
mv C.results/adf.rkf t21.C.DZP

AMS_JOBNAME=N $AMSBIN/ams <<eor
```

(continues on next page)

(continued from previous page)

```

System
  Atoms
    N 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create N file=$AMSRESOURCES/ADF/DZP/N
  Relativity Level=None
EndEngine
eor
mv N.results/adf.rkf t21.N.DZP

#####
# prepare H2O
#####

AMS_JOBNAME=H2O $AMSBIN/ams <<eor
System
  atoms
    O      -1.46800      2.60500      1.37700
    H      -0.95200      3.29800      0.96500
    H      -1.16100      1.79900      0.96100
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fragments
    H      t21.H.DZP
    O      t21.O.DZP
  end
  noprint BAS FUNCTIONS
  numericalquality GOOD
  scf
    converge 1.0e-06 1.0e-06
    iterations 100
  end
  symmetry NOSYM
  symmetrytolerance 1e-2
  title Input generated by PyADF and later modified
  xc
    lda
  end
  Relativity Level=None
EndEngine
eor

mv H2O.results/adf.rkf t21.h2o

```

Afterwards, the FDE calculation is performed. In addition to the nonfrozen

(continues on next page)

(continued from previous page)

```
# acetonitrile molecule, three different fragments are used for the solvent
# water molecules. The first two fragments frag1 and frag2 are relaxed (in up to
# two freeze-and-thaw cycles), while the third fragment is used for the
# remaining 10 solvent molecules. Since a calculation of the shielding is
# performed afterwards, the option has to be included.
```

```
#####
# and the embedding calculation
#####
```

```
AMS_JOBNAME=FDE $AMSBIN/ams <<eor
```

```
System
```

```
atoms
  C      0.83000      0.66100     -0.44400
  N      0.00000      0.00000      0.00000
  C      1.87800      1.55900     -0.81900
  H      1.78500      2.40300     -0.13500
  H      1.76200      1.94900     -1.83000
  H      2.82900      1.12200     -0.51300
  O     -1.46800      2.60500      1.37700      adf.f=frag1|1
  H     -0.95200      3.29800      0.96500      adf.f=frag1|1
  H     -1.16100      1.79900      0.96100      adf.f=frag1|1
  O      2.40400     -2.51000     -0.36200      adf.f=frag2|1
  H      2.70000     -3.41900     -0.40900      adf.f=frag2|1
  H      1.77500     -2.50000      0.35900      adf.f=frag2|1
  O     -3.22800     -1.61500      1.18500      adf.f=frag3|1
  H     -3.33300     -2.55300      1.03000      adf.f=frag3|1
  H     -3.14200     -1.23600      0.31000      adf.f=frag3|1
  O      0.84000     -2.61200      2.89000      adf.f=frag3|2
  H      0.58800     -3.43700      3.30500      adf.f=frag3|2
  H      0.02500     -2.11500      2.82900      adf.f=frag3|2
  O      2.95400     -0.85100      2.99700      adf.f=frag3|3
  H      2.12000     -1.22400      2.71200      adf.f=frag3|3
  H      2.71800     -0.24100      3.69600      adf.f=frag3|3
  O      3.62200     -0.74000     -2.19300      adf.f=frag3|4
  H      3.05100     -1.25200     -1.62100      adf.f=frag3|4
  H      4.08100     -0.14200     -1.60200      adf.f=frag3|4
  O     -3.80000     -1.13100     -1.71100      adf.f=frag3|5
  H     -3.02600     -0.80900     -2.17400      adf.f=frag3|5
  H     -4.31600     -0.34500     -1.53300      adf.f=frag3|5
  O     -1.77100     -3.79600     -2.15500      adf.f=frag3|6
  H     -2.71500     -3.79000     -2.31700      adf.f=frag3|6
  H     -1.65100     -3.19400     -1.42100      adf.f=frag3|6
  O      1.60000     -0.17800     -3.98800      adf.f=frag3|7
  H      2.40800     -0.18200     -3.47500      adf.f=frag3|7
  H      1.13900     -0.97100     -3.71300      adf.f=frag3|7
  O     -1.63900     -1.73400      3.28100      adf.f=frag3|8
  H     -1.97000     -1.69700      4.17900      adf.f=frag3|8
  H     -2.38200     -2.04200      2.76400      adf.f=frag3|8
  O      1.57900      2.85500      2.45800      adf.f=frag3|9
  H      0.92600      2.71500      3.14400      adf.f=frag3|9
  H      1.85200      3.76600      2.57000      adf.f=frag3|9
  O     -3.44400      2.36700      3.13700      adf.f=frag3|10
  H     -2.70200      2.29200      2.53700      adf.f=frag3|10
  H     -3.47300      3.29500      3.36800      adf.f=frag3|10
end
end
```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
  end
  fragments
    H      t21.H.DZP
    C      t21.C.DZP
    N      t21.N.DZP
    frag1  t21.h2o
    frag2  t21.h2o
    frag3  t21.h2o
  end
  fdefragments
    frag1 type=FDE &
      fdeoptions RELAX
      RELAXCYCLES 2
    SubEnd
    frag2 type=FDE &
      fdeoptions RELAX
      RELAXCYCLES 2
    SubEnd
    frag3 type=FDE &
      FDEENSTYPE SCFexact
    SubEnd
  end
  noprint BAS FUNCTIONS
  numericalquality GOOD
  save TAPE10
  scf
    converge 1.0e-07 1.0e-07
    iterations 100
  end
  symmetrytolerance 1e-2
  title Input generated by PyADF and later modified
  xc
    gga BP86
  end
  Relativity Level=None
EndEngine
eor

# Finally, the calculation of the NMR shielding of the nitrogen atom is
# performed using the NMR program.

$AMSBIN/nmr <<eor
tape10file FDE.results/TAPE10
adffile FDE.results/adf.rkf
NMR

```

(continues on next page)

(continued from previous page)

```

out tens iso
nuc 3
END
eor

```

Example: FDE NMR spin-spin coupling: NH3-H2O

Download FDE_CPL_NH3-H2O.run

```

#!/bin/sh

# This example demonstrates calculation of NMR spin-spin couplings (J coupling)
# in case of frozen density embedding (FDE). It performs single point runs for
# H2O and NH3 with PBE/(ZORA/jcpl basis) (all-electron) and uses these fragments
# in:
# - an FDE embedding calculation calculation in which water in presence of a
#   frozen ammonia is computed (first the electron density / KS orbitals with
#   ADF then the NMR J couplings with CPL (scalar code branch))
# - a corresponding FDE freeze-thaw calculation followed by calculation of NMR J
#   couplings with CPL scalar, then spin-orbit code branch

# First NH3 with PBE and an all electron TZP basis set. No cpl calculation for
# NH3, thus regular basis is OK. This is not shown. Next H2O with PBE and an all
# electron ZORA/jcpl basis set:

# NH3 PBE/TZP (no cpl calculation for NH3, thus regular basis is OK)

AMS_JOBNAME=NH3 $AMSBIN/ams <<eor
System
  atoms
    N      -1.39559      -0.02156      0.00004
    H      -1.62981       0.96110     -0.10622
    H      -1.86277     -0.51254     -0.75597
    H      -1.83355     -0.33077      0.86231
  end
end

Task SinglePoint

Engine ADF
  title NH3 PBE/TZP single point
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type TZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  symmetry NOSYM
  xc
    gga PBE

```

(continues on next page)

(continued from previous page)

```

end
  Relativity Level=None
EndEngine
eor

mv NH3.results/adf.rkf t21.ammonia

# H2O PBE/(ZORA/jcpl)

AMS_JOBNAME=H2O $AMSBIN/ams <<eor
System
  atoms
    O      1.56850      0.10589      0.00001
    H      0.60674     -0.03396     -0.00063
    H      1.94052     -0.78000      0.00022
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type ZORA/jcpl
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  symmetry NOSYM
  title H2O PBE/(ZORA/jcpl) single point
  xc
    gga PBE
  end
  Relativity Level=None
EndEngine

eor
mv H2O.results/adf.rkf t21.water

# NH3-H2O: FDE calculation of H2O in presence of frozen NH3

AMS_JOBNAME=FDE $AMSBIN/ams <<eor
System
  atoms
    O      1.56850      0.10589      0.00001      adf.f=frag1
    H      0.60674     -0.03396     -0.00063      adf.f=frag1
    H      1.94052     -0.78000      0.00022      adf.f=frag1
    N     -1.39559     -0.02156      0.00004      adf.f=frag2
    H     -1.62981      0.96110     -0.10622      adf.f=frag2
  end
end

```

(continues on next page)

(continued from previous page)

```

      H      -1.86277      -0.51254      -0.75597      adf.f=frag2
      H      -1.83355      -0.33077      0.86231      adf.f=frag2
    end
  end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    pw91k
  end
  fragments
    frag1 t21.water
    frag2 t21.ammonia
  end
  fdefragments
    frag2 type=FDE
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  save TAPE10
  symmetry NOSYM
  title NH3-H2O PBE/PW91k/(ZORA/jcpl) FDE single point calculation (no freeze-thaw)
  xc
    gga PBE
  end
  Relativity Level=None
EndEngine
eor

# NH3-H2O CPL calculation J(O-H) in water H-bond donor

"$AMSBIN/cpl" <<eor
tape10file FDE.results/TAPE10
adffile FDE.results/adf.rkf
GGA
NMRCoupling
  fc
  dso
  pso
  AtomPert 1
  AtomResp 2
  scf iterations=15 converge=1.0e-05
End
eor
rm TAPE21 TAPE10 logfile

# NH3-H2O FDE calculation (1 freeze-thaw cycle)

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=FDE1 $AMSBIN/ams <<eor
System
  atoms
    O      1.56850      0.10589      0.00001      adf.f=frag1
    H      0.60674     -0.03396     -0.00063      adf.f=frag1
    H      1.94052     -0.78000      0.00022      adf.f=frag1
    N     -1.39559     -0.02156      0.00004      adf.f=frag2
    H     -1.62981      0.96110     -0.10622      adf.f=frag2
    H     -1.86277     -0.51254     -0.75597      adf.f=frag2
    H     -1.83355     -0.33077      0.86231      adf.f=frag2
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    pw91k
    relaxcycles 1
  end
  fragments
    frag1 t21.water
    frag2 t21.ammonia
  end
  fdefragments
    frag2 type=FDE &
    fdeoptions RELAX
  SubEnd
end
noprnt BAS FUNCTIONS
numericalquality Good
save TAPE10
symmetry NOSYM
title NH3-H2O PBE/PW91k/(ZORA/jcpl) FDE single point calculation (1 freeze-thaw
↪cycle)
xc
  gga PBE
end
Relativity Level=None
EndEngine
eor

# NH3-H2O CPL calculation J(O-H) in water H-bond donor
# tests scalar code branch (no sd term)

"$AMSBIN/cpl" <<eor
tape10file FDE1.results/TAPE10
adffile FDE1.results/adf.rkf
GGA

```

(continues on next page)

(continued from previous page)

```

NMRCoupling
  fc
  dso
  pso
  AtomPert 1
  AtomResp 2
  scf iterations=15 converge=1.0e-05
End
eor
rm logfile

# NH3-H2O CPL calculation J(O-H) in water H-bond donor
# tests spin-orbit code branch (sd term)

"$AMSBIN/cpl" <<eor
tape10file FDE1.results/TAPE10
adffile FDE1.results/adf.rkf
GGA
NMRCoupling
  fc
  sd
  dso
  pso
  AtomPert 1
  AtomResp 2
  scf iterations=15 converge=1.0e-05
End
eor
rm t21.H t21.N t21.O t21.water t21.ammonia

```

Example: Subsystem TDDFT, coupled FDE excitation energies

Download SUBEXCI_dimer.run

```

#!/bin/sh

# This is example for coupled FDE calculation of excitation energies. The
# subsystem TDDFT code couples the monomer excitations to obtain the excited
# states of the total system (often denoted as coupled frozen density embedding,
# FDEc).

# First the isolated fragments are calculated, the TAPE21's of these fragments
# are t21.iso.rho1 and t21.iso.rho2. Next uncoupled FDE excitation energies are
# calculated in which one fragment is frozen and the other active. The key ALLOW
# PARTIALSUPERFRAGS is necessary to be able to use subsystem information for
# only one subsystem from a TAPE21 file of a previous FDE calculation.

#####
# PREPARATION OF ISOLATED FRAGMENTS
#####

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  C      1.05754858422573    -1.70701086799077    -3.50000000000000
  O      2.28164544472573    -1.70701086799077    -3.50000000000000
  C      0.20221626882573    -0.49944933059077    -3.50000000000000
  H      0.49106545372573    -2.67285236319077    -3.50000000000000
  C     -1.19491351307427    -0.64892031589077    -3.50000000000000
  C      0.76942690052573     0.78743686120923    -3.50000000000000
  C     -2.02186702237427     0.47538393990923    -3.50000000000000
  H     -1.62606655117427    -1.65281003349077    -3.50000000000000
  C     -0.05719256647427     1.90851291410923    -3.50000000000000
  H      1.85606600152573     0.87752625020923    -3.50000000000000
  C     -1.45186603427427     1.75322106580923    -3.50000000000000
  H     -3.10608163477427     0.35931991730923    -3.50000000000000
  H      0.37787441672573     2.90894982040923    -3.50000000000000
  H     -2.09570824397427     2.63406412680923    -3.50000000000000
end
end

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core none
    type DZP
  end
  noprint BAS FUNCTIONS
  scf
    converge 1.0e-8
  end
  symmetry NOSYM
  title Fragment no.          1; (isolated)
  xc
    gga BECKE88 PERDEW86
  end
  Relativity Level=None
EndEngine

eor

mv Iso1.results/adf.rkf t21.iso.rho1

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
atoms
  C      2.00708906832899     0.06235850568037     3.50000000000000
  O      2.61913749857899     1.12245748356614     3.50000000000000
  C      0.53364394260760    -0.07460023943380     3.50000000000000
  H      2.56029077395134    -0.91115102374797     3.50000000000000
  C     -0.03547527794391    -1.35928561559301     3.50000000000000
  C     -0.29722687542061     1.06006167281502     3.50000000000000
  C     -1.42262807969967    -1.51329623449550     3.50000000000000
  H      0.61834220104568    -2.23461995830645     3.50000000000000
  C     -1.68141695030640     0.90472624158027     3.50000000000000
  H      0.16807297559397     2.04616343352651     3.50000000000000

```

(continues on next page)

(continued from previous page)

```

      C      -2.24426699857796      -0.38074233566867      3.50000000000000
      H      -1.86422099386266      -2.51028564328820      3.50000000000000
      H      -2.33028723444571       1.78172375452933      3.50000000000000
      H      -3.32902057100121      -0.49790451479758      3.50000000000000
    end
  end

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core none
    type DZP
  end
  noprint BAS FUNCTIONS
  scf
    converge 1.0e-8
  end
  symmetry NOSYM
  title Fragment no.          2; (isolated)
  xc
    gga BECKE88 PERDEW86
  end
  Relativity Level=None
EndEngine

eor

mv Iso2.results/adf.rkf t21.iso.rho2

#####
# FROZEN-DENSITY EMBEDDING CALCULATIONS
# CK: first TDDFT then TDA
#####

AMS_JOBNAME=Emb1 $AMSBIN/ams <<eor
System
  atoms
    C      1.05754858422573      -1.70701086799077      -3.50000000000000      adf.
    ↪f=rho1
    O      2.28164544472573      -1.70701086799077      -3.50000000000000      adf.
    ↪f=rho1
    C      0.20221626882573      -0.49944933059077      -3.50000000000000      adf.
    ↪f=rho1
    H      0.49106545372573      -2.67285236319077      -3.50000000000000      adf.
    ↪f=rho1
    C      -1.19491351307427      -0.64892031589077      -3.50000000000000      adf.
    ↪f=rho1
    C      0.76942690052573       0.78743686120923      -3.50000000000000      adf.
    ↪f=rho1
    C      -2.02186702237427       0.47538393990923      -3.50000000000000      adf.
    ↪f=rho1
    H      -1.62606655117427      -1.65281003349077      -3.50000000000000      adf.
    ↪f=rho1

```

(continues on next page)

(continued from previous page)

```

      C      -0.05719256647427      1.90851291410923      -3.500000000000000      adf.
↪ f=rho1
      H      1.85606600152573      0.87752625020923      -3.500000000000000      adf.
↪ f=rho1
      C     -1.45186603427427      1.75322106580923      -3.500000000000000      adf.
↪ f=rho1
      H     -3.10608163477427      0.35931991730923      -3.500000000000000      adf.
↪ f=rho1
      H      0.37787441672573      2.90894982040923      -3.500000000000000      adf.
↪ f=rho1
      H     -2.09570824397427      2.63406412680923      -3.500000000000000      adf.
↪ f=rho1
      C      2.00708906832899      0.06235850568037      3.500000000000000      adf.
↪ f=rho2
      O      2.61913749857899      1.12245748356614      3.500000000000000      adf.
↪ f=rho2
      C      0.53364394260760     -0.07460023943380      3.500000000000000      adf.
↪ f=rho2
      H      2.56029077395134     -0.91115102374797      3.500000000000000      adf.
↪ f=rho2
      C     -0.03547527794391     -1.35928561559301      3.500000000000000      adf.
↪ f=rho2
      C     -0.29722687542061      1.06006167281502      3.500000000000000      adf.
↪ f=rho2
      C     -1.42262807969967     -1.51329623449550      3.500000000000000      adf.
↪ f=rho2
      H      0.61834220104568     -2.23461995830645      3.500000000000000      adf.
↪ f=rho2
      C     -1.68141695030640      0.90472624158027      3.500000000000000      adf.
↪ f=rho2
      H      0.16807297559397      2.04616343352651      3.500000000000000      adf.
↪ f=rho2
      C     -2.24426699857796     -0.38074233566867      3.500000000000000      adf.
↪ f=rho2
      H     -1.86422099386266     -2.51028564328820      3.500000000000000      adf.
↪ f=rho2
      H     -2.33028723444571      1.78172375452933      3.500000000000000      adf.
↪ f=rho2
      H     -3.32902057100121     -0.49790451479758      3.500000000000000      adf.
↪ f=rho2
      end
end

```

Task SinglePoint

```

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  excitations
    analytical
    cdspectrum
    lowest 20
    onlysing
    velocity
  end

```

(continues on next page)

(continued from previous page)

```

fde
  pw91k
end
fragments
  rho1 t21.iso.rho1
  rho2 t21.iso.rho2
end
fdefragments
  rho1 subfrag=active
  rho2 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
scf
  converge 1.0e-8
end
symmetry NOSYM
title Fragment no.          1; relaxed; TDDFT
xc
  gga BECKE88 PERDEW86
end
Relativity Level=None
EndEngine

eor

mv Emb1.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=TDA1 $AMSBIN/ams <<eor
System
atoms
  C          1.05754858422573    -1.70701086799077    -3.50000000000000    adf.
↪ f=rho1
  O          2.28164544472573    -1.70701086799077    -3.50000000000000    adf.
↪ f=rho1
  C          0.20221626882573    -0.49944933059077    -3.50000000000000    adf.
↪ f=rho1
  H          0.49106545372573    -2.67285236319077    -3.50000000000000    adf.
↪ f=rho1
  C          -1.19491351307427    -0.64892031589077    -3.50000000000000    adf.
↪ f=rho1
  C          0.76942690052573     0.78743686120923     -3.50000000000000    adf.
↪ f=rho1
  C          -2.02186702237427     0.47538393990923     -3.50000000000000    adf.
↪ f=rho1
  H          -1.62606655117427    -1.65281003349077    -3.50000000000000    adf.
↪ f=rho1
  C          -0.05719256647427     1.90851291410923     -3.50000000000000    adf.
↪ f=rho1
  H          1.85606600152573     0.87752625020923     -3.50000000000000    adf.
↪ f=rho1
  C          -1.45186603427427     1.75322106580923     -3.50000000000000    adf.
↪ f=rho1
  H          -3.10608163477427     0.35931991730923     -3.50000000000000    adf.
↪ f=rho1
  H          0.37787441672573     2.90894982040923     -3.50000000000000    adf.
↪ f=rho1
  H          -2.09570824397427     2.63406412680923     -3.50000000000000    adf.

```

(continues on next page)

(continued from previous page)

```

→f=rho1
  C      2.00708906832899    0.06235850568037    3.50000000000000    adf.
→f=rho2
  O      2.61913749857899    1.12245748356614    3.50000000000000    adf.
→f=rho2
  C      0.53364394260760   -0.07460023943380    3.50000000000000    adf.
→f=rho2
  H      2.56029077395134   -0.91115102374797    3.50000000000000    adf.
→f=rho2
  C     -0.03547527794391   -1.35928561559301    3.50000000000000    adf.
→f=rho2
  C     -0.29722687542061    1.06006167281502    3.50000000000000    adf.
→f=rho2
  C     -1.42262807969967   -1.51329623449550    3.50000000000000    adf.
→f=rho2
  H      0.61834220104568   -2.23461995830645    3.50000000000000    adf.
→f=rho2
  C     -1.68141695030640    0.90472624158027    3.50000000000000    adf.
→f=rho2
  H      0.16807297559397    2.04616343352651    3.50000000000000    adf.
→f=rho2
  C     -2.24426699857796   -0.38074233566867    3.50000000000000    adf.
→f=rho2
  H     -1.86422099386266   -2.51028564328820    3.50000000000000    adf.
→f=rho2
  H     -2.33028723444571    1.78172375452933    3.50000000000000    adf.
→f=rho2
  H     -3.32902057100121   -0.49790451479758    3.50000000000000    adf.
→f=rho2
  end
end

```

Task SinglePoint

Engine ADF

```

allow PARTIALSUPERFRAGS
eprint
  sfo NOEIG NOOVL NOORBPOP
end
excitations
  analytical
  cdspectrum
  lowest 20
  onlysing
  velocity
end
fde
  pw91k
end
fragments
  rho1 t21.emb.rho1
  rho2 t21.emb.rho1
end
fdefragments
  rho1 subfrag=active
  rho2 subfrag=rho2 type=fde
end

```

(continues on next page)

(continued from previous page)

```

noprnt BAS FUNCTIONS
scf
  converge 1.0e-8
end
symmetry NOSYM
tda
title Fragment no.          1; relaxed; TDA
xc
  gga BECKE88 PERDEW86
end
  Relativity Level=None
EndEngine
eor

mv TDA1.results/adf.rkf t21.emb.rho1_TDA

AMS_JOBNAME=Emb2 $AMSBIN/ams <<eor
System
atoms
  C          1.05754858422573    -1.70701086799077    -3.50000000000000    adf.
↪f=rho1
  O          2.28164544472573    -1.70701086799077    -3.50000000000000    adf.
↪f=rho1
  C          0.20221626882573    -0.49944933059077    -3.50000000000000    adf.
↪f=rho1
  H          0.49106545372573    -2.67285236319077    -3.50000000000000    adf.
↪f=rho1
  C          -1.19491351307427    -0.64892031589077    -3.50000000000000    adf.
↪f=rho1
  C          0.76942690052573     0.78743686120923    -3.50000000000000    adf.
↪f=rho1
  C          -2.02186702237427     0.47538393990923    -3.50000000000000    adf.
↪f=rho1
  H          -1.62606655117427    -1.65281003349077    -3.50000000000000    adf.
↪f=rho1
  C          -0.05719256647427     1.90851291410923    -3.50000000000000    adf.
↪f=rho1
  H          1.85606600152573     0.87752625020923    -3.50000000000000    adf.
↪f=rho1
  C          -1.45186603427427     1.75322106580923    -3.50000000000000    adf.
↪f=rho1
  H          -3.10608163477427     0.35931991730923    -3.50000000000000    adf.
↪f=rho1
  H          0.37787441672573     2.90894982040923    -3.50000000000000    adf.
↪f=rho1
  H          -2.09570824397427     2.63406412680923    -3.50000000000000    adf.
↪f=rho1
  C          2.00708906832899     0.06235850568037     3.50000000000000    adf.
↪f=rho2
  O          2.61913749857899     1.12245748356614     3.50000000000000    adf.
↪f=rho2
  C          0.53364394260760    -0.07460023943380     3.50000000000000    adf.
↪f=rho2
  H          2.56029077395134    -0.91115102374797     3.50000000000000    adf.
↪f=rho2
  C          -0.03547527794391    -1.35928561559301     3.50000000000000    adf.
↪f=rho2

```

(continues on next page)

(continued from previous page)

```

      C      -0.29722687542061      1.06006167281502      3.500000000000000      adf.
↪ f=rho2
      C      -1.42262807969967      -1.51329623449550      3.500000000000000      adf.
↪ f=rho2
      H      0.61834220104568      -2.23461995830645      3.500000000000000      adf.
↪ f=rho2
      C      -1.68141695030640      0.90472624158027      3.500000000000000      adf.
↪ f=rho2
      H      0.16807297559397      2.04616343352651      3.500000000000000      adf.
↪ f=rho2
      C      -2.24426699857796      -0.38074233566867      3.500000000000000      adf.
↪ f=rho2
      H      -1.86422099386266      -2.51028564328820      3.500000000000000      adf.
↪ f=rho2
      H      -2.33028723444571      1.78172375452933      3.500000000000000      adf.
↪ f=rho2
      H      -3.32902057100121      -0.49790451479758      3.500000000000000      adf.
↪ f=rho2
      end
end

```

Task SinglePoint

Engine ADF

```

allow PARTIALSUPERFRAGS
eprint
  sfo NOEIG NOOVL NOORBPOP
end
excitations
  analytical
  cdspectrum
  lowest 20
  onlysing
  velocity
end
fde
  pw91k
end
fragments
  rho1 t21.emb.rho1
  rho2 t21.iso.rho2
end
fdefragments
  rho1 subfrag=active type=fde
  rho2 subfrag=active
end
noprnt BAS FUNCTIONS
scf
  converge 1.0e-8
end
symmetry NOSYM
title Fragment no.          2; relaxed; TDDFT
xc
  gga BECKE88 PERDEW86
end
Relativity Level=None
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor
mv Emb2.results/adf.rkf t21.emb.rho2

AMS_JOBNAME=TDA2 $AMSBIN/ams <<eor
System
  atoms
    C      1.05754858422573      -1.70701086799077      -3.50000000000000      adf.
    ↪f=rho1
    O      2.28164544472573      -1.70701086799077      -3.50000000000000      adf.
    ↪f=rho1
    C      0.20221626882573      -0.49944933059077      -3.50000000000000      adf.
    ↪f=rho1
    H      0.49106545372573      -2.67285236319077      -3.50000000000000      adf.
    ↪f=rho1
    C      -1.19491351307427      -0.64892031589077      -3.50000000000000      adf.
    ↪f=rho1
    C      0.76942690052573      0.78743686120923      -3.50000000000000      adf.
    ↪f=rho1
    C      -2.02186702237427      0.47538393990923      -3.50000000000000      adf.
    ↪f=rho1
    H      -1.62606655117427      -1.65281003349077      -3.50000000000000      adf.
    ↪f=rho1
    C      -0.05719256647427      1.90851291410923      -3.50000000000000      adf.
    ↪f=rho1
    H      1.85606600152573      0.87752625020923      -3.50000000000000      adf.
    ↪f=rho1
    C      -1.45186603427427      1.75322106580923      -3.50000000000000      adf.
    ↪f=rho1
    H      -3.10608163477427      0.35931991730923      -3.50000000000000      adf.
    ↪f=rho1
    H      0.37787441672573      2.90894982040923      -3.50000000000000      adf.
    ↪f=rho1
    H      -2.09570824397427      2.63406412680923      -3.50000000000000      adf.
    ↪f=rho1
    C      2.00708906832899      0.06235850568037      3.50000000000000      adf.
    ↪f=rho2
    O      2.61913749857899      1.12245748356614      3.50000000000000      adf.
    ↪f=rho2
    C      0.53364394260760      -0.07460023943380      3.50000000000000      adf.
    ↪f=rho2
    H      2.56029077395134      -0.91115102374797      3.50000000000000      adf.
    ↪f=rho2
    C      -0.03547527794391      -1.35928561559301      3.50000000000000      adf.
    ↪f=rho2
    C      -0.29722687542061      1.06006167281502      3.50000000000000      adf.
    ↪f=rho2
    C      -1.42262807969967      -1.51329623449550      3.50000000000000      adf.
    ↪f=rho2
    H      0.61834220104568      -2.23461995830645      3.50000000000000      adf.
    ↪f=rho2
    C      -1.68141695030640      0.90472624158027      3.50000000000000      adf.
    ↪f=rho2
    H      0.16807297559397      2.04616343352651      3.50000000000000      adf.
    ↪f=rho2
    C      -2.24426699857796      -0.38074233566867      3.50000000000000      adf.
    ↪f=rho2

```

(continues on next page)

(continued from previous page)

```

      H      -1.86422099386266      -2.51028564328820      3.50000000000000      adf.
↪f=rho2
      H      -2.33028723444571      1.78172375452933      3.50000000000000      adf.
↪f=rho2
      H      -3.32902057100121      -0.49790451479758      3.50000000000000      adf.
↪f=rho2
    end
  end
end

```

Task SinglePoint

Engine ADF

```

  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  excitations
    analytical
    cdspectrum
    lowest 20
    onlysing
    velocity
  end
  fde
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
    rho2 subfrag=active
  end
  noprint BAS FUNCTIONS
  scf
    converge 1.0e-8
  end
  symmetry NOSYM
  tda
  title Fragment no.          2; relaxed; TDA
  xc
    gga BECKE88 PERDEW86
  end
  Relativity Level=None
EndEngine
eor

```

mv TDA2.results/adf.rkf t21.emb.rho2_TDA

```

#####
# SUBSYS EXCITATIONS CALCULATION
#####

AMS_JOBNAME=TDDFT $AMSBIN/ams <<eor
System
  atoms

```

(continues on next page)

(continued from previous page)

C	1.05754858422573	-1.70701086799077	-3.50000000000000	adf.
↪f=rho1				
O	2.28164544472573	-1.70701086799077	-3.50000000000000	adf.
↪f=rho1				
C	0.20221626882573	-0.49944933059077	-3.50000000000000	adf.
↪f=rho1				
H	0.49106545372573	-2.67285236319077	-3.50000000000000	adf.
↪f=rho1				
C	-1.19491351307427	-0.64892031589077	-3.50000000000000	adf.
↪f=rho1				
C	0.76942690052573	0.78743686120923	-3.50000000000000	adf.
↪f=rho1				
C	-2.02186702237427	0.47538393990923	-3.50000000000000	adf.
↪f=rho1				
H	-1.62606655117427	-1.65281003349077	-3.50000000000000	adf.
↪f=rho1				
C	-0.05719256647427	1.90851291410923	-3.50000000000000	adf.
↪f=rho1				
H	1.85606600152573	0.87752625020923	-3.50000000000000	adf.
↪f=rho1				
C	-1.45186603427427	1.75322106580923	-3.50000000000000	adf.
↪f=rho1				
H	-3.10608163477427	0.35931991730923	-3.50000000000000	adf.
↪f=rho1				
H	0.37787441672573	2.90894982040923	-3.50000000000000	adf.
↪f=rho1				
H	-2.09570824397427	2.63406412680923	-3.50000000000000	adf.
↪f=rho1				
C	2.00708906832899	0.06235850568037	3.50000000000000	adf.
↪f=rho2				
O	2.61913749857899	1.12245748356614	3.50000000000000	adf.
↪f=rho2				
C	0.53364394260760	-0.07460023943380	3.50000000000000	adf.
↪f=rho2				
H	2.56029077395134	-0.91115102374797	3.50000000000000	adf.
↪f=rho2				
C	-0.03547527794391	-1.35928561559301	3.50000000000000	adf.
↪f=rho2				
C	-0.29722687542061	1.06006167281502	3.50000000000000	adf.
↪f=rho2				
C	-1.42262807969967	-1.51329623449550	3.50000000000000	adf.
↪f=rho2				
H	0.61834220104568	-2.23461995830645	3.50000000000000	adf.
↪f=rho2				
C	-1.68141695030640	0.90472624158027	3.50000000000000	adf.
↪f=rho2				
H	0.16807297559397	2.04616343352651	3.50000000000000	adf.
↪f=rho2				
C	-2.24426699857796	-0.38074233566867	3.50000000000000	adf.
↪f=rho2				
H	-1.86422099386266	-2.51028564328820	3.50000000000000	adf.
↪f=rho2				
H	-2.33028723444571	1.78172375452933	3.50000000000000	adf.
↪f=rho2				
H	-3.32902057100121	-0.49790451479758	3.50000000000000	adf.
↪f=rho2				
end				

(continues on next page)

(continued from previous page)

```

end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  diffuse
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho1 subfrag=active
    rho2 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  scf
    converge 1.0e-8
  end
  subexci
    couplblock
    cthres 10000.00
    sfthres 0.00010000
  end
  symmetry NOSYM
  title COUPLED SUBSYSTEM EXCITATIONS; TDDFT
  xc
    gga BECKE88 PERDEW86
  end
  Relativity Level=None
EndEngine
eor

AMS_JOBNAME=TDA $AMSBIN/ams <<eor
System
  atoms
    C      1.05754858422573   -1.70701086799077   -3.50000000000000   adf.
    ↪f=rho1
    O      2.28164544472573   -1.70701086799077   -3.50000000000000   adf.
    ↪f=rho1
    C      0.20221626882573   -0.49944933059077   -3.50000000000000   adf.
    ↪f=rho1
    H      0.49106545372573   -2.67285236319077   -3.50000000000000   adf.
    ↪f=rho1
    C      -1.19491351307427   -0.64892031589077   -3.50000000000000   adf.
    ↪f=rho1
    C      0.76942690052573    0.78743686120923    -3.50000000000000   adf.
    ↪f=rho1
    C      -2.02186702237427    0.47538393990923    -3.50000000000000   adf.
    ↪f=rho1
    H      -1.62606655117427   -1.65281003349077   -3.50000000000000   adf.

```

(continues on next page)

(continued from previous page)

```

→f=rho1
  C      -0.05719256647427      1.90851291410923      -3.500000000000000      adf.
→f=rho1
  H      1.85606600152573      0.87752625020923      -3.500000000000000      adf.
→f=rho1
  C     -1.45186603427427      1.75322106580923      -3.500000000000000      adf.
→f=rho1
  H     -3.10608163477427      0.35931991730923      -3.500000000000000      adf.
→f=rho1
  H      0.37787441672573      2.90894982040923      -3.500000000000000      adf.
→f=rho1
  H     -2.09570824397427      2.63406412680923      -3.500000000000000      adf.
→f=rho1
  C      2.00708906832899      0.06235850568037      3.500000000000000      adf.
→f=rho2
  O      2.61913749857899      1.12245748356614      3.500000000000000      adf.
→f=rho2
  C      0.53364394260760     -0.07460023943380      3.500000000000000      adf.
→f=rho2
  H      2.56029077395134     -0.91115102374797      3.500000000000000      adf.
→f=rho2
  C     -0.03547527794391     -1.35928561559301      3.500000000000000      adf.
→f=rho2
  C     -0.29722687542061      1.06006167281502      3.500000000000000      adf.
→f=rho2
  C     -1.42262807969967     -1.51329623449550      3.500000000000000      adf.
→f=rho2
  H      0.61834220104568     -2.23461995830645      3.500000000000000      adf.
→f=rho2
  C     -1.68141695030640      0.90472624158027      3.500000000000000      adf.
→f=rho2
  H      0.16807297559397      2.04616343352651      3.500000000000000      adf.
→f=rho2
  C     -2.24426699857796     -0.38074233566867      3.500000000000000      adf.
→f=rho2
  H     -1.86422099386266     -2.51028564328820      3.500000000000000      adf.
→f=rho2
  H     -2.33028723444571      1.78172375452933      3.500000000000000      adf.
→f=rho2
  H     -3.32902057100121     -0.49790451479758      3.500000000000000      adf.
→f=rho2
  end
end

```

Task SinglePoint

```

Engine ADF
  allow PARTIALSUPERFRAGS
  diffuse
  eprint
  sfo NOEIG NOOVL NOORBPOP
  end
  fde
  pw91k
  end
  fragments
  rho1 t21.emb.rho1_TDA

```

(continues on next page)

(continued from previous page)

```

    rho2 t21.emb.rho2_TDA
end
fdefragments
    rho1 subfrag=active
    rho2 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
scf
    converge 1.0e-8
end
subexci
    couplblock
    cthres 10000.00
    sfthres 0.00010000
    tda
    cicoupl
end
symmetry NOSYM
title COUPLED SUBSYSTEM EXCITATIONS; TDA
xc
    gga BECKE88 PERDEW86
end
Relativity Level=None
EndEngine
eor

```

Example: FDE and COSMO: H2O-NH3

Download LoCOSMO_H2O-NH3.run

```

#!/bin/sh

# This is example for a calculation of FDE and (localized) COSMO in ADF in case
# of closed shell fragments.

# It performs single point runs for H2 O and NH3 in COSMO (water) and uses these
# fragments in a freeze-and-thaw calculations. Recommended is to limit the
# number of freeze-and-thaw cycles in such calculations where FDE and COSMO are
# combined, because the FT convergence criterion may not be met in a finite
# number of cycles, although the density is practically converged.

# In the freeze-and-thaw cycles LoCosmo is included in the SOLVATION key, thus
# the local COSMO will be used in the calculation. A cutoff radius (Angstrom)
# must be specified after the LoCOSMO subargument, in this case it is 3.0
# Angstrom. All surface charges within this radius from any atom of the active
# fragment are included in the active charge space.

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System
atoms
    H          0.0201  0.6299  0.0000
    O         -0.0370  1.6130  0.0000
    H          0.8936  1.9007  0.0000

```

(continues on next page)

(continued from previous page)

```
    end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
end
  symmetry NOSYM
  title H2O isolated
  xc
    gga BP86
  end
EndEngine
eor
mv Iso1.results/adf.rkf t21.iso.rho1

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
  atoms
    N      -0.0370  -1.4327  0.0000
    H       0.8110  -2.0086  0.0000
    H     -0.5850  -1.6987  0.8244
    H     -0.5850  -1.6987 -0.8244
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
end
  symmetry NOSYM
  title NH3 isolated
  xc
    gga BP86
```

(continues on next page)

(continued from previous page)

```

    end
EndEngine
eor
mv Iso2.results/adf.rkf t21.iso.rho2

$AMSBIN/ams <<eor
System
  atoms
    H      0.0201  0.6299  0.0000  adf.f=frag1
    O     -0.0370  1.6130  0.0000  adf.f=frag1
    H      0.8936  1.9007  0.0000  adf.f=frag1
    N     -0.0370 -1.4327  0.0000  adf.f=frag2
    H      0.8110 -2.0086  0.0000  adf.f=frag2
    H     -0.5850 -1.6987  0.8244  adf.f=frag2
    H     -0.5850 -1.6987 -0.8244  adf.f=frag2
  end
end

Task SinglePoint

Engine ADF
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  fde
    pw91k
    relaxcycles 3
  end
  fragments
    frag1 t21.iso.rho1
    frag2 t21.iso.rho2
  end
  fdefragments
    frag2 type=FDE &
      FDEOPTIONS RELAX
    SubEnd
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
    charged LoCOSMO 3.0
  end
  symmetry NOSYM
  title FT cycles for H2O-NH3
  xc
    gga BP86
  end
EndEngine
eor

```

Example: FDE and COSMO: H2O-NH3

Download LoCOSMO_H2O-NH3_TDDFT.run

```
#!/bin/sh

# This is example for a calculation of excitation energies using FDE and
# localized COSMO, which is based on the LoCOSMO_H2O-NH3 example. The difference
# is that it includes the calculation of excitation energies (EXCITATION block
# key), and performs only 1 freeze-and-thaw cycle for H2 O and NH3 in COSMO
# (water). The input for the fragment calculations are not repeated here.

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System
  atoms
    H      0.0201  0.6299  0.0000
    O     -0.0370  1.6130  0.0000
    H      0.8936  1.9007  0.0000
  end
end

Task SinglePoint

Engine ADF
  title H2O isolated
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
  end
  symmetry NOSYM
  xc
    gga BP86
  end
EndEngine
eor
mv Iso1.results/adf.rkf t21.iso.rho1

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
  atoms
    N     -0.0370 -1.4327  0.0000
    H      0.8110 -2.0086  0.0000
    H     -0.5850 -1.6987  0.8244
    H     -0.5850 -1.6987 -0.8244
  end
end

Task SinglePoint
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title NH3 isolated
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
  end
  symmetry NOSYM
  xc
    gga BP86
  end
EndEngine

eor
mv Iso2.results/adf.rkf t21.iso.rho2

$AMSBIN/ams <<eor
System
  atoms
    H      0.0201   0.6299   0.0000   adf.f=frag1
    O     -0.0370   1.6130   0.0000   adf.f=frag1
    H      0.8936   1.9007   0.0000   adf.f=frag1
    N     -0.0370  -1.4327   0.0000   adf.f=frag2
    H      0.8110  -2.0086   0.0000   adf.f=frag2
    H     -0.5850  -1.6987   0.8244   adf.f=frag2
    H     -0.5850  -1.6987  -0.8244   adf.f=frag2
  end
end

Task SinglePoint

Engine ADF
  title FT cycles for H2O-NH3
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  excitations
  end
  fde
    pw91k
    relaxcycles 1
  end
  fragments
    frag1 t21.iso.rho1
    frag2 t21.iso.rho2
  end
  fdefragments
    frag2 type=FDE &

```

(continues on next page)

(continued from previous page)

```

      FDEOPTIONS RELAX
    SubEnd
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  solvation
    charged LoCOSMO 3.0
  end
  symmetry NOSYM
  xc
    gga BP86
  end
EndEngine
eor

```

15.2.5 QM/MM calculations

15.2.6 Quild: Quantum-regions Interconnected by Local Descriptions

- Quild manual: [Quild examples](https://www.scm.com/doc.2024/Quild/Example_inputfiles.html) (https://www.scm.com/doc.2024/Quild/Example_inputfiles.html)

15.2.7 DIM/QM: Discrete Interaction Model/Quantum Mechanics

Example: DRF: H2O and H2O

Download DIMQM_DRF_BE.run

```

#!/bin/sh

$AMSBIN/ams <<eor
System
  atoms
    O      2.698990442000      0.000000000000      -0.000314732000
    H      1.927785302000      0.000000000000      -0.591074192000
    H      3.470195581000      0.000000000000      -0.591074192000
  end
end

Task SinglePoint

Engine ADF
  dimpar
    GROUP mol2
    3
    O      -0.801009558000      0.000000000000      -0.000314732000 pol=5.7494
    ↪char=-0.7134114435520156
    H      -1.572214698000      -0.000000000000      -0.591074192000 pol=2.7927
    ↪char=0.3567057217727492
    H      -0.029804419000      -0.000000000000      -0.591074192000 pol=2.7927
    ↪char=0.3567057217727492
    SUBEND
  end

```

(continues on next page)

(continued from previous page)

```

dimqm
  drf
end
basis
  core Large
  type TZP
end
symmetry NOSYM
Relativity
  Level None
End
EndEngine
eor

```

Example: DRF: hyperpolarizability H2O in water

Download DIMQM_DRF_Hyperpol.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to use DRF. Here, the hyperpolarizability is
# calculated of a water molecule surrounded by an environment of 127 water
# molecules. See also: C.R. Jacob, J. Neugebauer, L. Jensen and L. Visscher,
# Comparison of frozen-density embedding and discrete reaction field solvent
# models for molecular properties, Physical Chemistry Chemical Physics 8, 2349
# (2006)

$AMSBIN/ams <<eor
System
  atoms
    O      0.0000    0.0000    0.0000
    H     -0.7568    0.0000    0.5860
    H      0.7568    0.0000    0.5860
  end
end

Task SinglePoint

Engine ADF
  title DRF-TEST H2O in H2O
  dimqm
    DRF
  end
  externals
    O   4   water 2, -0.6690,    -6.0223,    -6.2499,    -2.3894,    9.3005,    3.0236
    H   5   water 2,  0.3345,    -6.9347,    -6.2642,    -2.1006,    0.0690,    1.5118
    H   6   water 2,  0.3345,    -5.5621,    -6.8017,    -1.7570,    0.0690,    1.5118
    ANAL 2
    O   7   water 3, -0.6690,    -0.5907,     4.8257,    -1.7097,    9.3005,    3.0236
    H   8   water 3,  0.3345,    -1.4937,     5.1420,    -1.6831,    0.0690,    1.5118
    H   9   water 3,  0.3345,    -0.0655,     5.5766,    -1.4333,    0.0690,    1.5118
  end
end

```

(continues on next page)

(continued from previous page)

ANAL 2							
O 10	water 4,	-0.6690,	2.3651,	-0.2666,	1.1699,	9.3005,	3.0236
H 11	water 4,	0.3345,	2.2615,	-1.1034,	1.6229,	0.0690,	1.5118
H 12	water 4,	0.3345,	3.1322,	-0.3900,	0.6111,	0.0690,	1.5118
ANAL 2							
O 13	water 5,	-0.6690,	-8.9796,	-1.9359,	-5.7076,	9.3005,	3.0236
H 14	water 5,	0.3345,	-8.3124,	-2.2437,	-5.0941,	0.0690,	1.5118
H 15	water 5,	0.3345,	-8.7198,	-2.3076,	-6.5504,	0.0690,	1.5118
ANAL 2							
O 16	water 6,	-0.6690,	-5.6969,	-2.2033,	0.2741,	9.3005,	3.0236
H 17	water 6,	0.3345,	-4.8479,	-2.1094,	-0.1577,	0.0690,	1.5118
H 18	water 6,	0.3345,	-6.3368,	-2.0090,	-0.4106,	0.0690,	1.5118
ANAL 2							
O 19	water 7,	-0.6690,	-3.4684,	-4.8700,	-5.9433,	9.3005,	3.0236
H 20	water 7,	0.3345,	-4.3144,	-5.1084,	-5.5645,	0.0690,	1.5118
H 21	water 7,	0.3345,	-3.6551,	-4.1011,	-6.4819,	0.0690,	1.5118
ANAL 2							
O 22	water 8,	-0.6690,	-7.4969,	-3.4704,	-3.5082,	9.3005,	3.0236
H 23	water 8,	0.3345,	-7.2745,	-4.3985,	-3.5808,	0.0690,	1.5118
H 24	water 8,	0.3345,	-8.1668,	-3.4372,	-2.8253,	0.0690,	1.5118
ANAL 2							
O 25	water 9,	-0.6690,	-0.5357,	-3.4594,	-10.9181,	9.3005,	3.0236
H 26	water 9,	0.3345,	0.2718,	-3.7131,	-10.4712,	0.0690,	1.5118
H 27	water 9,	0.3345,	-1.1951,	-3.4329,	-10.2249,	0.0690,	1.5118
ANAL 2							
O 28	water 10,	-0.6690,	-4.2195,	2.2934,	4.6878,	9.3005,	3.0236
H 29	water 10,	0.3345,	-3.9117,	1.4378,	4.9869,	0.0690,	1.5118
H 30	water 10,	0.3345,	-3.8849,	2.3695,	3.7943,	0.0690,	1.5118
ANAL 2							
O 31	water 11,	-0.6690,	0.8931,	-5.9761,	-1.5221,	9.3005,	3.0236
H 32	water 11,	0.3345,	0.8044,	-6.1702,	-2.4552,	0.0690,	1.5118
H 33	water 11,	0.3345,	0.4898,	-5.1144,	-1.4172,	0.0690,	1.5118
ANAL 2							
O 34	water 12,	-0.6690,	0.5778,	-0.8986,	-9.9576,	9.3005,	3.0236
H 35	water 12,	0.3345,	1.0965,	-1.2400,	-10.6860,	0.0690,	1.5118
H 36	water 12,	0.3345,	0.0709,	-1.6505,	-9.6513,	0.0690,	1.5118
ANAL 2							
O 37	water 13,	-0.6690,	-7.3305,	-0.8007,	-1.8143,	9.3005,	3.0236
H 38	water 13,	0.3345,	-7.0622,	-1.0105,	-2.7088,	0.0690,	1.5118
H 39	water 13,	0.3345,	-8.1064,	-1.3406,	-1.6640,	0.0690,	1.5118
ANAL 2							
O 40	water 14,	-0.6690,	2.7991,	-3.6051,	-6.9353,	9.3005,	3.0236
H 41	water 14,	0.3345,	3.7133,	-3.5041,	-6.6702,	0.0690,	1.5118
H 42	water 14,	0.3345,	2.3002,	-3.1634,	-6.2483,	0.0690,	1.5118
ANAL 2							
O 43	water 15,	-0.6690,	-6.0718,	-5.7718,	-4.9959,	9.3005,	3.0236
H 44	water 15,	0.3345,	-5.9353,	-6.5906,	-5.4724,	0.0690,	1.5118
H 45	water 15,	0.3345,	-5.9143,	-5.9987,	-4.0795,	0.0690,	1.5118
ANAL 2							
O 46	water 16,	-0.6690,	-0.8710,	-6.0513,	0.7837,	9.3005,	3.0236
H 47	water 16,	0.3345,	-0.1617,	-5.5424,	0.3911,	0.0690,	1.5118
H 48	water 16,	0.3345,	-0.9154,	-6.8479,	0.2550,	0.0690,	1.5118
ANAL 2							
O 49	water 17,	-0.6690,	-3.8761,	-2.6555,	2.3219,	9.3005,	3.0236
H 50	water 17,	0.3345,	-4.6665,	-2.5032,	1.8041,	0.0690,	1.5118
H 51	water 17,	0.3345,	-4.1060,	-3.3810,	2.9024,	0.0690,	1.5118
ANAL 2							

(continues on next page)

(continued from previous page)

O	52	water 18,	-0.6690,	2.7564,	-3.6188,	1.9534,	9.3005,	3.0236
H	53	water 18,	0.3345,	2.7865,	-3.5376,	1.0002,	0.0690,	1.5118
H	54	water 18,	0.3345,	3.3823,	-2.9672,	2.2693,	0.0690,	1.5118
ANAL 2								
O	55	water 19,	-0.6690,	-0.6609,	-3.6923,	-1.5511,	9.3005,	3.0236
H	56	water 19,	0.3345,	-1.2586,	-3.4903,	-0.8312,	0.0690,	1.5118
H	57	water 19,	0.3345,	-0.1127,	-2.9121,	-1.6334,	0.0690,	1.5118
ANAL 2								
O	58	water 20,	-0.6690,	3.5653,	-0.1379,	-3.4865,	9.3005,	3.0236
H	59	water 20,	0.3345,	3.4730,	-1.0831,	-3.6058,	0.0690,	1.5118
H	60	water 20,	0.3345,	4.3918,	0.0785,	-3.9181,	0.0690,	1.5118
ANAL 2								
O	61	water 21,	-0.6690,	2.8079,	-2.9333,	-3.4058,	9.3005,	3.0236
H	62	water 21,	0.3345,	2.0176,	-3.2231,	-3.8614,	0.0690,	1.5118
H	63	water 21,	0.3345,	3.5200,	-3.4054,	-3.8373,	0.0690,	1.5118
ANAL 2								
O	64	water 22,	-0.6690,	-3.0280,	-4.0184,	-2.9686,	9.3005,	3.0236
H	65	water 22,	0.3345,	-2.9833,	-3.9686,	-3.9234,	0.0690,	1.5118
H	66	water 22,	0.3345,	-2.1153,	-3.9764,	-2.6835,	0.0690,	1.5118
ANAL 2								
O	67	water 23,	-0.6690,	-2.6269,	2.2878,	-1.7246,	9.3005,	3.0236
H	68	water 23,	0.3345,	-3.3175,	2.9420,	-1.6184,	0.0690,	1.5118
H	69	water 23,	0.3345,	-1.8157,	2.7657,	-1.5521,	0.0690,	1.5118
ANAL 2								
O	70	water 24,	-0.6690,	-5.7904,	0.2934,	-6.9759,	9.3005,	3.0236
H	71	water 24,	0.3345,	-5.2884,	1.1025,	-7.0732,	0.0690,	1.5118
H	72	water 24,	0.3345,	-6.4866,	0.3633,	-7.6290,	0.0690,	1.5118
ANAL 2								
O	73	water 25,	-0.6690,	-4.9194,	2.8572,	-6.6807,	9.3005,	3.0236
H	74	water 25,	0.3345,	-4.1208,	2.8574,	-6.1531,	0.0690,	1.5118
H	75	water 25,	0.3345,	-4.6111,	2.9479,	-7.5822,	0.0690,	1.5118
ANAL 2								
O	76	water 26,	-0.6690,	1.5750,	-6.5856,	1.9188,	9.3005,	3.0236
H	77	water 26,	0.3345,	1.9374,	-5.6997,	1.9225,	0.0690,	1.5118
H	78	water 26,	0.3345,	0.6464,	-6.4639,	1.7216,	0.0690,	1.5118
ANAL 2								
O	79	water 27,	-0.6690,	-3.9796,	-1.4339,	-8.6954,	9.3005,	3.0236
H	80	water 27,	0.3345,	-4.5199,	-1.0671,	-7.9956,	0.0690,	1.5118
H	81	water 27,	0.3345,	-4.3002,	-1.0113,	-9.4921,	0.0690,	1.5118
ANAL 2								
O	82	water 28,	-0.6690,	-0.8980,	-1.0815,	-4.3428,	9.3005,	3.0236
H	83	water 28,	0.3345,	-0.6188,	-0.2290,	-4.6764,	0.0690,	1.5118
H	84	water 28,	0.3345,	-0.3369,	-1.2371,	-3.5832,	0.0690,	1.5118
ANAL 2								
O	85	water 29,	-0.6690,	2.8053,	-5.0592,	4.4727,	9.3005,	3.0236
H	86	water 29,	0.3345,	2.7908,	-4.5603,	3.6560,	0.0690,	1.5118
H	87	water 29,	0.3345,	2.4078,	-4.4744,	5.1179,	0.0690,	1.5118
ANAL 2								
O	88	water 30,	-0.6690,	3.1724,	-3.0925,	-0.6766,	9.3005,	3.0236
H	89	water 30,	0.3345,	3.2306,	-3.1480,	-1.6304,	0.0690,	1.5118
H	90	water 30,	0.3345,	3.7164,	-2.3393,	-0.4468,	0.0690,	1.5118
ANAL 2								
O	91	water 31,	-0.6690,	-4.4977,	3.3377,	0.6679,	9.3005,	3.0236
H	92	water 31,	0.3345,	-4.9024,	2.7604,	0.0205,	0.0690,	1.5118
H	93	water 31,	0.3345,	-5.2078,	3.5562,	1.2712,	0.0690,	1.5118
ANAL 2								
O	94	water 32,	-0.6690,	0.7528,	3.7841,	-3.5468,	9.3005,	3.0236

(continues on next page)

(continued from previous page)

H	95	water	32,	0.3345,	0.2600,	4.0986,	-2.7890,	0.0690,	1.5118
H	96	water	32,	0.3345,	1.5200,	3.3523,	-3.1712,	0.0690,	1.5118
ANAL 2									
O	97	water	33,	-0.6690,	0.6169,	-8.3945,	-4.2494,	9.3005,	3.0236
H	98	water	33,	0.3345,	-0.2327,	-8.7666,	-4.4857,	0.0690,	1.5118
H	99	water	33,	0.3345,	0.6722,	-7.5835,	-4.7547,	0.0690,	1.5118
ANAL 2									
O	100	water	34,	-0.6690,	-1.0012,	-5.6281,	-4.5428,	9.3005,	3.0236
H	101	water	34,	0.3345,	-1.4754,	-5.6715,	-5.3731,	0.0690,	1.5118
H	102	water	34,	0.3345,	-1.5387,	-6.1335,	-3.9331,	0.0690,	1.5118
ANAL 2									
O	103	water	35,	-0.6690,	0.6896,	-3.4643,	-4.9164,	9.3005,	3.0236
H	104	water	35,	0.3345,	0.0219,	-4.1296,	-4.7498,	0.0690,	1.5118
H	105	water	35,	0.3345,	0.2328,	-2.6316,	-4.7984,	0.0690,	1.5118
ANAL 2									
O	106	water	36,	-0.6690,	-2.1739,	-3.4893,	-8.6965,	9.3005,	3.0236
H	107	water	36,	0.3345,	-2.5934,	-4.2938,	-9.0013,	0.0690,	1.5118
H	108	water	36,	0.3345,	-2.8829,	-2.8473,	-8.6625,	0.0690,	1.5118
ANAL 2									
O	109	water	37,	-0.6690,	-3.1332,	-1.6040,	-1.3286,	9.3005,	3.0236
H	110	water	37,	0.3345,	-3.0590,	-2.4135,	-1.8339,	0.0690,	1.5118
H	111	water	37,	0.3345,	-3.2876,	-0.9250,	-1.9853,	0.0690,	1.5118
ANAL 2									
O	112	water	38,	-0.6690,	-2.7516,	-6.7877,	-2.6294,	9.3005,	3.0236
H	113	water	38,	0.3345,	-3.5480,	-7.1086,	-3.0525,	0.0690,	1.5118
H	114	water	38,	0.3345,	-2.8732,	-5.8397,	-2.5775,	0.0690,	1.5118
ANAL 2									
O	115	water	39,	-0.6690,	-2.5918,	2.9114,	-8.7408,	9.3005,	3.0236
H	116	water	39,	0.3345,	-2.6283,	3.8661,	-8.6824,	0.0690,	1.5118
H	117	water	39,	0.3345,	-1.7080,	2.6872,	-8.4499,	0.0690,	1.5118
ANAL 2									
O	118	water	40,	-0.6690,	-9.3024,	-2.6424,	-1.5753,	9.3005,	3.0236
H	119	water	40,	0.3345,	-9.9294,	-2.0331,	-1.1858,	0.0690,	1.5118
H	120	water	40,	0.3345,	-9.2070,	-3.3371,	-0.9237,	0.0690,	1.5118
ANAL 2									
O	121	water	41,	-0.6690,	-1.8562,	-9.1674,	-5.3470,	9.3005,	3.0236
H	122	water	41,	0.3345,	-2.3294,	-9.8602,	-5.8077,	0.0690,	1.5118
H	123	water	41,	0.3345,	-2.4022,	-8.9693,	-4.5862,	0.0690,	1.5118
ANAL 2									
O	124	water	42,	-0.6690,	-5.7252,	-2.4694,	-5.8976,	9.3005,	3.0236
H	125	water	42,	0.3345,	-6.1500,	-2.5840,	-5.0476,	0.0690,	1.5118
H	126	water	42,	0.3345,	-5.6141,	-1.5226,	-5.9843,	0.0690,	1.5118
ANAL 2									
O	127	water	43,	-0.6690,	-3.3825,	0.0095,	-3.5627,	9.3005,	3.0236
H	128	water	43,	0.3345,	-3.0805,	0.6489,	-2.9177,	0.0690,	1.5118
H	129	water	43,	0.3345,	-2.5797,	-0.3852,	-3.9029,	0.0690,	1.5118
ANAL 2									
O	130	water	44,	-0.6690,	-5.9824,	0.2454,	-4.3661,	9.3005,	3.0236
H	131	water	44,	0.3345,	-5.1025,	0.4269,	-4.0360,	0.0690,	1.5118
H	132	water	44,	0.3345,	-5.9262,	0.4186,	-5.3057,	0.0690,	1.5118
ANAL 2									
O	133	water	45,	-0.6690,	4.7647,	0.6670,	-7.3969,	9.3005,	3.0236
H	134	water	45,	0.3345,	4.6954,	0.5448,	-6.4501,	0.0690,	1.5118
H	135	water	45,	0.3345,	3.8600,	0.7691,	-7.6922,	0.0690,	1.5118
ANAL 2									
O	136	water	46,	-0.6690,	0.6049,	-1.4649,	-2.0801,	9.3005,	3.0236
H	137	water	46,	0.3345,	1.5609,	-1.4717,	-2.0332,	0.0690,	1.5118

(continues on next page)

(continued from previous page)

H 138	water 46,	0.3345,	0.3326,	-0.9204,	-1.3415,	0.0690,	1.5118
ANAL 2							
O 139	water 47,	-0.6690,	-2.7599,	-0.3793,	1.0454,	9.3005,	3.0236
H 140	water 47,	0.3345,	-3.1126,	-0.7184,	0.2228,	0.0690,	1.5118
H 141	water 47,	0.3345,	-3.0830,	-0.9851,	1.7124,	0.0690,	1.5118
ANAL 2							
O 142	water 48,	-0.6690,	-2.8683,	1.9384,	2.3701,	9.3005,	3.0236
H 143	water 48,	0.3345,	-3.4277,	2.5156,	1.8504,	0.0690,	1.5118
H 144	water 48,	0.3345,	-2.7961,	1.1400,	1.8470,	0.0690,	1.5118
ANAL 2							
O 145	water 49,	-0.6690,	-5.7630,	1.8173,	-1.3700,	9.3005,	3.0236
H 146	water 49,	0.3345,	-5.8465,	1.0390,	-1.9209,	0.0690,	1.5118
H 147	water 49,	0.3345,	-6.6060,	1.8853,	-0.9219,	0.0690,	1.5118
ANAL 2							
O 148	water 50,	-0.6690,	-3.0562,	6.2727,	-1.6414,	9.3005,	3.0236
H 149	water 50,	0.3345,	-3.9270,	5.9633,	-1.3923,	0.0690,	1.5118
H 150	water 50,	0.3345,	-2.9607,	7.1103,	-1.1881,	0.0690,	1.5118
ANAL 2							
O 151	water 51,	-0.6690,	2.4606,	1.9450,	-2.0022,	9.3005,	3.0236
H 152	water 51,	0.3345,	2.8071,	1.1437,	-2.3947,	0.0690,	1.5118
H 153	water 51,	0.3345,	1.7993,	1.6407,	-1.3806,	0.0690,	1.5118
ANAL 2							
O 154	water 52,	-0.6690,	-0.8297,	1.8046,	-5.0085,	9.3005,	3.0236
H 155	water 52,	0.3345,	-0.3315,	2.4831,	-4.5529,	0.0690,	1.5118
H 156	water 52,	0.3345,	-0.6508,	1.9580,	-5.9361,	0.0690,	1.5118
ANAL 2							
O 157	water 53,	-0.6690,	-3.0963,	3.1475,	-4.6319,	9.3005,	3.0236
H 158	water 53,	0.3345,	-2.3095,	2.6128,	-4.7377,	0.0690,	1.5118
H 159	water 53,	0.3345,	-2.7695,	4.0450,	-4.5698,	0.0690,	1.5118
ANAL 2							
O 160	water 54,	-0.6690,	-2.9391,	-4.1930,	0.1352,	9.3005,	3.0236
H 161	water 54,	0.3345,	-2.3195,	-4.9152,	0.2382,	0.0690,	1.5118
H 162	water 54,	0.3345,	-3.1844,	-3.9582,	1.0301,	0.0690,	1.5118
ANAL 2							
O 163	water 55,	-0.6690,	-5.7159,	2.6060,	-9.7518,	9.3005,	3.0236
H 164	water 55,	0.3345,	-5.0101,	2.1773,	-10.2358,	0.0690,	1.5118
H 165	water 55,	0.3345,	-6.3940,	1.9351,	-9.6725,	0.0690,	1.5118
ANAL 2							
O 166	water 56,	-0.6690,	6.2695,	3.1997,	-2.9652,	9.3005,	3.0236
H 167	water 56,	0.3345,	6.4762,	3.9915,	-2.4687,	0.0690,	1.5118
H 168	water 56,	0.3345,	5.3686,	3.3305,	-3.2607,	0.0690,	1.5118
ANAL 2							
O 169	water 57,	-0.6690,	0.7339,	-1.8844,	2.7237,	9.3005,	3.0236
H 170	water 57,	0.3345,	1.2467,	-1.5058,	3.4378,	0.0690,	1.5118
H 171	water 57,	0.3345,	1.1959,	-2.6920,	2.4989,	0.0690,	1.5118
ANAL 2							
O 172	water 58,	-0.6690,	4.9752,	-1.1454,	0.0349,	9.3005,	3.0236
H 173	water 58,	0.3345,	5.2875,	-0.3193,	-0.3341,	0.0690,	1.5118
H 174	water 58,	0.3345,	5.7725,	-1.6403,	0.2233,	0.0690,	1.5118
ANAL 2							
O 175	water 59,	-0.6690,	-1.7496,	-1.8578,	3.9802,	9.3005,	3.0236
H 176	water 59,	0.3345,	-0.9639,	-1.9885,	3.4495,	0.0690,	1.5118
H 177	water 59,	0.3345,	-2.4606,	-2.2142,	3.4475,	0.0690,	1.5118
ANAL 2							
O 178	water 60,	-0.6690,	-2.0308,	5.8210,	-4.5295,	9.3005,	3.0236
H 179	water 60,	0.3345,	-1.9811,	5.7326,	-3.5777,	0.0690,	1.5118
H 180	water 60,	0.3345,	-2.5794,	6.5926,	-4.6702,	0.0690,	1.5118

(continues on next page)

(continued from previous page)

ANAL 2							
O 181	water 61,	-0.6690,	-4.7217,	3.9768,	-2.7147,	9.3005,	3.0236
H 182	water 61,	0.3345,	-4.0442,	3.5964,	-3.2736,	0.0690,	1.5118
H 183	water 61,	0.3345,	-5.2852,	3.2381,	-2.4846,	0.0690,	1.5118
ANAL 2							
O 184	water 62,	-0.6690,	-0.1740,	2.5699,	-7.5593,	9.3005,	3.0236
H 185	water 62,	0.3345,	-0.1065,	3.5022,	-7.3532,	0.0690,	1.5118
H 186	water 62,	0.3345,	0.5851,	2.3916,	-8.1144,	0.0690,	1.5118
ANAL 2							
O 187	water 63,	-0.6690,	-1.5247,	-11.1982,	-7.2697,	9.3005,	3.0236
H 188	water 63,	0.3345,	-0.5802,	-11.0500,	-7.3172,	0.0690,	1.5118
H 189	water 63,	0.3345,	-1.6552,	-12.0487,	-7.6888,	0.0690,	1.5118
ANAL 2							
O 190	water 64,	-0.6690,	2.1613,	-9.1672,	2.4984,	9.3005,	3.0236
H 191	water 64,	0.3345,	2.1295,	-8.2119,	2.4479,	0.0690,	1.5118
H 192	water 64,	0.3345,	1.2538,	-9.4294,	2.6528,	0.0690,	1.5118
ANAL 2							
O 193	water 65,	-0.6690,	-6.7304,	3.8130,	2.3606,	9.3005,	3.0236
H 194	water 65,	0.3345,	-7.6519,	4.0716,	2.3705,	0.0690,	1.5118
H 195	water 65,	0.3345,	-6.3024,	4.4286,	2.9555,	0.0690,	1.5118
ANAL 2							
O 196	water 66,	-0.6690,	1.9295,	-3.0572,	6.3163,	9.3005,	3.0236
H 197	water 66,	0.3345,	2.4859,	-2.7944,	7.0495,	0.0690,	1.5118
H 198	water 66,	0.3345,	1.0479,	-3.0968,	6.6868,	0.0690,	1.5118
ANAL 2							
O 199	water 67,	-0.6690,	-6.1294,	-4.2386,	-7.7881,	9.3005,	3.0236
H 200	water 67,	0.3345,	-5.9027,	-3.6840,	-7.0417,	0.0690,	1.5118
H 201	water 67,	0.3345,	-7.0434,	-4.0256,	-7.9761,	0.0690,	1.5118
ANAL 2							
O 202	water 68,	-0.6690,	-12.0077,	-2.4353,	-6.0001,	9.3005,	3.0236
H 203	water 68,	0.3345,	-11.7598,	-3.2400,	-6.4553,	0.0690,	1.5118
H 204	water 68,	0.3345,	-11.1844,	-1.9604,	-5.8871,	0.0690,	1.5118
ANAL 2							
O 205	water 69,	-0.6690,	3.1564,	2.3885,	1.9597,	9.3005,	3.0236
H 206	water 69,	0.3345,	2.7744,	1.6226,	1.5314,	0.0690,	1.5118
H 207	water 69,	0.3345,	2.5063,	2.6469,	2.6129,	0.0690,	1.5118
ANAL 2							
O 208	water 70,	-0.6690,	2.4177,	8.1317,	-2.7903,	9.3005,	3.0236
H 209	water 70,	0.3345,	3.2979,	7.7921,	-2.9516,	0.0690,	1.5118
H 210	water 70,	0.3345,	2.4177,	8.9993,	-3.1946,	0.0690,	1.5118
ANAL 2							
O 211	water 71,	-0.6690,	-10.2768,	0.0535,	-7.3704,	9.3005,	3.0236
H 212	water 71,	0.3345,	-9.6914,	-0.5671,	-6.9364,	0.0690,	1.5118
H 213	water 71,	0.3345,	-10.9610,	0.2293,	-6.7246,	0.0690,	1.5118
ANAL 2							
O 214	water 72,	-0.6690,	2.1317,	-4.3290,	-12.7197,	9.3005,	3.0236
H 215	water 72,	0.3345,	2.9926,	-4.7445,	-12.7694,	0.0690,	1.5118
H 216	water 72,	0.3345,	1.6300,	-4.8877,	-12.1262,	0.0690,	1.5118
ANAL 2							
O 217	water 73,	-0.6690,	-8.7835,	-6.3924,	-1.6020,	9.3005,	3.0236
H 218	water 73,	0.3345,	-8.9261,	-5.5450,	-1.1804,	0.0690,	1.5118
H 219	water 73,	0.3345,	-9.3978,	-6.4013,	-2.3359,	0.0690,	1.5118
ANAL 2							
O 220	water 74,	-0.6690,	-3.8469,	5.8279,	-7.3208,	9.3005,	3.0236
H 221	water 74,	0.3345,	-4.5008,	6.2386,	-6.7552,	0.0690,	1.5118
H 222	water 74,	0.3345,	-3.1746,	6.4993,	-7.4365,	0.0690,	1.5118
ANAL 2							

(continues on next page)

(continued from previous page)

O 223	water 75,	-0.6690,	7.8985,	0.3862,	-0.4660,	9.3005,	3.0236
H 224	water 75,	0.3345,	7.7708,	0.2351,	0.4704,	0.0690,	1.5118
H 225	water 75,	0.3345,	7.1082,	0.8491,	-0.7440,	0.0690,	1.5118
ANAL 2							
O 226	water 76,	-0.6690,	-5.4240,	-8.2086,	-6.6502,	9.3005,	3.0236
H 227	water 76,	0.3345,	-5.7234,	-8.8913,	-6.0498,	0.0690,	1.5118
H 228	water 76,	0.3345,	-4.6627,	-8.5904,	-7.0868,	0.0690,	1.5118
ANAL 2							
O 229	water 77,	-0.6690,	3.2564,	-3.6039,	-9.7256,	9.3005,	3.0236
H 230	water 77,	0.3345,	2.9998,	-4.0224,	-8.9040,	0.0690,	1.5118
H 231	water 77,	0.3345,	4.1288,	-3.2504,	-9.5522,	0.0690,	1.5118
ANAL 2							
O 232	water 78,	-0.6690,	1.9939,	-6.2830,	-6.3501,	9.3005,	3.0236
H 233	water 78,	0.3345,	2.9264,	-6.4297,	-6.5082,	0.0690,	1.5118
H 234	water 78,	0.3345,	1.8631,	-5.3529,	-6.5343,	0.0690,	1.5118
ANAL 2							
O 235	water 79,	-0.6690,	2.2430,	1.1482,	-8.6661,	9.3005,	3.0236
H 236	water 79,	0.3345,	1.6065,	0.4905,	-8.9464,	0.0690,	1.5118
H 237	water 79,	0.3345,	2.6610,	1.4379,	-9.4769,	0.0690,	1.5118
ANAL 2							
O 238	water 80,	-0.6690,	-7.7698,	0.3830,	-8.8444,	9.3005,	3.0236
H 239	water 80,	0.3345,	-8.0150,	-0.2954,	-9.4735,	0.0690,	1.5118
H 240	water 80,	0.3345,	-8.5940,	0.6307,	-8.4256,	0.0690,	1.5118
ANAL 2							
O 241	water 81,	-0.6690,	-4.5307,	-0.6035,	-11.1722,	9.3005,	3.0236
H 242	water 81,	0.3345,	-3.8351,	0.0538,	-11.1889,	0.0690,	1.5118
H 243	water 81,	0.3345,	-4.2161,	-1.3000,	-11.7484,	0.0690,	1.5118
ANAL 2							
O 244	water 82,	-0.6690,	1.6394,	-10.2154,	-2.5027,	9.3005,	3.0236
H 245	water 82,	0.3345,	2.3686,	-9.8106,	-2.0331,	0.0690,	1.5118
H 246	water 82,	0.3345,	1.2256,	-9.4915,	-2.9727,	0.0690,	1.5118
ANAL 2							
O 247	water 83,	-0.6690,	-6.0760,	-1.3905,	4.7551,	9.3005,	3.0236
H 248	water 83,	0.3345,	-6.4040,	-1.0391,	3.9274,	0.0690,	1.5118
H 249	water 83,	0.3345,	-6.6344,	-2.1475,	4.9320,	0.0690,	1.5118
ANAL 2							
O 250	water 84,	-0.6690,	-8.1106,	2.6426,	0.3785,	9.3005,	3.0236
H 251	water 84,	0.3345,	-8.6162,	1.9182,	0.7470,	0.0690,	1.5118
H 252	water 84,	0.3345,	-7.5392,	2.9239,	1.0930,	0.0690,	1.5118
ANAL 2							
O 253	water 85,	-0.6690,	2.4867,	-1.6369,	-11.7542,	9.3005,	3.0236
H 254	water 85,	0.3345,	2.3496,	-1.6019,	-12.7008,	0.0690,	1.5118
H 255	water 85,	0.3345,	2.5971,	-2.5681,	-11.5623,	0.0690,	1.5118
ANAL 2							
O 256	water 86,	-0.6690,	2.9006,	-7.8697,	-1.2172,	9.3005,	3.0236
H 257	water 86,	0.3345,	3.2004,	-8.2218,	-0.3792,	0.0690,	1.5118
H 258	water 86,	0.3345,	2.1597,	-7.3080,	-0.9897,	0.0690,	1.5118
ANAL 2							
O 259	water 87,	-0.6690,	4.0836,	3.9644,	-0.1489,	9.3005,	3.0236
H 260	water 87,	0.3345,	3.7837,	3.9554,	0.7599,	0.0690,	1.5118
H 261	water 87,	0.3345,	3.5478,	3.3017,	-0.5847,	0.0690,	1.5118
ANAL 2							
O 262	water 88,	-0.6690,	-0.0528,	5.3863,	-6.6165,	9.3005,	3.0236
H 263	water 88,	0.3345,	0.7584,	5.5704,	-6.1430,	0.0690,	1.5118
H 264	water 88,	0.3345,	-0.7337,	5.4118,	-5.9443,	0.0690,	1.5118
ANAL 2							
O 265	water 89,	-0.6690,	0.0921,	-7.0690,	-9.1123,	9.3005,	3.0236

(continues on next page)

(continued from previous page)

H 266	water 89,	0.3345,	-0.8143,	-7.0535,	-8.8052,	0.0690,	1.5118
H 267	water 89,	0.3345,	0.6140,	-7.1527,	-8.3143,	0.0690,	1.5118
ANAL 2							
O 268	water 90,	-0.6690,	-6.8138,	-3.3648,	2.6731,	9.3005,	3.0236
H 269	water 90,	0.3345,	-6.3319,	-4.1487,	2.9367,	0.0690,	1.5118
H 270	water 90,	0.3345,	-6.3884,	-3.0831,	1.8633,	0.0690,	1.5118
ANAL 2							
O 271	water 91,	-0.6690,	5.4902,	1.5948,	-0.8761,	9.3005,	3.0236
H 272	water 91,	0.3345,	5.5884,	2.4297,	-0.4186,	0.0690,	1.5118
H 273	water 91,	0.3345,	5.5594,	1.8202,	-1.8038,	0.0690,	1.5118
ANAL 2							
O 274	water 92,	-0.6690,	-5.5811,	6.0788,	-0.6043,	9.3005,	3.0236
H 275	water 92,	0.3345,	-5.7564,	5.2131,	-0.9729,	0.0690,	1.5118
H 276	water 92,	0.3345,	-5.9128,	6.6907,	-1.2613,	0.0690,	1.5118
ANAL 2							
O 277	water 93,	-0.6690,	8.8753,	2.8928,	-3.7493,	9.3005,	3.0236
H 278	water 93,	0.3345,	7.9691,	3.1073,	-3.5279,	0.0690,	1.5118
H 279	water 93,	0.3345,	9.3254,	2.8541,	-2.9054,	0.0690,	1.5118
ANAL 2							
O 280	water 94,	-0.6690,	1.9868,	5.9861,	-4.9235,	9.3005,	3.0236
H 281	water 94,	0.3345,	2.0426,	6.7481,	-4.3470,	0.0690,	1.5118
H 282	water 94,	0.3345,	1.6201,	5.2949,	-4.3722,	0.0690,	1.5118
ANAL 2							
O 283	water 95,	-0.6690,	-6.5048,	1.8881,	8.2333,	9.3005,	3.0236
H 284	water 95,	0.3345,	-6.1127,	1.0795,	7.9039,	0.0690,	1.5118
H 285	water 95,	0.3345,	-7.3475,	1.6153,	8.5961,	0.0690,	1.5118
ANAL 2							
O 286	water 96,	-0.6690,	-3.2286,	-12.1274,	-4.3924,	9.3005,	3.0236
H 287	water 96,	0.3345,	-2.3268,	-12.4460,	-4.3539,	0.0690,	1.5118
H 288	water 96,	0.3345,	-3.6082,	-12.5733,	-5.1495,	0.0690,	1.5118
ANAL 2							
O 289	water 97,	-0.6690,	-8.7177,	-5.3273,	-5.8158,	9.3005,	3.0236
H 290	water 97,	0.3345,	-8.7728,	-4.4507,	-6.1962,	0.0690,	1.5118
H 291	water 97,	0.3345,	-7.8414,	-5.6346,	-6.0479,	0.0690,	1.5118
ANAL 2							
O 292	water 98,	-0.6690,	-10.4764,	-5.1159,	-3.3291,	9.3005,	3.0236
H 293	water 98,	0.3345,	-10.2133,	-5.2516,	-4.2394,	0.0690,	1.5118
H 294	water 98,	0.3345,	-10.9495,	-4.2839,	-3.3380,	0.0690,	1.5118
ANAL 2							
O 295	water 99,	-0.6690,	-2.7377,	-6.7273,	-8.1468,	9.3005,	3.0236
H 296	water 99,	0.3345,	-3.3330,	-6.3292,	-8.7818,	0.0690,	1.5118
H 297	water 99,	0.3345,	-3.1152,	-6.5089,	-7.2948,	0.0690,	1.5118
ANAL 2							
O 298	water 100,	-0.6690,	-0.5217,	1.4280,	-11.3190,	9.3005,	3.0236
H 299	water 100,	0.3345,	-1.4669,	1.5705,	-11.3684,	0.0690,	1.5118
H 300	water 100,	0.3345,	-0.4260,	0.6368,	-10.7889,	0.0690,	1.5118
ANAL 2							
O 301	water 101,	-0.6690,	-3.1946,	1.9538,	-11.0821,	9.3005,	3.0236
H 302	water 101,	0.3345,	-3.2495,	2.7344,	-11.6332,	0.0690,	1.5118
H 303	water 101,	0.3345,	-2.8520,	2.2733,	-10.2474,	0.0690,	1.5118
ANAL 2							
O 304	water 102,	-0.6690,	4.5346,	-2.0080,	3.3549,	9.3005,	3.0236
H 305	water 102,	0.3345,	5.0305,	-1.1959,	3.4577,	0.0690,	1.5118
H 306	water 102,	0.3345,	5.1502,	-2.6977,	3.6031,	0.0690,	1.5118
ANAL 2							
O 307	water 103,	-0.6690,	0.8621,	6.9715,	-0.8485,	9.3005,	3.0236
H 308	water 103,	0.3345,	1.4108,	6.8975,	-0.0677,	0.0690,	1.5118

(continues on next page)

(continued from previous page)

H 309	water 103,	0.3345,	1.4106,	7.4310,	-1.4842,	0.0690,	1.5118
ANAL 2							
O 310	water 104,	-0.6690,	-0.9493,	9.0170,	-1.1625,	9.3005,	3.0236
H 311	water 104,	0.3345,	-0.2815,	8.3384,	-1.0636,	0.0690,	1.5118
H 312	water 104,	0.3345,	-0.7553,	9.4228,	-2.0074,	0.0690,	1.5118
ANAL 2							
O 313	water 105,	-0.6690,	-4.0581,	-9.7236,	-3.3874,	9.3005,	3.0236
H 314	water 105,	0.3345,	-4.4897,	-9.8495,	-2.5424,	0.0690,	1.5118
H 315	water 105,	0.3345,	-3.7570,	-10.5977,	-3.6353,	0.0690,	1.5118
ANAL 2							
O 316	water 106,	-0.6690,	5.5055,	-1.6390,	-11.7299,	9.3005,	3.0236
H 317	water 106,	0.3345,	4.6196,	-1.3194,	-11.5594,	0.0690,	1.5118
H 318	water 106,	0.3345,	5.8834,	-0.9915,	-12.3250,	0.0690,	1.5118
ANAL 2							
O 319	water 107,	-0.6690,	-8.0985,	0.7307,	3.8635,	9.3005,	3.0236
H 320	water 107,	0.3345,	-7.7375,	1.4208,	4.4200,	0.0690,	1.5118
H 321	water 107,	0.3345,	-8.6955,	0.2490,	4.4359,	0.0690,	1.5118
ANAL 2							
O 322	water 108,	-0.6690,	4.5436,	-4.5512,	-4.7929,	9.3005,	3.0236
H 323	water 108,	0.3345,	4.6064,	-5.1929,	-5.5003,	0.0690,	1.5118
H 324	water 108,	0.3345,	4.5660,	-5.0746,	-3.9919,	0.0690,	1.5118
ANAL 2							
O 325	water 109,	-0.6690,	8.4875,	0.8021,	-5.4202,	9.3005,	3.0236
H 326	water 109,	0.3345,	8.0204,	1.1624,	-6.1739,	0.0690,	1.5118
H 327	water 109,	0.3345,	8.7010,	1.5653,	-4.8834,	0.0690,	1.5118
ANAL 2							
O 328	water 110,	-0.6690,	-7.9508,	2.4432,	-3.8256,	9.3005,	3.0236
H 329	water 110,	0.3345,	-7.3888,	2.8104,	-4.5078,	0.0690,	1.5118
H 330	water 110,	0.3345,	-7.5612,	1.5919,	-3.6267,	0.0690,	1.5118
ANAL 2							
O 331	water 111,	-0.6690,	-1.7889,	-8.4203,	-0.5295,	9.3005,	3.0236
H 332	water 111,	0.3345,	-2.2353,	-7.9598,	-1.2400,	0.0690,	1.5118
H 333	water 111,	0.3345,	-1.0075,	-8.7920,	-0.9386,	0.0690,	1.5118
ANAL 2							
O 334	water 112,	-0.6690,	-8.0755,	3.4368,	-10.6340,	9.3005,	3.0236
H 335	water 112,	0.3345,	-7.1592,	3.3044,	-10.3910,	0.0690,	1.5118
H 336	water 112,	0.3345,	-8.1904,	2.9154,	-11.4284,	0.0690,	1.5118
ANAL 2							
O 337	water 113,	-0.6690,	-9.5459,	-4.4615,	0.4290,	9.3005,	3.0236
H 338	water 113,	0.3345,	-10.4955,	-4.5770,	0.3975,	0.0690,	1.5118
H 339	water 113,	0.3345,	-9.3158,	-4.6171,	1.3449,	0.0690,	1.5118
ANAL 2							
O 340	water 114,	-0.6690,	-0.8791,	-13.1523,	-4.0194,	9.3005,	3.0236
H 341	water 114,	0.3345,	-0.4970,	-13.8941,	-3.5505,	0.0690,	1.5118
H 342	water 114,	0.3345,	-1.1450,	-13.5144,	-4.8646,	0.0690,	1.5118
ANAL 2							
O 343	water 115,	-0.6690,	-6.9397,	2.4469,	5.6391,	9.3005,	3.0236
H 344	water 115,	0.3345,	-6.7580,	2.1754,	6.5388,	0.0690,	1.5118
H 345	water 115,	0.3345,	-6.0782,	2.4962,	5.2250,	0.0690,	1.5118
ANAL 2							
O 346	water 116,	-0.6690,	-6.5700,	6.2697,	-3.7013,	9.3005,	3.0236
H 347	water 116,	0.3345,	-5.9806,	5.5298,	-3.5557,	0.0690,	1.5118
H 348	water 116,	0.3345,	-6.5995,	6.3690,	-4.6528,	0.0690,	1.5118
ANAL 2							
O 349	water 117,	-0.6690,	-3.6991,	7.9896,	-4.8411,	9.3005,	3.0236
H 350	water 117,	0.3345,	-4.4722,	8.3090,	-5.3064,	0.0690,	1.5118
H 351	water 117,	0.3345,	-3.7830,	8.3527,	-3.9595,	0.0690,	1.5118

(continues on next page)

(continued from previous page)

```

ANAL 2
O 352      water 118, -0.6690,  -6.5334,  5.5889,  -6.4765,  9.3005,  3.0236
H 353      water 118,  0.3345,  -6.0589,  4.7600,  -6.5391,  0.0690,  1.5118
H 354      water 118,  0.3345,  -6.6138,  5.8880,  -7.3821,  0.0690,  1.5118
ANAL 2
O 355      water 119, -0.6690,   6.0369, -0.5485,  -4.9230,  9.3005,  3.0236
H 356      water 119,  0.3345,   6.9450, -0.2473,  -4.9487,  0.0690,  1.5118
H 357      water 119,  0.3345,   5.9883, -1.2214,  -5.6020,  0.0690,  1.5118
ANAL 2
O 358      water 120, -0.6690,  -2.7088, -0.0648,   5.8336,  9.3005,  3.0236
H 359      water 120,  0.3345,  -2.0780,  0.6506,   5.7543,  0.0690,  1.5118
H 360      water 120,  0.3345,  -2.3160, -0.7863,   5.3424,  0.0690,  1.5118
ANAL 2
O 361      water 121, -0.6690,  -5.2890, -0.1781,   7.0195,  9.3005,  3.0236
H 362      water 121,  0.3345,  -4.4159,  0.1300,   6.7767,  0.0690,  1.5118
H 363      water 121,  0.3345,  -5.6072, -0.6345,   6.2406,  0.0690,  1.5118
ANAL 2
O 364      water 122, -0.6690,  -1.2183,  5.6595,   1.5861,  9.3005,  3.0236
H 365      water 122,  0.3345,  -1.0245,  5.3015,   0.7198,  0.0690,  1.5118
H 366      water 122,  0.3345,  -2.1428,  5.9036,   1.5432,  0.0690,  1.5118
ANAL 2
O 367      water 123, -0.6690,   6.8915, -2.7911,   0.6554,  9.3005,  3.0236
H 368      water 123,  0.3345,   7.5727, -2.4526,   0.0744,  0.0690,  1.5118
H 369      water 123,  0.3345,   7.3617, -3.0616,   1.4439,  0.0690,  1.5118
ANAL 2
O 370      water 124, -0.6690,   4.0041,  3.6736,  -5.0404,  9.3005,  3.0236
H 371      water 124,  0.3345,   4.3507,  3.1112,  -5.7330,  0.0690,  1.5118
H 372      water 124,  0.3345,   3.5308,  4.3631,  -5.5061,  0.0690,  1.5118
ANAL 2
O 373      water 125, -0.6690,  -1.1523,  3.7231,   3.3874,  9.3005,  3.0236
H 374      water 125,  0.3345,  -1.5693,  2.9944,   2.9278,  0.0690,  1.5118
H 375      water 125,  0.3345,  -1.1728,  4.4454,   2.7598,  0.0690,  1.5118
ANAL 2
O 376      water 126, -0.6690,   4.7668,  6.6724,  -2.9741,  9.3005,  3.0236
H 377      water 126,  0.3345,   5.4307,  6.2764,  -2.4097,  0.0690,  1.5118
H 378      water 126,  0.3345,   4.2200,  5.9378,  -3.2526,  0.0690,  1.5118
ANAL 2
O 379      water 127, -0.6690,  -0.7662, -1.9711, -13.2247,  9.3005,  3.0236
H 380      water 127,  0.3345,   0.1253, -2.3133, -13.2901,  0.0690,  1.5118
H 381      water 127,  0.3345,  -1.0164, -2.1267, -12.3140,  0.0690,  1.5118
ANAL 2
O 382      water 128, -0.6690,  -4.0473,  6.6758,   1.6220,  9.3005,  3.0236
H 383      water 128,  0.3345,  -4.1338,  7.6099,   1.8123,  0.0690,  1.5118
H 384      water 128,  0.3345,  -4.6763,  6.5154,   0.9186,  0.0690,  1.5118
ANAL 2
end
response
  allcomponents
  dynahyp
  hyperpol 0.0428 [Hartree]
end
Basis Core=None
symmetry NOSYM
Relativity
  Level None
End
EndEngine

```

(continues on next page)

(continued from previous page)

eor

Example: DRF: scripting tool

Download DIMQM_DRF_plams.run

```

#!/bin/sh

# The Discrete Reaction Field (DRF) method is a polarizable QM/MM method. For
# each type of solvent molecule, the DRF method requires two parameters, atomic
# polarizabilities and atomic charges. The main program reads the QM and DRF
# regions, splits the DRF region into unique molecules, computes the atomic
# charges of a single DRF molecule for each unique type, assigns the atomic
# charges and atomic polarizabilities for all the DRF molecules and defines the
# QM_DRF settings. This simple script works for initial configurations that come
# from a MD simulation, for example.

# In this example a python script is used for DRF calculations, that uses PLAMS
# (Python Library for Automating Molecular Simulation). PLAMS takes care of
# input preparation, job execution, file management and output processing, see
# also the PLAMS documentation in the Scripting manual. The DRF python script
# has default settings which can be easily modified if this is required. In the
# simplest case the user just needs to provide the QM and DRF regions (in xyz
# format). Typically the user may also want to choose the functional, basis set
# and numerical quality for the QM and DRF region. By default, atomic charges
# that are used for the DRF are computed with LDA functional, DZP basis set and
# normal numerical quality. Also by default, atomic polarizabilities (computed
# with the Thole's model) are taken from an inner database for the elements
# H, C, N, O, F, S, Cl, Br, and I [J.Phys.Chem.A 102 (1998) 2399].
# For the other elements up to U (Z=92) the inner database also include atomic
# polarizabilities, however, those are not optimized and not tested,
# and no reference paper exists.
#
# The main program defines a series of functions
# for general settings for a DRF calculation, reading QM and DRF regions,
# classifying DRF molecules of the same type (first by formula and then for
# configurations for a given formula), computing, for a given settings, the
# charges for a single molecule of unique DRF type and assigning the atomic
# charges for the rest of molecules that belong to a given DRF type (preserving
# atom orders).

# The DRF python script DIMQM_DRF_plams.py users will probably want to change or
# extend:

# =====
# from DIMQM_DRF_plams_module import full_DIMQM_DRF

# qm_region_filename = 'qm.xyz'
# drf_region_filename = 'drf.xyz'

# settings.input.AMS.Task = 'SinglePoint'
# settings.input.ADF.Basis.Type = 'TZP'
# settings.input.ADF.XC['_1'] = 'GGA BLYP'
# settings.input.ADF.NumericalQuality = 'Normal'

```

(continues on next page)

(continued from previous page)

```
# full_DIMQM_DRF(qm_region_filename, drf_region_filename,
#               settings, drf_charges_type='MDC-q charges',
#               drf_fragment_settings=None)
# =====

# This DRF python script DIMQM_DRF_plams.py imports DIMQM_DRF_plams_module.py,
# which contains a script full_DIMQM_DRF that splits the DRF region into unique
# molecules, computes the atomic charges of a single DRF molecule for each
# unique type, assigns the atomic charges and atomic polarizabilities for all
# the DRF molecules and defines the QM_DRF settings.

# The run script DIMQM_DRF_plams.run contains an example, how one could use the
# DIMQM_DRF_plams.py script. In this simple example both the QM and DRF region
# consists of a Formic acid molecule.

cp $AMSHOME/examples/adf/DIMQM_DRF_plams/formic_acid_qm.xyz qm.xyz
cp $AMSHOME/examples/adf/DIMQM_DRF_plams/formic_acid_drf.xyz drf.xyz
cp $AMSHOME/examples/adf/DIMQM_DRF_plams/DIMQM_DRF_plams_module.py .
cp $AMSHOME/examples/adf/DIMQM_DRF_plams/DIMQM_DRF_plams.py .

$AMSBIN/plams DIMQM_DRF_plams.py

# Every time you run a PLAMS script, a uniquely named working directory is
# created (plams.*****). This folder will contain one subdirectory per job. Each
# job directory contains the job's input and results files. In this case there
# will be 1 directory for the ADF calculation of the atomic charges that are
# used for DRF. Next there is a directory which calculates the full system.
```

Example: DRF2: Polarizability N2 on Ag68 + H2O

Download DIMQM_DRF2.run

```
#!/bin/sh

# == Expert option ==

# This example shows how to run DRF2, which is a combination of the
# Discrete Reaction Field and the PIM method of DIM/QM. This allows
# for treatment of systems such as a solvated nanoparticle using
# DRF with gaussian screening for the solvent, and PIM for the
# nanoparticle. Allows for geometry optimizations in "DRF" as well,
# as long as done with gaussian screening.

#####
# STATIC POLARIZABILITY
#####

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
atoms
  N      -0.000006   -0.000060   2.302488
  N      0.000019    0.000041   3.408628
```

(continues on next page)

(continued from previous page)

```

end
end

Task SinglePoint

Engine ADF
  title DRF2 Static Polarizability, N2 on Ag68 + H2O
  aoresponse
    alda
  end
  beckegrid
    quality good
  end
  dimpar
    Ag
    rad 1.4445
    drude 9.2 0.17 eV
    bound 5.0
    char 0.000000
    SUBEND
    O
    rad 0.90
    char 0.6
    STATIC
    SUBEND
    H
    rad 0.45
    char -0.3
    STATIC
    SUBEND
    XYZ
    71
    Ag      -1.2626801699   -1.1212553334   -7.5641602542
    Ag      -1.5751210922    0.5238327185   -9.9892089940
    Ag      -4.1814870442   -1.7663886735   -7.6050834452
    Ag      -0.8822430837   -2.7600722440   -5.1959892962
    Ag      -2.1240266195   -3.8206731623   -2.8525807753
    Ag       3.4578336576   -2.6744062081   -2.8525742581
    Ag      -3.7149452090   -3.2988294197   -5.2034646499
    Ag       1.8985756093   -2.1890139391   -5.1959881717
    Ag       0.6946811325   -3.3828052555   -2.8061234013
    Ag       4.7143519584   -1.5678241605   -5.2034549930
    Ag       1.6023915608   -0.5328957432   -7.5641613132
    Ag       1.2412345786    1.1021928389   -9.9892023582
    Ag       4.5392237030    0.0244593089   -7.6050682929
    Ag       0.0000106997    0.0000013921   -5.1462708001
    Ag      -0.3396832259    1.6541471619   -7.5641597129
    Ag      -2.8450227342   -0.5497019461   -5.1959955618
    Ag       2.8314207151    0.6159878635   -5.1959875699
    Ag      -3.1884901403    1.0603809604   -7.5634515357
    Ag      -1.2364094731   -1.0979217456   -2.7987978362
    Ag       1.5690420034   -0.5218070047   -2.7987993856
    Ag       4.3708278508    0.0708740258   -2.8525785565
    Ag      -4.0450216512   -1.6573690296   -2.8525892410
    Ag       2.5125751829    2.2311280445   -7.5634444475
    Ag       0.6759414795   -3.2915128984   -7.5634430672
    Ag       0.3339235029   -1.6260239766   -9.9892067983

```

(continues on next page)

(continued from previous page)

```

Ag      1.0324285615    -5.0274542660    -5.1718100987
Ag      -2.2484187072    -3.9433040680    -7.6050830302
Ag       3.6204971713    -2.7380910382    -7.6050765656
Ag      -2.4569103660    -2.1817169842    -9.8785349524
Ag      -1.7752961456    -5.4191572521    -5.2192070180
Ag       3.7672926986    -4.2809622136    -5.2191965533
Ag       3.1179002480    -1.0369024811    -9.8785348598
Ag      -1.9491576017     2.1440839896    -5.1959915042
Ag       2.5822650861     2.2930127465    -2.8061239177
Ag      -0.3326165571     1.6197266638    -2.7987957984
Ag       0.9464626101     2.7387205045    -5.1959886567
Ag      -0.5598334280    -4.3819335958    -9.8593641366
Ag      -0.2204924851    -6.0299810786    -7.5512447020
Ag       2.5790329655    -5.4550834512    -7.5512427315
Ag       2.2414383913    -3.8066764388    -9.8593649949
Ag      -2.2907828197     3.9188443502    -7.6050826773
Ag       0.5610225957     4.5044771077    -7.6050819796
Ag      -4.8701069022     1.6196298364    -5.1718125544
Ag      -3.2769317991     1.0897966386    -2.8061340012
Ag      -0.6609450333     3.2186205924    -9.8785392784
Ag      -5.5910570566    -1.1220840757    -5.2192067211
Ag      -2.2467815447     3.7498049589    -2.8525803584
Ag      -0.9993904347     4.8666585643    -5.2034637574
Ag      -3.8054729020     4.2470446290    -5.2192106249
Ag      -3.5149221622     2.6758039407    -9.8593694452
Ag      -4.4173760657    -0.0377981351    -9.8593712497
Ag      -6.0137475245     0.4940463872    -7.5512522368
Ag      -5.1118586671     3.2059431066    -7.5512501894
Ag       0.5871922586     4.3317735603    -2.8525794711
Ag       1.8237836111     5.4030432621    -5.2192000459
Ag       3.8377073288     3.4078339914    -5.1718059272
Ag       5.5807980727     1.1721205307    -5.2191937875
Ag       3.4347425354     4.9610463596    -7.5512390021
Ag       4.0747942310     1.7061247432    -9.8593564188
Ag       5.3323750373     2.8240364209    -7.5512331190
Ag       2.1759755136     3.8444690680    -9.8593641559
Ag      -1.8817544351     2.1073913325    -0.4836595729
Ag       0.8989635719     2.6784284394    -0.4836553279
Ag       0.0000000000     0.0000000000     0.0000000000
Ag       2.7659350940     0.5759533343    -0.4836497308
Ag      -2.7690678527    -0.5606913044    -0.4836604335
Ag      -0.8841719671    -2.6833451220    -0.4836610364
Ag       1.8701101821    -2.1177433283    -0.4836551986
O        -4.069283      -3.055450       0.358275
H        -5.031565      -3.283620       0.404829
H        -3.843952      -4.017650       0.299391
SUBEND
end
dimqm
  DRF2
  ALGORITHM BRUTE
end
basis
  core none
  type TZP
end
symmetry NOSYM

```

(continues on next page)

(continued from previous page)

```

xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY
#####

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title DRF2 Frequency-Dependent Polarizability, N2 on Ag68 + H2O
  aoresponse
    alda
      frequencies 3.55 [eV]
      lifetime 0.0036749
    end
  beckegrid
    quality good
  end
  dimpar
    Ag
      rad 1.4445
      drude 9.2 0.17 eV
      bound 5.0
      char 0.000000
    SUBEND
    O
      rad 0.90
      char 0.6
    STATIC
    SUBEND
    H
      rad 0.45
      char -0.3
    STATIC
    SUBEND
    XYZ
    71
    Ag      -1.2626801699   -1.1212553334   -7.5641602542
    Ag      -1.5751210922    0.5238327185   -9.9892089940
    Ag      -4.1814870442   -1.7663886735   -7.6050834452
    Ag      -0.8822430837   -2.7600722440   -5.1959892962

```

(continues on next page)

(continued from previous page)

Ag	-2.1240266195	-3.8206731623	-2.8525807753
Ag	3.4578336576	-2.6744062081	-2.8525742581
Ag	-3.7149452090	-3.2988294197	-5.2034646499
Ag	1.8985756093	-2.1890139391	-5.1959881717
Ag	0.6946811325	-3.3828052555	-2.8061234013
Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366
Ag	-0.2204924851	-6.0299810786	-7.5512447020
Ag	2.5790329655	-5.4550834512	-7.5512427315
Ag	2.2414383913	-3.8066764388	-9.8593649949
Ag	-2.2907828197	3.9188443502	-7.6050826773
Ag	0.5610225957	4.5044771077	-7.6050819796
Ag	-4.8701069022	1.6196298364	-5.1718125544
Ag	-3.2769317991	1.0897966386	-2.8061340012
Ag	-0.6609450333	3.2186205924	-9.8785392784
Ag	-5.5910570566	-1.1220840757	-5.2192067211
Ag	-2.2467815447	3.7498049589	-2.8525803584
Ag	-0.9993904347	4.8666585643	-5.2034637574
Ag	-3.8054729020	4.2470446290	-5.2192106249
Ag	-3.5149221622	2.6758039407	-9.8593694452
Ag	-4.4173760657	-0.0377981351	-9.8593712497
Ag	-6.0137475245	0.4940463872	-7.5512522368
Ag	-5.1118586671	3.2059431066	-7.5512501894
Ag	0.5871922586	4.3317735603	-2.8525794711
Ag	1.8237836111	5.4030432621	-5.2192000459
Ag	3.8377073288	3.4078339914	-5.1718059272
Ag	5.5807980727	1.1721205307	-5.2191937875
Ag	3.4347425354	4.9610463596	-7.5512390021
Ag	4.0747942310	1.7061247432	-9.8593564188
Ag	5.3323750373	2.8240364209	-7.5512331190
Ag	2.1759755136	3.8444690680	-9.8593641559

(continues on next page)

(continued from previous page)

```

    Ag    -1.8817544351    2.1073913325    -0.4836595729
    Ag     0.8989635719    2.6784284394    -0.4836553279
    Ag     0.0000000000    0.0000000000    0.0000000000
    Ag     2.7659350940    0.5759533343    -0.4836497308
    Ag    -2.7690678527    -0.5606913044    -0.4836604335
    Ag    -0.8841719671    -2.6833451220    -0.4836610364
    Ag     1.8701101821    -2.1177433283    -0.4836551986
    O      -4.069283      -3.055450      0.358275
    H      -5.031565      -3.283620      0.404829
    H      -3.843952      -4.017650      0.299391
  SUBEND
end
dimgm
  DRF2
  ALGORITHM BRUTE
  FREQUENCY
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY WITH LOCAL FIELDS
#####

AMS_JOBNAME=third $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006    -0.000060    2.302488
    N       0.000019     0.000041    3.408628
  end
end

Task SinglePoint

Engine ADF
  title DRF2 Frequency-Dependent Polarizability w/ Local Fields, N2 on Ag68 + H2O
  aoresponse
    alda
    frequencies 3.55 [eV]
    lifetime 0.0036749
  end
  beckegrid
    quality good
  end
  dimpar

```

(continues on next page)

(continued from previous page)

```

Ag
rad 1.4445
drude 9.2 0.17 eV
bound 5.0
char 0.000000
SUBEND
O
rad 0.90
char 0.6
STATIC
SUBEND
H
rad 0.45
char -0.3
STATIC
SUBEND
XYZ
71
Ag      -1.2626801699   -1.1212553334   -7.5641602542
Ag      -1.5751210922    0.5238327185   -9.9892089940
Ag      -4.1814870442   -1.7663886735   -7.6050834452
Ag      -0.8822430837   -2.7600722440   -5.1959892962
Ag      -2.1240266195   -3.8206731623   -2.8525807753
Ag       3.4578336576   -2.6744062081   -2.8525742581
Ag      -3.7149452090   -3.2988294197   -5.2034646499
Ag       1.8985756093   -2.1890139391   -5.1959881717
Ag       0.6946811325   -3.3828052555   -2.8061234013
Ag       4.7143519584   -1.5678241605   -5.2034549930
Ag       1.6023915608   -0.5328957432   -7.5641613132
Ag       1.2412345786    1.1021928389   -9.9892023582
Ag       4.5392237030    0.0244593089   -7.6050682929
Ag       0.0000106997    0.0000013921   -5.1462708001
Ag      -0.3396832259    1.6541471619   -7.5641597129
Ag      -2.8450227342   -0.5497019461   -5.1959955618
Ag       2.8314207151    0.6159878635   -5.1959875699
Ag      -3.1884901403    1.0603809604   -7.5634515357
Ag      -1.2364094731   -1.0979217456   -2.7987978362
Ag       1.5690420034   -0.5218070047   -2.7987993856
Ag       4.3708278508    0.0708740258   -2.8525785565
Ag      -4.0450216512   -1.6573690296   -2.8525892410
Ag       2.5125751829    2.2311280445   -7.5634444475
Ag       0.6759414795   -3.2915128984   -7.5634430672
Ag       0.3339235029   -1.6260239766   -9.9892067983
Ag       1.0324285615   -5.0274542660   -5.1718100987
Ag      -2.2484187072   -3.9433040680   -7.6050830302
Ag       3.6204971713   -2.7380910382   -7.6050765656
Ag      -2.4569103660   -2.1817169842   -9.8785349524
Ag      -1.7752961456   -5.4191572521   -5.2192070180
Ag       3.7672926986   -4.2809622136   -5.2191965533
Ag       3.1179002480   -1.0369024811   -9.8785348598
Ag      -1.9491576017    2.1440839896   -5.1959915042
Ag       2.5822650861    2.2930127465   -2.8061239177
Ag      -0.3326165571    1.6197266638   -2.7987957984
Ag       0.9464626101    2.7387205045   -5.1959886567
Ag      -0.5598334280   -4.3819335958   -9.8593641366
Ag      -0.2204924851   -6.0299810786   -7.5512447020
Ag       2.5790329655   -5.4550834512   -7.5512427315

```

(continues on next page)

(continued from previous page)

```

Ag      2.2414383913   -3.8066764388   -9.8593649949
Ag      -2.2907828197    3.9188443502   -7.6050826773
Ag       0.5610225957    4.5044771077   -7.6050819796
Ag      -4.8701069022    1.6196298364   -5.1718125544
Ag      -3.2769317991    1.0897966386   -2.8061340012
Ag      -0.6609450333    3.2186205924   -9.8785392784
Ag      -5.5910570566   -1.1220840757   -5.2192067211
Ag      -2.2467815447    3.7498049589   -2.8525803584
Ag      -0.9993904347    4.8666585643   -5.2034637574
Ag      -3.8054729020    4.2470446290   -5.2192106249
Ag      -3.5149221622    2.6758039407   -9.8593694452
Ag      -4.4173760657   -0.0377981351   -9.8593712497
Ag      -6.0137475245    0.4940463872   -7.5512522368
Ag      -5.1118586671    3.2059431066   -7.5512501894
Ag       0.5871922586    4.3317735603   -2.8525794711
Ag       1.8237836111    5.4030432621   -5.2192000459
Ag       3.8377073288    3.4078339914   -5.1718059272
Ag       5.5807980727    1.1721205307   -5.2191937875
Ag       3.4347425354    4.9610463596   -7.5512390021
Ag       4.0747942310    1.7061247432   -9.8593564188
Ag       5.3323750373    2.8240364209   -7.5512331190
Ag       2.1759755136    3.8444690680   -9.8593641559
Ag      -1.8817544351    2.1073913325   -0.4836595729
Ag       0.8989635719    2.6784284394   -0.4836553279
Ag       0.0000000000    0.0000000000    0.0000000000
Ag       2.7659350940    0.5759533343   -0.4836497308
Ag      -2.7690678527   -0.5606913044   -0.4836604335
Ag      -0.8841719671   -2.6833451220   -0.4836610364
Ag       1.8701101821   -2.1177433283   -0.4836551986
O       -4.069283      -3.055450       0.358275
H       -5.031565      -3.283620       0.404829
H       -3.843952      -4.017650       0.299391
SUBEND
end
dimqm
  DRF2
  ALGORITHM DIRECT
  FREQUENCY
  LOCALFIELD
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: CPIM: excitation energies N2 on silver cluster Ag68

Download DIMQM_CPIM_Excitations.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to calculate excitation energies with the
# Capacitance Polarizability Interaction Model (CPIM). Key EXCITATIONS is used.

$AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title DIM/QM Excitations Test, N2 on Ag68
  beckegrid
    quality good
  end
  dimpar
    Ag
    pol 49.9843
    cap 2.7529
    SUBEND
    XYZ
    68
    Ag      -1.2626801699   -1.1212553334   -7.5641602542
    Ag      -1.5751210922    0.5238327185   -9.9892089940
    Ag      -4.1814870442   -1.7663886735   -7.6050834452
    Ag      -0.8822430837   -2.7600722440   -5.1959892962
    Ag      -2.1240266195   -3.8206731623   -2.8525807753
    Ag       3.4578336576   -2.6744062081   -2.8525742581
    Ag     -3.7149452090   -3.2988294197   -5.2034646499
    Ag      1.8985756093   -2.1890139391   -5.1959881717
    Ag      0.6946811325   -3.3828052555   -2.8061234013
    Ag      4.7143519584   -1.5678241605   -5.2034549930
    Ag      1.6023915608   -0.5328957432   -7.5641613132
    Ag      1.2412345786    1.1021928389   -9.9892023582
    Ag      4.5392237030    0.0244593089   -7.6050682929
    Ag      0.0000106997    0.0000013921   -5.1462708001
    Ag     -0.3396832259    1.6541471619   -7.5641597129
    Ag     -2.8450227342   -0.5497019461   -5.1959955618
    Ag      2.8314207151    0.6159878635   -5.1959875699
    Ag     -3.1884901403    1.0603809604   -7.5634515357
    Ag     -1.2364094731   -1.0979217456   -2.7987978362
    Ag      1.5690420034   -0.5218070047   -2.7987993856
    Ag      4.3708278508    0.0708740258   -2.8525785565
    Ag     -4.0450216512   -1.6573690296   -2.8525892410
    Ag      2.5125751829    2.2311280445   -7.5634444475
  end
end

```

(continues on next page)

(continued from previous page)

```

Ag      0.6759414795   -3.2915128984   -7.5634430672
Ag      0.3339235029   -1.6260239766   -9.9892067983
Ag      1.0324285615   -5.0274542660   -5.1718100987
Ag     -2.2484187072   -3.9433040680   -7.6050830302
Ag      3.6204971713   -2.7380910382   -7.6050765656
Ag     -2.4569103660   -2.1817169842   -9.8785349524
Ag     -1.7752961456   -5.4191572521   -5.2192070180
Ag      3.7672926986   -4.2809622136   -5.2191965533
Ag      3.1179002480   -1.0369024811   -9.8785348598
Ag     -1.9491576017    2.1440839896   -5.1959915042
Ag      2.5822650861    2.2930127465   -2.8061239177
Ag     -0.3326165571    1.6197266638   -2.7987957984
Ag      0.9464626101    2.7387205045   -5.1959886567
Ag     -0.5598334280   -4.3819335958   -9.8593641366
Ag     -0.2204924851   -6.0299810786   -7.5512447020
Ag      2.5790329655   -5.4550834512   -7.5512427315
Ag      2.2414383913   -3.8066764388   -9.8593649949
Ag     -2.2907828197    3.9188443502   -7.6050826773
Ag      0.5610225957    4.5044771077   -7.6050819796
Ag     -4.8701069022    1.6196298364   -5.1718125544
Ag     -3.2769317991    1.0897966386   -2.8061340012
Ag     -0.6609450333    3.2186205924   -9.8785392784
Ag     -5.5910570566   -1.1220840757   -5.2192067211
Ag     -2.2467815447    3.7498049589   -2.8525803584
Ag     -0.9993904347    4.8666585643   -5.2034637574
Ag     -3.8054729020    4.2470446290   -5.2192106249
Ag     -3.5149221622    2.6758039407   -9.8593694452
Ag     -4.4173760657   -0.0377981351   -9.8593712497
Ag     -6.0137475245    0.4940463872   -7.5512522368
Ag     -5.1118586671    3.2059431066   -7.5512501894
Ag      0.5871922586    4.3317735603   -2.8525794711
Ag      1.8237836111    5.4030432621   -5.2192000459
Ag      3.8377073288    3.4078339914   -5.1718059272
Ag      5.5807980727    1.1721205307   -5.2191937875
Ag      3.4347425354    4.9610463596   -7.5512390021
Ag      4.0747942310    1.7061247432   -9.8593564188
Ag      5.3323750373    2.8240364209   -7.5512331190
Ag      2.1759755136    3.8444690680   -9.8593641559
Ag     -1.8817544351    2.1073913325   -0.4836595729
Ag      0.8989635719    2.6784284394   -0.4836553279
Ag      0.0000000000    0.0000000000    0.0000000000
Ag      2.7659350940    0.5759533343   -0.4836497308
Ag     -2.7690678527   -0.5606913044   -0.4836604335
Ag     -0.8841719671   -2.6833451220   -0.4836610364
Ag      1.8701101821   -2.1177433283   -0.4836551986
SUBEND
end
dimqm
  CPIM
end
excitations
  allowed
  davidson
end
  lowest 10
end
basis

```

(continues on next page)

(continued from previous page)

```

    core none
    type TZP
end
symmetry NOSYM
xc
    gga Becke Perdew
end
Relativity
    Level None
End
EndEngine
eor

```

Example: CPIM: polarizability N2 on silver cluster Ag68

Download DIMQM_JACOBI.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to do calculate static and frequency dependent
# polarizabilities with the Polarizability Interaction Model (PIM). The example
# consists of 3 calculations: static polarizability, frequency dependent, and
# with inclusion of effect of the local field.

# When the molecule interacts with a metal nanoparticle, there are two types of
# interactions: the image field and the local field. The image field is caused
# by the dipoles induced into the nanoparticle by the molecule's electron
# density. This is always taken into account in a DIM/QM calculation. The local
# field arises by direct interactions of the nanoparticle with an external
# field. Addition of the LOCALFIELD key causes the DIM/QM calculation to include
# this effect, but by default this is not included in a DIM/QM calculation.

#####
# STATIC POLARIZABILITY
#####

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N       0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Static Polarizability, N2 on Ag68
  aoresponse
  alda

```

(continues on next page)

(continued from previous page)

```

end
beckegrid
  quality good
end
dimpair
  Ag
  rad 1.4445
  drude 9.2 0.17 eV
  bound 5.0
  SUBEND
  XYZ
  68
  Ag      -1.2626801699   -1.1212553334   -7.5641602542
  Ag      -1.5751210922    0.5238327185   -9.9892089940
  Ag      -4.1814870442   -1.7663886735   -7.6050834452
  Ag      -0.8822430837   -2.7600722440   -5.1959892962
  Ag      -2.1240266195   -3.8206731623   -2.8525807753
  Ag       3.4578336576   -2.6744062081   -2.8525742581
  Ag      -3.7149452090   -3.2988294197   -5.2034646499
  Ag       1.8985756093   -2.1890139391   -5.1959881717
  Ag       0.6946811325   -3.3828052555   -2.8061234013
  Ag       4.7143519584   -1.5678241605   -5.2034549930
  Ag       1.6023915608   -0.5328957432   -7.5641613132
  Ag       1.2412345786    1.1021928389   -9.9892023582
  Ag       4.5392237030    0.0244593089   -7.6050682929
  Ag       0.0000106997    0.0000013921   -5.1462708001
  Ag      -0.3396832259    1.6541471619   -7.5641597129
  Ag      -2.8450227342   -0.5497019461   -5.1959955618
  Ag       2.8314207151    0.6159878635   -5.1959875699
  Ag      -3.1884901403    1.0603809604   -7.5634515357
  Ag      -1.2364094731   -1.0979217456   -2.7987978362
  Ag       1.5690420034   -0.5218070047   -2.7987993856
  Ag       4.3708278508    0.0708740258   -2.8525785565
  Ag      -4.0450216512   -1.6573690296   -2.8525892410
  Ag       2.5125751829    2.2311280445   -7.5634444475
  Ag       0.6759414795   -3.2915128984   -7.5634430672
  Ag       0.3339235029   -1.6260239766   -9.9892067983
  Ag       1.0324285615   -5.0274542660   -5.1718100987
  Ag      -2.2484187072   -3.9433040680   -7.6050830302
  Ag       3.6204971713   -2.7380910382   -7.6050765656
  Ag      -2.4569103660   -2.1817169842   -9.8785349524
  Ag      -1.7752961456   -5.4191572521   -5.2192070180
  Ag       3.7672926986   -4.2809622136   -5.2191965533
  Ag       3.1179002480   -1.0369024811   -9.8785348598
  Ag      -1.9491576017    2.1440839896   -5.1959915042
  Ag       2.5822650861    2.2930127465   -2.8061239177
  Ag      -0.3326165571    1.6197266638   -2.7987957984
  Ag       0.9464626101    2.7387205045   -5.1959886567
  Ag      -0.5598334280   -4.3819335958   -9.8593641366
  Ag      -0.2204924851   -6.0299810786   -7.5512447020
  Ag       2.5790329655   -5.4550834512   -7.5512427315
  Ag       2.2414383913   -3.8066764388   -9.8593649949
  Ag      -2.2907828197    3.9188443502   -7.6050826773
  Ag       0.5610225957    4.5044771077   -7.6050819796
  Ag      -4.8701069022    1.6196298364   -5.1718125544
  Ag      -3.2769317991    1.0897966386   -2.8061340012
  Ag      -0.6609450333    3.2186205924   -9.8785392784

```

(continues on next page)

(continued from previous page)

```

Ag      -5.5910570566   -1.1220840757   -5.2192067211
Ag      -2.2467815447    3.7498049589   -2.8525803584
Ag      -0.9993904347    4.8666585643   -5.2034637574
Ag      -3.8054729020    4.2470446290   -5.2192106249
Ag      -3.5149221622    2.6758039407   -9.8593694452
Ag      -4.4173760657   -0.0377981351   -9.8593712497
Ag      -6.0137475245    0.4940463872   -7.5512522368
Ag      -5.1118586671    3.2059431066   -7.5512501894
Ag      0.5871922586     4.3317735603   -2.8525794711
Ag      1.8237836111     5.4030432621   -5.2192000459
Ag      3.8377073288     3.4078339914   -5.1718059272
Ag      5.5807980727     1.1721205307   -5.2191937875
Ag      3.4347425354     4.9610463596   -7.5512390021
Ag      4.0747942310     1.7061247432   -9.8593564188
Ag      5.3323750373     2.8240364209   -7.5512331190
Ag      2.1759755136     3.8444690680   -9.8593641559
Ag      -1.8817544351     2.1073913325   -0.4836595729
Ag      0.8989635719     2.6784284394   -0.4836553279
Ag      0.0000000000     0.0000000000    0.0000000000
Ag      2.7659350940     0.5759533343   -0.4836497308
Ag      -2.7690678527    -0.5606913044   -0.4836604335
Ag      -0.8841719671    -2.6833451220   -0.4836610364
Ag      1.8701101821     -2.1177433283   -0.4836551986
SUBEND
end
dimqm
PIM
JACOBI
ALGORITHM BRUTE
end
basis
core none
type TZP
end
symmetry NOSYM
xc
gga Becke Perdew
end
Relativity
Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY
#####

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
atoms
N      -0.000006   -0.000060   2.302488
N      0.000019    0.000041   3.408628
end
end

```

(continues on next page)

(continued from previous page)

Task SinglePoint

Engine ADF

title PIM Frequency-Dependent Polarizability, N2 on Ag68

aoresponse

alda

frequencies 3.55 [eV]

lifetime 0.0036749

end

beckegrid

quality good

end

dimpair

Ag

rad 1.4445

drude 9.2 0.17 eV

bound 5.0

SUBEND

XYZ

68

Ag	-1.2626801699	-1.1212553334	-7.5641602542
Ag	-1.5751210922	0.5238327185	-9.9892089940
Ag	-4.1814870442	-1.7663886735	-7.6050834452
Ag	-0.8822430837	-2.7600722440	-5.1959892962
Ag	-2.1240266195	-3.8206731623	-2.8525807753
Ag	3.4578336576	-2.6744062081	-2.8525742581
Ag	-3.7149452090	-3.2988294197	-5.2034646499
Ag	1.8985756093	-2.1890139391	-5.1959881717
Ag	0.6946811325	-3.3828052555	-2.8061234013
Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366

(continues on next page)

(continued from previous page)

```

Ag      -0.2204924851   -6.0299810786   -7.5512447020
Ag      2.5790329655    -5.4550834512   -7.5512427315
Ag      2.2414383913    -3.8066764388   -9.8593649949
Ag      -2.2907828197    3.9188443502    -7.6050826773
Ag      0.5610225957     4.5044771077    -7.6050819796
Ag      -4.8701069022     1.6196298364    -5.1718125544
Ag      -3.2769317991     1.0897966386    -2.8061340012
Ag      -0.6609450333     3.2186205924    -9.8785392784
Ag      -5.5910570566    -1.1220840757    -5.2192067211
Ag      -2.2467815447     3.7498049589    -2.8525803584
Ag      -0.9993904347     4.8666585643    -5.2034637574
Ag      -3.8054729020     4.2470446290    -5.2192106249
Ag      -3.5149221622     2.6758039407    -9.8593694452
Ag      -4.4173760657    -0.0377981351    -9.8593712497
Ag      -6.0137475245     0.4940463872    -7.5512522368
Ag      -5.1118586671     3.2059431066    -7.5512501894
Ag      0.5871922586      4.3317735603    -2.8525794711
Ag      1.8237836111      5.4030432621    -5.2192000459
Ag      3.8377073288      3.4078339914    -5.1718059272
Ag      5.5807980727      1.1721205307    -5.2191937875
Ag      3.4347425354      4.9610463596    -7.5512390021
Ag      4.0747942310      1.7061247432    -9.8593564188
Ag      5.3323750373      2.8240364209    -7.5512331190
Ag      2.1759755136      3.8444690680    -9.8593641559
Ag      -1.8817544351      2.1073913325    -0.4836595729
Ag      0.8989635719      2.6784284394    -0.4836553279
Ag      0.0000000000      0.0000000000     0.0000000000
Ag      2.7659350940      0.5759533343    -0.4836497308
Ag      -2.7690678527     -0.5606913044    -0.4836604335
Ag      -0.8841719671     -2.6833451220    -0.4836610364
Ag      1.8701101821     -2.1177433283    -0.4836551986
SUBEND
end
dimqm
PIM
JACOBI
ALGORITHM BRUTE
FREQUENCY
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY WITH LOCAL FIELDS
#####

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=third $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006      -0.000060      2.302488
    N      0.000019      0.000041      3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Frequency-Dependent Polarizability w/ Local Fields, N2 on Ag68
  aoresponse
    alda
      frequencies 3.55 [eV]
      lifetime 0.0036749
    end
  beckegrid
    quality good
  end
  dimpar
    Ag
      rad 1.4445
      drude 9.2 0.17 eV
      bound 5.0
    SUBEND
    XYZ
    68
    Ag      -1.2626801699      -1.1212553334      -7.5641602542
    Ag      -1.5751210922      0.5238327185      -9.9892089940
    Ag      -4.1814870442      -1.7663886735      -7.6050834452
    Ag      -0.8822430837      -2.7600722440      -5.1959892962
    Ag      -2.1240266195      -3.8206731623      -2.8525807753
    Ag      3.4578336576      -2.6744062081      -2.8525742581
    Ag      -3.7149452090      -3.2988294197      -5.2034646499
    Ag      1.8985756093      -2.1890139391      -5.1959881717
    Ag      0.6946811325      -3.3828052555      -2.8061234013
    Ag      4.7143519584      -1.5678241605      -5.2034549930
    Ag      1.6023915608      -0.5328957432      -7.5641613132
    Ag      1.2412345786      1.1021928389      -9.9892023582
    Ag      4.5392237030      0.0244593089      -7.6050682929
    Ag      0.0000106997      0.0000013921      -5.1462708001
    Ag      -0.3396832259      1.6541471619      -7.5641597129
    Ag      -2.8450227342      -0.5497019461      -5.1959955618
    Ag      2.8314207151      0.6159878635      -5.1959875699
    Ag      -3.1884901403      1.0603809604      -7.5634515357
    Ag      -1.2364094731      -1.0979217456      -2.7987978362
    Ag      1.5690420034      -0.5218070047      -2.7987993856
    Ag      4.3708278508      0.0708740258      -2.8525785565
    Ag      -4.0450216512      -1.6573690296      -2.8525892410
    Ag      2.5125751829      2.2311280445      -7.5634444475
    Ag      0.6759414795      -3.2915128984      -7.5634430672
    Ag      0.3339235029      -1.6260239766      -9.9892067983
    Ag      1.0324285615      -5.0274542660      -5.1718100987
    Ag      -2.2484187072      -3.9433040680      -7.6050830302
    Ag      3.6204971713      -2.7380910382      -7.6050765656

```

(continues on next page)

(continued from previous page)

```

Ag      -2.4569103660    -2.1817169842    -9.8785349524
Ag      -1.7752961456    -5.4191572521    -5.2192070180
Ag       3.7672926986    -4.2809622136    -5.2191965533
Ag       3.1179002480    -1.0369024811    -9.8785348598
Ag      -1.9491576017     2.1440839896    -5.1959915042
Ag       2.5822650861     2.2930127465    -2.8061239177
Ag      -0.3326165571     1.6197266638    -2.7987957984
Ag       0.9464626101     2.7387205045    -5.1959886567
Ag      -0.5598334280    -4.3819335958    -9.8593641366
Ag      -0.2204924851    -6.0299810786    -7.5512447020
Ag       2.5790329655    -5.4550834512    -7.5512427315
Ag       2.2414383913    -3.8066764388    -9.8593649949
Ag      -2.2907828197     3.9188443502    -7.6050826773
Ag       0.5610225957     4.5044771077    -7.6050819796
Ag      -4.8701069022     1.6196298364    -5.1718125544
Ag      -3.2769317991     1.0897966386    -2.8061340012
Ag      -0.6609450333     3.2186205924    -9.8785392784
Ag      -5.5910570566    -1.1220840757    -5.2192067211
Ag      -2.2467815447     3.7498049589    -2.8525803584
Ag      -0.9993904347     4.8666585643    -5.2034637574
Ag      -3.8054729020     4.2470446290    -5.2192106249
Ag      -3.5149221622     2.6758039407    -9.8593694452
Ag      -4.4173760657    -0.0377981351    -9.8593712497
Ag      -6.0137475245     0.4940463872    -7.5512522368
Ag      -5.1118586671     3.2059431066    -7.5512501894
Ag       0.5871922586     4.3317735603    -2.8525794711
Ag       1.8237836111     5.4030432621    -5.2192000459
Ag       3.8377073288     3.4078339914    -5.1718059272
Ag       5.5807980727     1.1721205307    -5.2191937875
Ag       3.4347425354     4.9610463596    -7.5512390021
Ag       4.0747942310     1.7061247432    -9.8593564188
Ag       5.3323750373     2.8240364209    -7.5512331190
Ag       2.1759755136     3.8444690680    -9.8593641559
Ag      -1.8817544351     2.1073913325    -0.4836595729
Ag       0.8989635719     2.6784284394    -0.4836553279
Ag       0.0000000000     0.0000000000     0.0000000000
Ag       2.7659350940     0.5759533343    -0.4836497308
Ag      -2.7690678527    -0.5606913044    -0.4836604335
Ag      -0.8841719671    -2.6833451220    -0.4836610364
Ag       1.8701101821    -2.1177433283    -0.4836551986
SUBEND
end
dimqm
PIM
JACOBI
ALGORITHM DIRECT
FREQUENCY
LOCALFIELD
end
basis
core none
type TZP
end
symmetry NOSYM
xc
gga Becke Perdew
end

```

(continues on next page)

(continued from previous page)

```

    Relativity
      Level None
    End
  EndEngine
eor

```

Example: PIM: H2O on Ag2689

Download DIMQM_LOCAL.run

```

#!/bin/sh

$AMSBIN/ams <<eor
System
  atoms
    O      0.016560    0.127604    0.000000
    H      0.650009    0.566164    0.000000
    H     -0.666568    0.484010    0.000000
  end
end

Task SinglePoint

Engine ADF
  title ['Local Dim Test']
  allpoints
  beckegrid
    quality good
  end
  dimpar
    Ag
    rad=1.4445
    SUBEND
    XYZ
    $AMSHOME/examples/adf/DIMQM_LOCAL/ag2869.xyz
    SUBEND
  end
  dimqm
    PIM
    LOCALDIM
    debug
    PRINTLJPAR
    niter 2000
    CutOffDist 50.0
  end
  basis
    core None
    type TZP
  end
  symmetry nosym
  xc
    model SAOP
  end

```

(continues on next page)

(continued from previous page)

```

Relativity
  Level None
End
EndEngine

```

```
eor
```

Example: PIM: Polarizability with local fields

Download DIMQM_READLCLFLD.run

```

#!/bin/sh

#####
# FREQUENCY DEPENDENT POLARIZABILITY WITH LOCAL FIELDS
#####

$AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Frequency-Dependent Polarizability w/ Local Fields, N2 on Ag68
  aoresponse
    alda
      frequencies 3.55 [eV]
      lifetime 0.0036749
    end
  beckegrid
    quality good
  end
  dimpar
    Ag
    rad 1.4445
    drude 9.2 0.17 eV
    bound 5.0
    SUBEND
    XYZ
    68
    Ag      -1.2626801699   -1.1212553334   -7.5641602542
    Ag      -1.5751210922    0.5238327185   -9.9892089940
    Ag      -4.1814870442   -1.7663886735   -7.6050834452
    Ag      -0.8822430837   -2.7600722440   -5.1959892962
    Ag      -2.1240266195   -3.8206731623   -2.8525807753
    Ag      3.4578336576    -2.6744062081   -2.8525742581
    Ag      -3.7149452090   -3.2988294197   -5.2034646499
    Ag      1.8985756093    -2.1890139391   -5.1959881717
    Ag      0.6946811325    -3.3828052555   -2.8061234013

```

(continues on next page)

(continued from previous page)

Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366
Ag	-0.2204924851	-6.0299810786	-7.5512447020
Ag	2.5790329655	-5.4550834512	-7.5512427315
Ag	2.2414383913	-3.8066764388	-9.8593649949
Ag	-2.2907828197	3.9188443502	-7.6050826773
Ag	0.5610225957	4.5044771077	-7.6050819796
Ag	-4.8701069022	1.6196298364	-5.1718125544
Ag	-3.2769317991	1.0897966386	-2.8061340012
Ag	-0.6609450333	3.2186205924	-9.8785392784
Ag	-5.5910570566	-1.1220840757	-5.2192067211
Ag	-2.2467815447	3.7498049589	-2.8525803584
Ag	-0.9993904347	4.8666585643	-5.2034637574
Ag	-3.8054729020	4.2470446290	-5.2192106249
Ag	-3.5149221622	2.6758039407	-9.8593694452
Ag	-4.4173760657	-0.0377981351	-9.8593712497
Ag	-6.0137475245	0.4940463872	-7.5512522368
Ag	-5.1118586671	3.2059431066	-7.5512501894
Ag	0.5871922586	4.3317735603	-2.8525794711
Ag	1.8237836111	5.4030432621	-5.2192000459
Ag	3.8377073288	3.4078339914	-5.1718059272
Ag	5.5807980727	1.1721205307	-5.2191937875
Ag	3.4347425354	4.9610463596	-7.5512390021
Ag	4.0747942310	1.7061247432	-9.8593564188
Ag	5.3323750373	2.8240364209	-7.5512331190
Ag	2.1759755136	3.8444690680	-9.8593641559
Ag	-1.8817544351	2.1073913325	-0.4836595729
Ag	0.8989635719	2.6784284394	-0.4836553279
Ag	0.0000000000	0.0000000000	0.0000000000
Ag	2.7659350940	0.5759533343	-0.4836497308
Ag	-2.7690678527	-0.5606913044	-0.4836604335

(continues on next page)

(continued from previous page)

```

    Ag      -0.8841719671   -2.6833451220   -0.4836610364
    Ag      1.8701101821    -2.1177433283   -0.4836551986
  SUBEND
  LCLFLD
  $AMSHOME/examples/adf/DIMQM_READLCLFLD/lclfld.txt
  SUBEND
end
dimqm
  PIM
  FREQUENCY
  LocalField RESP
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: PIM: optimization N2 on silver cluster Ag68

Download DIMQM_Gradients.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to do a geometry optimization with the
# Polarizability Interaction Model (PIM).

$AMSBIN/ams <<eor
System
  atoms
    N      0.0000000000    0.0000000000    2.5000000000
    N      0.0000000000    0.0000000000    3.5000000000
  end
end

Task SinglePoint

Properties
  Gradients Yes
End

Engine ADF
  title DIM/QM Gradient Test, N2 on Ag68

```

(continues on next page)

(continued from previous page)

```

beckegrid
  quality good
end
dimpair
  Ag
  rad=1.4445
SUBEND
XYZ
68
Ag      -1.2626801699   -1.1212553334   -7.5641602542
Ag      -1.5751210922    0.5238327185   -9.9892089940
Ag      -4.1814870442   -1.7663886735   -7.6050834452
Ag      -0.8822430837   -2.7600722440   -5.1959892962
Ag      -2.1240266195   -3.8206731623   -2.8525807753
Ag       3.4578336576   -2.6744062081   -2.8525742581
Ag      -3.7149452090   -3.2988294197   -5.2034646499
Ag       1.8985756093   -2.1890139391   -5.1959881717
Ag       0.6946811325   -3.3828052555   -2.8061234013
Ag       4.7143519584   -1.5678241605   -5.2034549930
Ag       1.6023915608   -0.5328957432   -7.5641613132
Ag       1.2412345786    1.1021928389   -9.9892023582
Ag       4.5392237030    0.0244593089   -7.6050682929
Ag       0.0000106997    0.0000013921   -5.1462708001
Ag      -0.3396832259    1.6541471619   -7.5641597129
Ag      -2.8450227342   -0.5497019461   -5.1959955618
Ag       2.8314207151    0.6159878635   -5.1959875699
Ag      -3.1884901403    1.0603809604   -7.5634515357
Ag      -1.2364094731   -1.0979217456   -2.7987978362
Ag       1.5690420034   -0.5218070047   -2.7987993856
Ag       4.3708278508    0.0708740258   -2.8525785565
Ag      -4.0450216512   -1.6573690296   -2.8525892410
Ag       2.5125751829    2.2311280445   -7.5634444475
Ag       0.6759414795   -3.2915128984   -7.5634430672
Ag       0.3339235029   -1.6260239766   -9.9892067983
Ag       1.0324285615   -5.0274542660   -5.1718100987
Ag      -2.2484187072   -3.9433040680   -7.6050830302
Ag       3.6204971713   -2.7380910382   -7.6050765656
Ag      -2.4569103660   -2.1817169842   -9.8785349524
Ag      -1.7752961456   -5.4191572521   -5.2192070180
Ag       3.7672926986   -4.2809622136   -5.2191965533
Ag       3.1179002480   -1.0369024811   -9.8785348598
Ag      -1.9491576017    2.1440839896   -5.1959915042
Ag       2.5822650861    2.2930127465   -2.8061239177
Ag      -0.3326165571    1.6197266638   -2.7987957984
Ag       0.9464626101    2.7387205045   -5.1959886567
Ag      -0.5598334280   -4.3819335958   -9.8593641366
Ag      -0.2204924851   -6.0299810786   -7.5512447020
Ag       2.5790329655   -5.4550834512   -7.5512427315
Ag       2.2414383913   -3.8066764388   -9.8593649949
Ag      -2.2907828197    3.9188443502   -7.6050826773
Ag       0.5610225957    4.5044771077   -7.6050819796
Ag      -4.8701069022    1.6196298364   -5.1718125544
Ag      -3.2769317991    1.0897966386   -2.8061340012
Ag      -0.6609450333    3.2186205924   -9.8785392784
Ag      -5.5910570566   -1.1220840757   -5.2192067211
Ag      -2.2467815447    3.7498049589   -2.8525803584
Ag      -0.9993904347    4.8666585643   -5.2034637574

```

(continues on next page)

(continued from previous page)

```

Ag      -3.8054729020    4.2470446290   -5.2192106249
Ag      -3.5149221622    2.6758039407   -9.8593694452
Ag      -4.4173760657   -0.0377981351   -9.8593712497
Ag      -6.0137475245    0.4940463872   -7.5512522368
Ag      -5.1118586671    3.2059431066   -7.5512501894
Ag      0.5871922586     4.3317735603   -2.8525794711
Ag      1.8237836111     5.4030432621   -5.2192000459
Ag      3.8377073288     3.4078339914   -5.1718059272
Ag      5.5807980727     1.1721205307   -5.2191937875
Ag      3.4347425354     4.9610463596   -7.5512390021
Ag      4.0747942310     1.7061247432   -9.8593564188
Ag      5.3323750373     2.8240364209   -7.5512331190
Ag      2.1759755136     3.8444690680   -9.8593641559
Ag      -1.8817544351     2.1073913325   -0.4836595729
Ag      0.8989635719     2.6784284394   -0.4836553279
Ag      0.0000000000     0.0000000000    0.0000000000
Ag      2.7659350940     0.5759533343   -0.4836497308
Ag      -2.7690678527   -0.5606913044   -0.4836604335
Ag      -0.8841719671   -2.6833451220   -0.4836610364
Ag      1.8701101821   -2.1177433283   -0.4836551986
SUBEND
end
dimqm
PIM
ALGORITHM DIRECT
SCREEN EXP 1.0
FORCEFIELD LJ12-6
COORDDEPEND
CHEMISORPTION
COORDPAR  Ag    0.003000  0.000800  3.250000  3.650000  12.000000  9.448600  5.
↪669200
CHEMPAR   N      0.275000  0.052500  0.800000  0.900000  4.913000
DEBUG
end
basis
  core none
  type TZP
end
save TAPE21
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

```


Example: PIM: polarizability N2 on silver cluster Ag68

Download DIMQM_PIM_Pol.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to do calculate static and frequency dependent
# polarizabilities with the Polarizability Interaction Model (PIM). The example
# consists of 3 calculations: static polarizability, frequency dependent, and
# with inclusion of effect of the local field.

# When the molecule interacts with a metal nanoparticle, there are two types of
# interactions: the image field and the local field. The image field is caused
# by the dipoles induced into the nanoparticle by the molecule's electron
# density. This is always taken into account in a DIM/QM calculation. The local
# field arises by direct interactions of the nanoparticle with an external
# field. Addition of the LOCALFIELD key causes the DIM/QM calculation to include
# this effect, but by default this is not included in a DIM/QM calculation.

#####
# STATIC POLARIZABILITY
#####

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Static Polarizability, N2 on Ag68
  aoresponse
    alda
  end
  beckeGRID
    quality good
  end
  dimpar
    Ag
    rad 1.4445
    drude 9.2 0.17 eV
    bound 5.0
    SUBEND
    XYZ
    68
    Ag      -1.2626801699   -1.1212553334   -7.5641602542
    Ag      -1.5751210922    0.5238327185   -9.9892089940
    Ag      -4.1814870442   -1.7663886735   -7.6050834452
    Ag      -0.8822430837   -2.7600722440   -5.1959892962
    Ag      -2.1240266195   -3.8206731623   -2.8525807753

```

(continues on next page)

(continued from previous page)

Ag	3.4578336576	-2.6744062081	-2.8525742581
Ag	-3.7149452090	-3.2988294197	-5.2034646499
Ag	1.8985756093	-2.1890139391	-5.1959881717
Ag	0.6946811325	-3.3828052555	-2.8061234013
Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366
Ag	-0.2204924851	-6.0299810786	-7.5512447020
Ag	2.5790329655	-5.4550834512	-7.5512427315
Ag	2.2414383913	-3.8066764388	-9.8593649949
Ag	-2.2907828197	3.9188443502	-7.6050826773
Ag	0.5610225957	4.5044771077	-7.6050819796
Ag	-4.8701069022	1.6196298364	-5.1718125544
Ag	-3.2769317991	1.0897966386	-2.8061340012
Ag	-0.6609450333	3.2186205924	-9.8785392784
Ag	-5.5910570566	-1.1220840757	-5.2192067211
Ag	-2.2467815447	3.7498049589	-2.8525803584
Ag	-0.9993904347	4.8666585643	-5.2034637574
Ag	-3.8054729020	4.2470446290	-5.2192106249
Ag	-3.5149221622	2.6758039407	-9.8593694452
Ag	-4.4173760657	-0.0377981351	-9.8593712497
Ag	-6.0137475245	0.4940463872	-7.5512522368
Ag	-5.1118586671	3.2059431066	-7.5512501894
Ag	0.5871922586	4.3317735603	-2.8525794711
Ag	1.8237836111	5.4030432621	-5.2192000459
Ag	3.8377073288	3.4078339914	-5.1718059272
Ag	5.5807980727	1.1721205307	-5.2191937875
Ag	3.4347425354	4.9610463596	-7.5512390021
Ag	4.0747942310	1.7061247432	-9.8593564188
Ag	5.3323750373	2.8240364209	-7.5512331190
Ag	2.1759755136	3.8444690680	-9.8593641559
Ag	-1.8817544351	2.1073913325	-0.4836595729

(continues on next page)

(continued from previous page)

```

    Ag      0.8989635719    2.6784284394   -0.4836553279
    Ag      0.0000000000    0.0000000000    0.0000000000
    Ag      2.7659350940    0.5759533343   -0.4836497308
    Ag     -2.7690678527   -0.5606913044   -0.4836604335
    Ag     -0.8841719671   -2.6833451220   -0.4836610364
    Ag      1.8701101821   -2.1177433283   -0.4836551986
  SUBEND
end
dimqm
  PIM
  ALGORITHM BRUTE
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY
#####

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006    -0.000060    2.302488
    N       0.000019     0.000041    3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Frequency-Dependent Polarizability, N2 on Ag68
  aoresponse
    alda
    frequencies 3.55 [eV]
    lifetime 0.0036749
  end
  beckegrid
    quality good
  end
  dimpar
    Ag
    rad 1.4445
    drude 9.2 0.17 eV
    bound 5.0
  SUBEND

```

(continues on next page)

(continued from previous page)

XYZ			
68			
Ag	-1.2626801699	-1.1212553334	-7.5641602542
Ag	-1.5751210922	0.5238327185	-9.9892089940
Ag	-4.1814870442	-1.7663886735	-7.6050834452
Ag	-0.8822430837	-2.7600722440	-5.1959892962
Ag	-2.1240266195	-3.8206731623	-2.8525807753
Ag	3.4578336576	-2.6744062081	-2.8525742581
Ag	-3.7149452090	-3.2988294197	-5.2034646499
Ag	1.8985756093	-2.1890139391	-5.1959881717
Ag	0.6946811325	-3.3828052555	-2.8061234013
Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366
Ag	-0.2204924851	-6.0299810786	-7.5512447020
Ag	2.5790329655	-5.4550834512	-7.5512427315
Ag	2.2414383913	-3.8066764388	-9.8593649949
Ag	-2.2907828197	3.9188443502	-7.6050826773
Ag	0.5610225957	4.5044771077	-7.6050819796
Ag	-4.8701069022	1.6196298364	-5.1718125544
Ag	-3.2769317991	1.0897966386	-2.8061340012
Ag	-0.6609450333	3.2186205924	-9.8785392784
Ag	-5.5910570566	-1.1220840757	-5.2192067211
Ag	-2.2467815447	3.7498049589	-2.8525803584
Ag	-0.9993904347	4.8666585643	-5.2034637574
Ag	-3.8054729020	4.2470446290	-5.2192106249
Ag	-3.5149221622	2.6758039407	-9.8593694452
Ag	-4.4173760657	-0.0377981351	-9.8593712497
Ag	-6.0137475245	0.4940463872	-7.5512522368
Ag	-5.1118586671	3.2059431066	-7.5512501894
Ag	0.5871922586	4.3317735603	-2.8525794711
Ag	1.8237836111	5.4030432621	-5.2192000459

(continues on next page)

(continued from previous page)

```

      Ag      3.8377073288      3.4078339914      -5.1718059272
      Ag      5.5807980727      1.1721205307      -5.2191937875
      Ag      3.4347425354      4.9610463596      -7.5512390021
      Ag      4.0747942310      1.7061247432      -9.8593564188
      Ag      5.3323750373      2.8240364209      -7.5512331190
      Ag      2.1759755136      3.8444690680      -9.8593641559
      Ag      -1.8817544351      2.1073913325      -0.4836595729
      Ag      0.8989635719      2.6784284394      -0.4836553279
      Ag      0.0000000000      0.0000000000      0.0000000000
      Ag      2.7659350940      0.5759533343      -0.4836497308
      Ag      -2.7690678527      -0.5606913044      -0.4836604335
      Ag      -0.8841719671      -2.6833451220      -0.4836610364
      Ag      1.8701101821      -2.1177433283      -0.4836551986
    SUBEND
  end
  dimqm
  PIM
  ALGORITHM BRUTE
  FREQUENCY
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine

eor

#####
# FREQUENCY DEPENDENT POLARIZABILITY WITH LOCAL FIELDS
#####

AMS_JOBNAME=third $AMSBIN/ams <<eor
System
  atoms
    N      -0.000006      -0.000060      2.302488
    N      0.000019      0.000041      3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Frequency-Dependent Polarizability w/ Local Fields, N2 on Ag68
  aoresponse
    alda
    frequencies 3.55 [eV]
    lifetime 0.0036749
  end
  beckegrid

```

(continues on next page)

(continued from previous page)

```

quality good
end
dimpair
  Ag
  rad 1.4445
  drude 9.2 0.17 eV
  bound 5.0
SUBEND
XYZ
68
Ag      -1.2626801699   -1.1212553334   -7.5641602542
Ag      -1.5751210922    0.5238327185   -9.9892089940
Ag      -4.1814870442   -1.7663886735   -7.6050834452
Ag      -0.8822430837   -2.7600722440   -5.1959892962
Ag      -2.1240266195   -3.8206731623   -2.8525807753
Ag       3.4578336576   -2.6744062081   -2.8525742581
Ag      -3.7149452090   -3.2988294197   -5.2034646499
Ag       1.8985756093   -2.1890139391   -5.1959881717
Ag       0.6946811325   -3.3828052555   -2.8061234013
Ag       4.7143519584   -1.5678241605   -5.2034549930
Ag       1.6023915608   -0.5328957432   -7.5641613132
Ag       1.2412345786    1.1021928389   -9.9892023582
Ag       4.5392237030    0.0244593089   -7.6050682929
Ag       0.0000106997    0.0000013921   -5.1462708001
Ag      -0.3396832259    1.6541471619   -7.5641597129
Ag      -2.8450227342   -0.5497019461   -5.1959955618
Ag       2.8314207151    0.6159878635   -5.1959875699
Ag      -3.1884901403    1.0603809604   -7.5634515357
Ag      -1.2364094731   -1.0979217456   -2.7987978362
Ag       1.5690420034   -0.5218070047   -2.7987993856
Ag       4.3708278508    0.0708740258   -2.8525785565
Ag      -4.0450216512   -1.6573690296   -2.8525892410
Ag       2.5125751829    2.2311280445   -7.5634444475
Ag       0.6759414795   -3.2915128984   -7.5634430672
Ag       0.3339235029   -1.6260239766   -9.9892067983
Ag       1.0324285615   -5.0274542660   -5.1718100987
Ag      -2.2484187072   -3.9433040680   -7.6050830302
Ag       3.6204971713   -2.7380910382   -7.6050765656
Ag      -2.4569103660   -2.1817169842   -9.8785349524
Ag      -1.7752961456   -5.4191572521   -5.2192070180
Ag       3.7672926986   -4.2809622136   -5.2191965533
Ag       3.1179002480   -1.0369024811   -9.8785348598
Ag      -1.9491576017    2.1440839896   -5.1959915042
Ag       2.5822650861    2.2930127465   -2.8061239177
Ag      -0.3326165571    1.6197266638   -2.7987957984
Ag       0.9464626101    2.7387205045   -5.1959886567
Ag      -0.5598334280   -4.3819335958   -9.8593641366
Ag      -0.2204924851   -6.0299810786   -7.5512447020
Ag       2.5790329655   -5.4550834512   -7.5512427315
Ag       2.2414383913   -3.8066764388   -9.8593649949
Ag      -2.2907828197    3.9188443502   -7.6050826773
Ag       0.5610225957    4.5044771077   -7.6050819796
Ag      -4.8701069022    1.6196298364   -5.1718125544
Ag      -3.2769317991    1.0897966386   -2.8061340012
Ag      -0.6609450333    3.2186205924   -9.8785392784
Ag      -5.5910570566   -1.1220840757   -5.2192067211
Ag      -2.2467815447    3.7498049589   -2.8525803584

```

(continues on next page)

(continued from previous page)

```

Ag      -0.9993904347    4.8666585643   -5.2034637574
Ag      -3.8054729020    4.2470446290   -5.2192106249
Ag      -3.5149221622    2.6758039407   -9.8593694452
Ag      -4.4173760657   -0.0377981351   -9.8593712497
Ag      -6.0137475245    0.4940463872   -7.5512522368
Ag      -5.1118586671    3.2059431066   -7.5512501894
Ag       0.5871922586    4.3317735603   -2.8525794711
Ag       1.8237836111    5.4030432621   -5.2192000459
Ag       3.8377073288    3.4078339914   -5.1718059272
Ag       5.5807980727    1.1721205307   -5.2191937875
Ag       3.4347425354    4.9610463596   -7.5512390021
Ag       4.0747942310    1.7061247432   -9.8593564188
Ag       5.3323750373    2.8240364209   -7.5512331190
Ag       2.1759755136    3.8444690680   -9.8593641559
Ag      -1.8817544351    2.1073913325   -0.4836595729
Ag       0.8989635719    2.6784284394   -0.4836553279
Ag       0.0000000000    0.0000000000    0.0000000000
Ag       2.7659350940    0.5759533343   -0.4836497308
Ag      -2.7690678527   -0.5606913044   -0.4836604335
Ag      -0.8841719671   -2.6833451220   -0.4836610364
Ag       1.8701101821   -2.1177433283   -0.4836551986
SUBEND
end
dimqm
  PIM
  ALGORITHM DIRECT
  FREQUENCY
  LOCALFIELD
end
basis
  core none
  type TZP
end
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: PIM: Raman scattering N2 on silver cluster Ag68

Download DIMQM_Raman.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to calculate Raman scattering with the
# Polarizability Interaction Model (PIM). AORESPONSE is used and numerical
# frequencies.

```

(continues on next page)

(continued from previous page)

```
# Allowing for all rigid motions gives a very different result, suggesting to the non-
→expert that the example may be wrong
```

```
$AMSBIN/ams <<eor
```

```
# RigidMotions AllowRotations=all AllowTranslations=all
```

```
# log
# debug RigidMotionsConfigModule
# debug NormalModes
# debug RigidMotionsProjectorModule
# end
```

```
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end
```

```
Task SinglePoint
```

```
Properties
  NormalModes True
  Raman True
```

```
End
```

```
Raman
  IncidentFrequency 3.55 [eV]
  Lifetime 0.0036749
```

```
End
```

```
Engine ADF
```

```
  title DIM/QM Raman Calculation, N2 on Ag68
```

```
  responseformalism AORESPONSE
```

```
  allpoints
```

```
  beckegrid
```

```
    quality good
```

```
end
```

```
dimpar
```

```
  Ag
```

```
  rad=1.4445
```

```
  drude 9.2 0.17 eV
```

```
  bound 5.0
```

```
  SUBEND
```

```
  XYZ
```

```
  68
```

```
  Ag      -1.2626801699   -1.1212553334   -7.5641602542
```

```
  Ag      -1.5751210922    0.5238327185   -9.9892089940
```

```
  Ag      -4.1814870442   -1.7663886735   -7.6050834452
```

```
  Ag      -0.8822430837   -2.7600722440   -5.1959892962
```

```
  Ag      -2.1240266195   -3.8206731623   -2.8525807753
```

```
  Ag      3.4578336576    -2.6744062081   -2.8525742581
```

```
  Ag      -3.7149452090   -3.2988294197   -5.2034646499
```

```
  Ag      1.8985756093    -2.1890139391   -5.1959881717
```

```
  Ag      0.6946811325    -3.3828052555   -2.8061234013
```

(continues on next page)

(continued from previous page)

Ag	4.7143519584	-1.5678241605	-5.2034549930
Ag	1.6023915608	-0.5328957432	-7.5641613132
Ag	1.2412345786	1.1021928389	-9.9892023582
Ag	4.5392237030	0.0244593089	-7.6050682929
Ag	0.0000106997	0.0000013921	-5.1462708001
Ag	-0.3396832259	1.6541471619	-7.5641597129
Ag	-2.8450227342	-0.5497019461	-5.1959955618
Ag	2.8314207151	0.6159878635	-5.1959875699
Ag	-3.1884901403	1.0603809604	-7.5634515357
Ag	-1.2364094731	-1.0979217456	-2.7987978362
Ag	1.5690420034	-0.5218070047	-2.7987993856
Ag	4.3708278508	0.0708740258	-2.8525785565
Ag	-4.0450216512	-1.6573690296	-2.8525892410
Ag	2.5125751829	2.2311280445	-7.5634444475
Ag	0.6759414795	-3.2915128984	-7.5634430672
Ag	0.3339235029	-1.6260239766	-9.9892067983
Ag	1.0324285615	-5.0274542660	-5.1718100987
Ag	-2.2484187072	-3.9433040680	-7.6050830302
Ag	3.6204971713	-2.7380910382	-7.6050765656
Ag	-2.4569103660	-2.1817169842	-9.8785349524
Ag	-1.7752961456	-5.4191572521	-5.2192070180
Ag	3.7672926986	-4.2809622136	-5.2191965533
Ag	3.1179002480	-1.0369024811	-9.8785348598
Ag	-1.9491576017	2.1440839896	-5.1959915042
Ag	2.5822650861	2.2930127465	-2.8061239177
Ag	-0.3326165571	1.6197266638	-2.7987957984
Ag	0.9464626101	2.7387205045	-5.1959886567
Ag	-0.5598334280	-4.3819335958	-9.8593641366
Ag	-0.2204924851	-6.0299810786	-7.5512447020
Ag	2.5790329655	-5.4550834512	-7.5512427315
Ag	2.2414383913	-3.8066764388	-9.8593649949
Ag	-2.2907828197	3.9188443502	-7.6050826773
Ag	0.5610225957	4.5044771077	-7.6050819796
Ag	-4.8701069022	1.6196298364	-5.1718125544
Ag	-3.2769317991	1.0897966386	-2.8061340012
Ag	-0.6609450333	3.2186205924	-9.8785392784
Ag	-5.5910570566	-1.1220840757	-5.2192067211
Ag	-2.2467815447	3.7498049589	-2.8525803584
Ag	-0.9993904347	4.8666585643	-5.2034637574
Ag	-3.8054729020	4.2470446290	-5.2192106249
Ag	-3.5149221622	2.6758039407	-9.8593694452
Ag	-4.4173760657	-0.0377981351	-9.8593712497
Ag	-6.0137475245	0.4940463872	-7.5512522368
Ag	-5.1118586671	3.2059431066	-7.5512501894
Ag	0.5871922586	4.3317735603	-2.8525794711
Ag	1.8237836111	5.4030432621	-5.2192000459
Ag	3.8377073288	3.4078339914	-5.1718059272
Ag	5.5807980727	1.1721205307	-5.2191937875
Ag	3.4347425354	4.9610463596	-7.5512390021
Ag	4.0747942310	1.7061247432	-9.8593564188
Ag	5.3323750373	2.8240364209	-7.5512331190
Ag	2.1759755136	3.8444690680	-9.8593641559
Ag	-1.8817544351	2.1073913325	-0.4836595729
Ag	0.8989635719	2.6784284394	-0.4836553279
Ag	0.0000000000	0.0000000000	0.0000000000
Ag	2.7659350940	0.5759533343	-0.4836497308
Ag	-2.7690678527	-0.5606913044	-0.4836604335

(continues on next page)

(continued from previous page)

```

    Ag      -0.8841719671   -2.6833451220   -0.4836610364
    Ag      1.8701101821   -2.1177433283   -0.4836551986
    SUBEND
end
dimqm
  PIM
  ALGORITHM DIRECT
  SCREEN EXP 1.0
  FORCEFIELD LJ12-6
  COORDDEPEND
  CHEMISORPTION
  COORDPAR Ag 0.003000 0.000800 3.250000 3.650000 12.000000 9.448600 5.
→ 669200
  CHEMPAR N 0.275000 0.052500 0.800000 0.900000 4.913000
  FREQUENCY
  LOCALFIELD
end
basis
  core none
  type TZP
end
save TAPE21
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: PIM: SEROA calculation N2 on silver cluster Ag68

Download DIMQM_SEROA.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to calculate Surface-Enhanced Raman Optical
# Activity (SEROA) with the Polarizability Interaction Model (PIM). AORESPONSE
# is used and numerical frequencies.

$AMSBIN/ams <<eor
System
  atoms
    N      -0.000097   -0.000310   2.997901
    N      0.000076    0.000133   4.095604
  end
end
Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Properties
  VROA
End
Raman
  IncidentFrequency 5.0 [eV]
  Lifetime 0.0037
End

Engine ADF
  title DIM/QM SEROA Calculation, N2 on Ag68
  dimqm
    PIM
    ALGORITHM DIRECT
    SCREEN GAU 1.0
    FORCEFIELD LJ12-6
    FREQUENCY
    LOCALFIELD
  end
  exactdensity
  NumericalQuality Good
  basis
    type TZP
  end
  symmetry NoSym
  dimpar
    Ag
    rad=1.4445
    drude 5.0 0.1 eV
    bound 5.0
  SUBEND
  XYZ
  68
  Ag      -1.2626801699   -1.1212553334   -7.5641602542
  Ag      -1.5751210922    0.5238327185   -9.9892089940
  Ag      -4.1814870442   -1.7663886735   -7.6050834452
  Ag      -0.8822430837   -2.7600722440   -5.1959892962
  Ag      -2.1240266195   -3.8206731623   -2.8525807753
  Ag       3.4578336576   -2.6744062081   -2.8525742581
  Ag      -3.7149452090   -3.2988294197   -5.2034646499
  Ag       1.8985756093   -2.1890139391   -5.1959881717
  Ag       0.6946811325   -3.3828052555   -2.8061234013
  Ag       4.7143519584   -1.5678241605   -5.2034549930
  Ag       1.6023915608   -0.5328957432   -7.5641613132
  Ag       1.2412345786    1.1021928389   -9.9892023582
  Ag       4.5392237030    0.0244593089   -7.6050682929
  Ag       0.0000106997    0.0000013921   -5.1462708001
  Ag      -0.3396832259    1.6541471619   -7.5641597129
  Ag      -2.8450227342   -0.5497019461   -5.1959955618
  Ag       2.8314207151    0.6159878635   -5.1959875699
  Ag      -3.1884901403    1.0603809604   -7.5634515357
  Ag      -1.2364094731   -1.0979217456   -2.7987978362
  Ag       1.5690420034   -0.5218070047   -2.7987993856
  Ag       4.3708278508    0.0708740258   -2.8525785565
  Ag      -4.0450216512   -1.6573690296   -2.8525892410
  Ag       2.5125751829    2.2311280445   -7.5634444475
  Ag       0.6759414795   -3.2915128984   -7.5634430672
  Ag       0.3339235029   -1.6260239766   -9.9892067983

```

(continues on next page)

(continued from previous page)

```

Ag      1.0324285615    -5.0274542660    -5.1718100987
Ag      -2.2484187072    -3.9433040680    -7.6050830302
Ag       3.6204971713    -2.7380910382    -7.6050765656
Ag      -2.4569103660    -2.1817169842    -9.8785349524
Ag      -1.7752961456    -5.4191572521    -5.2192070180
Ag       3.7672926986    -4.2809622136    -5.2191965533
Ag       3.1179002480    -1.0369024811    -9.8785348598
Ag      -1.9491576017     2.1440839896    -5.1959915042
Ag       2.5822650861     2.2930127465    -2.8061239177
Ag      -0.3326165571     1.6197266638    -2.7987957984
Ag       0.9464626101     2.7387205045    -5.1959886567
Ag      -0.5598334280    -4.3819335958    -9.8593641366
Ag      -0.2204924851    -6.0299810786    -7.5512447020
Ag       2.5790329655    -5.4550834512    -7.5512427315
Ag       2.2414383913    -3.8066764388    -9.8593649949
Ag      -2.2907828197     3.9188443502    -7.6050826773
Ag       0.5610225957     4.5044771077    -7.6050819796
Ag      -4.8701069022     1.6196298364    -5.1718125544
Ag      -3.2769317991     1.0897966386    -2.8061340012
Ag      -0.6609450333     3.2186205924    -9.8785392784
Ag      -5.5910570566    -1.1220840757    -5.2192067211
Ag      -2.2467815447     3.7498049589    -2.8525803584
Ag      -0.9993904347     4.8666585643    -5.2034637574
Ag      -3.8054729020     4.2470446290    -5.2192106249
Ag      -3.5149221622     2.6758039407    -9.8593694452
Ag      -4.4173760657    -0.0377981351    -9.8593712497
Ag      -6.0137475245     0.4940463872    -7.5512522368
Ag      -5.1118586671     3.2059431066    -7.5512501894
Ag       0.5871922586     4.3317735603    -2.8525794711
Ag       1.8237836111     5.4030432621    -5.2192000459
Ag       3.8377073288     3.4078339914    -5.1718059272
Ag       5.5807980727     1.1721205307    -5.2191937875
Ag       3.4347425354     4.9610463596    -7.5512390021
Ag       4.0747942310     1.7061247432    -9.8593564188
Ag       5.3323750373     2.8240364209    -7.5512331190
Ag       2.1759755136     3.8444690680    -9.8593641559
Ag      -1.8817544351     2.1073913325    -0.4836595729
Ag       0.8989635719     2.6784284394    -0.4836553279
Ag       0.0000000000     0.0000000000     0.0000000000
Ag       2.7659350940     0.5759533343    -0.4836497308
Ag      -2.7690678527    -0.5606913044    -0.4836604335
Ag      -0.8841719671    -2.6833451220    -0.4836610364
Ag       1.8701101821    -2.1177433283    -0.4836551986
SUBEND
end
Relativity
  Level None
End
EndEngine
eor

```

Example: PIM: Multipole Method N2 on silver cluster Ag1415

Download DIMQM_PIM_CMM.run

```

#!/bin/sh

# == Expert option ==

# This example demonstrates how to do a single point calculation with the
# Polarizability Interaction Model (PIM), for a large metal cluster.

$AMSBIN/ams <<eor
System
  atoms
    N      -0.000006   -0.000060   2.302488
    N      0.000019    0.000041   3.408628
  end
end

Task SinglePoint

Engine ADF
  title PIM Cell Multipole Method Test, N2 on Ag1415
  dimqm
    PIM
    ALGORITHM MULTI
    MULTIPLIER 0.683 0.517 1.1301
  end
  basis
    core none
    type TZP
  end
  symmetry NOSYM
  xc
    gga Becke Perdew
  end
  beckegrid
    quality good
  end
  Relativity
    Level None
End
  dimpar
    Ag
    rad 1.4445
    SUBEND
    XYZ
    1415
    Ag      0.00000000   0.00000000  -17.21195420
    Ag      2.88900000   0.00000000  -17.21195420
    Ag      5.77800000   0.00000000  -17.21195420
    Ag      8.66700000   0.00000000  -17.21195420
    Ag     11.55600000   0.00000000  -17.21195420
    Ag     14.44500000   0.00000000  -17.21195420
    Ag     17.33400000   0.00000000  -17.21195420
    Ag     20.22300000   0.00000000  -17.21195420

```

(continues on next page)

(continued from previous page)

Ag	1.29138300	2.58276600	-17.21195420
Ag	4.18038300	2.58276600	-17.21195420
Ag	7.06938300	2.58276600	-17.21195420
Ag	9.95838300	2.58276600	-17.21195420
Ag	12.84738300	2.58276600	-17.21195420
Ag	15.73638300	2.58276600	-17.21195420
Ag	18.62538300	2.58276600	-17.21195420
Ag	2.58276600	5.16553200	-17.21195420
Ag	5.47176600	5.16553200	-17.21195420
Ag	8.36076600	5.16553200	-17.21195420
Ag	11.24976600	5.16553200	-17.21195420
Ag	14.13876600	5.16553200	-17.21195420
Ag	17.02776600	5.16553200	-17.21195420
Ag	3.87414900	7.74829800	-17.21195420
Ag	6.76314900	7.74829800	-17.21195420
Ag	9.65214900	7.74829800	-17.21195420
Ag	12.54114900	7.74829800	-17.21195420
Ag	15.43014900	7.74829800	-17.21195420
Ag	5.16553200	10.33106400	-17.21195420
Ag	8.05453200	10.33106400	-17.21195420
Ag	10.94353200	10.33106400	-17.21195420
Ag	13.83253200	10.33106400	-17.21195420
Ag	6.45691500	12.91383000	-17.21195420
Ag	9.34591500	12.91383000	-17.21195420
Ag	12.23491500	12.91383000	-17.21195420
Ag	7.74829800	15.49659600	-17.21195420
Ag	10.63729800	15.49659600	-17.21195420
Ag	9.03968100	18.07936200	-17.21195420
Ag	1.29716100	0.80314200	-14.75919320
Ag	4.18616100	0.80314200	-14.75919320
Ag	7.07516100	0.80314200	-14.75919320
Ag	9.96416100	0.80314200	-14.75919320
Ag	12.85316100	0.80314200	-14.75919320
Ag	15.74216100	0.80314200	-14.75919320
Ag	18.63116100	0.80314200	-14.75919320
Ag	2.58854400	3.38590800	-14.75919320
Ag	5.47754400	3.38590800	-14.75919320
Ag	8.36654400	3.38590800	-14.75919320
Ag	11.25554400	3.38590800	-14.75919320
Ag	14.14454400	3.38590800	-14.75919320
Ag	17.03354400	3.38590800	-14.75919320
Ag	3.87992700	5.96867400	-14.75919320
Ag	6.76892700	5.96867400	-14.75919320
Ag	9.65792700	5.96867400	-14.75919320
Ag	12.54692700	5.96867400	-14.75919320
Ag	15.43592700	5.96867400	-14.75919320
Ag	5.17131000	8.55144000	-14.75919320
Ag	8.06031000	8.55144000	-14.75919320
Ag	10.94931000	8.55144000	-14.75919320
Ag	13.83831000	8.55144000	-14.75919320
Ag	6.46269300	11.13420600	-14.75919320
Ag	9.35169300	11.13420600	-14.75919320
Ag	12.24069300	11.13420600	-14.75919320
Ag	7.75407600	13.71697200	-14.75919320
Ag	10.64307600	13.71697200	-14.75919320
Ag	9.04545900	16.29973800	-14.75919320
Ag	2.59432200	1.60628400	-12.30643220

(continues on next page)

(continued from previous page)

Ag	5.48332200	1.60628400	-12.30643220
Ag	8.37232200	1.60628400	-12.30643220
Ag	11.26132200	1.60628400	-12.30643220
Ag	14.15032200	1.60628400	-12.30643220
Ag	17.03932200	1.60628400	-12.30643220
Ag	3.88570500	4.18905000	-12.30643220
Ag	6.77470500	4.18905000	-12.30643220
Ag	9.66370500	4.18905000	-12.30643220
Ag	12.55270500	4.18905000	-12.30643220
Ag	15.44170500	4.18905000	-12.30643220
Ag	5.17708800	6.77181600	-12.30643220
Ag	8.06608800	6.77181600	-12.30643220
Ag	10.95508800	6.77181600	-12.30643220
Ag	13.84408800	6.77181600	-12.30643220
Ag	6.46847100	9.35458200	-12.30643220
Ag	9.35747100	9.35458200	-12.30643220
Ag	12.24647100	9.35458200	-12.30643220
Ag	7.75985400	11.93734800	-12.30643220
Ag	10.64885400	11.93734800	-12.30643220
Ag	9.05123700	14.52011400	-12.30643220
Ag	3.89148300	2.40942600	-9.85367120
Ag	6.78048300	2.40942600	-9.85367120
Ag	9.66948300	2.40942600	-9.85367120
Ag	12.55848300	2.40942600	-9.85367120
Ag	15.44748300	2.40942600	-9.85367120
Ag	5.18286600	4.99219200	-9.85367120
Ag	8.07186600	4.99219200	-9.85367120
Ag	10.96086600	4.99219200	-9.85367120
Ag	13.84986600	4.99219200	-9.85367120
Ag	6.47424900	7.57495800	-9.85367120
Ag	9.36324900	7.57495800	-9.85367120
Ag	12.25224900	7.57495800	-9.85367120
Ag	7.76563200	10.15772400	-9.85367120
Ag	10.65463200	10.15772400	-9.85367120
Ag	9.05701500	12.74049000	-9.85367120
Ag	5.18864400	3.21256800	-7.40091020
Ag	8.07764400	3.21256800	-7.40091020
Ag	10.96664400	3.21256800	-7.40091020
Ag	13.85564400	3.21256800	-7.40091020
Ag	6.48002700	5.79533400	-7.40091020
Ag	9.36902700	5.79533400	-7.40091020
Ag	12.25802700	5.79533400	-7.40091020
Ag	7.77141000	8.37810000	-7.40091020
Ag	10.66041000	8.37810000	-7.40091020
Ag	9.06279300	10.96086600	-7.40091020
Ag	6.48580500	4.01571000	-4.94814920
Ag	9.37480500	4.01571000	-4.94814920
Ag	12.26380500	4.01571000	-4.94814920
Ag	7.77718800	6.59847600	-4.94814920
Ag	10.66618800	6.59847600	-4.94814920
Ag	9.06857100	9.18124200	-4.94814920
Ag	7.78296600	4.81885200	-2.49538820
Ag	10.67196600	4.81885200	-2.49538820
Ag	9.07434900	7.40161800	-2.49538820
Ag	9.08012700	5.62199400	-0.04262720
Ag	-1.28560500	2.09163600	-15.69234020
Ag	0.01155600	2.89188900	-13.23957920

(continues on next page)

(continued from previous page)

Ag	1.30871700	3.69214200	-10.78681820
Ag	2.60587800	4.49239500	-8.33405720
Ag	3.90303900	5.29264800	-5.88129620
Ag	5.20020000	6.09290100	-3.42853520
Ag	6.49736100	6.89315400	-0.97577420
Ag	0.00577800	4.67440200	-15.69234020
Ag	1.30293900	5.47465500	-13.23957920
Ag	2.60010000	6.27490800	-10.78681820
Ag	3.89726100	7.07516100	-8.33405720
Ag	5.19442200	7.87541400	-5.88129620
Ag	6.49158300	8.67566700	-3.42853520
Ag	1.29716100	7.25716800	-15.69234020
Ag	2.59432200	8.05742100	-13.23957920
Ag	3.89148300	8.85767400	-10.78681820
Ag	5.18864400	9.65792700	-8.33405720
Ag	6.48580500	10.45818000	-5.88129620
Ag	2.58854400	9.83993400	-15.69234020
Ag	3.88570500	10.64018700	-13.23957920
Ag	5.18286600	11.44044000	-10.78681820
Ag	6.48002700	12.24069300	-8.33405720
Ag	3.87992700	12.42270000	-15.69234020
Ag	5.17708800	13.22295300	-13.23957920
Ag	6.47424900	14.02320600	-10.78681820
Ag	5.17131000	15.00546600	-15.69234020
Ag	6.46847100	15.80571900	-13.23957920
Ag	6.46269300	17.58823200	-15.69234020
Ag	-2.57121000	4.18327200	-14.17272620
Ag	-1.27404900	4.98352500	-11.71996520
Ag	0.02311200	5.78377800	-9.26720420
Ag	1.32027300	6.58403100	-6.81444320
Ag	2.61743400	7.38428400	-4.36168220
Ag	3.91459500	8.18453700	-1.90892120
Ag	-1.27982700	6.76603800	-14.17272620
Ag	0.01733400	7.56629100	-11.71996520
Ag	1.31449500	8.36654400	-9.26720420
Ag	2.61165600	9.16679700	-6.81444320
Ag	3.90881700	9.96705000	-4.36168220
Ag	0.01155600	9.34880400	-14.17272620
Ag	1.30871700	10.14905700	-11.71996520
Ag	2.60587800	10.94931000	-9.26720420
Ag	3.90303900	11.74956300	-6.81444320
Ag	1.30293900	11.93157000	-14.17272620
Ag	2.60010000	12.73182300	-11.71996520
Ag	3.89726100	13.53207600	-9.26720420
Ag	2.59432200	14.51433600	-14.17272620
Ag	3.89148300	15.31458900	-11.71996520
Ag	3.88570500	17.09710200	-14.17272620
Ag	-3.85681500	6.27490800	-12.65311220
Ag	-2.55965400	7.07516100	-10.20035120
Ag	-1.26249300	7.87541400	-7.74759020
Ag	0.03466800	8.67566700	-5.29482920
Ag	1.33182900	9.47592000	-2.84206820
Ag	-2.56543200	8.85767400	-12.65311220
Ag	-1.26827100	9.65792700	-10.20035120
Ag	0.02889000	10.45818000	-7.74759020
Ag	1.32605100	11.25843300	-5.29482920
Ag	-1.27404900	11.44044000	-12.65311220

(continues on next page)

(continued from previous page)

Ag	0.02311200	12.24069300	-10.20035120
Ag	1.32027300	13.04094600	-7.74759020
Ag	0.01733400	14.02320600	-12.65311220
Ag	1.31449500	14.82345900	-10.20035120
Ag	1.30871700	16.60597200	-12.65311220
Ag	-5.14242000	8.36654400	-11.13349820
Ag	-3.84525900	9.16679700	-8.68073720
Ag	-2.54809800	9.96705000	-6.22797620
Ag	-1.25093700	10.76730300	-3.77521520
Ag	-3.85103700	10.94931000	-11.13349820
Ag	-2.55387600	11.74956300	-8.68073720
Ag	-1.25671500	12.54981600	-6.22797620
Ag	-2.55965400	13.53207600	-11.13349820
Ag	-1.26249300	14.33232900	-8.68073720
Ag	-1.26827100	16.11484200	-11.13349820
Ag	-6.42802500	10.45818000	-9.61388420
Ag	-5.13086400	11.25843300	-7.16112320
Ag	-3.83370300	12.05868600	-4.70836220
Ag	-5.13664200	13.04094600	-9.61388420
Ag	-3.83948100	13.84119900	-7.16112320
Ag	-3.84525900	15.62371200	-9.61388420
Ag	-7.71363000	12.54981600	-8.09427020
Ag	-6.41646900	13.35006900	-5.64150920
Ag	-6.42224700	15.13258200	-8.09427020
Ag	-8.99923500	14.64145200	-6.57465620
Ag	1.29138300	0.79811860	-19.66831060
Ag	4.18038300	0.79811860	-19.66831060
Ag	7.06938300	0.79811860	-19.66831060
Ag	9.95838300	0.79811860	-19.66831060
Ag	12.84738300	0.79811860	-19.66831060
Ag	15.73638300	0.79811860	-19.66831060
Ag	18.62538300	0.79811860	-19.66831060
Ag	2.58276600	1.59623720	-22.12466710
Ag	5.47176600	1.59623720	-22.12466710
Ag	8.36076600	1.59623720	-22.12466710
Ag	11.24976600	1.59623720	-22.12466710
Ag	14.13876600	1.59623720	-22.12466710
Ag	17.02776600	1.59623720	-22.12466710
Ag	3.87414900	2.39435580	-24.58102350
Ag	6.76314900	2.39435580	-24.58102350
Ag	9.65214900	2.39435580	-24.58102350
Ag	12.54114900	2.39435580	-24.58102350
Ag	15.43014900	2.39435580	-24.58102350
Ag	5.16553200	3.19247430	-27.03737990
Ag	8.05453200	3.19247430	-27.03737990
Ag	10.94353200	3.19247430	-27.03737990
Ag	13.83253200	3.19247430	-27.03737990
Ag	6.45691500	3.99059290	-29.49373640
Ag	9.34591500	3.99059290	-29.49373640
Ag	12.23491500	3.99059290	-29.49373640
Ag	7.74829800	4.78871150	-31.95009280
Ag	10.63729800	4.78871150	-31.95009280
Ag	9.03968100	5.58683010	-34.40644920
Ag	2.58854400	3.37901740	-19.67419920
Ag	5.47754400	3.37901740	-19.67419920
Ag	8.36654400	3.37901740	-19.67419920
Ag	11.25554400	3.37901740	-19.67419920

(continues on next page)

(continued from previous page)

Ag	14.14454400	3.37901740	-19.67419920
Ag	17.03354400	3.37901740	-19.67419920
Ag	3.87992700	4.17713600	-22.13055570
Ag	6.76892700	4.17713600	-22.13055570
Ag	9.65792700	4.17713600	-22.13055570
Ag	12.54692700	4.17713600	-22.13055570
Ag	15.43592700	4.17713600	-22.13055570
Ag	5.17131000	4.97525460	-24.58691210
Ag	8.06031000	4.97525460	-24.58691210
Ag	10.94931000	4.97525460	-24.58691210
Ag	13.83831000	4.97525460	-24.58691210
Ag	6.46269300	5.77337320	-27.04326850
Ag	9.35169300	5.77337320	-27.04326850
Ag	12.24069300	5.77337320	-27.04326850
Ag	7.75407600	6.57149180	-29.49962500
Ag	10.64307600	6.57149180	-29.49962500
Ag	9.04545900	7.36961040	-31.95598140
Ag	3.88570500	5.95991630	-19.68008780
Ag	6.77470500	5.95991630	-19.68008780
Ag	9.66370500	5.95991630	-19.68008780
Ag	12.55270500	5.95991630	-19.68008780
Ag	15.44170500	5.95991630	-19.68008780
Ag	5.17708800	6.75803490	-22.13644430
Ag	8.06608800	6.75803490	-22.13644430
Ag	10.95508800	6.75803490	-22.13644430
Ag	13.84408800	6.75803490	-22.13644430
Ag	6.46847100	7.55615350	-24.59280070
Ag	9.35747100	7.55615350	-24.59280070
Ag	12.24647100	7.55615350	-24.59280070
Ag	7.75985400	8.35427210	-27.04915710
Ag	10.64885400	8.35427210	-27.04915710
Ag	9.05123700	9.15239070	-29.50551360
Ag	5.18286600	8.54081520	-19.68597640
Ag	8.07186600	8.54081520	-19.68597640
Ag	10.96086600	8.54081520	-19.68597640
Ag	13.84986600	8.54081520	-19.68597640
Ag	6.47424900	9.33893370	-22.14233290
Ag	9.36324900	9.33893370	-22.14233290
Ag	12.25224900	9.33893370	-22.14233290
Ag	7.76563200	10.13705230	-24.59868930
Ag	10.65463200	10.13705230	-24.59868930
Ag	9.05701500	10.93517090	-27.05504570
Ag	6.48002700	11.12171400	-19.69186500
Ag	9.36902700	11.12171400	-19.69186500
Ag	12.25802700	11.12171400	-19.69186500
Ag	7.77141000	11.91983260	-22.14822150
Ag	10.66041000	11.91983260	-22.14822150
Ag	9.06279300	12.71795120	-24.60457790
Ag	7.77718800	13.70261290	-19.69775360
Ag	10.66618800	13.70261290	-19.69775360
Ag	9.06857100	14.50073150	-22.15411010
Ag	9.07434900	16.28351170	-19.70364220
Ag	-1.28560500	2.09158990	-18.73163170
Ag	0.01155600	4.67159600	-18.73477270
Ag	1.30871700	7.25160210	-18.73791370
Ag	2.60587800	9.83160820	-18.74105470
Ag	3.90303900	12.41161430	-18.74419570

(continues on next page)

(continued from previous page)

Ag	5.20020000	14.99162040	-18.74733670
Ag	6.49736100	17.57162650	-18.75047770
Ag	0.00577800	2.88970850	-21.18798810
Ag	1.30293900	5.46971460	-21.19112910
Ag	2.60010000	8.04972070	-21.19427010
Ag	3.89726100	10.62972680	-21.19741110
Ag	5.19442200	13.20973290	-21.20055210
Ag	6.49158300	15.78973900	-21.20369310
Ag	1.29716100	3.68782700	-23.64434460
Ag	2.59432200	6.26783310	-23.64748560
Ag	3.89148300	8.84783930	-23.65062660
Ag	5.18864400	11.42784540	-23.65376760
Ag	6.48580500	14.00785150	-23.65690860
Ag	2.58854400	4.48594560	-26.10070100
Ag	3.88570500	7.06595170	-26.10384200
Ag	5.18286600	9.64595780	-26.10698300
Ag	6.48002700	12.22596400	-26.11012400
Ag	3.87992700	5.28406420	-28.55705740
Ag	5.17708800	7.86407030	-28.56019840
Ag	6.47424900	10.44407640	-28.56333940
Ag	5.17131000	6.08218280	-31.01341390
Ag	6.46847100	8.66218890	-31.01655490
Ag	6.46269300	6.88030140	-33.46977030
Ag	-2.57121000	4.18317970	-20.25130920
Ag	-1.27404900	6.76318580	-20.25445020
Ag	0.02311200	9.34319200	-20.25759120
Ag	1.32027300	11.92319810	-20.26073220
Ag	2.61743400	14.50320420	-20.26387320
Ag	3.91459500	17.08321030	-20.26701420
Ag	-1.27982700	4.98129830	-22.70766560
Ag	0.01733400	7.56130440	-22.71080660
Ag	1.31449500	10.14131050	-22.71394760
Ag	2.61165600	12.72131660	-22.71708860
Ag	3.90881700	15.30132280	-22.72022960
Ag	0.01155600	5.77941690	-25.16402210
Ag	1.30871700	8.35942300	-25.16716310
Ag	2.60587800	10.93942910	-25.17030410
Ag	3.90303900	13.51943520	-25.17344510
Ag	1.30293900	6.57753550	-27.62037850
Ag	2.60010000	9.15754160	-27.62351950
Ag	3.89726100	11.73754770	-27.62666050
Ag	2.59432200	7.37565410	-30.07673490
Ag	3.89148300	9.95566020	-30.07987590
Ag	3.88570500	8.17377270	-32.53309140
Ag	-3.85681500	6.27476960	-21.77098670
Ag	-2.55965400	8.85477570	-21.77412770
Ag	-1.26249300	11.43478180	-21.77726870
Ag	0.03466800	14.01478790	-21.78040970
Ag	1.33182900	16.59479400	-21.78355070
Ag	-2.56543200	7.07288820	-24.22734310
Ag	-1.26827100	9.65289430	-24.23048410
Ag	0.02889000	12.23290040	-24.23362510
Ag	1.32605100	14.81290650	-24.23676610
Ag	-1.27404900	7.87100680	-26.68369960
Ag	0.02311200	10.45101290	-26.68684060
Ag	1.32027300	13.03101900	-26.68998160
Ag	0.01733400	8.66912540	-29.14005600

(continues on next page)

(continued from previous page)

Ag	1.31449500	11.24913150	-29.14319700
Ag	1.30871700	9.46724390	-31.59641240
Ag	-5.14242000	8.36635950	-23.29066420
Ag	-3.84525900	10.94636560	-23.29380520
Ag	-2.54809800	13.52637170	-23.29694620
Ag	-1.25093700	16.10637780	-23.30008720
Ag	-3.85103700	9.16447810	-25.74702060
Ag	-2.55387600	11.74448420	-25.75016160
Ag	-1.25671500	14.32449030	-25.75330260
Ag	-2.55965400	9.96259660	-28.20337710
Ag	-1.26249300	12.54260270	-28.20651810
Ag	-1.26827100	10.76071520	-30.65973350
Ag	-6.42802500	10.45794930	-24.81034170
Ag	-5.13086400	13.03795540	-24.81348270
Ag	-3.83370300	15.61796160	-24.81662370
Ag	-5.13664200	11.25606790	-27.26669810
Ag	-3.83948100	13.83607400	-27.26983910
Ag	-3.84525900	12.05418650	-29.72305460
Ag	-7.71363000	12.54953920	-26.33001920
Ag	-6.41646900	15.12954530	-26.33316020
Ag	-6.42224700	13.34765780	-28.78637560
Ag	-8.99923500	14.64112910	-27.84969670
Ag	1.29138300	-2.08950160	-18.73006600
Ag	4.18038300	-2.08950160	-18.73006600
Ag	7.06938300	-2.08950160	-18.73006600
Ag	9.95838300	-2.08950160	-18.73006600
Ag	12.84738300	-2.08950160	-18.73006600
Ag	15.73638300	-2.08950160	-18.73006600
Ag	18.62538300	-2.08950160	-18.73006600
Ag	2.58276600	-4.17900320	-20.24817770
Ag	5.47176600	-4.17900320	-20.24817770
Ag	8.36076600	-4.17900320	-20.24817770
Ag	11.24976600	-4.17900320	-20.24817770
Ag	14.13876600	-4.17900320	-20.24817770
Ag	17.02776600	-4.17900320	-20.24817770
Ag	3.87414900	-6.26850480	-21.76628950
Ag	6.76314900	-6.26850480	-21.76628950
Ag	9.65214900	-6.26850480	-21.76628950
Ag	12.54114900	-6.26850480	-21.76628950
Ag	15.43014900	-6.26850480	-21.76628950
Ag	5.16553200	-8.35800630	-23.28440130
Ag	8.05453200	-8.35800630	-23.28440130
Ag	10.94353200	-8.35800630	-23.28440130
Ag	13.83253200	-8.35800630	-23.28440130
Ag	6.45691500	-10.44750790	-24.80251300
Ag	9.34591500	-10.44750790	-24.80251300
Ag	12.23491500	-10.44750790	-24.80251300
Ag	7.74829800	-12.53700950	-26.32062480
Ag	10.63729800	-12.53700950	-26.32062480
Ag	9.03968100	-14.62651110	-27.83873660
Ag	2.58854400	-1.29756040	-21.18646630
Ag	5.47754400	-1.29756040	-21.18646630
Ag	8.36654400	-1.29756040	-21.18646630
Ag	11.25554400	-1.29756040	-21.18646630
Ag	14.14454400	-1.29756040	-21.18646630
Ag	17.03354400	-1.29756040	-21.18646630
Ag	3.87992700	-3.38706200	-22.70457810

(continues on next page)

(continued from previous page)

Ag	6.76892700	-3.38706200	-22.70457810
Ag	9.65792700	-3.38706200	-22.70457810
Ag	12.54692700	-3.38706200	-22.70457810
Ag	15.43592700	-3.38706200	-22.70457810
Ag	5.17131000	-5.47656350	-24.22268990
Ag	8.06031000	-5.47656350	-24.22268990
Ag	10.94931000	-5.47656350	-24.22268990
Ag	13.83831000	-5.47656350	-24.22268990
Ag	6.46269300	-7.56606510	-25.74080160
Ag	9.35169300	-7.56606510	-25.74080160
Ag	12.24069300	-7.56606510	-25.74080160
Ag	7.75407600	-9.65556670	-27.25891340
Ag	10.64307600	-9.65556670	-27.25891340
Ag	9.04545900	-11.74506830	-28.77702510
Ag	3.88570500	-0.50561920	-23.64286670
Ag	6.77470500	-0.50561920	-23.64286670
Ag	9.66370500	-0.50561920	-23.64286670
Ag	12.55270500	-0.50561920	-23.64286670
Ag	15.44170500	-0.50561920	-23.64286670
Ag	5.17708800	-2.59512070	-25.16097840
Ag	8.06608800	-2.59512070	-25.16097840
Ag	10.95508800	-2.59512070	-25.16097840
Ag	13.84408800	-2.59512070	-25.16097840
Ag	6.46847100	-4.68462230	-26.67909020
Ag	9.35747100	-4.68462230	-26.67909020
Ag	12.24647100	-4.68462230	-26.67909020
Ag	7.75985400	-6.77412390	-28.19720200
Ag	10.64885400	-6.77412390	-28.19720200
Ag	9.05123700	-8.86362550	-29.71531370
Ag	5.18286600	0.28632210	-26.09926700
Ag	8.07186600	0.28632210	-26.09926700
Ag	10.96086600	0.28632210	-26.09926700
Ag	13.84986600	0.28632210	-26.09926700
Ag	6.47424900	-1.80317950	-27.61737880
Ag	9.36324900	-1.80317950	-27.61737880
Ag	12.25224900	-1.80317950	-27.61737880
Ag	7.76563200	-3.89268110	-29.13549060
Ag	10.65463200	-3.89268110	-29.13549060
Ag	9.05701500	-5.98218270	-30.65360230
Ag	6.48002700	1.07826330	-28.55566740
Ag	9.36902700	1.07826330	-28.55566740
Ag	12.25802700	1.07826330	-28.55566740
Ag	7.77141000	-1.01123830	-30.07377920
Ag	10.66041000	-1.01123830	-30.07377920
Ag	9.06279300	-3.10073990	-31.59189090
Ag	7.77718800	1.87020450	-31.01206770
Ag	10.66618800	1.87020450	-31.01206770
Ag	9.06857100	-0.21929710	-32.53017950
Ag	9.07434900	2.66214570	-33.46846810
Ag	-1.28560500	-0.79896240	-19.67078050
Ag	0.01155600	-0.00468390	-22.12548280
Ag	1.30871700	0.78959460	-24.58018500
Ag	2.60587800	1.58387300	-27.03488730
Ag	3.90303900	2.37815150	-29.48958950
Ag	5.20020000	3.17243000	-31.94429180
Ag	6.49736100	3.96670840	-34.39899400
Ag	0.00577800	-2.88846400	-21.18889230

(continues on next page)

(continued from previous page)

Ag	1.30293900	-2.09418550	-23.64359460
Ag	2.60010000	-1.29990700	-26.09829680
Ag	3.89726100	-0.50562860	-28.55299900
Ag	5.19442200	0.28864990	-31.00770130
Ag	6.49158300	1.08292840	-33.46240350
Ag	1.29716100	-4.97796550	-22.70700410
Ag	2.59432200	-4.18368710	-25.16170630
Ag	3.89148300	-3.38940860	-27.61640860
Ag	5.18864400	-2.59513010	-30.07111080
Ag	6.48580500	-1.80085170	-32.52581300
Ag	2.58854400	-7.06746710	-24.22511580
Ag	3.88570500	-6.27318870	-26.67981810
Ag	5.18286600	-5.47891020	-29.13452030
Ag	6.48002700	-4.68463170	-31.58922260
Ag	3.87992700	-9.15696870	-25.74322760
Ag	5.17708800	-8.36269030	-28.19792980
Ag	6.47424900	-7.56841180	-30.65263210
Ag	5.17131000	-11.24647030	-27.26133940
Ag	6.46847100	-10.45219180	-29.71604160
Ag	6.46269300	-13.33597190	-28.77945110
Ag	-2.57121000	-1.59792470	-22.12960690
Ag	-1.27404900	-0.80364630	-24.58430910
Ag	0.02311200	-0.00936780	-27.03901140
Ag	1.32027300	0.78491070	-29.49371360
Ag	2.61743400	1.57918910	-31.94841590
Ag	3.91459500	2.37346760	-34.40311810
Ag	-1.27982700	-3.68742630	-23.64771870
Ag	0.01733400	-2.89314790	-26.10242090
Ag	1.31449500	-2.09886940	-28.55712310
Ag	2.61165600	-1.30459090	-31.01182540
Ag	3.90881700	-0.51031250	-33.46652760
Ag	0.01155600	-5.77692790	-25.16583040
Ag	1.30871700	-4.98264940	-27.62053270
Ag	2.60587800	-4.18837100	-30.07523490
Ag	3.90303900	-3.39409250	-32.52993720
Ag	1.30293900	-7.86642950	-26.68394220
Ag	2.60010000	-7.07215100	-29.13864440
Ag	3.89726100	-6.27787260	-31.59334670
Ag	2.59432200	-9.95593110	-28.20205390
Ag	3.89148300	-9.16165260	-30.65675620
Ag	3.88570500	-12.04543270	-29.72016570
Ag	-3.85681500	-2.39688710	-24.58843320
Ag	-2.55965400	-1.60260860	-27.04313550
Ag	-1.26249300	-0.80833020	-29.49783770
Ag	0.03466800	-0.01405170	-31.95254000
Ag	1.33182900	0.78022680	-34.40724220
Ag	-2.56543200	-4.48638870	-26.10654500
Ag	-1.26827100	-3.69211020	-28.56124720
Ag	0.02889000	-2.89783180	-31.01594950
Ag	1.32605100	-2.10355330	-33.47065170
Ag	-1.27404900	-6.57589030	-27.62465680
Ag	0.02311200	-5.78161180	-30.07935900
Ag	1.32027300	-4.98733340	-32.53406130
Ag	0.01733400	-8.66539190	-29.14276850
Ag	1.31449500	-7.87111340	-31.59747080
Ag	1.30871700	-10.75489350	-30.66088030
Ag	-5.14242000	-3.19584950	-27.04725960

(continues on next page)

(continued from previous page)

Ag	-3.84525900	-2.40157100	-29.50196180
Ag	-2.54809800	-1.60729260	-31.95666410
Ag	-1.25093700	-0.81301410	-34.41136630
Ag	-3.85103700	-5.28535110	-28.56537130
Ag	-2.55387600	-4.49107260	-31.02007360
Ag	-1.25671500	-3.69679410	-33.47477580
Ag	-2.55965400	-7.37485270	-30.08348310
Ag	-1.26249300	-6.58057420	-32.53818540
Ag	-1.26827100	-9.46435420	-31.60159490
Ag	-6.42802500	-3.99481190	-29.50608590
Ag	-5.13086400	-3.20053340	-31.96078820
Ag	-3.83370300	-2.40625490	-34.41549040
Ag	-5.13664200	-6.08431340	-31.02419770
Ag	-3.83948100	-5.29003500	-33.47889990
Ag	-3.84525900	-8.17381500	-32.54230950
Ag	-7.71363000	-4.79377420	-31.96491230
Ag	-6.41646900	-3.99949580	-34.41961450
Ag	-6.42224700	-6.88327580	-33.48302400
Ag	-8.99923500	-5.59273660	-34.42373860
Ag	1.29138300	-2.08950160	-15.69384240
Ag	4.18038300	-2.08950160	-15.69384240
Ag	7.06938300	-2.08950160	-15.69384240
Ag	9.95838300	-2.08950160	-15.69384240
Ag	12.84738300	-2.08950160	-15.69384240
Ag	15.73638300	-2.08950160	-15.69384240
Ag	18.62538300	-2.08950160	-15.69384240
Ag	2.58276600	-4.17900320	-14.17573070
Ag	5.47176600	-4.17900320	-14.17573070
Ag	8.36076600	-4.17900320	-14.17573070
Ag	11.24976600	-4.17900320	-14.17573070
Ag	14.13876600	-4.17900320	-14.17573070
Ag	17.02776600	-4.17900320	-14.17573070
Ag	3.87414900	-6.26850480	-12.65761890
Ag	6.76314900	-6.26850480	-12.65761890
Ag	9.65214900	-6.26850480	-12.65761890
Ag	12.54114900	-6.26850480	-12.65761890
Ag	15.43014900	-6.26850480	-12.65761890
Ag	5.16553200	-8.35800630	-11.13950710
Ag	8.05453200	-8.35800630	-11.13950710
Ag	10.94353200	-8.35800630	-11.13950710
Ag	13.83253200	-8.35800630	-11.13950710
Ag	6.45691500	-10.44750790	-9.62139540
Ag	9.34591500	-10.44750790	-9.62139540
Ag	12.23491500	-10.44750790	-9.62139540
Ag	7.74829800	-12.53700950	-8.10328360
Ag	10.63729800	-12.53700950	-8.10328360
Ag	9.03968100	-14.62651110	-6.58517180
Ag	2.58854400	-4.18095390	-17.20609270
Ag	5.47754400	-4.18095390	-17.20609270
Ag	8.36654400	-4.18095390	-17.20609270
Ag	11.25554400	-4.18095390	-17.20609270
Ag	14.14454400	-4.18095390	-17.20609270
Ag	17.03354400	-4.18095390	-17.20609270
Ag	3.87992700	-6.27045540	-15.68798100
Ag	6.76892700	-6.27045540	-15.68798100
Ag	9.65792700	-6.27045540	-15.68798100
Ag	12.54692700	-6.27045540	-15.68798100

(continues on next page)

(continued from previous page)

Ag	15.43592700	-6.27045540	-15.68798100
Ag	5.17131000	-8.35995700	-14.16986920
Ag	8.06031000	-8.35995700	-14.16986920
Ag	10.94931000	-8.35995700	-14.16986920
Ag	13.83831000	-8.35995700	-14.16986920
Ag	6.46269300	-10.44945860	-12.65175740
Ag	9.35169300	-10.44945860	-12.65175740
Ag	12.24069300	-10.44945860	-12.65175740
Ag	7.75407600	-12.53896020	-11.13364570
Ag	10.64307600	-12.53896020	-11.13364570
Ag	9.04545900	-14.62846180	-9.61553390
Ag	3.88570500	-6.27240610	-18.71834310
Ag	6.77470500	-6.27240610	-18.71834310
Ag	9.66370500	-6.27240610	-18.71834310
Ag	12.55270500	-6.27240610	-18.71834310
Ag	15.44170500	-6.27240610	-18.71834310
Ag	5.17708800	-8.36190770	-17.20023130
Ag	8.06608800	-8.36190770	-17.20023130
Ag	10.95508800	-8.36190770	-17.20023130
Ag	13.84408800	-8.36190770	-17.20023130
Ag	6.46847100	-10.45140930	-15.68211950
Ag	9.35747100	-10.45140930	-15.68211950
Ag	12.24647100	-10.45140930	-15.68211950
Ag	7.75985400	-12.54091090	-14.16400780
Ag	10.64885400	-12.54091090	-14.16400780
Ag	9.05123700	-14.63041250	-12.64589600
Ag	5.18286600	-8.36385840	-20.23059340
Ag	8.07186600	-8.36385840	-20.23059340
Ag	10.96086600	-8.36385840	-20.23059340
Ag	13.84986600	-8.36385840	-20.23059340
Ag	6.47424900	-10.45336000	-18.71248160
Ag	9.36324900	-10.45336000	-18.71248160
Ag	12.25224900	-10.45336000	-18.71248160
Ag	7.76563200	-12.54286160	-17.19436980
Ag	10.65463200	-12.54286160	-17.19436980
Ag	9.05701500	-14.63236320	-15.67625810
Ag	6.48002700	-10.45531070	-21.74284370
Ag	9.36902700	-10.45531070	-21.74284370
Ag	12.25802700	-10.45531070	-21.74284370
Ag	7.77141000	-12.54481230	-20.22473190
Ag	10.66041000	-12.54481230	-20.22473190
Ag	9.06279300	-14.63431380	-18.70662010
Ag	7.77718800	-12.54676290	-23.25509400
Ag	10.66618800	-12.54676290	-23.25509400
Ag	9.06857100	-14.63626450	-21.73698220
Ag	9.07434900	-14.63821520	-24.76734430
Ag	-1.28560500	-2.58537580	-17.21191500
Ag	0.01155600	-4.67449080	-18.72586340
Ag	1.30871700	-6.76360580	-20.23981180
Ag	2.60587800	-8.85272080	-21.75376020
Ag	3.90303900	-10.94183580	-23.26770860
Ag	5.20020000	-13.03095090	-24.78165710
Ag	6.49736100	-15.12006590	-26.29560550
Ag	0.00577800	-4.67487740	-15.69380320
Ag	1.30293900	-6.76399240	-17.20775160
Ag	2.60010000	-8.85310740	-18.72170000
Ag	3.89726100	-10.94222240	-20.23564850

(continues on next page)

(continued from previous page)

Ag	5.19442200	-13.03133740	-21.74959690
Ag	6.49158300	-15.12045250	-23.26354530
Ag	1.29716100	-6.76437890	-14.17569140
Ag	2.59432200	-8.85349400	-15.68963980
Ag	3.89148300	-10.94260900	-17.20358830
Ag	5.18864400	-13.03172400	-18.71753670
Ag	6.48580500	-15.12083900	-20.23148510
Ag	2.58854400	-8.85388050	-12.65757970
Ag	3.88570500	-10.94299550	-14.17152810
Ag	5.18286600	-13.03211060	-15.68547650
Ag	6.48002700	-15.12122560	-17.19942490
Ag	3.87992700	-10.94338210	-11.13946790
Ag	5.17708800	-13.03249710	-12.65341630
Ag	6.47424900	-15.12161220	-14.16736470
Ag	5.17131000	-13.03288370	-9.62135610
Ag	6.46847100	-15.12199870	-11.13530460
Ag	6.46269300	-15.12238530	-8.10324440
Ag	-2.57121000	-5.17075150	-17.21187570
Ag	-1.27404900	-7.25986660	-18.72582410
Ag	0.02311200	-9.34898160	-20.23977260
Ag	1.32027300	-11.43809660	-21.75372100
Ag	2.61743400	-13.52721160	-23.26766940
Ag	3.91459500	-15.61632660	-24.78161780
Ag	-1.27982700	-7.26025310	-15.69376390
Ag	0.01733400	-9.34936810	-17.20771240
Ag	1.31449500	-11.43848320	-18.72166080
Ag	2.61165600	-13.52759820	-20.23560920
Ag	3.90881700	-15.61671320	-21.74955760
Ag	0.01155600	-9.34975470	-14.17565220
Ag	1.30871700	-11.43886970	-15.68960060
Ag	2.60587800	-13.52798470	-17.20354900
Ag	3.90303900	-15.61709980	-18.71749740
Ag	1.30293900	-11.43925630	-12.65754040
Ag	2.60010000	-13.52837130	-14.17148880
Ag	3.89726100	-15.61748630	-15.68543730
Ag	2.59432200	-13.52875790	-11.13942870
Ag	3.89148300	-15.61787290	-12.65337710
Ag	3.88570500	-15.61825950	-9.62131690
Ag	-3.85681500	-7.75612730	-17.21183650
Ag	-2.55965400	-9.84524230	-18.72578490
Ag	-1.26249300	-11.93435730	-20.23973330
Ag	0.03466800	-14.02347240	-21.75368170
Ag	1.33182900	-16.11258740	-23.26763020
Ag	-2.56543200	-9.84562890	-15.69372470
Ag	-1.26827100	-11.93474390	-17.20767310
Ag	0.02889000	-14.02385890	-18.72162150
Ag	1.32605100	-16.11297400	-20.23557000
Ag	-1.27404900	-11.93513050	-14.17561290
Ag	0.02311200	-14.02424550	-15.68956140
Ag	1.32027300	-16.11336050	-17.20350980
Ag	0.01733400	-14.02463210	-12.65750120
Ag	1.31449500	-16.11374710	-14.17144960
Ag	1.30871700	-16.11413370	-11.13938940
Ag	-5.14242000	-10.34150310	-17.21179720
Ag	-3.84525900	-12.43061810	-18.72574560
Ag	-2.54809800	-14.51973310	-20.23969410
Ag	-1.25093700	-16.60884810	-21.75364250

(continues on next page)

(continued from previous page)

Ag	-3.85103700	-12.43100470	-15.69368550
Ag	-2.55387600	-14.52011970	-17.20763390
Ag	-1.25671500	-16.60923470	-18.72158230
Ag	-2.55965400	-14.52050620	-14.17557370
Ag	-1.26249300	-16.60962130	-15.68952210
Ag	-1.26827100	-16.61000780	-12.65746190
Ag	-6.42802500	-12.92687880	-17.21175800
Ag	-5.13086400	-15.01599390	-18.72570640
Ag	-3.83370300	-17.10510890	-20.23965480
Ag	-5.13664200	-15.01638040	-15.69364620
Ag	-3.83948100	-17.10549540	-17.20759460
Ag	-3.84525900	-17.10588200	-14.17553450
Ag	-7.71363000	-15.51225460	-17.21171870
Ag	-6.41646900	-17.60136960	-18.72566720
Ag	-6.42224700	-17.60175620	-15.69360700
Ag	-8.99923500	-18.09763040	-17.21167950
Ag	2.58854400	-1.28641120	-13.23381950
Ag	5.47754400	-1.28641120	-13.23381950
Ag	8.36654400	-1.28641120	-13.23381950
Ag	11.25554400	-1.28641120	-13.23381950
Ag	14.14454400	-1.28641120	-13.23381950
Ag	17.03354400	-1.28641120	-13.23381950
Ag	3.87992700	-0.48829260	-10.77746310
Ag	6.76892700	-0.48829260	-10.77746310
Ag	9.65792700	-0.48829260	-10.77746310
Ag	12.54692700	-0.48829260	-10.77746310
Ag	15.43592700	-0.48829260	-10.77746310
Ag	5.17131000	0.30982600	-8.32110660
Ag	8.06031000	0.30982600	-8.32110660
Ag	10.94931000	0.30982600	-8.32110660
Ag	13.83831000	0.30982600	-8.32110660
Ag	6.46269300	1.10794450	-5.86475020
Ag	9.35169300	1.10794450	-5.86475020
Ag	12.24069300	1.10794450	-5.86475020
Ag	7.75407600	1.90606310	-3.40839380
Ag	10.64307600	1.90606310	-3.40839380
Ag	9.04545900	2.70418170	-0.95203730
Ag	3.88570500	-3.37094100	-11.71204120
Ag	6.77470500	-3.37094100	-11.71204120
Ag	9.66370500	-3.37094100	-11.71204120
Ag	12.55270500	-3.37094100	-11.71204120
Ag	15.44170500	-3.37094100	-11.71204120
Ag	5.17708800	-2.57282240	-9.25568480
Ag	8.06608800	-2.57282240	-9.25568480
Ag	10.95508800	-2.57282240	-9.25568480
Ag	13.84408800	-2.57282240	-9.25568480
Ag	6.46847100	-1.77470390	-6.79932840
Ag	9.35747100	-1.77470390	-6.79932840
Ag	12.24647100	-1.77470390	-6.79932840
Ag	7.75985400	-0.97658530	-4.34297190
Ag	10.64885400	-0.97658530	-4.34297190
Ag	9.05123700	-0.17846670	-1.88661550
Ag	5.18286600	-5.45547080	-10.19026300
Ag	8.07186600	-5.45547080	-10.19026300
Ag	10.96086600	-5.45547080	-10.19026300
Ag	13.84986600	-5.45547080	-10.19026300
Ag	6.47424900	-4.65735220	-7.73390650

(continues on next page)

(continued from previous page)

Ag	9.36324900	-4.65735220	-7.73390650
Ag	12.25224900	-4.65735220	-7.73390650
Ag	7.76563200	-3.85923370	-5.27755010
Ag	10.65463200	-3.85923370	-5.27755010
Ag	9.05701500	-3.06111510	-2.82119370
Ag	6.48002700	-7.54000060	-8.66848470
Ag	9.36902700	-7.54000060	-8.66848470
Ag	12.25802700	-7.54000060	-8.66848470
Ag	7.77141000	-6.74188200	-6.21212830
Ag	10.66041000	-6.74188200	-6.21212830
Ag	9.06279300	-5.94376350	-3.75577180
Ag	7.77718800	-9.62453040	-7.14670640
Ag	10.66618800	-9.62453040	-7.14670640
Ag	9.06857100	-8.82641190	-4.69035000
Ag	9.07434900	-11.70906020	-5.62492820
Ag	-1.28560500	-0.79888770	-14.75310360
Ag	0.01155600	-2.88431030	-13.23407290
Ag	1.30871700	-4.96973280	-11.71504230
Ag	2.60587800	-7.05515540	-10.19601160
Ag	3.90303900	-9.14057790	-8.67698100
Ag	5.20020000	-11.22600050	-7.15795030
Ag	6.49736100	-13.31142310	-5.63891960
Ag	0.00577800	-0.00076910	-12.29674720
Ag	1.30293900	-2.08619170	-10.77771650
Ag	2.60010000	-4.17161430	-9.25868580
Ag	3.89726100	-6.25703680	-7.73965520
Ag	5.19442200	-8.34245940	-6.22062450
Ag	6.49158300	-10.42788190	-4.70159390
Ag	1.29716100	0.79734940	-9.84039070
Ag	2.59432200	-1.28807310	-8.32136010
Ag	3.89148300	-3.37349570	-6.80232940
Ag	5.18864400	-5.45891820	-5.28329870
Ag	6.48580500	-7.54434080	-3.76426810
Ag	2.58854400	1.59546800	-7.38403430
Ag	3.88570500	-0.48995450	-5.86500360
Ag	5.18286600	-2.57537710	-4.34597300
Ag	6.48002700	-4.66079960	-2.82694230
Ag	3.87992700	2.39358660	-4.92767790
Ag	5.17708800	0.30816410	-3.40864720
Ag	6.47424900	-1.77725850	-1.88961650
Ag	5.17131000	3.19170520	-2.47132140
Ag	6.46847100	1.10628270	-0.95229080
Ag	6.46269300	3.98982380	-0.01496500
Ag	-2.57121000	-1.59777550	-12.29425300
Ag	-1.27404900	-3.68319800	-10.77522230
Ag	0.02311200	-5.76862060	-9.25619170
Ag	1.32027300	-7.85404310	-7.73716100
Ag	2.61743400	-9.93946570	-6.21813040
Ag	3.91459500	-12.02488820	-4.69909970
Ag	-1.27982700	-0.79965690	-9.83789660
Ag	0.01733400	-2.88507940	-8.31886590
Ag	1.31449500	-4.97050200	-6.79983520
Ag	2.61165600	-7.05592450	-5.28080460
Ag	3.90881700	-9.14134710	-3.76177390
Ag	0.01155600	-0.00153830	-7.38154010
Ag	1.30871700	-2.08696080	-5.86250950
Ag	2.60587800	-4.17238340	-4.34347880

(continues on next page)

(continued from previous page)

Ag	3.90303900	-6.25780590	-2.82444810
Ag	1.30293900	0.79658030	-4.92518370
Ag	2.60010000	-1.28884220	-3.40615300
Ag	3.89726100	-3.37426480	-1.88712240
Ag	2.59432200	1.59469890	-2.46882730
Ag	3.89148300	-0.49072370	-0.94979660
Ag	3.88570500	2.39281750	-0.01247080
Ag	-3.85681500	-2.39666320	-9.83540240
Ag	-2.55965400	-4.48208570	-8.31637170
Ag	-1.26249300	-6.56750830	-6.79734110
Ag	0.03466800	-8.65293080	-5.27831040
Ag	1.33182900	-10.73835340	-3.75927980
Ag	-2.56543200	-1.59854460	-7.37904600
Ag	-1.26827100	-3.68396710	-5.86001530
Ag	0.02889000	-5.76938970	-4.34098460
Ag	1.32605100	-7.85481230	-2.82195400
Ag	-1.27404900	-0.80042600	-4.92268950
Ag	0.02311200	-2.88584860	-3.40365890
Ag	1.32027300	-4.97127110	-1.88462820
Ag	0.01733400	-0.00230740	-2.46633310
Ag	1.31449500	-2.08773000	-0.94730240
Ag	1.30871700	0.79581120	-0.00997670
Ag	-5.14242000	-3.19555090	-7.37655180
Ag	-3.84525900	-5.28097350	-5.85752110
Ag	-2.54809800	-7.36639600	-4.33849050
Ag	-1.25093700	-9.45181860	-2.81945980
Ag	-3.85103700	-2.39743230	-4.92019540
Ag	-2.55387600	-4.48285490	-3.40116470
Ag	-1.25671500	-6.56827740	-1.88213400
Ag	-2.55965400	-1.59931370	-2.46383890
Ag	-1.26249300	-3.68473630	-0.94480830
Ag	-1.26827100	-0.80119510	-0.00748250
Ag	-6.42802500	-3.99443860	-4.91770120
Ag	-5.13086400	-6.07986120	-3.39867050
Ag	-3.83370300	-8.16528370	-1.87963990
Ag	-5.13664200	-3.19632000	-2.46134480
Ag	-3.83948100	-5.28174260	-0.94231410
Ag	-3.84525900	-2.39820150	-0.00498830
Ag	-7.71363000	-4.79332640	-2.45885060
Ag	-6.41646900	-6.87874890	-0.93981990
Ag	-6.42224700	-3.99520780	-0.00249420
Ag	-8.99923500	-5.59221410	0.00000000
Ag	-2.88900000	0.00000000	-17.21195420
Ag	-5.77800000	0.00000000	-17.21195420
Ag	-8.66700000	0.00000000	-17.21195420
Ag	-11.55600000	0.00000000	-17.21195420
Ag	-14.44500000	0.00000000	-17.21195420
Ag	-17.33400000	0.00000000	-17.21195420
Ag	-20.22300000	0.00000000	-17.21195420
Ag	-4.18038300	2.08950160	-18.73006600
Ag	-7.06938300	2.08950160	-18.73006600
Ag	-9.95838300	2.08950160	-18.73006600
Ag	-12.84738300	2.08950160	-18.73006600
Ag	-15.73638300	2.08950160	-18.73006600
Ag	-18.62538300	2.08950160	-18.73006600
Ag	-5.47176600	4.17900320	-20.24817770
Ag	-8.36076600	4.17900320	-20.24817770

(continues on next page)

(continued from previous page)

Ag	-11.24976600	4.17900320	-20.24817770
Ag	-14.13876600	4.17900320	-20.24817770
Ag	-17.02776600	4.17900320	-20.24817770
Ag	-6.76314900	6.26850480	-21.76628950
Ag	-9.65214900	6.26850480	-21.76628950
Ag	-12.54114900	6.26850480	-21.76628950
Ag	-15.43014900	6.26850480	-21.76628950
Ag	-8.05453200	8.35800630	-23.28440130
Ag	-10.94353200	8.35800630	-23.28440130
Ag	-13.83253200	8.35800630	-23.28440130
Ag	-9.34591500	10.44750790	-24.80251300
Ag	-12.23491500	10.44750790	-24.80251300
Ag	-10.63729800	12.53700950	-26.32062480
Ag	-4.18616100	2.09145230	-15.69970390
Ag	-7.07516100	2.09145230	-15.69970390
Ag	-9.96416100	2.09145230	-15.69970390
Ag	-12.85316100	2.09145230	-15.69970390
Ag	-15.74216100	2.09145230	-15.69970390
Ag	-18.63116100	2.09145230	-15.69970390
Ag	-2.58854400	4.18095390	-17.21781570
Ag	-5.47754400	4.18095390	-17.21781570
Ag	-8.36654400	4.18095390	-17.21781570
Ag	-11.25554400	4.18095390	-17.21781570
Ag	-14.14454400	4.18095390	-17.21781570
Ag	-17.03354400	4.18095390	-17.21781570
Ag	-3.87992700	6.27045540	-18.73592740
Ag	-6.76892700	6.27045540	-18.73592740
Ag	-9.65792700	6.27045540	-18.73592740
Ag	-12.54692700	6.27045540	-18.73592740
Ag	-15.43592700	6.27045540	-18.73592740
Ag	-5.17131000	8.35995700	-20.25403920
Ag	-8.06031000	8.35995700	-20.25403920
Ag	-10.94931000	8.35995700	-20.25403920
Ag	-13.83831000	8.35995700	-20.25403920
Ag	-6.46269300	10.44945860	-21.77215100
Ag	-9.35169300	10.44945860	-21.77215100
Ag	-12.24069300	10.44945860	-21.77215100
Ag	-7.75407600	12.53896020	-23.29026270
Ag	-10.64307600	12.53896020	-23.29026270
Ag	-9.04545900	14.62846180	-24.80837450
Ag	-5.48332200	4.18290450	-14.18745360
Ag	-8.37232200	4.18290450	-14.18745360
Ag	-11.26132200	4.18290450	-14.18745360
Ag	-14.15032200	4.18290450	-14.18745360
Ag	-17.03932200	4.18290450	-14.18745360
Ag	-3.88570500	6.27240610	-15.70556530
Ag	-6.77470500	6.27240610	-15.70556530
Ag	-9.66370500	6.27240610	-15.70556530
Ag	-12.55270500	6.27240610	-15.70556530
Ag	-15.44170500	6.27240610	-15.70556530
Ag	-5.17708800	8.36190770	-17.22367710
Ag	-8.06608800	8.36190770	-17.22367710
Ag	-10.95508800	8.36190770	-17.22367710
Ag	-13.84408800	8.36190770	-17.22367710
Ag	-6.46847100	10.45140930	-18.74178890
Ag	-9.35747100	10.45140930	-18.74178890
Ag	-12.24647100	10.45140930	-18.74178890

(continues on next page)

(continued from previous page)

Ag	-7.75985400	12.54091090	-20.25990060
Ag	-10.64885400	12.54091090	-20.25990060
Ag	-9.05123700	14.63041250	-21.77801240
Ag	-6.78048300	6.27435680	-12.67520330
Ag	-9.66948300	6.27435680	-12.67520330
Ag	-12.55848300	6.27435680	-12.67520330
Ag	-15.44748300	6.27435680	-12.67520330
Ag	-5.18286600	8.36385840	-14.19331500
Ag	-8.07186600	8.36385840	-14.19331500
Ag	-10.96086600	8.36385840	-14.19331500
Ag	-13.84986600	8.36385840	-14.19331500
Ag	-6.47424900	10.45336000	-15.71142680
Ag	-9.36324900	10.45336000	-15.71142680
Ag	-12.25224900	10.45336000	-15.71142680
Ag	-7.76563200	12.54286160	-17.22953860
Ag	-10.65463200	12.54286160	-17.22953860
Ag	-9.05701500	14.63236320	-18.74765030
Ag	-8.07764400	8.36580910	-11.16295300
Ag	-10.96664400	8.36580910	-11.16295300
Ag	-13.85564400	8.36580910	-11.16295300
Ag	-6.48002700	10.45531070	-12.68106470
Ag	-9.36902700	10.45531070	-12.68106470
Ag	-12.25802700	10.45531070	-12.68106470
Ag	-7.77141000	12.54481230	-14.19917650
Ag	-10.66041000	12.54481230	-14.19917650
Ag	-9.06279300	14.63431380	-15.71728830
Ag	-9.37480500	10.45726140	-9.65070270
Ag	-12.26380500	10.45726140	-9.65070270
Ag	-7.77718800	12.54676290	-11.16881440
Ag	-10.66618800	12.54676290	-11.16881440
Ag	-9.06857100	14.63626450	-12.68692620
Ag	-10.67196600	12.54871360	-8.13845230
Ag	-9.07434900	14.63821520	-9.65656410
Ag	-1.30293900	6.76399240	-17.21615680
Ag	-2.60010000	8.85310740	-15.70220840
Ag	-3.89726100	10.94222240	-14.18825990
Ag	-5.19442200	13.03133740	-12.67431150
Ag	-6.49158300	15.12045250	-11.16036310
Ag	-2.59432200	8.85349400	-18.73426860
Ag	-3.89148300	10.94260900	-17.22032010
Ag	-5.18864400	13.03172400	-15.70637170
Ag	-6.48580500	15.12083900	-14.19242330
Ag	-3.88570500	10.94299550	-20.25238030
Ag	-5.18286600	13.03211060	-18.73843190
Ag	-6.48002700	15.12122560	-17.22448350
Ag	-5.17708800	13.03249710	-21.77049210
Ag	-6.47424900	15.12161220	-20.25654370
Ag	-6.46847100	15.12199870	-23.28860380
Ag	-0.01733400	9.34936810	-17.21619600
Ag	-1.31449500	11.43848320	-15.70224760
Ag	-2.61165600	13.52759820	-14.18829920
Ag	-3.90881700	15.61671320	-12.67435080
Ag	-1.30871700	11.43886970	-18.73430780
Ag	-2.60587800	13.52798470	-17.22035940
Ag	-3.90303900	15.61709980	-15.70641100
Ag	-2.60010000	13.52837130	-20.25241960
Ag	-3.89726100	15.61748630	-18.73847110

(continues on next page)

(continued from previous page)

Ag	-3.89148300	15.61787290	-21.77053130
Ag	1.26827100	11.93474390	-17.21623530
Ag	-0.02889000	14.02385890	-15.70228690
Ag	-1.32605100	16.11297400	-14.18833840
Ag	-0.02311200	14.02424550	-18.73434700
Ag	-1.32027300	16.11336050	-17.22039860
Ag	-1.31449500	16.11374710	-20.25245880
Ag	2.55387600	14.52011970	-17.21627450
Ag	1.25671500	16.60923470	-15.70232610
Ag	1.26249300	16.60962130	-18.73438630
Ag	3.83948100	17.10549540	-17.21631380
Ag	-4.18038300	-0.79811860	-19.66831060
Ag	-7.06938300	-0.79811860	-19.66831060
Ag	-9.95838300	-0.79811860	-19.66831060
Ag	-12.84738300	-0.79811860	-19.66831060
Ag	-15.73638300	-0.79811860	-19.66831060
Ag	-18.62538300	-0.79811860	-19.66831060
Ag	-5.47176600	-1.59623720	-22.12466710
Ag	-8.36076600	-1.59623720	-22.12466710
Ag	-11.24976600	-1.59623720	-22.12466710
Ag	-14.13876600	-1.59623720	-22.12466710
Ag	-17.02776600	-1.59623720	-22.12466710
Ag	-6.76314900	-2.39435580	-24.58102350
Ag	-9.65214900	-2.39435580	-24.58102350
Ag	-12.54114900	-2.39435580	-24.58102350
Ag	-15.43014900	-2.39435580	-24.58102350
Ag	-8.05453200	-3.19247430	-27.03737990
Ag	-10.94353200	-3.19247430	-27.03737990
Ag	-13.83253200	-3.19247430	-27.03737990
Ag	-9.34591500	-3.99059290	-29.49373640
Ag	-12.23491500	-3.99059290	-29.49373640
Ag	-10.63729800	-4.78871150	-31.95009280
Ag	-2.58854400	1.28641120	-21.19008890
Ag	-5.47754400	1.28641120	-21.19008890
Ag	-8.36654400	1.28641120	-21.19008890
Ag	-11.25554400	1.28641120	-21.19008890
Ag	-14.14454400	1.28641120	-21.19008890
Ag	-17.03354400	1.28641120	-21.19008890
Ag	-3.87992700	0.48829260	-23.64644530
Ag	-6.76892700	0.48829260	-23.64644530
Ag	-9.65792700	0.48829260	-23.64644530
Ag	-12.54692700	0.48829260	-23.64644530
Ag	-15.43592700	0.48829260	-23.64644530
Ag	-5.17131000	-0.30982600	-26.10280180
Ag	-8.06031000	-0.30982600	-26.10280180
Ag	-10.94931000	-0.30982600	-26.10280180
Ag	-13.83831000	-0.30982600	-26.10280180
Ag	-6.46269300	-1.10794450	-28.55915820
Ag	-9.35169300	-1.10794450	-28.55915820
Ag	-12.24069300	-1.10794450	-28.55915820
Ag	-7.75407600	-1.90606310	-31.01551460
Ag	-10.64307600	-1.90606310	-31.01551460
Ag	-9.04545900	-2.70418170	-33.47187110
Ag	-3.88570500	3.37094100	-22.71186720
Ag	-6.77470500	3.37094100	-22.71186720
Ag	-9.66370500	3.37094100	-22.71186720
Ag	-12.55270500	3.37094100	-22.71186720

(continues on next page)

(continued from previous page)

Ag	-15.44170500	3.37094100	-22.71186720
Ag	-5.17708800	2.57282240	-25.16822360
Ag	-8.06608800	2.57282240	-25.16822360
Ag	-10.95508800	2.57282240	-25.16822360
Ag	-13.84408800	2.57282240	-25.16822360
Ag	-6.46847100	1.77470390	-27.62458000
Ag	-9.35747100	1.77470390	-27.62458000
Ag	-12.24647100	1.77470390	-27.62458000
Ag	-7.75985400	0.97658530	-30.08093650
Ag	-10.64885400	0.97658530	-30.08093650
Ag	-9.05123700	0.17846670	-32.53729290
Ag	-5.18286600	5.45547080	-24.23364540
Ag	-8.07186600	5.45547080	-24.23364540
Ag	-10.96086600	5.45547080	-24.23364540
Ag	-13.84986600	5.45547080	-24.23364540
Ag	-6.47424900	4.65735220	-26.69000190
Ag	-9.36324900	4.65735220	-26.69000190
Ag	-12.25224900	4.65735220	-26.69000190
Ag	-7.76563200	3.85923370	-29.14635830
Ag	-10.65463200	3.85923370	-29.14635830
Ag	-9.05701500	3.06111510	-31.60271470
Ag	-6.48002700	7.54000060	-25.75542370
Ag	-9.36902700	7.54000060	-25.75542370
Ag	-12.25802700	7.54000060	-25.75542370
Ag	-7.77141000	6.74188200	-28.21178010
Ag	-10.66041000	6.74188200	-28.21178010
Ag	-9.06279300	5.94376350	-30.66813660
Ag	-7.77718800	9.62453040	-27.27720200
Ag	-10.66618800	9.62453040	-27.27720200
Ag	-9.06857100	8.82641190	-29.73355840
Ag	-9.07434900	11.70906020	-28.79898020
Ag	-1.30293900	2.08619170	-23.64619190
Ag	-2.60010000	4.17161430	-25.16522260
Ag	-3.89726100	6.25703680	-26.68425320
Ag	-5.19442200	8.34245940	-28.20328390
Ag	-6.49158300	10.42788190	-29.72231450
Ag	-2.59432200	1.28807310	-26.10254830
Ag	-3.89148300	3.37349570	-27.62157900
Ag	-5.18864400	5.45891820	-29.14060970
Ag	-6.48580500	7.54434080	-30.65964030
Ag	-3.88570500	0.48995450	-28.55890480
Ag	-5.18286600	2.57537710	-30.07793540
Ag	-6.48002700	4.66079960	-31.59696610
Ag	-5.17708800	-0.30816410	-31.01526120
Ag	-6.47424900	1.77725850	-32.53429190
Ag	-6.46847100	-1.10628270	-33.47161760
Ag	-0.01733400	2.88507940	-26.10504250
Ag	-1.31449500	4.97050200	-27.62407320
Ag	-2.61165600	7.05592450	-29.14310380
Ag	-3.90881700	9.14134710	-30.66213450
Ag	-1.30871700	2.08696080	-28.56139890
Ag	-2.60587800	4.17238340	-30.08042960
Ag	-3.90303900	6.25780590	-31.59946030
Ag	-2.60010000	1.28884220	-31.01775540
Ag	-3.89726100	3.37426480	-32.53678600
Ag	-3.89148300	0.49072370	-33.47411180
Ag	1.26827100	3.68396710	-28.56389310

(continues on next page)

(continued from previous page)

Ag	-0.02889000	5.76938970	-30.08292380
Ag	-1.32605100	7.85481230	-31.60195440
Ag	-0.02311200	2.88584860	-31.02024950
Ag	-1.32027300	4.97127110	-32.53928020
Ag	-1.31449500	2.08773000	-33.47660600
Ag	2.55387600	4.48285490	-31.02274370
Ag	1.25671500	6.56827740	-32.54177440
Ag	1.26249300	3.68473630	-33.47910010
Ag	3.83948100	5.28174260	-33.48159430
Ag	-4.18038300	-2.58276600	-17.21195420
Ag	-7.06938300	-2.58276600	-17.21195420
Ag	-9.95838300	-2.58276600	-17.21195420
Ag	-12.84738300	-2.58276600	-17.21195420
Ag	-15.73638300	-2.58276600	-17.21195420
Ag	-18.62538300	-2.58276600	-17.21195420
Ag	-5.47176600	-5.16553200	-17.21195420
Ag	-8.36076600	-5.16553200	-17.21195420
Ag	-11.24976600	-5.16553200	-17.21195420
Ag	-14.13876600	-5.16553200	-17.21195420
Ag	-17.02776600	-5.16553200	-17.21195420
Ag	-6.76314900	-7.74829800	-17.21195420
Ag	-9.65214900	-7.74829800	-17.21195420
Ag	-12.54114900	-7.74829800	-17.21195420
Ag	-15.43014900	-7.74829800	-17.21195420
Ag	-8.05453200	-10.33106400	-17.21195420
Ag	-10.94353200	-10.33106400	-17.21195420
Ag	-13.83253200	-10.33106400	-17.21195420
Ag	-9.34591500	-12.91383000	-17.21195420
Ag	-12.23491500	-12.91383000	-17.21195420
Ag	-10.63729800	-15.49659600	-17.21195420
Ag	-2.58854400	-3.38590800	-19.66471520
Ag	-5.47754400	-3.38590800	-19.66471520
Ag	-8.36654400	-3.38590800	-19.66471520
Ag	-11.25554400	-3.38590800	-19.66471520
Ag	-14.14454400	-3.38590800	-19.66471520
Ag	-17.03354400	-3.38590800	-19.66471520
Ag	-3.87992700	-5.96867400	-19.66471520
Ag	-6.76892700	-5.96867400	-19.66471520
Ag	-9.65792700	-5.96867400	-19.66471520
Ag	-12.54692700	-5.96867400	-19.66471520
Ag	-15.43592700	-5.96867400	-19.66471520
Ag	-5.17131000	-8.55144000	-19.66471520
Ag	-8.06031000	-8.55144000	-19.66471520
Ag	-10.94931000	-8.55144000	-19.66471520
Ag	-13.83831000	-8.55144000	-19.66471520
Ag	-6.46269300	-11.13420600	-19.66471520
Ag	-9.35169300	-11.13420600	-19.66471520
Ag	-12.24069300	-11.13420600	-19.66471520
Ag	-7.75407600	-13.71697200	-19.66471520
Ag	-10.64307600	-13.71697200	-19.66471520
Ag	-9.04545900	-16.29973800	-19.66471520
Ag	-3.88570500	-4.18905000	-22.11747620
Ag	-6.77470500	-4.18905000	-22.11747620
Ag	-9.66370500	-4.18905000	-22.11747620
Ag	-12.55270500	-4.18905000	-22.11747620
Ag	-15.44170500	-4.18905000	-22.11747620
Ag	-5.17708800	-6.77181600	-22.11747620

(continues on next page)

(continued from previous page)

Ag	-8.06608800	-6.77181600	-22.11747620
Ag	-10.95508800	-6.77181600	-22.11747620
Ag	-13.84408800	-6.77181600	-22.11747620
Ag	-6.46847100	-9.35458200	-22.11747620
Ag	-9.35747100	-9.35458200	-22.11747620
Ag	-12.24647100	-9.35458200	-22.11747620
Ag	-7.75985400	-11.93734800	-22.11747620
Ag	-10.64885400	-11.93734800	-22.11747620
Ag	-9.05123700	-14.52011400	-22.11747620
Ag	-5.18286600	-4.99219200	-24.57023720
Ag	-8.07186600	-4.99219200	-24.57023720
Ag	-10.96086600	-4.99219200	-24.57023720
Ag	-13.84986600	-4.99219200	-24.57023720
Ag	-6.47424900	-7.57495800	-24.57023720
Ag	-9.36324900	-7.57495800	-24.57023720
Ag	-12.25224900	-7.57495800	-24.57023720
Ag	-7.76563200	-10.15772400	-24.57023720
Ag	-10.65463200	-10.15772400	-24.57023720
Ag	-9.05701500	-12.74049000	-24.57023720
Ag	-6.48002700	-5.79533400	-27.02299820
Ag	-9.36902700	-5.79533400	-27.02299820
Ag	-12.25802700	-5.79533400	-27.02299820
Ag	-7.77141000	-8.37810000	-27.02299820
Ag	-10.66041000	-8.37810000	-27.02299820
Ag	-9.06279300	-10.96086600	-27.02299820
Ag	-7.77718800	-6.59847600	-29.47575920
Ag	-10.66618800	-6.59847600	-29.47575920
Ag	-9.06857100	-9.18124200	-29.47575920
Ag	-9.07434900	-7.40161800	-31.92852020
Ag	-1.30293900	-5.47465500	-21.18432920
Ag	-2.60010000	-6.27490800	-23.63709020
Ag	-3.89726100	-7.07516100	-26.08985120
Ag	-5.19442200	-7.87541400	-28.54261220
Ag	-6.49158300	-8.67566700	-30.99537320
Ag	-2.59432200	-8.05742100	-21.18432920
Ag	-3.89148300	-8.85767400	-23.63709020
Ag	-5.18864400	-9.65792700	-26.08985120
Ag	-6.48580500	-10.45818000	-28.54261220
Ag	-3.88570500	-10.64018700	-21.18432920
Ag	-5.18286600	-11.44044000	-23.63709020
Ag	-6.48002700	-12.24069300	-26.08985120
Ag	-5.17708800	-13.22295300	-21.18432920
Ag	-6.47424900	-14.02320600	-23.63709020
Ag	-6.46847100	-15.80571900	-21.18432920
Ag	-0.01733400	-7.56629100	-22.70394320
Ag	-1.31449500	-8.36654400	-25.15670420
Ag	-2.61165600	-9.16679700	-27.60946520
Ag	-3.90881700	-9.96705000	-30.06222620
Ag	-1.30871700	-10.14905700	-22.70394320
Ag	-2.60587800	-10.94931000	-25.15670420
Ag	-3.90303900	-11.74956300	-27.60946520
Ag	-2.60010000	-12.73182300	-22.70394320
Ag	-3.89726100	-13.53207600	-25.15670420
Ag	-3.89148300	-15.31458900	-22.70394320
Ag	1.26827100	-9.65792700	-24.22355720
Ag	-0.02889000	-10.45818000	-26.67631820
Ag	-1.32605100	-11.25843300	-29.12907920

(continues on next page)

(continued from previous page)

Ag	-0.02311200	-12.24069300	-24.22355720
Ag	-1.32027300	-13.04094600	-26.67631820
Ag	-1.31449500	-14.82345900	-24.22355720
Ag	2.55387600	-11.74956300	-25.74317120
Ag	1.25671500	-12.54981600	-28.19593220
Ag	1.26249300	-14.33232900	-25.74317120
Ag	3.83948100	-13.84119900	-27.26278520
Ag	-4.18038300	-0.79811860	-14.75559780
Ag	-7.06938300	-0.79811860	-14.75559780
Ag	-9.95838300	-0.79811860	-14.75559780
Ag	-12.84738300	-0.79811860	-14.75559780
Ag	-15.73638300	-0.79811860	-14.75559780
Ag	-18.62538300	-0.79811860	-14.75559780
Ag	-5.47176600	-1.59623720	-12.29924130
Ag	-8.36076600	-1.59623720	-12.29924130
Ag	-11.24976600	-1.59623720	-12.29924130
Ag	-14.13876600	-1.59623720	-12.29924130
Ag	-17.02776600	-1.59623720	-12.29924130
Ag	-6.76314900	-2.39435580	-9.84288490
Ag	-9.65214900	-2.39435580	-9.84288490
Ag	-12.54114900	-2.39435580	-9.84288490
Ag	-15.43014900	-2.39435580	-9.84288490
Ag	-8.05453200	-3.19247430	-7.38652850
Ag	-10.94353200	-3.19247430	-7.38652850
Ag	-13.83253200	-3.19247430	-7.38652850
Ag	-9.34591500	-3.99059290	-4.93017200
Ag	-12.23491500	-3.99059290	-4.93017200
Ag	-10.63729800	-4.78871150	-2.47381560
Ag	-2.58854400	-3.37901740	-14.74970920
Ag	-5.47754400	-3.37901740	-14.74970920
Ag	-8.36654400	-3.37901740	-14.74970920
Ag	-11.25554400	-3.37901740	-14.74970920
Ag	-14.14454400	-3.37901740	-14.74970920
Ag	-17.03354400	-3.37901740	-14.74970920
Ag	-3.87992700	-4.17713600	-12.29335270
Ag	-6.76892700	-4.17713600	-12.29335270
Ag	-9.65792700	-4.17713600	-12.29335270
Ag	-12.54692700	-4.17713600	-12.29335270
Ag	-15.43592700	-4.17713600	-12.29335270
Ag	-5.17131000	-4.97525460	-9.83699630
Ag	-8.06031000	-4.97525460	-9.83699630
Ag	-10.94931000	-4.97525460	-9.83699630
Ag	-13.83831000	-4.97525460	-9.83699630
Ag	-6.46269300	-5.77337320	-7.38063990
Ag	-9.35169300	-5.77337320	-7.38063990
Ag	-12.24069300	-5.77337320	-7.38063990
Ag	-7.75407600	-6.57149180	-4.92428340
Ag	-10.64307600	-6.57149180	-4.92428340
Ag	-9.04545900	-7.36961040	-2.46792700
Ag	-3.88570500	-5.95991630	-14.74382060
Ag	-6.77470500	-5.95991630	-14.74382060
Ag	-9.66370500	-5.95991630	-14.74382060
Ag	-12.55270500	-5.95991630	-14.74382060
Ag	-15.44170500	-5.95991630	-14.74382060
Ag	-5.17708800	-6.75803490	-12.28746410
Ag	-8.06608800	-6.75803490	-12.28746410
Ag	-10.95508800	-6.75803490	-12.28746410

(continues on next page)

(continued from previous page)

Ag	-13.84408800	-6.75803490	-12.28746410
Ag	-6.46847100	-7.55615350	-9.83110770
Ag	-9.35747100	-7.55615350	-9.83110770
Ag	-12.24647100	-7.55615350	-9.83110770
Ag	-7.75985400	-8.35427210	-7.37475130
Ag	-10.64885400	-8.35427210	-7.37475130
Ag	-9.05123700	-9.15239070	-4.91839480
Ag	-5.18286600	-8.54081520	-14.73793200
Ag	-8.07186600	-8.54081520	-14.73793200
Ag	-10.96086600	-8.54081520	-14.73793200
Ag	-13.84986600	-8.54081520	-14.73793200
Ag	-6.47424900	-9.33893370	-12.28157550
Ag	-9.36324900	-9.33893370	-12.28157550
Ag	-12.25224900	-9.33893370	-12.28157550
Ag	-7.76563200	-10.13705230	-9.82521910
Ag	-10.65463200	-10.13705230	-9.82521910
Ag	-9.05701500	-10.93517090	-7.36886270
Ag	-6.48002700	-11.12171400	-14.73204340
Ag	-9.36902700	-11.12171400	-14.73204340
Ag	-12.25802700	-11.12171400	-14.73204340
Ag	-7.77141000	-11.91983260	-12.27568690
Ag	-10.66041000	-11.91983260	-12.27568690
Ag	-9.06279300	-12.71795120	-9.81933050
Ag	-7.77718800	-13.70261290	-14.72615480
Ag	-10.66618800	-13.70261290	-14.72615480
Ag	-9.06857100	-14.50073150	-12.26979830
Ag	-9.07434900	-16.28351170	-14.72026620
Ag	-1.30293900	-5.46971460	-13.23277930
Ag	-2.60010000	-8.04972070	-13.22963830
Ag	-3.89726100	-10.62972680	-13.22649730
Ag	-5.19442200	-13.20973290	-13.22335630
Ag	-6.49158300	-15.78973900	-13.22021530
Ag	-2.59432200	-6.26783310	-10.77642280
Ag	-3.89148300	-8.84783930	-10.77328180
Ag	-5.18864400	-11.42784540	-10.77014080
Ag	-6.48580500	-14.00785150	-10.76699980
Ag	-3.88570500	-7.06595170	-8.32006640
Ag	-5.18286600	-9.64595780	-8.31692540
Ag	-6.48002700	-12.22596400	-8.31378440
Ag	-5.17708800	-7.86407030	-5.86371000
Ag	-6.47424900	-10.44407640	-5.86056900
Ag	-6.46847100	-8.66218890	-3.40735350
Ag	-0.01733400	-7.56130440	-11.71310180
Ag	-1.31449500	-10.14131050	-11.70996080
Ag	-2.61165600	-12.72131660	-11.70681980
Ag	-3.90881700	-15.30132280	-11.70367880
Ag	-1.30871700	-8.35942300	-9.25674530
Ag	-2.60587800	-10.93942910	-9.25360430
Ag	-3.90303900	-13.51943520	-9.25046330
Ag	-2.60010000	-9.15754160	-6.80038890
Ag	-3.89726100	-11.73754770	-6.79724790
Ag	-3.89148300	-9.95566020	-4.34403250
Ag	1.26827100	-9.65289430	-10.19342430
Ag	-0.02889000	-12.23290040	-10.19028330
Ag	-1.32605100	-14.81290650	-10.18714230
Ag	-0.02311200	-10.45101290	-7.73706780
Ag	-1.32027300	-13.03101900	-7.73392680

(continues on next page)

(continued from previous page)

Ag	-1.31449500	-11.24913150	-5.28071140
Ag	2.55387600	-11.74448420	-8.67374680
Ag	1.25671500	-14.32449030	-8.67060580
Ag	1.26249300	-12.54260270	-6.21739030
Ag	3.83948100	-13.83607400	-7.15406930
Ag	-2.58854400	1.29756040	-13.23744210
Ag	-5.47754400	1.29756040	-13.23744210
Ag	-8.36654400	1.29756040	-13.23744210
Ag	-11.25554400	1.29756040	-13.23744210
Ag	-14.14454400	1.29756040	-13.23744210
Ag	-17.03354400	1.29756040	-13.23744210
Ag	-3.87992700	3.38706200	-11.71933030
Ag	-6.76892700	3.38706200	-11.71933030
Ag	-9.65792700	3.38706200	-11.71933030
Ag	-12.54692700	3.38706200	-11.71933030
Ag	-15.43592700	3.38706200	-11.71933030
Ag	-5.17131000	5.47656350	-10.20121850
Ag	-8.06031000	5.47656350	-10.20121850
Ag	-10.94931000	5.47656350	-10.20121850
Ag	-13.83831000	5.47656350	-10.20121850
Ag	-6.46269300	7.56606510	-8.68310680
Ag	-9.35169300	7.56606510	-8.68310680
Ag	-12.24069300	7.56606510	-8.68310680
Ag	-7.75407600	9.65556670	-7.16499500
Ag	-10.64307600	9.65556670	-7.16499500
Ag	-9.04545900	11.74506830	-5.64688330
Ag	-3.88570500	0.50561920	-10.78104170
Ag	-6.77470500	0.50561920	-10.78104170
Ag	-9.66370500	0.50561920	-10.78104170
Ag	-12.55270500	0.50561920	-10.78104170
Ag	-15.44170500	0.50561920	-10.78104170
Ag	-5.17708800	2.59512070	-9.26293000
Ag	-8.06608800	2.59512070	-9.26293000
Ag	-10.95508800	2.59512070	-9.26293000
Ag	-13.84408800	2.59512070	-9.26293000
Ag	-6.46847100	4.68462230	-7.74481820
Ag	-9.35747100	4.68462230	-7.74481820
Ag	-12.24647100	4.68462230	-7.74481820
Ag	-7.75985400	6.77412390	-6.22670640
Ag	-10.64885400	6.77412390	-6.22670640
Ag	-9.05123700	8.86362550	-4.70859470
Ag	-5.18286600	-0.28632210	-8.32464140
Ag	-8.07186600	-0.28632210	-8.32464140
Ag	-10.96086600	-0.28632210	-8.32464140
Ag	-13.84986600	-0.28632210	-8.32464140
Ag	-6.47424900	1.80317950	-6.80652960
Ag	-9.36324900	1.80317950	-6.80652960
Ag	-12.25224900	1.80317950	-6.80652960
Ag	-7.76563200	3.89268110	-5.28841780
Ag	-10.65463200	3.89268110	-5.28841780
Ag	-9.05701500	5.98218270	-3.77030610
Ag	-6.48002700	-1.07826330	-5.86824100
Ag	-9.36902700	-1.07826330	-5.86824100
Ag	-12.25802700	-1.07826330	-5.86824100
Ag	-7.77141000	1.01123830	-4.35012920
Ag	-10.66041000	1.01123830	-4.35012920
Ag	-9.06279300	3.10073990	-2.83201750

(continues on next page)

(continued from previous page)

```

Ag -7.77718800 -1.87020450 -3.41184070
Ag -10.66618800 -1.87020450 -3.41184070
Ag -9.06857100 0.21929710 -1.89372890
Ag -9.07434900 -2.66214570 -0.95544030
Ag -1.30293900 2.09418550 -10.78031380
Ag -2.60010000 1.29990700 -8.32561160
Ag -3.89726100 0.50562860 -5.87090940
Ag -5.19442200 -0.28864990 -3.41620710
Ag -6.49158300 -1.08292840 -0.96150490
Ag -2.59432200 4.18368710 -9.26220210
Ag -3.89148300 3.38940860 -6.80749980
Ag -5.18864400 2.59513010 -4.35279760
Ag -6.48580500 1.80085170 -1.89809540
Ag -3.88570500 6.27318870 -7.74409030
Ag -5.18286600 5.47891020 -5.28938810
Ag -6.48002700 4.68463170 -2.83468580
Ag -5.17708800 8.36269030 -6.22597860
Ag -6.47424900 7.56841180 -3.77127630
Ag -6.46847100 10.45219180 -4.70786680
Ag -0.01733400 2.89314790 -8.32148750
Ag -1.31449500 2.09886940 -5.86678530
Ag -2.61165600 1.30459090 -3.41208300
Ag -3.90881700 0.51031250 -0.95738080
Ag -1.30871700 4.98264940 -6.80337570
Ag -2.60587800 4.18837100 -4.34867350
Ag -3.90303900 3.39409250 -1.89397120
Ag -2.60010000 7.07215100 -5.28526400
Ag -3.89726100 6.27787260 -2.83056170
Ag -3.89148300 9.16165260 -3.76715220
Ag 1.26827100 3.69211020 -5.86266120
Ag -0.02889000 2.89783180 -3.40795890
Ag -1.32605100 2.10355330 -0.95325670
Ag -0.02311200 5.78161180 -4.34454940
Ag -1.32027300 4.98733340 -1.88984710
Ag -1.31449500 7.87111340 -2.82643760
Ag 2.55387600 4.49107260 -3.40383480
Ag 1.25671500 3.69679410 -0.94913260
Ag 1.26249300 6.58057420 -1.88572300
Ag 3.83948100 5.29003500 -0.94500850
SUBEND
end
EndEngine
eor

```

15.2.8 QM/FQ(F μ): Quantum Mechanics / Fluctuating Charges (and Fluctuating Dipoles)

Example: QM/FQ(F μ): 2-Methyloxirane (QM) in Water

Two examples: a QM/FQ calculation and a QM/FQF μ calculation.

Download FQQM_scf.run

```

#!/bin/bash

# QMFQ solvation calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.32246      0.46994     -0.44553
    C      0.03851      0.37791      0.32993
    O     -1.13145      0.98673     -0.28822
    C     -1.09292     -0.44743     -0.11660
    H     -0.99733     -1.01009     -1.04597
    H     -1.81522     -0.83104      0.60631
    H      0.10287      0.59921      1.39924
    H      2.07829     -0.18966      0.00080
    H      1.71275      1.49611     -0.42640
    H      1.17353      0.16408     -1.48893
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQ energy calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O      6.179      -4.919      2.699      1
    H      7.008      -4.361      2.695      1
    H      5.687      -4.779      3.558      1
    O      3.341      2.501      5.245      2
    H      2.813      2.455      6.093      2
    H      3.93       1.695      5.175      2
    O      2.692      8.795      -4.87      3

```

(continues on next page)

(continued from previous page)

H	3.592	8.369	-4.781	3
H	2.444	9.232	-4.005	3
O	-2.039	5.881	6.772	4
H	-3.025	6.045	6.742	4
H	-1.597	6.604	7.301	4
O	4.733	-3.969	5.277	5
H	3.944	-3.36	5.362	5
H	4.456	-4.904	5.497	5
O	-0.143	3.368	-8.787	6
H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22

(continues on next page)

(continued from previous page)

H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25
H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41

(continues on next page)

(continued from previous page)

H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44
H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60

(continues on next page)

(continued from previous page)

H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63
H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79

(continues on next page)

(continued from previous page)

H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82
H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98

(continues on next page)

(continued from previous page)

H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101
H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117

(continues on next page)

(continued from previous page)

H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120
H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136

(continues on next page)

(continued from previous page)

H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139
H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155

(continues on next page)

(continued from previous page)

H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158
H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174

(continues on next page)

(continued from previous page)

H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177
H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193

(continues on next page)

(continued from previous page)

H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196
H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212

(continues on next page)

(continued from previous page)

```

H      -5.324      6.26      7.16      212
H      -4.448      6.234      8.538      212
O      -7.198      8.279      2.233      213
H      -6.522      8.005      2.917      213
H      -7.442      9.239      2.372      213
O      -0.931     10.111      0.639      214
H      -0.955      9.372     -0.034      214
H      -0.074     10.065      1.154      214
O      6.652     -0.975     -5.911      215
H      6.955     -1.129     -6.852      215
H      6.039     -1.715     -5.634      215
O     11.643      1.502     -0.57      216
H     10.975      1.438      0.171      216
H     11.176      1.745     -1.42      216
O     -8.267     -2.766     -5.204      217
H     -8.194     -1.919     -5.73      217
H     -7.565     -3.41      -5.509      217
O      4.001     -4.795      1.063      218
H      4.818     -4.764      1.639      218
H      3.835     -5.737      0.771      218
O     -3.518     -0.073     -11.143      219
H     -4.375     -0.493     -11.442      219
H     -2.889     -0.009     -11.918      219
O      5.278      8.33      -4.17      220
H      5.812      8.57      -3.36      220
H      5.813      8.525     -4.992      220
O     -7.165      5.42      -3.118      221
H     -6.784      4.835     -2.402      221
H     -7.286      4.886     -3.955      221
O      4.501      8.636     -0.932      222
H      4.421      7.683     -1.224      222
H      3.623      9.097     -1.055      222
O     -1.648     -10.25      4.458      223
H     -2.159     -10.03      3.627      223
H     -2.211     -10.044      5.259      223
O     -1.212      7.616      8.694      224
H     -0.792      8.473      8.398      224
H     -2.05      7.814      9.203      224
O     -9.049      1.489      0.827      225
H     -8.587      2.255      1.272      225
H     -8.522      0.652      0.972      225
End
END
EndEngine
eor

```

Download FQQM_FQFMU_scf.run

```

#!/bin/bash

# QMFQ solvation calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.32246      0.46994     -0.44553
    C      0.03851      0.37791      0.32993

```

(continues on next page)

(continued from previous page)

```

O      -1.13145      0.98673      -0.28822
C      -1.09292      -0.44743      -0.11660
H      -0.99733      -1.01009      -1.04597
H      -1.81522      -0.83104      0.60631
H       0.10287      0.59921      1.39924
H       2.07829      -0.18966      0.00080
H       1.71275      1.49611      -0.42640
H       1.17353      0.16408      -1.48893
End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQFMU energy calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQFMU
    MolCharge 0.00
    Kernel GAUS

  AtomType
    Symbol O
    Chi 0.2908429850
    Eta 0.5625181140
    Alpha 2.2187983720
  End
  AtomType
    Symbol H
    Chi 0.1675711970
    Eta 0.6093265770
    Alpha 1.1906416090
  End
  Coords
O      6.179      -4.919      2.699      1
H      7.008      -4.361      2.695      1
H      5.687      -4.779      3.558      1
O      3.341      2.501      5.245      2
H      2.813      2.455      6.093      2
H      3.93       1.695      5.175      2
O      2.692      8.795      -4.87      3
H      3.592      8.369      -4.781      3
H      2.444      9.232      -4.005      3
O      -2.039      5.881      6.772      4
H      -3.025      6.045      6.742      4
H      -1.597      6.604      7.301      4
O      4.733      -3.969      5.277      5

```

(continues on next page)

(continued from previous page)

H	3.944	-3.36	5.362	5
H	4.456	-4.904	5.497	5
O	-0.143	3.368	-8.787	6
H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24

(continues on next page)

(continued from previous page)

H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25
H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43

(continues on next page)

(continued from previous page)

H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44
H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62

(continues on next page)

(continued from previous page)

H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63
H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81

(continues on next page)

(continued from previous page)

H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82
H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100

(continues on next page)

(continued from previous page)

H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101
H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119

(continues on next page)

(continued from previous page)

H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120
H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138

(continues on next page)

(continued from previous page)

H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139
H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157

(continues on next page)

(continued from previous page)

H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158
H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176

(continues on next page)

(continued from previous page)

H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177
H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195

(continues on next page)

(continued from previous page)

H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196
H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214

(continues on next page)

(continued from previous page)

```

H      -0.955      9.372     -0.034     214
H      -0.074     10.065      1.154     214
O       6.652     -0.975     -5.911     215
H       6.955     -1.129     -6.852     215
H       6.039     -1.715     -5.634     215
O      11.643      1.502     -0.57      216
H      10.975      1.438      0.171     216
H      11.176      1.745     -1.42     216
O      -8.267     -2.766     -5.204     217
H      -8.194     -1.919     -5.73     217
H      -7.565     -3.41      -5.509     217
O       4.001     -4.795      1.063     218
H       4.818     -4.764      1.639     218
H       3.835     -5.737      0.771     218
O      -3.518     -0.073     -11.143     219
H      -4.375     -0.493     -11.442     219
H      -2.889     -0.009     -11.918     219
O       5.278      8.33      -4.17     220
H       5.812      8.57      -3.36     220
H       5.813      8.525     -4.992     220
O      -7.165      5.42      -3.118     221
H      -6.784      4.835     -2.402     221
H      -7.286      4.886     -3.955     221
O       4.501      8.636     -0.932     222
H       4.421      7.683     -1.224     222
H       3.623      9.097     -1.055     222
O      -1.648     -10.25      4.458     223
H      -2.159     -10.03      3.627     223
H      -2.211     -10.044      5.259     223
O      -1.212      7.616      8.694     224
H      -0.792      8.473      8.398     224
H      -2.05      7.814      9.203     224
O      -9.049      1.489      0.827     225
H      -8.587      2.255      1.272     225
H      -8.522      0.652      0.972     225
End
END
EndEngine
eor

```

Example: QM/FQ(F μ): geometry optimization

Download FQQM_GO.run

```

#!/bin/bash

# QM/FQ geometry optimization of methyloxirane in water
# note the inclusion of non-electrostatic terms in the QMFQ block
# via the NonEle keyword

$AMSBIN/ams << eor
system
  Atoms
    C      1.31850905      0.47502665     -0.44755569
    C      0.04022051      0.38681907      0.33447493

```

(continues on next page)

(continued from previous page)

```

O      -1.15849182      0.98791679      -0.28490245
C      -1.08540829      -0.45486977      -0.11644722
H      -0.96598328      -1.02414973      -1.04262009
H      -1.81348643      -0.83430955       0.60457995
H       0.09244672       0.63108069       1.40043377
H       2.06109548      -0.21931967      -0.02383383
H       1.74548955       1.48727456      -0.40512799
H       1.15709853       0.18029096      -1.49437139
End
End

```

Task GeometryOptimization

```

Engine adf
  Relativity
    Level None
  End
  Basis
    Type TZP
    Core None
  End
  Symmetry NoSym
  Title QM/FQ Geometry optimization
  XC
    gga PBE
  End
  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    NonEle LJ
    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
O      6.179      -4.919      2.699      1
H      7.008      -4.361      2.695      1
H      5.687      -4.779      3.558      1
O      3.341      2.501      5.245      2
H      2.813      2.455      6.093      2
H      3.93       1.695      5.175      2
O      2.692      8.795      -4.87      3
H      3.592      8.369      -4.781      3
H      2.444      9.232      -4.005      3
O      -2.039      5.881      6.772      4
H      -3.025      6.045      6.742      4
H      -1.597      6.604      7.301      4
O      4.733      -3.969      5.277      5
H      3.944      -3.36       5.362      5
H      4.456      -4.904      5.497      5
O      -0.143      3.368      -8.787      6

```

(continues on next page)

(continued from previous page)

H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25

(continues on next page)

(continued from previous page)

H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44

(continues on next page)

(continued from previous page)

H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63

(continues on next page)

(continued from previous page)

H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82

(continues on next page)

(continued from previous page)

H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101

(continues on next page)

(continued from previous page)

H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120

(continues on next page)

(continued from previous page)

H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139

(continues on next page)

(continued from previous page)

H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158

(continues on next page)

(continued from previous page)

H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177

(continues on next page)

(continued from previous page)

H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196

(continues on next page)

(continued from previous page)

H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215

(continues on next page)

(continued from previous page)

```

H      6.955      -1.129      -6.852      215
H      6.039      -1.715      -5.634      215
O     11.643       1.502      -0.57       216
H     10.975       1.438       0.171      216
H     11.176       1.745      -1.42       216
O     -8.267      -2.766      -5.204      217
H     -8.194      -1.919      -5.73       217
H     -7.565      -3.41       -5.509      217
O      4.001      -4.795       1.063      218
H      4.818      -4.764       1.639      218
H      3.835      -5.737       0.771      218
O     -3.518      -0.073     -11.143      219
H     -4.375      -0.493     -11.442      219
H     -2.889      -0.009     -11.918      219
O      5.278       8.33       -4.17      220
H      5.812       8.57       -3.36      220
H      5.813       8.525      -4.992      220
O     -7.165       5.42       -3.118      221
H     -6.784       4.835      -2.402      221
H     -7.286       4.886      -3.955      221
O      4.501       8.636      -0.932      222
H      4.421       7.683      -1.224      222
H      3.623       9.097      -1.055      222
O     -1.648      -10.25       4.458      223
H     -2.159      -10.03       3.627      223
H     -2.211      -10.044       5.259      223
O     -1.212       7.616       8.694      224
H     -0.792       8.473       8.398      224
H     -2.05       7.814       9.203      224
O     -9.049       1.489       0.827      225
H     -8.587       2.255       1.272      225
H     -8.522       0.652       0.972      225
End
END
EndEngine
eor

```

Example: QM/FQ(F_μ): polarizability 2-Methyloxirane (AORESPONSE)

Two examples: a QM/FQ calculation and a QM/FQF_μ calculation.

Download FQQM_aoreponse.run

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.32246      0.46994     -0.44553
    C      0.03851      0.37791      0.32993
    O     -1.13145      0.98673     -0.28822
    C     -1.09292     -0.44743     -0.11660
    H     -0.99733     -1.01009     -1.04597

```

(continues on next page)

(continued from previous page)

```

      H      -1.81522      -0.83104      0.60631
      H       0.10287       0.59921      1.39924
      H       2.07829      -0.18966      0.00080
      H       1.71275       1.49611     -0.42640
      H       1.17353       0.16408     -1.48893
    End
  End
task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 0.0 0.5 [eV]
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQ molecular polarizability calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

  AtomType
    Symbol O
    Chi 0.189194
    Eta 0.523700
  End
  AtomType
    Symbol H
    Chi 0.012767
    Eta 0.537512
  End
  Coords
    O      6.179      -4.919      2.699      1
    H      7.008      -4.361      2.695      1
    H      5.687      -4.779      3.558      1
    O      3.341      2.501      5.245      2
    H      2.813      2.455      6.093      2
    H      3.93       1.695      5.175      2
    O      2.692      8.795      -4.87      3
    H      3.592      8.369      -4.781      3
    H      2.444      9.232      -4.005      3
    O     -2.039      5.881      6.772      4
    H     -3.025      6.045      6.742      4
    H     -1.597      6.604      7.301      4
    O      4.733     -3.969      5.277      5
    H      3.944     -3.36      5.362      5
    H      4.456     -4.904      5.497      5
    O     -0.143      3.368     -8.787      6

```

(continues on next page)

(continued from previous page)

H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25

(continues on next page)

(continued from previous page)

H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44

(continues on next page)

(continued from previous page)

H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63

(continues on next page)

(continued from previous page)

H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82

(continues on next page)

(continued from previous page)

H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101

(continues on next page)

(continued from previous page)

H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120

(continues on next page)

(continued from previous page)

H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139

(continues on next page)

(continued from previous page)

H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158

(continues on next page)

(continued from previous page)

H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177

(continues on next page)

(continued from previous page)

H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196

(continues on next page)

(continued from previous page)

H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215

(continues on next page)

(continued from previous page)

```

H      6.955      -1.129      -6.852      215
H      6.039      -1.715      -5.634      215
O     11.643       1.502      -0.57       216
H     10.975       1.438       0.171      216
H     11.176       1.745      -1.42       216
O     -8.267      -2.766      -5.204      217
H     -8.194      -1.919      -5.73       217
H     -7.565      -3.41       -5.509      217
O      4.001      -4.795       1.063      218
H      4.818      -4.764       1.639      218
H      3.835      -5.737       0.771      218
O     -3.518      -0.073     -11.143      219
H     -4.375      -0.493     -11.442      219
H     -2.889      -0.009     -11.918      219
O      5.278       8.33       -4.17       220
H      5.812       8.57       -3.36       220
H      5.813       8.525      -4.992      220
O     -7.165       5.42       -3.118      221
H     -6.784       4.835      -2.402      221
H     -7.286       4.886      -3.955      221
O      4.501       8.636      -0.932      222
H      4.421       7.683      -1.224      222
H      3.623       9.097      -1.055      222
O     -1.648      -10.25       4.458      223
H     -2.159      -10.03       3.627      223
H     -2.211      -10.044       5.259      223
O     -1.212       7.616       8.694      224
H     -0.792       8.473       8.398      224
H     -2.05       7.814       9.203      224
O     -9.049       1.489       0.827      225
H     -8.587       2.255       1.272      225
H     -8.522       0.652       0.972      225
End
END
EndEngine
eor

```

Download FQQM_FQFMU_aoresponse.run

```

#!/bin/bash

# QM/FQFMU polarizability calculation

$AMSBIN/ams << eor
system
Atoms
C      1.32246      0.46994     -0.44553
C      0.03851      0.37791      0.32993
O     -1.13145      0.98673     -0.28822
C     -1.09292     -0.44743     -0.11660
H     -0.99733     -1.01009     -1.04597
H     -1.81522     -0.83104      0.60631
H      0.10287      0.59921      1.39924
H      2.07829     -0.18966      0.00080
H      1.71275      1.49611     -0.42640
H      1.17353      0.16408     -1.48893
End

```

(continues on next page)

(continued from previous page)

```

End
task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 0.0 0.5 [eV]
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQFMU molecular polarizability calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQFMU
    Kernel GAUS
    MolCharge 0.00

  AtomType
    Symbol O
    Chi 0.2908429850
    Eta 0.5625181140
    Alpha 2.2187983720
  End
  AtomType
    Symbol H
    Chi 0.1675711970
    Eta 0.6093265770
    Alpha 1.1906416090
  End
  Coords
O      6.179      -4.919      2.699      1
H      7.008      -4.361      2.695      1
H      5.687      -4.779      3.558      1
O      3.341      2.501      5.245      2
H      2.813      2.455      6.093      2
H      3.93       1.695      5.175      2
O      2.692      8.795      -4.87      3
H      3.592      8.369      -4.781      3
H      2.444      9.232      -4.005      3
O      -2.039      5.881      6.772      4
H      -3.025      6.045      6.742      4
H      -1.597      6.604      7.301      4
O      4.733      -3.969      5.277      5
H      3.944      -3.36      5.362      5
H      4.456      -4.904      5.497      5
O      -0.143      3.368      -8.787      6
H      0.262      2.454      -8.8      6
H      -0.588      3.548      -9.665      6
O      0.957      0.844      -8.505      7

```

(continues on next page)

(continued from previous page)

H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25
H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26

(continues on next page)

(continued from previous page)

H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44
H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45

(continues on next page)

(continued from previous page)

H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63
H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64

(continues on next page)

(continued from previous page)

H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82
H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83

(continues on next page)

(continued from previous page)

H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101
H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102

(continues on next page)

(continued from previous page)

H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120
H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121

(continues on next page)

(continued from previous page)

H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139
H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140

(continues on next page)

(continued from previous page)

H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158
H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159

(continues on next page)

(continued from previous page)

H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177
H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178

(continues on next page)

(continued from previous page)

H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196
H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197

(continues on next page)

(continued from previous page)

H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215
H	6.955	-1.129	-6.852	215
H	6.039	-1.715	-5.634	215
O	11.643	1.502	-0.57	216

(continues on next page)

(continued from previous page)

```

H      10.975    1.438    0.171    216
H      11.176    1.745   -1.42    216
O      -8.267   -2.766   -5.204    217
H      -8.194   -1.919   -5.73    217
H      -7.565   -3.41    -5.509    217
O       4.001   -4.795    1.063    218
H       4.818   -4.764    1.639    218
H       3.835   -5.737    0.771    218
O      -3.518   -0.073   -11.143    219
H      -4.375   -0.493   -11.442    219
H      -2.889   -0.009   -11.918    219
O       5.278    8.33    -4.17    220
H       5.812    8.57    -3.36    220
H       5.813    8.525   -4.992    220
O      -7.165    5.42    -3.118    221
H      -6.784    4.835   -2.402    221
H      -7.286    4.886   -3.955    221
O       4.501    8.636   -0.932    222
H       4.421    7.683   -1.224    222
H       3.623    9.097   -1.055    222
O      -1.648   -10.25    4.458    223
H      -2.159   -10.03    3.627    223
H      -2.211   -10.044    5.259    223
O      -1.212    7.616    8.694    224
H      -0.792    8.473    8.398    224
H      -2.05    7.814    9.203    224
O      -9.049    1.489    0.827    225
H      -8.587    2.255    1.272    225
H      -8.522    0.652    0.972    225
End
END
EndEngine
eor

```

Example: QM/FQ(F_μ): polarizability 2-Methyloxirane (RESPONSE)

Two examples: a QM/FQ calculation and a QM/FQ F_μ calculation.

Download FQQM_response.run

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
Atoms
C      1.32246    0.46994   -0.44553
C      0.03851    0.37791    0.32993
O     -1.13145    0.98673   -0.28822
C     -1.09292   -0.44743   -0.11660
H     -0.99733   -1.01009   -1.04597
H     -1.81522   -0.83104    0.60631
H      0.10287    0.59921    1.39924
H      2.07829   -0.18966    0.00080

```

(continues on next page)

(continued from previous page)

```

      H      1.71275      1.49611      -0.42640
      H      1.17353      0.16408      -1.48893
    End
  End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  basis
    type TZP
    core none
  End
  response
    allcomponents True
    analytic True
    Frequencies 0.0 0.5 [eV]
  End
  symmetry NOSYM
  title QM/FQ molecular polarizability calculation
  xc
    gga PBE
  End

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O      6.179      -4.919      2.699      1
    H      7.008      -4.361      2.695      1
    H      5.687      -4.779      3.558      1
    O      3.341      2.501      5.245      2
    H      2.813      2.455      6.093      2
    H      3.93       1.695      5.175      2
    O      2.692      8.795      -4.87      3
    H      3.592      8.369      -4.781      3
    H      2.444      9.232      -4.005      3
    O      -2.039      5.881      6.772      4
    H      -3.025      6.045      6.742      4
    H      -1.597      6.604      7.301      4
    O      4.733      -3.969      5.277      5
    H      3.944      -3.36      5.362      5
    H      4.456      -4.904      5.497      5
    O      -0.143      3.368      -8.787      6

```

(continues on next page)

(continued from previous page)

H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25

(continues on next page)

(continued from previous page)

H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44

(continues on next page)

(continued from previous page)

H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63

(continues on next page)

(continued from previous page)

H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82

(continues on next page)

(continued from previous page)

H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101

(continues on next page)

(continued from previous page)

H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120

(continues on next page)

(continued from previous page)

H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139

(continues on next page)

(continued from previous page)

H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158

(continues on next page)

(continued from previous page)

H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177

(continues on next page)

(continued from previous page)

H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196

(continues on next page)

(continued from previous page)

H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215

(continues on next page)

(continued from previous page)

```

H      6.955      -1.129      -6.852      215
H      6.039      -1.715      -5.634      215
O      11.643      1.502      -0.57      216
H      10.975      1.438      0.171      216
H      11.176      1.745      -1.42      216
O      -8.267      -2.766      -5.204      217
H      -8.194      -1.919      -5.73      217
H      -7.565      -3.41      -5.509      217
O      4.001      -4.795      1.063      218
H      4.818      -4.764      1.639      218
H      3.835      -5.737      0.771      218
O      -3.518      -0.073      -11.143      219
H      -4.375      -0.493      -11.442      219
H      -2.889      -0.009      -11.918      219
O      5.278      8.33      -4.17      220
H      5.812      8.57      -3.36      220
H      5.813      8.525      -4.992      220
O      -7.165      5.42      -3.118      221
H      -6.784      4.835      -2.402      221
H      -7.286      4.886      -3.955      221
O      4.501      8.636      -0.932      222
H      4.421      7.683      -1.224      222
H      3.623      9.097      -1.055      222
O      -1.648      -10.25      4.458      223
H      -2.159      -10.03      3.627      223
H      -2.211      -10.044      5.259      223
O      -1.212      7.616      8.694      224
H      -0.792      8.473      8.398      224
H      -2.05      7.814      9.203      224
O      -9.049      1.489      0.827      225
H      -8.587      2.255      1.272      225
H      -8.522      0.652      0.972      225
End
END
EndEngine
eor

```

Download FQQM_FQFMU_response.run

```

#!/bin/bash

# QM/FQFMU polarizability calculation

$AMSBIN/ams << eor
system
Atoms
C      1.32246      0.46994      -0.44553
C      0.03851      0.37791      0.32993
O     -1.13145      0.98673      -0.28822
C     -1.09292     -0.44743     -0.11660
H     -0.99733     -1.01009     -1.04597
H     -1.81522     -0.83104      0.60631
H      0.10287      0.59921      1.39924
H      2.07829     -0.18966      0.00080
H      1.71275      1.49611     -0.42640
H      1.17353      0.16408     -1.48893
End

```

(continues on next page)

(continued from previous page)

```

End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
basis
  type TZP
  core none
End
response
  allcomponents True
  analytic True
  Frequencies 0.0 0.5 [eV]
End
symmetry NOSYM
title QM/FQFMU molecular polarizability calculation
xc
  gga PBE
End

QMFQ
  FORCEFIELD FQFMU
  Kernel GAUS
  MolCharge 0.00

  AtomType
    Symbol O
    Chi 0.2908429850
    Eta 0.5625181140
    Alpha 2.2187983720
  End
  AtomType
    Symbol H
    Chi 0.1675711970
    Eta 0.6093265770
    Alpha 1.1906416090
  End
Coords
O      6.179      -4.919      2.699      1
H      7.008      -4.361      2.695      1
H      5.687      -4.779      3.558      1
O      3.341      2.501      5.245      2
H      2.813      2.455      6.093      2
H      3.93       1.695      5.175      2
O      2.692      8.795      -4.87      3
H      3.592      8.369      -4.781      3
H      2.444      9.232      -4.005      3
O      -2.039      5.881      6.772      4
H      -3.025      6.045      6.742      4
H      -1.597      6.604      7.301      4
O      4.733      -3.969      5.277      5
H      3.944      -3.36      5.362      5
H      4.456      -4.904      5.497      5
O      -0.143      3.368      -8.787      6

```

(continues on next page)

(continued from previous page)

H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25

(continues on next page)

(continued from previous page)

H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44

(continues on next page)

(continued from previous page)

H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63

(continues on next page)

(continued from previous page)

H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82

(continues on next page)

(continued from previous page)

H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101

(continues on next page)

(continued from previous page)

H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120

(continues on next page)

(continued from previous page)

H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139

(continues on next page)

(continued from previous page)

H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158

(continues on next page)

(continued from previous page)

H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177

(continues on next page)

(continued from previous page)

H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196

(continues on next page)

(continued from previous page)

H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215

(continues on next page)

(continued from previous page)

```

H      6.955      -1.129      -6.852      215
H      6.039      -1.715      -5.634      215
O      11.643       1.502       -0.57       216
H      10.975       1.438       0.171       216
H      11.176       1.745       -1.42       216
O      -8.267      -2.766      -5.204      217
H      -8.194      -1.919      -5.73       217
H      -7.565      -3.41       -5.509      217
O      4.001      -4.795       1.063      218
H      4.818      -4.764       1.639      218
H      3.835      -5.737       0.771      218
O      -3.518      -0.073     -11.143      219
H      -4.375      -0.493     -11.442      219
H      -2.889      -0.009     -11.918      219
O      5.278       8.33       -4.17      220
H      5.812       8.57       -3.36      220
H      5.813       8.525      -4.992      220
O      -7.165       5.42       -3.118      221
H      -6.784       4.835      -2.402      221
H      -7.286       4.886      -3.955      221
O      4.501       8.636      -0.932      222
H      4.421       7.683      -1.224      222
H      3.623       9.097      -1.055      222
O      -1.648      -10.25       4.458      223
H      -2.159      -10.03       3.627      223
H      -2.211      -10.044       5.259      223
O      -1.212       7.616       8.694      224
H      -0.792       8.473       8.398      224
H      -2.05       7.814       9.203      224
O      -9.049       1.489       0.827      225
H      -8.587       2.255       1.272      225
H      -8.522       0.652       0.972      225
End
END
EndEngine
eor

```

Example: QM/FQ(F μ): excitations 2-Methyloxirane

Two examples: a QM/FQ calculation and a QM/FQF μ calculation.

Download FQQM_td.run

```

#!/bin/bash

# QMFQ excitations calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.32246      0.46994      -0.44553
    C      0.03851      0.37791      0.32993
    O     -1.13145      0.98673     -0.28822
    C     -1.09292     -0.44743     -0.11660
    H     -0.99733     -1.01009     -1.04597

```

(continues on next page)

(continued from previous page)

```

      H      -1.81522      -0.83104      0.60631
      H       0.10287       0.59921      1.39924
      H       2.07829      -0.18966      0.00080
      H       1.71275       1.49611     -0.42640
      H       1.17353       0.16408     -1.48893
    End
  End
task SinglePoint

Engine adf
  Relativity
    Level None
  End
  basis
    type TZP
    core none
  End
  excitations
    lowest 10
    onlysing True
  End
  symmetry NOSYM
  title QM/FQ excitations calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O      6.179      -4.919      2.699      1
    H      7.008      -4.361      2.695      1
    H      5.687      -4.779      3.558      1
    O      3.341       2.501       5.245      2
    H      2.813       2.455       6.093      2
    H      3.93       1.695       5.175      2
    O      2.692       8.795      -4.87      3
    H      3.592       8.369      -4.781      3
    H      2.444       9.232      -4.005      3
    O     -2.039       5.881       6.772      4
    H     -3.025       6.045       6.742      4
    H     -1.597       6.604       7.301      4
    O      4.733      -3.969       5.277      5
    H      3.944      -3.36       5.362      5
    H      4.456      -4.904       5.497      5

```

(continues on next page)

(continued from previous page)

O	-0.143	3.368	-8.787	6
H	0.262	2.454	-8.8	6
H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24

(continues on next page)

(continued from previous page)

O	-3.466	6.667	1.722	25
H	-2.758	6.783	1.026	25
H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43

(continues on next page)

(continued from previous page)

O	-4.427	3.296	5.288	44
H	-4.348	2.855	6.182	44
H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62

(continues on next page)

(continued from previous page)

O	0.167	8.19	-1.584	63
H	-0.233	8.98	-2.049	63
H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81

(continues on next page)

(continued from previous page)

O	8.142	-2.725	7.39	82
H	7.867	-3.625	7.728	82
H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100

(continues on next page)

(continued from previous page)

O	0.21	-0.312	8.228	101
H	1.026	-0.659	7.765	101
H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119

(continues on next page)

(continued from previous page)

O	5.055	-6.955	6.321	120
H	4.585	-7.29	7.138	120
H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138

(continues on next page)

(continued from previous page)

O	4.819	-9.959	3.19	139
H	5.303	-10.736	2.788	139
H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157

(continues on next page)

(continued from previous page)

O	5.173	0.414	4.591	158
H	5.914	0.938	4.169	158
H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176

(continues on next page)

(continued from previous page)

O	9.532	2.335	1.199	177
H	9.808	3.202	0.786	177
H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195

(continues on next page)

(continued from previous page)

O	-6.62	3.126	1.407	196
H	-5.909	2.655	1.93	196
H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214

(continues on next page)

(continued from previous page)

```

O      6.652      -0.975      -5.911      215
H      6.955      -1.129      -6.852      215
H      6.039      -1.715      -5.634      215
O     11.643       1.502      -0.57       216
H     10.975       1.438       0.171      216
H     11.176       1.745      -1.42       216
O     -8.267      -2.766      -5.204      217
H     -8.194      -1.919      -5.73       217
H     -7.565      -3.41       -5.509      217
O      4.001      -4.795       1.063      218
H      4.818      -4.764       1.639      218
H      3.835      -5.737       0.771      218
O     -3.518      -0.073     -11.143      219
H     -4.375      -0.493     -11.442      219
H     -2.889      -0.009     -11.918      219
O      5.278       8.33       -4.17       220
H      5.812       8.57       -3.36       220
H      5.813       8.525      -4.992      220
O     -7.165       5.42       -3.118      221
H     -6.784       4.835      -2.402      221
H     -7.286       4.886      -3.955      221
O      4.501       8.636      -0.932      222
H      4.421       7.683      -1.224      222
H      3.623       9.097      -1.055      222
O     -1.648      -10.25       4.458      223
H     -2.159      -10.03       3.627      223
H     -2.211      -10.044       5.259      223
O     -1.212       7.616       8.694      224
H     -0.792       8.473       8.398      224
H     -2.05       7.814       9.203      224
O     -9.049       1.489       0.827      225
H     -8.587       2.255       1.272      225
H     -8.522       0.652       0.972      225
End
END
EndEngine
eor

```

Download FQQM_FQFMU_td.run

```

#!/bin/bash

# QM/FQFMU excitations calculation

$AMSBIN/ams << eor
system
Atoms
C      1.32246      0.46994     -0.44553
C      0.03851      0.37791      0.32993
O     -1.13145      0.98673     -0.28822
C     -1.09292     -0.44743     -0.11660
H     -0.99733     -1.01009     -1.04597
H     -1.81522     -0.83104      0.60631
H      0.10287      0.59921      1.39924
H      2.07829     -0.18966      0.00080
H      1.71275      1.49611     -0.42640
H      1.17353      0.16408     -1.48893

```

(continues on next page)

(continued from previous page)

```

End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  basis
    type TZP
    core none
  End
  excitations
    lowest 10
    onlysing True
  End
  symmetry NOSYM
  title QM/FQFMU excitations calculation
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD FQFMU
    Kernel GAUS
    MolCharge 0.00

  AtomType
    Symbol O
    Chi 0.2908429850
    Eta 0.5625181140
    Alpha 2.2187983720
  End
  AtomType
    Symbol H
    Chi 0.1675711970
    Eta 0.6093265770
    Alpha 1.1906416090
  End
  Coords
    O      6.179      -4.919      2.699      1
    H      7.008      -4.361      2.695      1
    H      5.687      -4.779      3.558      1
    O      3.341      2.501      5.245      2
    H      2.813      2.455      6.093      2
    H      3.93       1.695      5.175      2
    O      2.692      8.795      -4.87      3
    H      3.592      8.369      -4.781     3
    H      2.444      9.232      -4.005     3
    O      -2.039      5.881      6.772      4
    H      -3.025      6.045      6.742      4
    H      -1.597      6.604      7.301      4
    O      4.733      -3.969      5.277      5
    H      3.944      -3.36      5.362      5
    H      4.456      -4.904      5.497      5
    O      -0.143      3.368      -8.787     6
    H      0.262      2.454      -8.8       6

```

(continues on next page)

(continued from previous page)

H	-0.588	3.548	-9.665	6
O	0.957	0.844	-8.505	7
H	1.915	0.563	-8.573	7
H	0.399	0.276	-9.11	7
O	-2.971	-5.482	6.927	8
H	-3.616	-6.141	7.313	8
H	-3.473	-4.692	6.574	8
O	3.049	3.883	-9.821	9
H	2.387	4.418	-9.297	9
H	2.574	3.376	-10.54	9
O	6.079	8.112	2.853	10
H	6.635	7.88	3.651	10
H	5.245	7.56	2.855	10
O	3.022	-6.207	8.919	11
H	2.452	-6.216	9.74	11
H	2.653	-5.546	8.265	11
O	1.49	1.433	10.208	12
H	2.352	1.441	10.715	12
H	0.73	1.581	10.84	12
O	-2.472	4.816	-5.151	13
H	-1.53	5.086	-5.349	13
H	-2.91	4.492	-5.99	13
O	-6.138	7.963	-4.272	14
H	-6.292	7.128	-3.744	14
H	-5.371	7.824	-4.898	14
O	6.384	-7.3	0.928	15
H	5.462	-7.396	0.554	15
H	6.379	-6.615	1.657	15
O	8.759	-0.26	-1.401	16
H	8.949	-1.242	-1.397	16
H	7.993	-0.066	-0.788	16
O	0.745	6.829	1.703	17
H	0.439	6.196	0.992	17
H	0.186	6.704	2.523	17
O	-10.018	-4.546	3.877	18
H	-9.098	-4.855	3.637	18
H	-10.69	-5.035	3.321	18
O	-3.63	-2.187	-1.384	19
H	-2.767	-2.462	-1.807	19
H	-3.822	-1.231	-1.607	19
O	1.942	-6.524	-8.737	20
H	0.996	-6.22	-8.852	20
H	2.391	-6.563	-9.63	20
O	-3.547	2.764	0.052	21
H	-3.23	1.901	-0.342	21
H	-2.83	3.455	-0.038	21
O	1.904	8.539	-7.933	22
H	2.085	8.395	-6.96	22
H	0.923	8.447	-8.106	22
O	5.07	6.46	-6.979	23
H	5.462	5.945	-6.216	23
H	5.106	7.438	-6.774	23
O	1.317	1.858	-4.009	24
H	0.789	2.105	-4.821	24
H	1.565	0.891	-4.054	24
O	-3.466	6.667	1.722	25
H	-2.758	6.783	1.026	25

(continues on next page)

(continued from previous page)

H	-3.233	5.891	2.308	25
O	9.374	-0.284	-4.021	26
H	9.226	-0.462	-3.048	26
H	8.904	0.56	-4.28	26
O	-1.567	-0.699	-9.148	27
H	-1.459	-1.69	-9.234	27
H	-2.068	-0.348	-9.939	27
O	2.355	-6.756	5.05	28
H	3.312	-6.948	5.27	28
H	2.119	-5.837	5.367	28
O	-11.241	2.669	-0.446	29
H	-10.442	2.227	-0.039	29
H	-12.069	2.351	0.017	29
O	-0.519	2.829	-2.219	30
H	0.293	2.675	-2.782	30
H	-0.756	1.984	-1.738	30
O	2.736	2.528	1.949	31
H	3.367	2.379	2.711	31
H	1.894	2.946	2.29	31
O	-3.662	-3.579	1.114	32
H	-2.722	-3.33	1.349	32
H	-3.879	-3.238	0.2	32
O	-4.354	-0.05	9.809	33
H	-4.059	-0.99	9.982	33
H	-4.437	0.098	8.824	33
O	-8.16	-1.139	0.546	34
H	-8.636	-1.849	1.066	34
H	-7.667	-1.558	-0.216	34
O	-1.843	-1.194	6.421	35
H	-1.115	-0.876	7.029	35
H	-1.582	-1.022	5.471	35
O	-1.16	-3.054	2.421	36
H	-0.235	-2.945	2.057	36
H	-1.147	-3.716	3.171	36
O	-0.447	2.125	-6.198	37
H	-0.425	2.996	-6.688	37
H	0.061	1.437	-6.716	37
O	0.34	-7.527	7.536	38
H	0.901	-7.234	6.761	38
H	0.225	-8.52	7.508	38
O	-1.493	-5.793	-0.627	39
H	-2.034	-5.067	-1.052	39
H	-2.041	-6.249	0.074	39
O	3.987	0.323	-6.433	40
H	3.903	0.239	-7.426	40
H	4.943	0.201	-6.168	40
O	0.987	-6.627	0.39	41
H	0.661	-7.469	0.819	41
H	0.249	-6.221	-0.15	41
O	-9.847	1.488	4.432	42
H	-10.021	0.672	3.882	42
H	-10.581	2.151	4.286	42
O	2.111	10.191	-2.495	43
H	2.186	10.37	-1.514	43
H	1.935	11.049	-2.977	43
O	-4.427	3.296	5.288	44
H	-4.348	2.855	6.182	44

(continues on next page)

(continued from previous page)

H	-4.246	2.626	4.568	44
O	10.082	3.061	-2.716	45
H	10.773	3.744	-2.482	45
H	10.172	2.812	-3.68	45
O	4.76	-3.022	-4.717	46
H	5.405	-3.261	-3.991	46
H	4.172	-3.806	-4.913	46
O	3.545	-7.379	0.472	47
H	3.686	-8.159	-0.137	47
H	2.571	-7.157	0.508	47
O	7.795	2.559	-1.356	48
H	7.891	1.812	-0.698	48
H	8.689	2.776	-1.747	48
O	3.429	-0.252	-9.178	49
H	3.495	0.04	-10.133	49
H	3.756	-1.193	-9.094	49
O	-3.579	2.402	-10.241	50
H	-3.406	1.508	-10.654	50
H	-2.873	3.047	-10.534	50
O	1.105	-2.91	-1.017	51
H	0.927	-2.797	-0.04	51
H	2.018	-3.296	-1.147	51
O	-0.849	3.983	0.308	52
H	-0.713	3.325	-0.433	52
H	-0.973	4.898	-0.077	52
O	6.657	2.671	4.09	53
H	7.3	3.358	3.752	53
H	5.874	3.127	4.513	53
O	-1.501	6.653	-0.432	54
H	-1.883	6.036	-1.12	54
H	-0.862	7.286	-0.869	54
O	3.395	-4.498	-1.626	55
H	3.676	-4.53	-0.667	55
H	4.202	-4.558	-2.213	55
O	-0.792	1.114	-11.733	56
H	-0.455	0.182	-11.865	56
H	-0.023	1.721	-11.532	56
O	9.721	-2.916	-1.66	57
H	9.417	-2.736	-2.596	57
H	9.34	-3.787	-1.348	57
O	-7.087	-4.974	-5.981	58
H	-7.388	-4.844	-6.925	58
H	-6.088	-4.953	-5.943	58
O	4.858	8.204	6.274	59
H	4.557	8.898	6.929	59
H	4.59	7.298	6.6	59
O	-5.74	4.317	-0.952	60
H	-4.795	3.992	-0.963	60
H	-5.777	5.221	-0.525	60
O	4.091	6.159	-2.019	61
H	3.956	5.352	-1.444	61
H	3.21	6.456	-2.388	61
O	0.259	-1.583	-11.55	62
H	0.456	-2.193	-10.783	62
H	1.112	-1.18	-11.882	62
O	0.167	8.19	-1.584	63
H	-0.233	8.98	-2.049	63

(continues on next page)

(continued from previous page)

H	0.999	7.909	-2.062	63
O	5.904	5.593	-4.57	64
H	5.781	4.816	-3.953	64
H	5.595	6.43	-4.118	64
O	1.853	2.264	7.653	65
H	2.031	1.992	8.599	65
H	0.866	2.341	7.509	65
O	-3.917	-8.529	3.889	66
H	-3.102	-8.099	3.5	66
H	-3.747	-8.76	4.847	66
O	-5.078	7.76	3.832	67
H	-4.485	7.317	3.159	67
H	-5.5	7.064	4.413	67
O	-5.333	-7.661	-6.49	68
H	-5.485	-7.46	-7.457	68
H	-4.51	-7.187	-6.176	68
O	1.603	9.353	1.706	69
H	1.306	8.406	1.576	69
H	2.011	9.452	2.614	69
O	-8.588	7.768	-2.072	70
H	-8.096	8.409	-1.483	70
H	-8.101	6.895	-2.096	70
O	8.949	-5.62	0.186	71
H	8.046	-5.232	0.372	71
H	9.636	-5.141	0.731	71
O	-2.56	-3.378	-9.638	72
H	-2.169	-4.295	-9.725	72
H	-2.903	-3.077	-10.528	72
O	4.132	5.755	7.273	73
H	3.367	5.418	7.822	73
H	4.613	4.982	6.859	73
O	-8.001	-0.706	-7.091	74
H	-8.965	-0.793	-7.341	74
H	-7.795	0.252	-6.889	74
O	1.985	-9.965	1.717	75
H	1.164	-10.041	1.152	75
H	1.726	-9.72	2.651	75
O	-0.889	-3.751	7.35	76
H	-1.637	-4.413	7.286	76
H	-1.14	-2.918	6.857	76
O	6.447	-8.648	-3.384	77
H	6.956	-8.025	-2.791	77
H	7.079	-9.101	-4.013	77
O	-10.087	1.376	-3.258	78
H	-10.346	1.756	-2.37	78
H	-10.584	1.853	-3.982	78
O	-7.721	-6.978	-4.007	79
H	-7.044	-7.461	-4.562	79
H	-7.673	-5.998	-4.2	79
O	3.742	-9.925	-0.53	80
H	4.013	-10.88	-0.645	80
H	3.147	-9.841	0.269	80
O	2.643	11.407	0.185	81
H	3.532	11.713	0.526	81
H	2.357	10.591	0.686	81
O	8.142	-2.725	7.39	82
H	7.867	-3.625	7.728	82

(continues on next page)

(continued from previous page)

H	8.341	-2.124	8.164	82
O	6.161	3.092	-3.472	83
H	6.808	3.021	-2.713	83
H	6.61	2.81	-4.32	83
O	-0.296	-10.611	0.551	84
H	0.082	-11.185	-0.175	84
H	-1.124	-11.036	0.916	84
O	8.597	-7.332	-1.93	85
H	9.074	-6.978	-2.734	85
H	8.663	-6.67	-1.184	85
O	6.902	-2.876	0.076	86
H	7.286	-2.931	0.998	86
H	6.464	-1.986	-0.05	86
O	-6.753	2.76	8.111	87
H	-7.086	3.694	8.246	87
H	-6.953	2.467	7.176	87
O	-7.552	-4.988	2.842	88
H	-7.782	-4.906	1.872	88
H	-7.032	-5.829	2.991	88
O	-8.182	-7.7	-1.006	89
H	-7.682	-7.051	-1.581	89
H	-7.896	-8.632	-1.23	89
O	8.372	-3.157	2.438	90
H	8.557	-3.167	3.421	90
H	9.221	-2.98	1.941	90
O	-6.198	-1.22	-3.217	91
H	-6.53	-0.276	-3.211	91
H	-5.626	-1.367	-4.024	91
O	4.677	1.242	0.094	92
H	4.368	1.864	-0.625	92
H	4.105	1.361	0.906	92
O	-2.993	-1.195	3.495	93
H	-3.849	-1.308	2.99	93
H	-2.282	-1.76	3.075	93
O	-3.81	7.752	-5.745	94
H	-3.268	7.416	-6.515	94
H	-3.233	7.809	-4.93	94
O	-2.693	4.73	3.854	95
H	-2.342	3.925	3.376	95
H	-3.179	4.443	4.679	95
O	1.001	-0.574	4.81	96
H	0.553	0.313	4.696	96
H	1.648	-0.72	4.062	96
O	-7.658	3.829	-5.601	97
H	-7.06	3.029	-5.656	97
H	-8.518	3.635	-6.073	97
O	1.26	6.271	8.504	98
H	1.441	6.387	7.527	98
H	0.355	6.637	8.721	98
O	-2.775	-9.109	0.291	99
H	-2.86	-8.211	0.723	99
H	-1.809	-9.316	0.139	99
O	3.256	-1.013	2.987	100
H	3.539	-1.259	2.06	100
H	3.855	-0.293	3.338	100
O	0.21	-0.312	8.228	101
H	1.026	-0.659	7.765	101

(continues on next page)

(continued from previous page)

H	0.428	0.548	8.688	101
O	5.422	-0.784	-1.655	102
H	5.497	-0.764	-2.652	102
H	4.972	0.05	-1.337	102
O	-1.59	-4.154	-5.957	103
H	-1.997	-4.976	-5.559	103
H	-1.274	-3.551	-5.225	103
O	0.51	-8.72	3.751	104
H	1.317	-8.458	4.28	104
H	-0.042	-9.364	4.281	104
O	-2.594	-6.607	-5.182	105
H	-3.233	-6.683	-4.416	105
H	-1.761	-7.12	-4.974	105
O	-5.857	7.025	-0.001	106
H	-4.915	7.129	0.32	106
H	-6.458	7.622	0.53	106
O	-0.705	-2.368	10.335	107
H	-0.302	-2.039	9.481	107
H	-1.387	-3.071	10.133	107
O	-0.613	6.667	3.919	108
H	-0.003	6.582	4.707	108
H	-1.404	6.068	4.044	108
O	3.935	-9.377	-3.564	109
H	4.784	-8.856	-3.476	109
H	3.704	-9.789	-2.683	109
O	6.435	-3.938	-2.832	110
H	7.169	-3.555	-3.391	110
H	6.591	-3.706	-1.872	110
O	6.896	8.206	0.362	111
H	6.777	8.065	1.345	111
H	6.022	8.469	-0.045	111
O	-0.931	-3.296	-2.501	112
H	-0.842	-2.655	-3.264	112
H	-0.122	-3.232	-1.917	112
O	-2.26	-0.566	-6.382	113
H	-3.181	-0.898	-6.176	113
H	-2.061	-0.717	-7.35	113
O	-3.942	-6.403	0.843	114
H	-4.632	-6.735	1.485	114
H	-3.718	-5.452	1.057	114
O	-6.161	-3.718	7.927	115
H	-6.312	-3.364	8.85	115
H	-5.542	-3.107	7.433	115
O	-3.529	2.117	11.116	116
H	-2.591	2.344	11.376	116
H	-3.524	1.334	10.494	116
O	11.264	0.732	2.673	117
H	10.509	1.161	2.179	117
H	11.435	1.232	3.522	117
O	5.878	4.725	-8.717	118
H	5.363	5.296	-8.078	118
H	5.285	4.457	-9.477	118
O	6.383	-1.828	5.578	119
H	5.775	-2.616	5.484	119
H	7.277	-2.134	5.904	119
O	5.055	-6.955	6.321	120
H	4.585	-7.29	7.138	120

(continues on next page)

(continued from previous page)

H	5.653	-7.672	5.963	120
O	-2.944	-5.135	9.603	121
H	-2.164	-5.688	9.895	121
H	-3.022	-5.167	8.607	121
O	-7.242	2.071	5.296	122
H	-8.153	1.824	4.966	122
H	-6.948	2.921	4.859	122
O	-4.801	-10.888	0.386	123
H	-4.064	-10.22	0.494	123
H	-5.563	-10.466	-0.105	123
O	1.498	-2.946	1.749	124
H	2.0	-2.206	2.198	124
H	2.01	-3.8	1.842	124
O	2.527	9.263	4.264	125
H	1.982	9.895	4.815	125
H	3.379	9.052	4.743	125
O	7.852	1.576	-5.351	126
H	7.338	0.737	-5.531	126
H	8.162	1.969	-6.217	126
O	-5.735	4.508	-7.708	127
H	-6.255	4.132	-6.941	127
H	-4.806	4.137	-7.694	127
O	1.852	5.922	-3.635	128
H	1.113	5.297	-3.387	128
H	2.305	5.592	-4.463	128
O	-4.456	1.801	2.702	129
H	-3.992	2.104	1.869	129
H	-4.646	0.821	2.64	129
O	0.803	-5.527	-3.252	130
H	1.341	-5.551	-2.41	130
H	0.008	-4.934	-3.122	130
O	-7.448	4.67	3.716	131
H	-7.111	4.066	2.994	131
H	-8.163	5.263	3.348	131
O	3.596	-0.597	8.511	132
H	3.424	-0.862	9.46	132
H	4.549	-0.31	8.412	132
O	8.133	5.499	3.039	133
H	8.974	5.936	2.719	133
H	7.642	5.11	2.26	133
O	-1.186	3.025	6.358	134
H	-1.453	3.989	6.371	134
H	-1.716	2.523	7.041	134
O	1.391	6.827	5.842	135
H	1.717	6.033	5.329	135
H	1.576	7.659	5.32	135
O	8.48	0.178	3.175	136
H	8.689	-0.233	4.062	136
H	8.429	1.172	3.272	136
O	5.491	-2.645	-8.951	137
H	6.099	-3.205	-8.389	137
H	5.372	-3.076	-9.846	137
O	5.858	-6.18	-7.286	138
H	5.479	-6.48	-8.161	138
H	5.775	-6.917	-6.615	138
O	4.819	-9.959	3.19	139
H	5.303	-10.736	2.788	139

(continues on next page)

(continued from previous page)

H	4.151	-9.607	2.534	139
O	-10.22	-2.106	-2.896	140
H	-11.165	-1.943	-3.179	140
H	-9.63	-2.132	-3.703	140
O	9.523	0.622	5.574	141
H	10.389	0.614	6.075	141
H	8.774	0.824	6.205	141
O	3.768	2.327	-2.459	142
H	2.96	2.318	-3.048	142
H	4.573	2.567	-3.002	142
O	9.057	-3.727	5.016	143
H	8.826	-3.519	5.967	143
H	9.288	-4.696	4.934	143
O	-3.865	-9.077	-2.573	144
H	-3.642	-9.53	-1.71	144
H	-3.999	-8.099	-2.412	144
O	7.735	6.089	-1.411	145
H	7.706	6.786	-0.695	145
H	6.871	6.092	-1.914	145
O	2.451	-7.59	-6.329	146
H	2.186	-7.189	-7.206	146
H	3.252	-8.175	-6.459	146
O	10.049	4.728	0.155	147
H	9.866	5.617	0.576	147
H	10.223	4.852	-0.822	147
O	-6.754	6.196	5.779	148
H	-7.052	5.609	5.027	148
H	-7.543	6.682	6.156	148
O	0.795	-3.52	-9.602	149
H	0.443	-4.455	-9.558	149
H	1.511	-3.401	-8.915	149
O	-7.039	1.511	-3.64	150
H	-6.551	1.817	-2.823	150
H	-8.024	1.548	-3.473	150
O	-3.164	-9.103	6.758	151
H	-3.773	-8.477	7.245	151
H	-2.413	-9.373	7.36	151
O	-5.629	1.786	-5.896	152
H	-4.658	1.779	-5.658	152
H	-6.169	1.508	-5.102	152
O	7.288	2.496	7.375	153
H	7.76	3.141	7.975	153
H	7.083	2.941	6.503	153
O	-0.563	-1.687	-4.735	154
H	0.383	-1.395	-4.876	154
H	-1.178	-1.082	-5.241	154
O	0.097	5.872	-7.772	155
H	-0.007	4.886	-7.9	155
H	-0.289	6.353	-8.559	155
O	0.263	3.329	2.77	156
H	-0.195	2.506	3.107	156
H	-0.167	3.625	1.917	156
O	-5.112	-3.742	3.386	157
H	-6.023	-4.152	3.352	157
H	-4.724	-3.716	2.465	157
O	5.173	0.414	4.591	158
H	5.914	0.938	4.169	158

(continues on next page)

(continued from previous page)

H	5.536	-0.445	4.951	158
O	-0.54	9.346	4.364	159
H	-0.519	8.387	4.082	159
H	-1.136	9.862	3.749	159
O	-7.739	-2.707	-1.775	160
H	-7.119	-2.238	-2.405	160
H	-8.675	-2.642	-2.119	160
O	4.069	-1.93	0.595	161
H	4.054	-2.91	0.792	161
H	4.477	-1.777	-0.306	161
O	7.679	-4.202	-7.817	162
H	8.547	-4.383	-7.354	162
H	6.957	-4.751	-7.397	162
O	-4.112	-3.518	-7.265	163
H	-3.62	-3.431	-8.131	163
H	-3.457	-3.538	-6.51	163
O	-4.079	2.718	8.002	164
H	-4.036	1.739	7.799	164
H	-5.026	2.979	8.185	164
O	-0.788	-5.992	-8.417	165
H	-0.874	-5.596	-7.502	165
H	-1.656	-6.413	-8.68	165
O	-0.642	-8.0	-2.36	166
H	-1.093	-7.251	-1.876	166
H	-0.617	-7.798	-3.339	166
O	-5.431	-4.01	-2.659	167
H	-6.327	-3.586	-2.795	167
H	-4.768	-3.311	-2.392	167
O	1.622	-4.606	7.267	168
H	0.644	-4.448	7.405	168
H	2.063	-3.751	6.996	168
O	-9.426	-1.829	3.261	169
H	-8.578	-1.754	3.786	169
H	-9.786	-2.759	3.34	169
O	10.397	-2.728	0.938	170
H	9.987	-2.336	0.114	170
H	11.372	-2.508	0.962	170
O	-3.49	-10.263	-4.969	171
H	-2.767	-9.841	-5.517	171
H	-3.819	-9.607	-4.289	171
O	-1.521	-7.2	2.797	172
H	-1.357	-6.413	3.392	172
H	-0.828	-7.899	2.97	172
O	2.563	-4.792	-5.31	173
H	1.916	-4.727	-4.55	173
H	2.546	-5.719	-5.685	173
O	2.837	-2.181	6.366	174
H	2.273	-1.594	5.785	174
H	3.201	-1.646	7.128	174
O	-4.032	-6.368	-2.157	175
H	-4.673	-5.671	-2.479	175
H	-4.118	-6.467	-1.165	175
O	-3.248	1.69	-4.498	176
H	-2.674	2.482	-4.291	176
H	-2.676	0.943	-4.835	176
O	9.532	2.335	1.199	177
H	9.808	3.202	0.786	177

(continues on next page)

(continued from previous page)

H	8.539	2.233	1.129	177
O	4.296	6.036	3.312	178
H	4.884	5.765	4.074	178
H	3.344	6.057	3.617	178
O	-4.003	0.618	-2.093	179
H	-3.993	0.617	-3.093	179
H	-4.888	0.953	-1.769	179
O	6.312	5.31	5.167	180
H	6.936	5.315	4.386	180
H	6.368	6.187	5.644	180
O	-6.267	-0.421	5.288	181
H	-7.045	-1.049	5.313	181
H	-6.538	0.461	5.671	181
O	-4.077	0.335	6.986	182
H	-4.824	-0.155	6.539	182
H	-3.207	-0.105	6.762	182
O	-1.592	10.18	-2.288	183
H	-2.521	10.21	-2.657	183
H	-1.428	10.996	-1.734	183
O	-1.179	1.277	4.006	184
H	-1.662	0.404	3.942	184
H	-1.541	1.802	4.776	184
O	-5.857	-7.312	2.548	185
H	-5.09	-7.722	3.042	185
H	-6.533	-8.017	2.337	185
O	8.543	-2.902	-4.126	186
H	8.959	-3.487	-4.823	186
H	8.449	-1.973	-4.484	186
O	-2.288	4.779	9.339	187
H	-2.796	3.953	9.585	187
H	-2.061	4.754	8.366	187
O	-3.934	-3.208	5.916	188
H	-3.188	-2.542	5.928	188
H	-4.429	-3.137	5.05	188
O	-0.872	-9.88	-6.056	189
H	-0.065	-10.416	-5.807	189
H	-0.715	-8.918	-5.833	189
O	-2.461	4.695	-2.278	190
H	-2.779	4.946	-3.192	190
H	-1.851	3.906	-2.342	190
O	6.344	-0.092	7.977	191
H	6.51	-0.546	7.101	191
H	6.343	0.899	7.843	191
O	-5.698	-0.661	2.606	192
H	-5.841	-0.727	3.593	192
H	-6.565	-0.816	2.132	192
O	-4.029	-2.72	10.246	193
H	-5.009	-2.685	10.442	193
H	-3.786	-3.634	9.923	193
O	2.832	-3.188	-7.657	194
H	2.732	-3.704	-6.806	194
H	3.768	-3.282	-7.996	194
O	1.073	-10.115	-2.625	195
H	0.46	-9.352	-2.419	195
H	1.445	-10.004	-3.547	195
O	-6.62	3.126	1.407	196
H	-5.909	2.655	1.93	196

(continues on next page)

(continued from previous page)

H	-6.194	3.705	0.711	196
O	-0.677	8.512	-5.231	197
H	-0.896	9.254	-4.597	197
H	0.11	8.001	-4.887	197
O	4.12	4.53	0.653	198
H	4.223	5.225	1.364	198
H	3.485	3.824	0.967	198
O	-8.221	-2.456	5.669	199
H	-8.808	-2.293	6.463	199
H	-7.852	-3.384	5.712	199
O	2.898	4.605	-5.775	200
H	3.521	4.999	-6.45	200
H	2.968	3.608	-5.798	200
O	-8.042	-4.503	0.126	201
H	-7.787	-3.888	-0.62	201
H	-9.001	-4.768	0.027	201
O	0.142	-7.397	-5.046	202
H	0.431	-6.604	-4.511	202
H	0.919	-7.748	-5.568	202
O	-5.157	-1.438	-5.812	203
H	-5.788	-0.913	-6.384	203
H	-4.908	-2.285	-6.281	203
O	-1.04	-5.021	4.465	204
H	-1.767	-5.433	5.015	204
H	-0.158	-5.409	4.733	204
O	6.958	4.266	0.911	205
H	5.988	4.074	0.766	205
H	7.395	4.46	0.033	205
O	7.345	0.71	0.51	206
H	7.532	0.27	1.389	206
H	6.36	0.714	0.342	206
O	2.18	-0.941	-4.851	207
H	2.768	-1.736	-4.7	207
H	2.46	-0.474	-5.689	207
O	1.874	4.72	4.35	208
H	1.127	4.286	3.847	208
H	2.47	4.016	4.736	208
O	-3.182	3.268	-7.397	209
H	-2.609	2.52	-7.062	209
H	-3.481	3.066	-8.33	209
O	-6.334	1.42	-0.932	210
H	-7.057	0.73	-0.933	210
H	-6.418	1.991	-0.115	210
O	-11.485	0.121	1.494	211
H	-10.502	-0.004	1.358	211
H	-11.916	-0.768	1.646	211
O	-4.428	6.45	7.562	212
H	-5.324	6.26	7.16	212
H	-4.448	6.234	8.538	212
O	-7.198	8.279	2.233	213
H	-6.522	8.005	2.917	213
H	-7.442	9.239	2.372	213
O	-0.931	10.111	0.639	214
H	-0.955	9.372	-0.034	214
H	-0.074	10.065	1.154	214
O	6.652	-0.975	-5.911	215
H	6.955	-1.129	-6.852	215

(continues on next page)

(continued from previous page)

```

H      6.039      -1.715      -5.634      215
O      11.643       1.502       -0.57      216
H      10.975       1.438        0.171      216
H      11.176       1.745       -1.42      216
O      -8.267       -2.766       -5.204      217
H      -8.194       -1.919       -5.73      217
H      -7.565       -3.41        -5.509      217
O       4.001       -4.795        1.063      218
H       4.818       -4.764        1.639      218
H       3.835       -5.737        0.771      218
O      -3.518        -0.073       -11.143      219
H      -4.375        -0.493       -11.442      219
H      -2.889        -0.009       -11.918      219
O       5.278        8.33         -4.17      220
H       5.812        8.57         -3.36      220
H       5.813        8.525        -4.992      220
O      -7.165        5.42         -3.118      221
H      -6.784        4.835        -2.402      221
H      -7.286        4.886        -3.955      221
O       4.501        8.636        -0.932      222
H       4.421        7.683        -1.224      222
H       3.623        9.097        -1.055      222
O      -1.648       -10.25         4.458      223
H      -2.159       -10.03         3.627      223
H      -2.211       -10.044         5.259      223
O      -1.212        7.616         8.694      224
H      -0.792        8.473         8.398      224
H      -2.05        7.814         9.203      224
O      -9.049        1.489         0.827      225
H      -8.587        2.255         1.272      225
H      -8.522        0.652         0.972      225
End
END
EndEngine
eor

```

Example: QM/FDE/FQ: excitations of acrolein in water

Three examples: a QM/FDE/FQ calculation with the frozen-layer response modeled with FQ, one without the response, and one with no explicit FQ layer.

Download FQQM_FDE_FDERESP.run

```

#!/bin/bash

# This example shows how to perform an excited-state calculation
# of an organic molecule in aqueous solution using the QM/FDE/FQ model
# In this example the response of the FDE layer is also included
# by means of the FQ method

# The calculation starts with the solute embedded within an FQ environment

AMS_JOBNAME="acrolein" "$AMSBIN/ams" <<EOF
System

```

(continues on next page)

(continued from previous page)

```

Atoms
  C    26.163000    27.087000    27.854000
  O    25.922000    26.598000    28.918000
  H    25.425000    27.661000    27.251000
  C    27.541000    26.980000    27.309000
  C    27.781000    27.369000    26.027000
  H    28.266000    26.451000    27.925000
  H    28.823000    27.287000    25.727000
  H    27.066000    27.797000    25.330000
End
End

Task SinglePoint

Engine ADF
  Title Acrolein PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O    28.826000    25.183000    30.762000    1
    H    28.995000    26.089000    31.149000    1
    H    28.144000    24.706000    31.315000    1
    O    27.763000    31.250000    26.749000    2
    H    27.469000    30.950000    25.842000    2
    H    26.974000    31.279000    27.363000    2
    O    24.563000    24.510000    25.661000    3

```

(continues on next page)

(continued from previous page)

```

H      25.293000    24.179000    25.064000    3
H      23.710000    24.040000    25.436000    3
O      24.219000    23.640000    28.272000    4
H      23.531000    22.942000    28.076000    4
H      24.474000    24.103000    27.423000    4
O      22.979000    24.696000    30.549000    5
H      23.726000    24.648000    29.886000    5
H      23.222000    24.170000    31.364000    5
O      22.709000    27.494000    30.324000    6
H      23.077000    26.584000    30.512000    6
H      22.782000    27.689000    29.346000    6
O      29.009000    27.562000    32.091000    7
H      28.267000    27.944000    31.541000    7
H      29.871000    28.003000    31.840000    7
O      26.815000    24.369000    24.266000    8
H      27.032000    25.081000    23.598000    8
H      27.472000    24.407000    25.018000    8
O      26.727000    23.089000    28.975000    9
H      26.980000    23.432000    29.879000    9
H      25.761000    23.284000    28.803000    9
O      25.883000    31.425000    28.603000    10
H      25.156000    31.260000    29.269000    10
H      26.624000    31.936000    29.038000    10
O      29.317000    29.573000    27.978000    11
H      30.130000    29.270000    27.481000    11
H      28.782000    30.188000    27.398000    11
O      24.110000    29.703000    24.837000    12
H      23.685000    28.874000    25.201000    12
H      23.551000    30.064000    24.091000    12
O      26.708000    30.327000    24.312000    13
H      25.716000    30.396000    24.419000    13
H      26.920000    29.651000    23.606000    13
O      30.565000    24.816000    28.707000    14
H      30.237000    24.502000    27.816000    14
H      29.793000    24.898000    29.337000    14
O      28.442000    23.780000    26.550000    15
H      27.844000    23.801000    27.351000    15
H      28.454000    22.857000    26.166000    15

```

End

End

EndEngine

EOF

mv acrolein.results/adf.rkf t21.acrolein

The QM water layer is then simulated

#H2O B3LYP/DZP

AMS_JOBNAME=H2O "\$AMSBIN/ams" <<EOF

System

Atoms

```

O      23.219000    27.243000    25.752000
H      22.533000    27.083000    25.042000
H      23.738000    26.403000    25.909000
O      27.812000    28.937000    30.049000
H      28.442000    28.831000    29.280000
H      26.915000    28.573000    29.797000

```

(continues on next page)

(continued from previous page)

```

      O      23.304000      28.960000      27.797000
      H      23.864000      29.646000      27.332000
      H      23.228000      28.146000      27.220000
End
End

Task SinglePoint

Engine ADF
  Title H2O PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O      28.826000      25.183000      30.762000      1
    H      28.995000      26.089000      31.149000      1
    H      28.144000      24.706000      31.315000      1
    O      27.763000      31.250000      26.749000      2
    H      27.469000      30.950000      25.842000      2
    H      26.974000      31.279000      27.363000      2
    O      24.563000      24.510000      25.661000      3
    H      25.293000      24.179000      25.064000      3
    H      23.710000      24.040000      25.436000      3
    O      24.219000      23.640000      28.272000      4
    H      23.531000      22.942000      28.076000      4
    H      24.474000      24.103000      27.423000      4
    O      22.979000      24.696000      30.549000      5
    H      23.726000      24.648000      29.886000      5

```

(continues on next page)

(continued from previous page)

```

H      23.222000    24.170000    31.364000    5
O      22.709000    27.494000    30.324000    6
H      23.077000    26.584000    30.512000    6
H      22.782000    27.689000    29.346000    6
O      29.009000    27.562000    32.091000    7
H      28.267000    27.944000    31.541000    7
H      29.871000    28.003000    31.840000    7
O      26.815000    24.369000    24.266000    8
H      27.032000    25.081000    23.598000    8
H      27.472000    24.407000    25.018000    8
O      26.727000    23.089000    28.975000    9
H      26.980000    23.432000    29.879000    9
H      25.761000    23.284000    28.803000    9
O      25.883000    31.425000    28.603000    10
H      25.156000    31.260000    29.269000    10
H      26.624000    31.936000    29.038000    10
O      29.317000    29.573000    27.978000    11
H      30.130000    29.270000    27.481000    11
H      28.782000    30.188000    27.398000    11
O      24.110000    29.703000    24.837000    12
H      23.685000    28.874000    25.201000    12
H      23.551000    30.064000    24.091000    12
O      26.708000    30.327000    24.312000    13
H      25.716000    30.396000    24.419000    13
H      26.920000    29.651000    23.606000    13
O      30.565000    24.816000    28.707000    14
H      30.237000    24.502000    27.816000    14
H      29.793000    24.898000    29.337000    14
O      28.442000    23.780000    26.550000    15
H      27.844000    23.801000    27.351000    15
H      28.454000    22.857000    26.166000    15
End
End
EndEngine
EOF

mv H2O.results/adf.rkf t21.H2O

# Finally, the QM/FDE/FQ calculation is performed
# The response of the FDE layer is activated with the FDERESP keyword

AMS_JOBNAME=FDE "$AMSBIN/ams" <<EOF
System
Atoms
C      26.163000    27.087000    27.854000    adf.f=frag1
O      25.922000    26.598000    28.918000    adf.f=frag1
H      25.425000    27.661000    27.251000    adf.f=frag1
C      27.541000    26.980000    27.309000    adf.f=frag1
C      27.781000    27.369000    26.027000    adf.f=frag1
H      28.266000    26.451000    27.925000    adf.f=frag1
H      28.823000    27.287000    25.727000    adf.f=frag1
H      27.066000    27.797000    25.330000    adf.f=frag1
O      23.219000    27.243000    25.752000    adf.f=frag2 adf.imol=1
H      22.533000    27.083000    25.042000    adf.f=frag2 adf.imol=1
H      23.738000    26.403000    25.909000    adf.f=frag2 adf.imol=1
O      27.812000    28.937000    30.049000    adf.f=frag2 adf.imol=2
H      28.442000    28.831000    29.280000    adf.f=frag2 adf.imol=2

```

(continues on next page)

(continued from previous page)

```

      H      26.915000      28.573000      29.797000      adf.f=frag2 adf.imol=2
      O      23.304000      28.960000      27.797000      adf.f=frag2 adf.imol=3
      H      23.864000      29.646000      27.332000      adf.f=frag2 adf.imol=3
      H      23.228000      28.146000      27.220000      adf.f=frag2 adf.imol=3
    End
  End

Task SinglePoint

Engine ADF
  Title Acrolein-H2O PBE/PW91K/DZ  FDE single point with interaction energy
  SymmetryTolerance 1e-2
  STOFit
  Relativity
    Level None
  End
  XC
    GGA PBE
  End
  ExactDensity
  FDE
    PW91K
    GGAPOTXFD PBEx
    GGAPOTCFD PBEc
    FULLGRID
    ENERGY
  End
  Fragments
    frag1 t21.acrolein
    frag2 t21.H2O
  End
  FDEFragments
    frag2 type=FDE
  End
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit
  Excitations
    LOWEST 4
    ONLYSING True
  End

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    FDERESP
    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767

```

(continues on next page)

(continued from previous page)

```

Eta 0.537512
End
Coords
O    28.826000    25.183000    30.762000    1
H    28.995000    26.089000    31.149000    1
H    28.144000    24.706000    31.315000    1
O    27.763000    31.250000    26.749000    2
H    27.469000    30.950000    25.842000    2
H    26.974000    31.279000    27.363000    2
O    24.563000    24.510000    25.661000    3
H    25.293000    24.179000    25.064000    3
H    23.710000    24.040000    25.436000    3
O    24.219000    23.640000    28.272000    4
H    23.531000    22.942000    28.076000    4
H    24.474000    24.103000    27.423000    4
O    22.979000    24.696000    30.549000    5
H    23.726000    24.648000    29.886000    5
H    23.222000    24.170000    31.364000    5
O    22.709000    27.494000    30.324000    6
H    23.077000    26.584000    30.512000    6
H    22.782000    27.689000    29.346000    6
O    29.009000    27.562000    32.091000    7
H    28.267000    27.944000    31.541000    7
H    29.871000    28.003000    31.840000    7
O    26.815000    24.369000    24.266000    8
H    27.032000    25.081000    23.598000    8
H    27.472000    24.407000    25.018000    8
O    26.727000    23.089000    28.975000    9
H    26.980000    23.432000    29.879000    9
H    25.761000    23.284000    28.803000    9
O    25.883000    31.425000    28.603000    10
H    25.156000    31.260000    29.269000    10
H    26.624000    31.936000    29.038000    10
O    29.317000    29.573000    27.978000    11
H    30.130000    29.270000    27.481000    11
H    28.782000    30.188000    27.398000    11
O    24.110000    29.703000    24.837000    12
H    23.685000    28.874000    25.201000    12
H    23.551000    30.064000    24.091000    12
O    26.708000    30.327000    24.312000    13
H    25.716000    30.396000    24.419000    13
H    26.920000    29.651000    23.606000    13
O    30.565000    24.816000    28.707000    14
H    30.237000    24.502000    27.816000    14
H    29.793000    24.898000    29.337000    14
O    28.442000    23.780000    26.550000    15
H    27.844000    23.801000    27.351000    15
H    28.454000    22.857000    26.166000    15
End
End
EndEngine
EOF

```

Download FQQM_FDE_noFDERESP.run

#!/bin/bash

(continues on next page)

(continued from previous page)

```

# This example shows how to perform an excited-state calculation
# of an organic molecule in aqueous solution using the QM/FDE/FQ model
# In this example the response of the FDE layer is not included

# The calculation starts with the solute embedded within an FQ environment

AMS_JOBNAME="acrolein" "$AMSBIN/ams" <<EOF
System
  Atoms
    C   26.163000   27.087000   27.854000
    O   25.922000   26.598000   28.918000
    H   25.425000   27.661000   27.251000
    C   27.541000   26.980000   27.309000
    C   27.781000   27.369000   26.027000
    H   28.266000   26.451000   27.925000
    H   28.823000   27.287000   25.727000
    H   27.066000   27.797000   25.330000
  End
End

Task SinglePoint

Engine ADF
  Title Acrolein PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00

    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512

```

(continues on next page)

(continued from previous page)

```

End
Coords
O 28.826000 25.183000 30.762000 1
H 28.995000 26.089000 31.149000 1
H 28.144000 24.706000 31.315000 1
O 27.763000 31.250000 26.749000 2
H 27.469000 30.950000 25.842000 2
H 26.974000 31.279000 27.363000 2
O 24.563000 24.510000 25.661000 3
H 25.293000 24.179000 25.064000 3
H 23.710000 24.040000 25.436000 3
O 24.219000 23.640000 28.272000 4
H 23.531000 22.942000 28.076000 4
H 24.474000 24.103000 27.423000 4
O 22.979000 24.696000 30.549000 5
H 23.726000 24.648000 29.886000 5
H 23.222000 24.170000 31.364000 5
O 22.709000 27.494000 30.324000 6
H 23.077000 26.584000 30.512000 6
H 22.782000 27.689000 29.346000 6
O 29.009000 27.562000 32.091000 7
H 28.267000 27.944000 31.541000 7
H 29.871000 28.003000 31.840000 7
O 26.815000 24.369000 24.266000 8
H 27.032000 25.081000 23.598000 8
H 27.472000 24.407000 25.018000 8
O 26.727000 23.089000 28.975000 9
H 26.980000 23.432000 29.879000 9
H 25.761000 23.284000 28.803000 9
O 25.883000 31.425000 28.603000 10
H 25.156000 31.260000 29.269000 10
H 26.624000 31.936000 29.038000 10
O 29.317000 29.573000 27.978000 11
H 30.130000 29.270000 27.481000 11
H 28.782000 30.188000 27.398000 11
O 24.110000 29.703000 24.837000 12
H 23.685000 28.874000 25.201000 12
H 23.551000 30.064000 24.091000 12
O 26.708000 30.327000 24.312000 13
H 25.716000 30.396000 24.419000 13
H 26.920000 29.651000 23.606000 13
O 30.565000 24.816000 28.707000 14
H 30.237000 24.502000 27.816000 14
H 29.793000 24.898000 29.337000 14
O 28.442000 23.780000 26.550000 15
H 27.844000 23.801000 27.351000 15
H 28.454000 22.857000 26.166000 15
End
End
EndEngine
EOF

mv acrolein.results/adf.rkf t21.acrolein

# The QM water layer is then simulated

#H2O B3LYP/DZP

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=H2O "$AMSBIN/ams" <<EOF
System
  Atoms
    O    23.219000    27.243000    25.752000
    H    22.533000    27.083000    25.042000
    H    23.738000    26.403000    25.909000
    O    27.812000    28.937000    30.049000
    H    28.442000    28.831000    29.280000
    H    26.915000    28.573000    29.797000
    O    23.304000    28.960000    27.797000
    H    23.864000    29.646000    27.332000
    H    23.228000    28.146000    27.220000
  End
End

Task SinglePoint

Engine ADF
  Title H2O PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    AtomType
      Symbol O
      Chi 0.189194
      Eta 0.523700
    End
    AtomType
      Symbol H
      Chi 0.012767
      Eta 0.537512
    End
  Coords
    O    28.826000    25.183000    30.762000    1
    H    28.995000    26.089000    31.149000    1
    H    28.144000    24.706000    31.315000    1
    O    27.763000    31.250000    26.749000    2
    H    27.469000    30.950000    25.842000    2

```

(continues on next page)

(continued from previous page)

```

H      26.974000    31.279000    27.363000    2
O      24.563000    24.510000    25.661000    3
H      25.293000    24.179000    25.064000    3
H      23.710000    24.040000    25.436000    3
O      24.219000    23.640000    28.272000    4
H      23.531000    22.942000    28.076000    4
H      24.474000    24.103000    27.423000    4
O      22.979000    24.696000    30.549000    5
H      23.726000    24.648000    29.886000    5
H      23.222000    24.170000    31.364000    5
O      22.709000    27.494000    30.324000    6
H      23.077000    26.584000    30.512000    6
H      22.782000    27.689000    29.346000    6
O      29.009000    27.562000    32.091000    7
H      28.267000    27.944000    31.541000    7
H      29.871000    28.003000    31.840000    7
O      26.815000    24.369000    24.266000    8
H      27.032000    25.081000    23.598000    8
H      27.472000    24.407000    25.018000    8
O      26.727000    23.089000    28.975000    9
H      26.980000    23.432000    29.879000    9
H      25.761000    23.284000    28.803000    9
O      25.883000    31.425000    28.603000    10
H      25.156000    31.260000    29.269000    10
H      26.624000    31.936000    29.038000    10
O      29.317000    29.573000    27.978000    11
H      30.130000    29.270000    27.481000    11
H      28.782000    30.188000    27.398000    11
O      24.110000    29.703000    24.837000    12
H      23.685000    28.874000    25.201000    12
H      23.551000    30.064000    24.091000    12
O      26.708000    30.327000    24.312000    13
H      25.716000    30.396000    24.419000    13
H      26.920000    29.651000    23.606000    13
O      30.565000    24.816000    28.707000    14
H      30.237000    24.502000    27.816000    14
H      29.793000    24.898000    29.337000    14
O      28.442000    23.780000    26.550000    15
H      27.844000    23.801000    27.351000    15
H      28.454000    22.857000    26.166000    15
End
End
EndEngine
EOF

mv H2O.results/adf.rkf t21.H2O

# Finally, the QM/FDE/FQ calculation is performed

AMS_JOBNAME=FDE "$AMSBIN/ams" <<EOF
System
Atoms
C      26.163000    27.087000    27.854000    adf.f=frag1
O      25.922000    26.598000    28.918000    adf.f=frag1
H      25.425000    27.661000    27.251000    adf.f=frag1
C      27.541000    26.980000    27.309000    adf.f=frag1
C      27.781000    27.369000    26.027000    adf.f=frag1

```

(continues on next page)

(continued from previous page)

```

H      28.266000    26.451000    27.925000    adf.f=frag1
H      28.823000    27.287000    25.727000    adf.f=frag1
H      27.066000    27.797000    25.330000    adf.f=frag1
O      23.219000    27.243000    25.752000    adf.f=frag2 adf.imol=1
H      22.533000    27.083000    25.042000    adf.f=frag2 adf.imol=1
H      23.738000    26.403000    25.909000    adf.f=frag2 adf.imol=1
O      27.812000    28.937000    30.049000    adf.f=frag2 adf.imol=2
H      28.442000    28.831000    29.280000    adf.f=frag2 adf.imol=2
H      26.915000    28.573000    29.797000    adf.f=frag2 adf.imol=2
O      23.304000    28.960000    27.797000    adf.f=frag2 adf.imol=3
H      23.864000    29.646000    27.332000    adf.f=frag2 adf.imol=3
H      23.228000    28.146000    27.220000    adf.f=frag2 adf.imol=3
End
End

Task SinglePoint

Engine ADF
  Title Acrolein-H2O PBE/PW91K/DZ   FDE single point with interaction energy
  SymmetryTolerance 1e-2
  STOFit
  Relativity
    Level None
  End
  XC
    GGA PBE
  End
  ExactDensity
  FDE
    PW91K
    GGAPOTXFD PBEx
    GGAPOTCFD PBEC
    FULLGRID
    ENERGY
  End
  Fragments
    frag1 t21.acrolein
    frag2 t21.H2O
  End
  FDEFragments
    frag2 type=FDE
  End
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit
  Excitations
    LOWEST 4
    ONLYSING True
  End

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    AtomType

```

(continues on next page)

(continued from previous page)

```

Symbol O
Chi 0.189194
Eta 0.523700
End
AtomType
Symbol H
Chi 0.012767
Eta 0.537512
End
Coords
O 28.826000 25.183000 30.762000 1
H 28.995000 26.089000 31.149000 1
H 28.144000 24.706000 31.315000 1
O 27.763000 31.250000 26.749000 2
H 27.469000 30.950000 25.842000 2
H 26.974000 31.279000 27.363000 2
O 24.563000 24.510000 25.661000 3
H 25.293000 24.179000 25.064000 3
H 23.710000 24.040000 25.436000 3
O 24.219000 23.640000 28.272000 4
H 23.531000 22.942000 28.076000 4
H 24.474000 24.103000 27.423000 4
O 22.979000 24.696000 30.549000 5
H 23.726000 24.648000 29.886000 5
H 23.222000 24.170000 31.364000 5
O 22.709000 27.494000 30.324000 6
H 23.077000 26.584000 30.512000 6
H 22.782000 27.689000 29.346000 6
O 29.009000 27.562000 32.091000 7
H 28.267000 27.944000 31.541000 7
H 29.871000 28.003000 31.840000 7
O 26.815000 24.369000 24.266000 8
H 27.032000 25.081000 23.598000 8
H 27.472000 24.407000 25.018000 8
O 26.727000 23.089000 28.975000 9
H 26.980000 23.432000 29.879000 9
H 25.761000 23.284000 28.803000 9
O 25.883000 31.425000 28.603000 10
H 25.156000 31.260000 29.269000 10
H 26.624000 31.936000 29.038000 10
O 29.317000 29.573000 27.978000 11
H 30.130000 29.270000 27.481000 11
H 28.782000 30.188000 27.398000 11
O 24.110000 29.703000 24.837000 12
H 23.685000 28.874000 25.201000 12
H 23.551000 30.064000 24.091000 12
O 26.708000 30.327000 24.312000 13
H 25.716000 30.396000 24.419000 13
H 26.920000 29.651000 23.606000 13
O 30.565000 24.816000 28.707000 14
H 30.237000 24.502000 27.816000 14
H 29.793000 24.898000 29.337000 14
O 28.442000 23.780000 26.550000 15
H 27.844000 23.801000 27.351000 15
H 28.454000 22.857000 26.166000 15
End
End

```

(continues on next page)

(continued from previous page)

```
EndEngine
EOF
```

Download FQQM_FDE_noFQ.run

```
#!/bin/bash

# In this example, the FDE method is used to simulate the absorption
# spectrum of acrolein in water.
# Normally, the FDE method neglects to include the response of the frozen
# layer, however this assumption can lead to large systematic errors
# One way to include the response of the environment in a very cost-efficient
# way is to resort to the FQ method, as shown below

AMS_JOBNAME="acrolein" "$AMSBIN/ams" <<EOF
System
  Atoms
    C    26.163000    27.087000    27.854000
    O    25.922000    26.598000    28.918000
    H    25.425000    27.661000    27.251000
    C    27.541000    26.980000    27.309000
    C    27.781000    27.369000    26.027000
    H    28.266000    26.451000    27.925000
    H    28.823000    27.287000    25.727000
    H    27.066000    27.797000    25.330000
  End
End

Task SinglePoint

Engine ADF
  Title Acrolein PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit
EndEngine
EOF

mv acrolein.results/adf.rkf t21.acrolein

#H2O B3LYP/DZP
AMS_JOBNAME=H2O "$AMSBIN/ams" <<EOF
```

(continues on next page)

(continued from previous page)

```

System
  Atoms
    O    23.219000    27.243000    25.752000
    H    22.533000    27.083000    25.042000
    H    23.738000    26.403000    25.909000
    O    27.812000    28.937000    30.049000
    H    28.442000    28.831000    29.280000
    H    26.915000    28.573000    29.797000
    O    23.304000    28.960000    27.797000
    H    23.864000    29.646000    27.332000
    H    23.228000    28.146000    27.220000
  End
End

Task SinglePoint

Engine ADF
  Title H2O PBE/DZ single point
  Symmetrytolerance 1e-2
  Relativity
    Level None
  End
  Basis
    Type DZ
    Core None
  End
  XC
    GGA PBE
  End
  ExactDensity
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit

EndEngine
EOF

mv H2O.results/adf.rkf t21.H2O

# Having converged the two QM layers the FDE calculation can be carried out
# The response of the frozen layer is modeled using the FQ method, note the use
# of the FDERESP keyword in the QMFQ block

AMS_JOBNAME=FDE "$AMSBIN/ams" <<EOF
System
  Atoms
    C    26.163000    27.087000    27.854000    adf.f=frag1
    O    25.922000    26.598000    28.918000    adf.f=frag1
    H    25.425000    27.661000    27.251000    adf.f=frag1
    C    27.541000    26.980000    27.309000    adf.f=frag1
    C    27.781000    27.369000    26.027000    adf.f=frag1
    H    28.266000    26.451000    27.925000    adf.f=frag1
    H    28.823000    27.287000    25.727000    adf.f=frag1
    H    27.066000    27.797000    25.330000    adf.f=frag1

```

(continues on next page)

(continued from previous page)

```

O    23.219000    27.243000    25.752000    adf.f=frag2 adf.imol=1
H    22.533000    27.083000    25.042000    adf.f=frag2 adf.imol=1
H    23.738000    26.403000    25.909000    adf.f=frag2 adf.imol=1
O    27.812000    28.937000    30.049000    adf.f=frag2 adf.imol=2
H    28.442000    28.831000    29.280000    adf.f=frag2 adf.imol=2
H    26.915000    28.573000    29.797000    adf.f=frag2 adf.imol=2
O    23.304000    28.960000    27.797000    adf.f=frag2 adf.imol=3
H    23.864000    29.646000    27.332000    adf.f=frag2 adf.imol=3
H    23.228000    28.146000    27.220000    adf.f=frag2 adf.imol=3
End
End

Task SinglePoint

Engine ADF
  Title Acrolein-H2O PBE/PW91K/DZ  FDE single point with interaction energy
  SymmetryTolerance 1e-2
  STOFit
  Relativity
    Level None
  End
  XC
    GGA PBE
  End
  ExactDensity
  FDE
    PW91K
    GGAPOTXFD PBEx
    GGAPOTCFD PBEc
    FULLGRID
    ENERGY
  End
  Fragments
    frag1 t21.acrolein
    frag2 t21.H2O
  End
  FDEFragments
    frag2 type=FDE
  End
  EPrint
    SFO NOEIG NOOVL NOORBPOP
    SCF NOPOP
  End
  NoPrint BAS FUNCTIONS
  NoSymFit
  Excitations
    LOWEST 4
    ONLYSING True
  End

  QMFQ
    FORCEFIELD FQ
    MolCharge 0.00
    FDERESP
    AtomType
      Symbol O
      Chi 0.189194

```

(continues on next page)

(continued from previous page)

```

      Eta 0.523700
    End
  AtomType
    Symbol H
    Chi 0.012767
    Eta 0.537512
  End
End
EndEngine
EOF

```

Example: QM/wFQ(F_μ): 2-Methyloxirane (QM) with Sodium nanoparticle

Two examples: a QM/wFQ calculation with the standard and RQ force field.

Download wFQ_na_aoresponse.run

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.18331100      0.30836400      12.88256390
    C      -0.10063900      0.21633400      13.65802391
    O      -1.27059900      0.82515400      13.03987391
    C      -1.23206900     -0.60900600      13.21149389
    H      -1.13647900     -1.17166600      12.28212391
    H      -1.95436900     -0.99261600      13.93440391
    H      -0.03627900      0.43763400      14.72733389
    H      1.93914100     -0.35123600      13.32889391
    H      1.57360100      1.33453400      12.90169392
    H      1.03438100      0.00250400      11.83916391
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 2.5 [eV]
    lifetime 0.004
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQ molecular polarizability calculation
  xc
    gga PBE

```

(continues on next page)

(continued from previous page)

```

End
QMFQ
  FORCEFIELD wFQ

  AtomType
    Symbol Na
  End
  Coords
    Na      -6.33750000      -2.11250000      -2.11250000      1
    Na      -6.33750000      -2.11250000      2.11250000      1
    Na      -6.33750000      2.11250000      -2.11250000      1
    Na      -6.33750000      2.11250000      2.11250000      1
    Na      -2.11250000      -6.33750000      -2.11250000      1
    Na      -2.11250000      -6.33750000      2.11250000      1
    Na      -2.11250000      -2.11250000      -6.33750000      1
    Na      -4.22500000      -4.22500000      -4.22500000      1
    Na      -2.11250000      -2.11250000      -2.11250000      1
    Na      -4.22500000      -4.22500000      0.00000000      1
    Na      -2.11250000      -2.11250000      2.11250000      1
    Na      -4.22500000      -4.22500000      4.22500000      1
    Na      -2.11250000      -2.11250000      6.33750000      1
    Na      -2.11250000      2.11250000      -6.33750000      1
    Na      -4.22500000      0.00000000      -4.22500000      1
    Na      -2.11250000      2.11250000      -2.11250000      1
    Na      -4.22500000      0.00000000      0.00000000      1
    Na      -2.11250000      2.11250000      2.11250000      1
    Na      -4.22500000      0.00000000      4.22500000      1
    Na      -2.11250000      2.11250000      6.33750000      1
    Na      -4.22500000      4.22500000      -4.22500000      1
    Na      -2.11250000      6.33750000      -2.11250000      1
    Na      -4.22500000      4.22500000      0.00000000      1
    Na      -2.11250000      6.33750000      2.11250000      1
    Na      -4.22500000      6.33750000      2.11250000      1
    Na      -4.22500000      4.22500000      4.22500000      1
    Na      2.11250000      -6.33750000      -2.11250000      1
    Na      2.11250000      -6.33750000      2.11250000      1
    Na      2.11250000      -2.11250000      -6.33750000      1
    Na      0.00000000      -4.22500000      -4.22500000      1
    Na      2.11250000      -2.11250000      -2.11250000      1
    Na      0.00000000      -4.22500000      0.00000000      1
    Na      2.11250000      -2.11250000      2.11250000      1
    Na      0.00000000      -4.22500000      4.22500000      1
    Na      2.11250000      -2.11250000      6.33750000      1
    Na      2.11250000      2.11250000      -6.33750000      1
    Na      0.00000000      0.00000000      -4.22500000      1
    Na      2.11250000      2.11250000      -2.11250000      1
    Na      0.00000000      0.00000000      0.00000000      1
    Na      2.11250000      2.11250000      2.11250000      1
    Na      0.00000000      0.00000000      4.22500000      1
    Na      2.11250000      2.11250000      6.33750000      1
    Na      0.00000000      4.22500000      -4.22500000      1
    Na      2.11250000      6.33750000      -2.11250000      1
    Na      0.00000000      4.22500000      0.00000000      1
    Na      2.11250000      6.33750000      2.11250000      1
    Na      0.00000000      4.22500000      4.22500000      1
    Na      4.22500000      -4.22500000      -4.22500000      1
    Na      6.33750000      -2.11250000      -2.11250000      1
    Na      4.22500000      -4.22500000      0.00000000      1

```

(continues on next page)

(continued from previous page)

```

      Na      6.33750000      -2.11250000      2.11250000      1
      Na      4.22500000      -4.22500000      4.22500000      1
      Na      4.22500000      0.00000000     -4.22500000      1
      Na      6.33750000      2.11250000     -2.11250000      1
      Na      4.22500000      0.00000000      0.00000000      1
      Na      6.33750000      2.11250000      2.11250000      1
      Na      4.22500000      0.00000000      4.22500000      1
      Na      4.22500000      4.22500000     -4.22500000      1
      Na      4.22500000      4.22500000      0.00000000      1
      Na      4.22500000      4.22500000      4.22500000      1
    End
  END

EndEngine
eor

```

Download wFQ_RQ_na_aoresponse.run

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.18331100      0.30836400      12.88256390
    C      -0.10063900      0.21633400      13.65802391
    O      -1.27059900      0.82515400      13.03987391
    C      -1.23206900     -0.60900600      13.21149389
    H      -1.13647900     -1.17166600      12.28212391
    H      -1.95436900     -0.99261600      13.93440391
    H      -0.03627900      0.43763400      14.72733389
    H      1.93914100     -0.35123600      13.32889391
    H      1.57360100      1.33453400      12.90169392
    H      1.03438100      0.00250400      11.83916391
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 2.5 [eV]
    lifetime 0.004
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  title QM/FQ molecular polarizability calculation
  xc

```

(continues on next page)

(continued from previous page)

```

gga PBE
End
QMFQ
FORCEFIELD wFQ_RQ

AtomType
  Symbol Na
End
Coords
  Na      -6.33750000    -2.11250000    -2.11250000    1
  Na      -6.33750000    -2.11250000     2.11250000    1
  Na      -6.33750000     2.11250000    -2.11250000    1
  Na      -6.33750000     2.11250000     2.11250000    1
  Na      -2.11250000    -6.33750000    -2.11250000    1
  Na      -2.11250000    -6.33750000     2.11250000    1
  Na      -2.11250000    -2.11250000    -6.33750000    1
  Na      -4.22500000    -4.22500000    -4.22500000    1
  Na      -2.11250000    -2.11250000    -2.11250000    1
  Na      -4.22500000    -4.22500000     0.00000000    1
  Na      -2.11250000    -2.11250000     2.11250000    1
  Na      -4.22500000    -4.22500000     4.22500000    1
  Na      -2.11250000    -2.11250000     6.33750000    1
  Na      -2.11250000     2.11250000    -6.33750000    1
  Na      -4.22500000     0.00000000    -4.22500000    1
  Na      -2.11250000     2.11250000    -2.11250000    1
  Na      -4.22500000     0.00000000     0.00000000    1
  Na      -2.11250000     2.11250000     2.11250000    1
  Na      -4.22500000     0.00000000     4.22500000    1
  Na      -2.11250000     2.11250000     6.33750000    1
  Na      -4.22500000     4.22500000    -4.22500000    1
  Na      -2.11250000     6.33750000    -2.11250000    1
  Na      -4.22500000     4.22500000     0.00000000    1
  Na      -2.11250000     6.33750000     2.11250000    1
  Na      -4.22500000     4.22500000     4.22500000    1
  Na      2.11250000    -6.33750000    -2.11250000    1
  Na      2.11250000    -6.33750000     2.11250000    1
  Na      2.11250000    -2.11250000    -6.33750000    1
  Na      0.00000000    -4.22500000    -4.22500000    1
  Na      2.11250000    -2.11250000    -2.11250000    1
  Na      0.00000000    -4.22500000     0.00000000    1
  Na      2.11250000    -2.11250000     2.11250000    1
  Na      0.00000000    -4.22500000     4.22500000    1
  Na      2.11250000    -2.11250000     6.33750000    1
  Na      0.00000000     2.11250000    -6.33750000    1
  Na      0.00000000     0.00000000    -4.22500000    1
  Na      2.11250000     2.11250000    -2.11250000    1
  Na      0.00000000     0.00000000     0.00000000    1
  Na      2.11250000     2.11250000     2.11250000    1
  Na      0.00000000     0.00000000     4.22500000    1
  Na      2.11250000     2.11250000     6.33750000    1
  Na      0.00000000     4.22500000    -4.22500000    1
  Na      2.11250000     6.33750000    -2.11250000    1
  Na      0.00000000     4.22500000     0.00000000    1
  Na      2.11250000     6.33750000     2.11250000    1
  Na      0.00000000     4.22500000     4.22500000    1
  Na      4.22500000    -4.22500000    -4.22500000    1
  Na      6.33750000    -2.11250000    -2.11250000    1

```

(continues on next page)

(continued from previous page)

```

      Na      4.22500000      -4.22500000      0.00000000      1
      Na      6.33750000      -2.11250000      2.11250000      1
      Na      4.22500000      -4.22500000      4.22500000      1
      Na      4.22500000      0.00000000      -4.22500000      1
      Na      6.33750000      2.11250000      -2.11250000      1
      Na      4.22500000      0.00000000      0.00000000      1
      Na      6.33750000      2.11250000      2.11250000      1
      Na      4.22500000      0.00000000      4.22500000      1
      Na      4.22500000      4.22500000      -4.22500000      1
      Na      4.22500000      4.22500000      0.00000000      1
      Na      4.22500000      4.22500000      4.22500000      1
End
END

EndEngine
eor

```

Example: QM/wFQ(F_{μ}): 2-Methyloxirane (QM) on a carbon sheet

Three examples: a QM/wFQ calculation with the standard and RQ force field, and a calculation with the GroundState keyword included, which adds FQ contribution to the ground-state SCF calculation, in addition to the response.

Download wFQ_carbon_aoresponse.run

```

#!/bin/bash

$AMSBIN/ams --delete-old-results << eor

system
  Atoms
    C      1.18331100      0.30836400      6.90139756
    C      -0.10063900      0.21633400      7.67685756
    O      -1.27059900      0.82515400      7.05870757
    C      -1.23206900      -0.60900600      7.23032752
    H      -1.13647900      -1.17166600      6.30095753
    H      -1.95436900      -0.99261600      7.95323756
    H      -0.03627900      0.43763400      8.74616751
    H      1.93914100      -0.35123600      7.34772757
    H      1.57360100      1.33453400      6.92052755
    H      1.03438100      0.00250400      5.85799757
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 0.50 [eV]
    lifetime 0.004
  End

```

(continues on next page)

(continued from previous page)

```

basis
  type TZP
  core none
End
symmetry NOSYM
xc
  gga PBE
End
QMFO
  FORCEFIELD wFO

AtomType
  Symbol C
End
Coords
  C      -2.46000000    -4.97098582    0.00000000    1
  C      -3.69000000    -2.84056332    0.00000000    1
  C      -4.92000000    -0.71014083    0.00000000    1
  C      -1.23000000    -5.68112665    0.00000000    1
  C      -0.00000000    -4.97098582    0.00000000    1
  C      -2.46000000    -3.55070416    0.00000000    1
  C      -1.23000000    -2.84056332    0.00000000    1
  C      -3.69000000    -1.42028166    0.00000000    1
  C      -2.46000000    -0.71014083    0.00000000    1
  C      -4.92000000     0.71014083    0.00000000    1
  C      -3.69000000     1.42028166    0.00000000    1
  C       1.23000000    -5.68112665    0.00000000    1
  C       2.46000000    -4.97098582    0.00000000    1
  C      -0.00000000    -3.55070416    0.00000000    1
  C       1.23000000    -2.84056332    0.00000000    1
  C      -1.23000000    -1.42028166    0.00000000    1
  C      -0.00000000    -0.71014083    0.00000000    1
  C      -2.46000000     0.71014083    0.00000000    1
  C      -1.23000000     1.42028166    0.00000000    1
  C      -3.69000000     2.84056332    0.00000000    1
  C      -2.46000000     3.55070416    0.00000000    1
  C       2.46000000    -3.55070416    0.00000000    1
  C       3.69000000    -2.84056332    0.00000000    1
  C       1.23000000    -1.42028166    0.00000000    1
  C       2.46000000    -0.71014083    0.00000000    1
  C      -0.00000000     0.71014083    0.00000000    1
  C       1.23000000     1.42028166    0.00000000    1
  C      -1.23000000     2.84056332    0.00000000    1
  C      -0.00000000     3.55070416    0.00000000    1
  C      -2.46000000     4.97098582    0.00000000    1
  C      -1.23000000     5.68112665    0.00000000    1
  C       3.69000000    -1.42028166    0.00000000    1
  C       4.92000000    -0.71014083    0.00000000    1
  C       2.46000000     0.71014083    0.00000000    1
  C       3.69000000     1.42028166    0.00000000    1
  C       1.23000000     2.84056332    0.00000000    1
  C       2.46000000     3.55070416    0.00000000    1
  C      -0.00000000     4.97098582    0.00000000    1
  C       1.23000000     5.68112665    0.00000000    1
  C       4.92000000     0.71014083    0.00000000    1
  C       3.69000000     2.84056332    0.00000000    1
  C       2.46000000     4.97098582    0.00000000    1

```

(continues on next page)

(continued from previous page)

```

End
END
EndEngine
eor

```

Download wFQ_RQ_carbon_aoresponse.run

```

#!/bin/bash

$AMSBIN/ams --delete-old-results << eor

system
  Atoms
    C      1.18331100      0.30836400      6.90139756
    C      -0.10063900      0.21633400      7.67685756
    O      -1.27059900      0.82515400      7.05870757
    C      -1.23206900     -0.60900600      7.23032752
    H      -1.13647900     -1.17166600      6.30095753
    H      -1.95436900     -0.99261600      7.95323756
    H      -0.03627900      0.43763400      8.74616751
    H      1.93914100     -0.35123600      7.34772757
    H      1.57360100      1.33453400      6.92052755
    H      1.03438100      0.00250400      5.85799757
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 0.50 [eV]
    lifetime 0.004
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD wFQ_RQ

  AtomType
    Symbol C
  End
  Coords
    C      -2.46000000     -4.97098582      0.00000000      1
    C      -3.69000000     -2.84056332      0.00000000      1
    C      -4.92000000     -0.71014083      0.00000000      1
    C      -1.23000000     -5.68112665      0.00000000      1
    C      -0.00000000     -4.97098582      0.00000000      1
    C      -2.46000000     -3.55070416      0.00000000      1

```

(continues on next page)

(continued from previous page)

```

C      -1.23000000      -2.84056332      0.00000000      1
C      -3.69000000      -1.42028166      0.00000000      1
C      -2.46000000      -0.71014083      0.00000000      1
C      -4.92000000       0.71014083      0.00000000      1
C      -3.69000000       1.42028166      0.00000000      1
C       1.23000000      -5.68112665      0.00000000      1
C       2.46000000      -4.97098582      0.00000000      1
C      -0.00000000      -3.55070416      0.00000000      1
C       1.23000000      -2.84056332      0.00000000      1
C      -1.23000000      -1.42028166      0.00000000      1
C      -0.00000000      -0.71014083      0.00000000      1
C      -2.46000000       0.71014083      0.00000000      1
C      -1.23000000       1.42028166      0.00000000      1
C      -3.69000000       2.84056332      0.00000000      1
C      -2.46000000       3.55070416      0.00000000      1
C       2.46000000      -3.55070416      0.00000000      1
C       3.69000000      -2.84056332      0.00000000      1
C       1.23000000      -1.42028166      0.00000000      1
C       2.46000000      -0.71014083      0.00000000      1
C      -0.00000000       0.71014083      0.00000000      1
C       1.23000000       1.42028166      0.00000000      1
C      -1.23000000       2.84056332      0.00000000      1
C      -0.00000000       3.55070416      0.00000000      1
C      -2.46000000       4.97098582      0.00000000      1
C      -1.23000000       5.68112665      0.00000000      1
C       3.69000000      -1.42028166      0.00000000      1
C       4.92000000      -0.71014083      0.00000000      1
C       2.46000000       0.71014083      0.00000000      1
C       3.69000000       1.42028166      0.00000000      1
C       1.23000000       2.84056332      0.00000000      1
C       2.46000000       3.55070416      0.00000000      1
C      -0.00000000       4.97098582      0.00000000      1
C       1.23000000       5.68112665      0.00000000      1
C       4.92000000       0.71014083      0.00000000      1
C       3.69000000       2.84056332      0.00000000      1
C       2.46000000       4.97098582      0.00000000      1
End
END
EndEngine
eor

```

Download wFQ_carbon_aoresponse_GS.run

```

#!/bin/bash

$AMSBIN/ams --delete-old-results << eor

system
  Atoms
    C      1.18331100      0.30836400      6.90139756
    C      -0.10063900      0.21633400      7.67685756
    O      -1.27059900      0.82515400      7.05870757
    C      -1.23206900     -0.60900600      7.23032752
    H      -1.13647900     -1.17166600      6.30095753
    H      -1.95436900     -0.99261600      7.95323756
    H      -0.03627900      0.43763400      8.74616751
    H       1.93914100     -0.35123600      7.34772757

```

(continues on next page)

(continued from previous page)

```

      H      1.57360100      1.33453400      6.92052755
      H      1.03438100      0.00250400      5.85799757
End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 0.50 [eV]
    lifetime 0.004
  End
  basis
    type TZP
    core none
  End
  symmetry NOSYM
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD wFQ
    groundstate

  AtomType
    Symbol C
  End
  Coords
    C      -2.46000000      -4.97098582      0.00000000      1
    C      -3.69000000      -2.84056332      0.00000000      1
    C      -4.92000000      -0.71014083      0.00000000      1
    C      -1.23000000      -5.68112665      0.00000000      1
    C      -0.00000000      -4.97098582      0.00000000      1
    C      -2.46000000      -3.55070416      0.00000000      1
    C      -1.23000000      -2.84056332      0.00000000      1
    C      -3.69000000      -1.42028166      0.00000000      1
    C      -2.46000000      -0.71014083      0.00000000      1
    C      -4.92000000      0.71014083      0.00000000      1
    C      -3.69000000      1.42028166      0.00000000      1
    C      1.23000000      -5.68112665      0.00000000      1
    C      2.46000000      -4.97098582      0.00000000      1
    C      -0.00000000      -3.55070416      0.00000000      1
    C      1.23000000      -2.84056332      0.00000000      1
    C      -1.23000000      -1.42028166      0.00000000      1
    C      -0.00000000      -0.71014083      0.00000000      1
    C      -2.46000000      0.71014083      0.00000000      1
    C      -1.23000000      1.42028166      0.00000000      1
    C      -3.69000000      2.84056332      0.00000000      1
    C      -2.46000000      3.55070416      0.00000000      1
    C      2.46000000      -3.55070416      0.00000000      1
    C      3.69000000      -2.84056332      0.00000000      1
    C      1.23000000      -1.42028166      0.00000000      1
    C      2.46000000      -0.71014083      0.00000000      1
    C      -0.00000000      0.71014083      0.00000000      1

```

(continues on next page)

(continued from previous page)

```

      C      1.23000000      1.42028166      0.00000000      1
      C     -1.23000000      2.84056332      0.00000000      1
      C     -0.00000000      3.55070416      0.00000000      1
      C     -2.46000000      4.97098582      0.00000000      1
      C     -1.23000000      5.68112665      0.00000000      1
      C      3.69000000     -1.42028166      0.00000000      1
      C      4.92000000     -0.71014083      0.00000000      1
      C      2.46000000      0.71014083      0.00000000      1
      C      3.69000000      1.42028166      0.00000000      1
      C      1.23000000      2.84056332      0.00000000      1
      C      2.46000000      3.55070416      0.00000000      1
      C     -0.00000000      4.97098582      0.00000000      1
      C      1.23000000      5.68112665      0.00000000      1
      C      4.92000000      0.71014083      0.00000000      1
      C      3.69000000      2.84056332      0.00000000      1
      C      2.46000000      4.97098582      0.00000000      1
End
END
EndEngine
eor

```

Example: QM/wFQ(F μ): 2-Methyloxirane (QM) with Silver nanoparticle

Two examples: a QM/wFQ calculation with the standard and RQ force field.

Download `wFQFmu_ag_aoresponse.run`

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.18331100      0.30836400      11.02349105
    C     -0.10063900      0.21633400      11.79895105
    O     -1.27059900      0.82515400      11.18080106
    C     -1.23206900     -0.60900600      11.35242101
    H     -1.13647900     -1.17166600      10.42305102
    H     -1.95436900     -0.99261600      12.07533106
    H     -0.03627900      0.43763400      12.86826100
    H      1.93914100     -0.35123600      11.46982106
    H      1.57360100      1.33453400      11.04262104
    H      1.03438100      0.00250400      9.98009106
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 3.5 [eV]

```

(continues on next page)

(continued from previous page)

```

lifetime 0.004
End
basis
  type DZP
  core none
End
symmetry NOSYM
xc
  gga PBE
End
QMFO
  FORCEFIELD wFQFmu

AtomType
  Symbol Ag
End
Coords
  Ag      -4.08000000    -2.04000000    -2.04000000    1
  Ag      -2.04000000    -4.08000000    -2.04000000    1
  Ag      -2.04000000    -2.04000000    -4.08000000    1
  Ag      -4.08000000    -2.04000000     2.04000000    1
  Ag      -2.04000000    -4.08000000     2.04000000    1
  Ag      -2.04000000    -2.04000000     0.00000000    1
  Ag      -2.04000000    -2.04000000     4.08000000    1
  Ag      -4.08000000     2.04000000    -2.04000000    1
  Ag      -2.04000000     0.00000000    -2.04000000    1
  Ag      -2.04000000     2.04000000    -4.08000000    1
  Ag      -4.08000000     0.00000000     0.00000000    1
  Ag      -4.08000000     2.04000000     2.04000000    1
  Ag      -2.04000000     0.00000000     2.04000000    1
  Ag      -2.04000000     2.04000000     0.00000000    1
  Ag      -2.04000000     2.04000000     4.08000000    1
  Ag      -2.04000000     4.08000000    -2.04000000    1
  Ag      -2.04000000     4.08000000     2.04000000    1
  Ag      0.00000000    -2.04000000    -2.04000000    1
  Ag      2.04000000    -4.08000000    -2.04000000    1
  Ag      2.04000000    -2.04000000    -4.08000000    1
  Ag      0.00000000    -4.08000000     0.00000000    1
  Ag      0.00000000    -2.04000000     2.04000000    1
  Ag      2.04000000    -4.08000000     2.04000000    1
  Ag      2.04000000    -2.04000000     0.00000000    1
  Ag      2.04000000    -2.04000000     4.08000000    1
  Ag      0.00000000     0.00000000    -4.08000000    1
  Ag      0.00000000     2.04000000    -2.04000000    1
  Ag      2.04000000     0.00000000    -2.04000000    1
  Ag      2.04000000     2.04000000    -4.08000000    1
  Ag      0.00000000     0.00000000     0.00000000    1
  Ag      0.00000000     2.04000000     2.04000000    1
  Ag      2.04000000     0.00000000     2.04000000    1
  Ag      2.04000000     2.04000000     0.00000000    1
  Ag      0.00000000     0.00000000     4.08000000    1
  Ag      2.04000000     2.04000000     4.08000000    1
  Ag      2.04000000     4.08000000    -2.04000000    1
  Ag      0.00000000     4.08000000     0.00000000    1
  Ag      2.04000000     4.08000000     2.04000000    1
  Ag      4.08000000    -2.04000000    -2.04000000    1
  Ag      4.08000000    -2.04000000     2.04000000    1

```

(continues on next page)

(continued from previous page)

```

      Ag      4.08000000      2.04000000      -2.04000000  1
      Ag      4.08000000      0.00000000      0.00000000  1
      Ag      4.08000000      2.04000000      2.04000000  1
    End
  END
EndEngine
eor

```

Download wFQFmu_RQRmu_ag_aoresponse.run

```

#!/bin/bash

# QMFQ polarizability calculation

$AMSBIN/ams << eor
system
  Atoms
    C      1.18331100      0.30836400      11.02349105
    C      -0.10063900      0.21633400      11.79895105
    O      -1.27059900      0.82515400      11.18080106
    C      -1.23206900     -0.60900600      11.35242101
    H      -1.13647900     -1.17166600      10.42305102
    H      -1.95436900     -0.99261600      12.07533106
    H      -0.03627900      0.43763400      12.86826100
    H      1.93914100     -0.35123600      11.46982106
    H      1.57360100      1.33453400      11.04262104
    H      1.03438100      0.00250400       9.98009106
  End
End

task SinglePoint

Engine adf
  Relativity
    Level None
  End
  aoresponse
    Frequencies 3.5 [eV]
    lifetime 0.004
  End
  basis
    type DZP
    core none
  End
  symmetry NOSYM
  xc
    gga PBE
  End
  QMFQ
    FORCEFIELD wFQFmu_RQRmu

  AtomType
    Symbol Ag
  End
  Coords
    Ag      -4.08000000     -2.04000000     -2.04000000  1
    Ag      -2.04000000     -4.08000000     -2.04000000  1

```

(continues on next page)

(continued from previous page)

Ag	-2.04000000	-2.04000000	-4.08000000	1
Ag	-4.08000000	-2.04000000	2.04000000	1
Ag	-2.04000000	-4.08000000	2.04000000	1
Ag	-2.04000000	-2.04000000	0.00000000	1
Ag	-2.04000000	-2.04000000	4.08000000	1
Ag	-4.08000000	2.04000000	-2.04000000	1
Ag	-2.04000000	0.00000000	-2.04000000	1
Ag	-2.04000000	2.04000000	-4.08000000	1
Ag	-4.08000000	0.00000000	0.00000000	1
Ag	-4.08000000	2.04000000	2.04000000	1
Ag	-2.04000000	0.00000000	2.04000000	1
Ag	-2.04000000	2.04000000	0.00000000	1
Ag	-2.04000000	2.04000000	4.08000000	1
Ag	-2.04000000	4.08000000	-2.04000000	1
Ag	-2.04000000	4.08000000	2.04000000	1
Ag	0.00000000	-2.04000000	-2.04000000	1
Ag	2.04000000	-4.08000000	-2.04000000	1
Ag	2.04000000	-2.04000000	-4.08000000	1
Ag	0.00000000	-4.08000000	0.00000000	1
Ag	0.00000000	-2.04000000	2.04000000	1
Ag	2.04000000	-4.08000000	2.04000000	1
Ag	2.04000000	-2.04000000	0.00000000	1
Ag	2.04000000	-2.04000000	4.08000000	1
Ag	0.00000000	0.00000000	-4.08000000	1
Ag	0.00000000	2.04000000	-2.04000000	1
Ag	2.04000000	0.00000000	-2.04000000	1
Ag	2.04000000	2.04000000	-4.08000000	1
Ag	0.00000000	0.00000000	0.00000000	1
Ag	0.00000000	2.04000000	2.04000000	1
Ag	2.04000000	0.00000000	2.04000000	1
Ag	2.04000000	2.04000000	0.00000000	1
Ag	0.00000000	0.00000000	4.08000000	1
Ag	2.04000000	2.04000000	4.08000000	1
Ag	2.04000000	4.08000000	-2.04000000	1
Ag	0.00000000	4.08000000	0.00000000	1
Ag	2.04000000	4.08000000	2.04000000	1
Ag	4.08000000	-2.04000000	-2.04000000	1
Ag	4.08000000	-2.04000000	2.04000000	1
Ag	4.08000000	2.04000000	-2.04000000	1
Ag	4.08000000	0.00000000	0.00000000	1
Ag	4.08000000	2.04000000	2.04000000	1
End				
END				
EndEngine				
eor				

Example: QM/wFQ(F μ): 2-Methyloxirane (QM) with Gold nanoparticle

A QM/wFQ calculation of the molecule's response as adsorbed on a gold nanoparticle.

Download `wFQFmu_RQRmu_au_response.run`

```
#!/bin/bash

$AMSBIN/ams --delete-old-results << eor

system
  Atoms
    C      1.18331100      0.30836400      11.02349105
    C      -0.10063900      0.21633400      11.79895105
    O      -1.27059900      0.82515400      11.18080106
    C      -1.23206900     -0.60900600      11.35242101
    H      -1.13647900     -1.17166600     10.42305102
    H      -1.95436900     -0.99261600     12.07533106
    H      -0.03627900      0.43763400     12.86826100
    H      1.93914100     -0.35123600     11.46982106
    H      1.57360100      1.33453400     11.04262104
    H      1.03438100      0.00250400      9.98009106
  End
End

task SinglePoint

Engine adf

  Relativity
    Level None
  End

  basis
    type DZP
    core none
  End

  symmetry NOSYM

  xc
    Hybrid B3LYP
  End

  QMFQ
    FORCEFIELD wFQFmu_RQRmu

    LifeFrequency 2.40746
    LifeState 2

    AtomType
      Symbol Au
    End
    Coords
      Au      -4.08000000     -2.04000000     -2.04000000  1
      Au      -2.04000000     -4.08000000     -2.04000000  1
      Au      -2.04000000     -2.04000000     -4.08000000  1
```

(continues on next page)

(continued from previous page)

```

Au      -4.08000000    -2.04000000    2.04000000  1
Au      -2.04000000    -4.08000000    2.04000000  1
Au      -2.04000000    -2.04000000    0.00000000  1
Au      -2.04000000    -2.04000000    4.08000000  1
Au      -4.08000000     2.04000000   -2.04000000  1
Au      -2.04000000     0.00000000   -2.04000000  1
Au      -2.04000000     2.04000000   -4.08000000  1
Au      -4.08000000     0.00000000     0.00000000  1
Au      -4.08000000     2.04000000     2.04000000  1
Au      -2.04000000     0.00000000     2.04000000  1
Au      -2.04000000     2.04000000     0.00000000  1
Au      -2.04000000     2.04000000     4.08000000  1
Au      -2.04000000     4.08000000   -2.04000000  1
Au      -2.04000000     4.08000000     2.04000000  1
Au       0.00000000   -2.04000000   -2.04000000  1
Au       2.04000000   -4.08000000   -2.04000000  1
Au       2.04000000   -2.04000000   -4.08000000  1
Au       0.00000000   -4.08000000     0.00000000  1
Au       0.00000000   -2.04000000     2.04000000  1
Au       2.04000000   -4.08000000     2.04000000  1
Au       2.04000000   -2.04000000     0.00000000  1
Au       2.04000000   -2.04000000     4.08000000  1
Au       0.00000000     0.00000000   -4.08000000  1
Au       0.00000000     2.04000000   -2.04000000  1
Au       2.04000000     0.00000000   -2.04000000  1
Au       2.04000000     2.04000000   -4.08000000  1
Au       0.00000000     0.00000000     0.00000000  1
Au       0.00000000     2.04000000     2.04000000  1
Au       2.04000000     0.00000000     2.04000000  1
Au       2.04000000     2.04000000     0.00000000  1
Au       0.00000000     0.00000000     4.08000000  1
Au       2.04000000     2.04000000     4.08000000  1
Au       2.04000000     4.08000000   -2.04000000  1
Au       0.00000000     4.08000000     0.00000000  1
Au       2.04000000     4.08000000     2.04000000  1
Au       4.08000000   -2.04000000   -2.04000000  1
Au       4.08000000   -2.04000000     2.04000000  1
Au       4.08000000     2.04000000   -2.04000000  1
Au       4.08000000     0.00000000     0.00000000  1
Au       4.08000000     2.04000000     2.04000000  1
End
END

EXCITATIONS
ALLOWED
LOWEST 3
ONLYSING
END

EndEngine
eor

```

15.3 Structure and Reactivity

15.3.1 Geometry Optimizations

Example: Geometry Optimization: H2O

Download `GO_H2O.run`

```
#!/bin/sh

"$AMSBIN/ams" <<eor

Task GeometryOptimization

System
  Atoms
    O 0.0 0.0 0.0
    H 1.0 0.0 0.0
    H 0.0 0.0 1.0
  End
End

Properties
  NormalModes Yes
End

Engine ADF
  Symmetry NoSym
  basis
    Type DZP
    CreateOutput Yes
  End
EndEngine

eor
```

Example: Restraint Geometry Optimization: H2O

Download `GO_restraint.run`

```
#!/bin/sh

# The restraint does not have to be satisfied at the start of the geometry
# optimization. An extra force is added to restrain the bond length, angle, or
# dihedral angle to a certain value.

# == angle restraint ==

AMS_JOBNAME=Angle $AMSBIN/ams <<eor
System
  atoms
    O      0.001356      0.000999      0.000000
    H      0.994442     -0.037855      0.000000
    H     -0.298554      0.948531      0.000000
  end
End
```

(continues on next page)

(continued from previous page)

```

    Symmetrize Yes
end

Task GeometryOptimization

Restrains
  Angle 3 1 2 125.0 10.0
End

Engine ADF
  title WATER geometry optimization with angle restraint
  basis
    type DZP
  end
EndEngine
eor

echo "Angle after optimization:"
$AMSBIN/amsreport Angle.results/adf.rkf -r angle#3#1#2

# == bond length restraint ==

AMS_JOBNAME=Bond $AMSBIN/ams <<eor
System
  atoms
    O      0.001356    0.000999    0.000000
    H      0.994442   -0.037855    0.000000
    H     -0.298554    0.948531    0.000000
  end
  Symmetrize Yes
end

Task GeometryOptimization

Restrains
  Distance 1 2 1.03 10.0
  Distance 1 3 1.03 10.0
end

Engine ADF
  title WATER Geometry Optimization with bond length restraint
  basis
    type DZP
  end
EndEngine
eor

echo "Bond-distances after optimization:"
$AMSBIN/amsreport Bond.results/adf.rkf -r distance#1#2
$AMSBIN/amsreport Bond.results/adf.rkf -r distance#1#3

# == Restraining dihedral ==

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=Dihedral $AMSBIN/ams <<eor
System
  atoms
    C      -0.004115   -0.000021   0.000023
    C      1.535711    0.000022   0.000008
    H     -0.399693    1.027812  -0.000082
    H     -0.399745   -0.513934   0.890139
    H     -0.399612   -0.513952  -0.890156
    H      1.931188    0.514066   0.890140
    H      1.931432    0.513819  -0.890121
    H      1.931281   -1.027824   0.000244
  end
end

Task GeometryOptimization

Restrains
  Dihedral 6 2 1 3 20.00 10.0
end

Engine ADF
  title Restraining dihedral of ethane
  basis
    type DZP
  end
  Symmetry NoSym
EndEngine
eor

echo "Dihedral after optimization:"
$AMSBIN/amsreport Dihedral.results/adf.rkf -r dihedral#6#2#1#3

```

Example: Constraint Geometry Optimization: H2O

Download GO_constraints.run

```

#!/bin/sh

# The key Constraints can only be used to enforce constraint in a geometry
# optimization. The Constraints do not have to be satisfied at the start
# of the geometry optimization.

# == Example for angle constraint for water ==

AMS_JOBNAME=angle $AMSBIN/ams <<eor

System
  Atoms
    O      0.001356    0.000999   0.000000
    H      0.994442   -0.037855   0.000000
    H     -0.298554    0.948531   0.000000
  End
End

```

(continues on next page)

(continued from previous page)

```

Task GeometryOptimization

GeometryOptimization
  Convergence Step=1.0e-3
End

Constraints
  Angle 3 1 2 125.0
End

Engine ADF
  Basis
    Type DZP
  End
EndEngine
eor

echo "Angle after optimization:"
$AMSBIN/amsreport angle.results/adf.rkf -r angle#3#1#2

# == Example for fixed-coordinates constraint for water ==

AMS_JOBNAME=fixed_coordinates $AMSBIN/ams <<eor

System
  Atoms
    O      0.001356    0.000999    0.000000
    H      0.994442   -0.037855    0.000000
    H     -0.298554    0.948531    0.000000
  End
End

Task GeometryOptimization

GeometryOptimization
  Convergence Step=1.0e-3
End

Constraints
  Coordinate 1 x 0.0
  Coordinate 1 y 0.0
  Coordinate 2 x 1.0
  Coordinate 2 y 0.0
End

Engine ADF
  symmetry NoSym
  Basis
    Type DZP
  End
  LinearScaling
    Overlap_Int 98
  End
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor

echo "Angle after optimization:"
$AMSBIN/amsreport fixed_coordinates.results/adf.rkf -r angle#3#1#2

# == Example for bond length constraint for water ==

AMS_JOBNAME=bond_length $AMSBIN/ams <<eor
System
  Atoms
    O      0.001356    0.000999    0.000000
    H      0.994442   -0.037855    0.000000
    H     -0.298554    0.948531    0.000000
  End
End

Task GeometryOptimization

GeometryOptimization
  Convergence Step=1.0e-3
End

Constraints
  Distance  1 2 1.03
  Distance  1 3 1.03
End

Engine ADF
  Symmetry NoSym
  Basis
  Type DZP
  End
EndEngine
eor

echo "Bonds distance after optimization:"
$AMSBIN/amsreport bond_length.results/adf.rkf -r distance#1#2
$AMSBIN/amsreport bond_length.results/adf.rkf -r distance#1#3

# == Example for dihedral angle constraint for ethane ==

AMS_JOBNAME=dihedral $AMSBIN/ams <<eor

Task GeometryOptimization

GeometryOptimization
  Convergence Step=1.0e-3
End

System
  Atoms
    C      -0.004115   -0.000021    0.000023
    C      1.535711    0.000022    0.000008

```

(continues on next page)

(continued from previous page)

```

      H      -0.399693      1.027812      -0.000082
      H      -0.399745      -0.513934      0.890139
      H      -0.399612      -0.513952      -0.890156
      H      1.931188      0.514066      0.890140
      H      1.931432      0.513819      -0.890121
      H      1.931281      -1.027824      0.000244
    End
  End

Constraints
  Dihedral 6 2 1 3 20.00
End

Engine ADF
  Symmetry NoSym
  Basis
    type DZP
  End
EndEngine
eor

echo "Dihedral after optimization:"
$AMSBIN/amsreport dihedral.results/adf.rkf -r dihedral#6#2#1#3

# == Example for Block constraint (with a dihedral constraint) for ethane ==

AMS_JOBNAME=block_and_dihedral $AMSBIN/ams <<eor
System
  Atoms
    C      -0.004115      -0.000021      0.000023 region=b1
    C      1.535711      0.000022      0.000008 region=b2
    H      -0.399693      1.027812      -0.000082 region=b1
    H      -0.399745      -0.513934      0.890139 region=b1
    H      -0.399612      -0.513952      -0.890156 region=b1
    H      1.931188      0.514066      0.890140 region=b2
    H      1.931432      0.513819      -0.890121 region=b2
    H      1.931281      -1.027824      0.000244 region=b2
  End
End

Task GeometryOptimization

GeometryOptimization
  Convergence Gradients=1.0e-4 Step=1.0e-3
End

Constraints
  Dihedral 6 2 1 3 20.00
  Block b1
  Block b2
End

Engine ADF
  Symmetry NoSym
  Basis

```

(continues on next page)

(continued from previous page)

```

        type DZP
    End
EndEngine
eor

echo "Dihedral after optimization:"
$AMSBIN/amsreport block_and_dihedral.results/adf.rkf -r dihedral#6#2#1#3
echo "Bonds distance after optimization:"
$AMSBIN/amsreport block_and_dihedral.results/adf.rkf -r distance#1#3
$AMSBIN/amsreport block_and_dihedral.results/adf.rkf -r distance#2#6

```

Example: Initial Hessian

Download InitHess.run

```

#!/bin/sh

# In this example the Hessian from a DFTB and a MOPAC calculation is used as a
# starting guess for the Hessian in an ADF geometry optimization of Isobutane.
# This example consist of 4 calculations:
# - MOPAC frequency calculation
# - DFTB frequency calculation
# - ADF geometry optimization with initial MOPAC Hessian
# - ADF geometry optimization with initial DFTB Hessian

# =====
# Generate MOPAC Hessian
# =====

AMS_JOBNAME=mopac_hessian $AMSBIN/ams << eor

Task SinglePoint

Properties
    NormalModes Yes
End

System
    Symmetrize
    Atoms
        C      -3.01417223      -2.81892970      0.27443080
        C      -2.32560254      -1.48669854     -0.04099291
        C      -0.81033566      -1.60274167      0.15652441
        H      -2.65505660      -3.61825489     -0.40916512
        H      -4.11459952      -2.71726364      0.16084942
        H      -2.80179295      -3.12071121      1.32226630
        H      -2.71211792      -0.71788031      0.66394035
        C      -2.65045192      -1.03659727     -1.46944155
        H      -0.32255475      -0.62449394     -0.04145480
        H      -0.38172118      -2.36329425     -0.53112669
        H      -0.58228356      -1.89634208      1.20336328
        H      -2.17532684      -0.05436369     -1.67852390
    
```

(continues on next page)

(continued from previous page)

```

      H      -3.74843413      -0.92249496      -1.59450083
      H      -2.28021380      -1.77910197      -2.20888365
    End
  End

Engine Mopac
EndEngine
eor

# =====
# Generate a dftb Hessian
# =====

AMS_JOBNAME=dftb_hessian $AMSBIN/ams <<eor

Task SinglePoint

Properties
  NormalModes True
End

System
  Symmetrize
  Atoms
    C      -3.014172230000      -2.818929700000      0.274430800000
    C      -2.325602540000      -1.486698540000      -0.040992910000
    C      -0.810335660000      -1.602741670000      0.156524410000
    H      -2.655056600000      -3.618254890000      -0.409165120000
    H      -4.114599520000      -2.717263640000      0.160849420000
    H      -2.801792950000      -3.120711210000      1.322266300000
    H      -2.712117920000      -0.717880310000      0.663940350000
    C      -2.650451920000      -1.036597270000      -1.469441550000
    H      -0.322554750000      -0.624493940000      -0.041454800000
    H      -0.381721180000      -2.363294250000      -0.531126690000
    H      -0.582283560000      -1.896342080000      1.203363280000
    H      -2.175326840000      -0.054363690000      -1.678523900000
    H      -3.748434130000      -0.922494960000      -1.594500830000
    H      -2.280213800000      -1.779101970000      -2.208883650000
  End

  Charge 0
End

Engine DFTB
  Model SCC-DFTB
  ResourcesDir DFTB.org/mio-1-1
  SCC
  End
EndEngine
eor

# Use the MOPAC Hessian generated earlier for ADF optimization

AMS_JOBNAME=adf_mopachessian "$AMSBIN/ams" <<eor
LoadSystem

```

(continues on next page)

(continued from previous page)

```

    File mopac_hessian.results/ams.rkf
End
Task GeometryOptimization
GeometryOptimization
    InitialHessian
        Type FromFile
        File mopac_hessian.results/mopac.rkf
    End
End
Engine ADF
EndEngine
eor

# Use the DFTB Hessian generated earlier for ADF optimization

AMS_JOBNAME=adf_dftbhessian "$AMSBIN/ams" <<eor
LoadSystem
    File dftb_hessian.results/ams.rkf
End
Task GeometryOptimization
GeometryOptimization
    InitialHessian
        Type FromFile
        File dftb_hessian.results/dftb.rkf
    End
End
Engine ADF
EndEngine
eor

```

Example: Geometry optimization with an external electric field or point charges: LiF

Download GO_LiF_Efield.run

```

#!/bin/sh

# In the first example a geometry optimization is performed with an external
# homogeneous electric field. In the second example a geometry optimization is
# performed with an external point charges

# Note that SYMMETRY NOSYM should be used. In case of point charges it is
# important to use the QPNEAR subkeyword of the BECKEGRID key with a large
# enough value that would include some of the point charges.

AMS_JOBNAME=Efield $AMSBIN/ams <<eor
System
    Atoms
        F      0.000000      0.800000      0.000000
        Li     0.000000     -0.800000      0.000000
    End
    ElectrostaticEmbedding
        ElectricField 0.0 0.0 0.01 [a.u.]
    End

```

(continues on next page)

(continued from previous page)

```

End

Task GeometryOptimization

GeometryOptimization
  Convergence Gradients=1E-5 Step=1E-3
End

Engine ADF
  Title LiF Geometry Optimization in the presence of electric field
  Basis
    type DZP
  End
  Symmetry NoSym
EndEngine
eor

AMS_JOBNAME=PointCharges $AMSBIN/ams <<eor
System
  Atoms
    F      0.000000      0.800000      0.000000
    Li     0.000000     -0.800000      0.000000
  End
  ElectrostaticEmbedding
    MultipolePotential
      Coordinates
        0.0 0.0  5.3  0.5
        0.0 0.0 -5.3 -0.5
      End
    End
  End
End
End

Task GeometryOptimization

GeometryOptimization
  Convergence Gradients=1E-5 Step=1E-3
End

RigidMotions
  AllowTranslations None
End

Engine ADF
  Title LiF Geometry Optimization in the presence of point charges
  BeckeGrid
    QPnear 20
  End
  Basis
    type DZP
  End
  Symmetry NoSym
EndEngine
eor

```

15.3.2 Transition States, Linear Transits, Intrinsic Reaction Coordinates

Example: LT, Frequencies, TS, and IRC: HCN

Download HCN.run

```
#!/bin/sh

# Linear Transit (PES scan)

AMS_JOBNAME=PES_Scan "$AMSBIN/ams" <<eor

Task PESScan
System
  Atoms
    C   0.00000000  0.00000000 -1.16013597
    N   0.00000000  0.00000000  0.00000000
    H   0.00000000  0.00000000  0.99666657
  End
End

PESScan
  CalcPropertiesAtPESPoints Yes
  ScanCoordinate
    nPoints 10
    Angle 3 2 1 180.0 0
  End
End

Engine ADF
  Basis
    Type DZP
  End
EndEngine
eor

# Transition state search starting from highest point in PES scan (i.e. PESPoint(7))

AMS_JOBNAME=TS_search "$AMSBIN/ams" <<eor

Task TransitionStateSearch

LoadSystem
  File PES_Scan.results/PESPoint(7).rkf
End

GeometryOptimization
  InitialHessian
    Type Calculate
  End
  Convergence Gradients=0.00001
End

Properties
  NormalModes Yes
End
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  Basis
    Type DZP
  End
EndEngine
eor

# IRC from TS

AMS_JOBNAME=IRC "$AMSBIN/ams" <<eor

Task IRC

LoadSystem
  File TS_search.results/adf.rkf
End

Engine ADF
  Basis
    Type DZP
  End
EndEngine
eor

```

Example: TS search using partial Hessian: C2H6 internal rotation

Download TS_C2H6.run

```

#!/bin/sh

# Frequently when searching for a transition state, one needs an accurate second
# derivatives matrix, a Hessian. An exact Hessian may be obtained analytically
# but this may be very expensive for large molecules. In such cases it may be
# beneficial to calculate Hessian matrix elements only for atoms directly
# involved in the reaction for which a transition state is sought for. The rest
# of the Hessian can then be approximated using a cheaper method.

# In this example, a saddle point of the ethane internal rotation around C-C
# bond is found. In principle, only hydrogen atoms contribute to the normal mode
# we are interested in. Therefore we calculate a partial Hessian matrix
# including hydrogen atoms only. For this purpose, the SelectedRegionForHessian
# key is used.
# In the calculation symmetry will be used.

AMS_JOBNAME=Partial_Hessian $AMSBIN/ams <<eor
System
  Symmetrize
    atoms
      C      0.000000000000      0.000000000000      0.767685465031
      C      0.000000000000      0.000000000000     -0.767685465031
      H      0.964354016767      0.347635559279      1.177128271450 region=hess
      H     -0.181115782790     -1.008972856410      1.177128271450 region=hess
      H     -0.783238233981      0.661337297125      1.177128271450 region=hess
      H     -0.500471876676      0.894626767091     -1.177128271450 region=hess
      H     -0.524533568868     -0.880734742626     -1.177128271450 region=hess

```

(continues on next page)

(continued from previous page)

```

      H      1.025005445540      -0.013892024465      -1.177128271450 region=hess
    end
  end

Task SinglePoint

Properties
  NormalModes Yes
  SelectedRegionForHessian hess
End

Engine ADF
  title Ethane transition state search using partial Hessian
  beckegrid
    quality good
  end
  basis
    core Large
    type DZ
    CreateOutput Yes
  end
EndEngine
eor

# After the Hessian is calculated, the resulting TAPE21 file is used for a
# subsequent transition state search:

AMS_JOBNAME=TS $AMSBIN/ams <<eor
LoadSystem
  File Partial_Hessian.results/ams.rkf
End

Task TransitionStateSearch

GeometryOptimization
  InitialHessian
    Type FromFile
    File Partial_Hessian.results/adf.rkf
  End
End

EngineRestart Partial_Hessian.results/adf.rkf

Engine ADF
  title Ethane transition state search using partial Hessian
  beckegrid
    quality good
  end
  basis
    core Large
    type DZ
  end
EndEngine

eor

# Important note: care should be taken to specify correct mode in the

```

(continues on next page)

(continued from previous page)

```
# TransitionState keyword. Because a significant part of the Hessian will not be
# calculated exactly, it is possible that it will have more than one negative
# eigenvalue, in which case the one we are interested in may not be the first
# one. In such a case, one needs to specify the correct mode number in the
# TransitionState keyword.
```

Example: Relativistic ZORA TS search: CH₄ + HgCl₂ <=> CH₃HgCl + HCl

Download TS_CH4_HgCl2.run

```
#!/bin/sh

# Compute the approximate initial hessian using DFTB:
AMS_JOBNAME=InitialHessian $AMSBIN/ams <<eor

System
  atoms
    C      0.049484    0.042994    0.000000
    H     -0.068980    0.638928   -0.915972
    H     -0.068980    0.638928    0.915972
    H     -0.841513   -0.626342    0.000000
    H      0.555494   -1.148227    0.000000
    Hg     2.303289   -0.007233    0.000000
    Cl     4.429752    0.776056    0.000000
    Cl     1.342057   -2.676083    0.000000
  end
  Symmetrize Yes
end

Task SinglePoint

Properties
  NormalModes Yes
End

Engine DFTB
  Model GFN1-xTB
EndEngine
eor

# A ZORA scalar relativistic Transition State calculation using the
# initial hessian computed by DFTB

AMS_JOBNAME=TS $AMSBIN/ams <<eor

LoadSystem
  File InitialHessian.results/dftb.rkf
End

EngineDebugging
  NeverQuiet True
End
```

(continues on next page)

(continued from previous page)

```

Task TransitionStateSearch

GeometryOptimization
  Convergence
    Energy 1.25e-6
  End
  InitialHessian
    Type FromFile
    File InitialHessian.results/dftb.rkf
  End
End

Properties
  PESPointCharacter Yes
End

Engine ADF
  Title Transition State: CH4 + HgCl2 <==> CH3HgCl + HCl
  basis
    Type TZP
    Core Small
    PerAtomType Symbol=Cl File=TZP/Cl.2p
  end
  relativity
    level scalar
    formalism ZORA
  end
EndEngine

eor

```

Example: TS reaction coordinate: F- + CH3Cl

Download TSRC_SN2.run

```

#!/bin/sh

# With the ReactionCoordinate block key one can specify a reaction coordinate along_
↳ which the
# transition state is sought for. This feature is especially useful when an
# accurate Hessian is not available.

# This example tries to find the TS for the S_N2 reaction of F^- + CH_3Cl <==> CH_3F_
↳ + Cl^-

$AMSBIN/ams <<eor
System
atoms
  C          0.000000    0.000000    0.000000
  H         -0.530807    0.919384693  0.012892
  H         -0.530807   -0.919384693  0.012892
  H          1.061614    0.000000    0.012892
  Cl          0.000000    0.000000   -2.124300
  F          0.000000    0.000000    2.019100

```

(continues on next page)

(continued from previous page)

```

    end
    charge -1
end

Task TransitionStateSearch

TransitionStateSearch
  ReactionCoordinate
    distance 1 5 1.0
    distance 1 6 -1.0
  end
End

Properties
  PESPointCharacter Yes
End

Engine ADF
  title Transition state search for Sn2 reaction of F- + CH3Cl
  beckegrid
    quality good
  end
  eprint
    sfo noeig noovl
  end
  basis
    core NONE
    type TZ2P
  end
  scf
    converge 1.0e-6 1.0e-6
    diis
      ok 0.01
    end
    iterations 99
  end
  xc
    gga OPBE
    lda VWN
  end
EndEngine
eor

```

Example: (non-)Linear Transit: H2O

Download Transit_H2O.run

```

#!/bin/sh

# AMS is capable of performing linear transits
# Here multiple coordinate descriptors are combined.
# This combines the individual coordinates into one compound coordinate,
# i.e. all coordinates will transit together through their respective ranges.

$AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    O      0.000000    0.000000    0.000000
    H      0.000000   -0.689440   -0.578509
    H      0.000000    0.689440   -0.578509
  end
end

Task PESSCAN

PESScan
  ScanCoordinate
    nPoints 4
    distance 1 2 0.8 1.5
    angle 2 1 3 100.0 120.0
  End
End

GeometryOptimization
  Convergence
    gradients 0.0001
  End
End

Engine ADF
  Basis
    Type DZP
  End
EndEngine
eor

```

15.3.3 Total energy, Multiplet States, S2, Localized hole, CEBE

Example: Total Energy calculation: H2O

Download `Energy_H2O.run`

```

#!/bin/sh

# If the TOTALENERGY is included the total energy will be calculated.

# ADF normally does not calculate the total energy of a system (the energy wrt bare
↪ nuclei and free electrons).
# However, ADF calculates the energy of the system with respect to fragment energies.
# By default, these fragments are the spherical spin-restricted neutral atoms, but
↪ one can also use larger fragments

# This example performs single point runs for H2O with PBE/DZP with frozen
# cores and all-electron and B3LYP/DZP with all-electron and HARTREEFOCK/DZP
# with all-electron. The tests run in C(2v) symmetry. Integration quality is good
# which should give total energies accurate at least up to 10^-4 atomic units.
# The key EXACTDENSITY is used for higher accuracy of the results.

```

(continues on next page)

(continued from previous page)

```

# Note that only energy difference comparisons are meaningful. These are the
# only energies that play a role in chemistry of course, and for this one does
# not need total energies.

# Remark: an earlier version of this example contained the undocumented key NOTOTEN.
# If one uses this undocumented key NOTOTEN the bond energy is not calculated.
# This may lead to an error in the AMS calculation.

# -----
# H2O PBE/DZP with frozen core
# -----

AMS_JOBNAME=FrozenCore $AMSBIN/ams <<eor
System
  atoms
    O      0.00000      0.00000      0.00000
    H      0.00000     -0.68944     -0.57851
    H      0.00000      0.68944     -0.57851
  end
end

Task SinglePoint

Engine ADF
  title H2O PBE/DZP (frozen core) single point calculation
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core Small
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  totalenergy
  xc
    gga PBE
  end
  Relativity
    Level None
  End
EndEngine
eor

# -----
# H2O PBE/DZP all-electron
# -----

AMS_JOBNAME=AllElectron $AMSBIN/ams <<eor
System
  atoms
    O      0.00000      0.00000      0.00000
    H      0.00000     -0.68944     -0.57851

```

(continues on next page)

(continued from previous page)

```

      H      0.00000      0.68944      -0.57851
    end
  end

Task SinglePoint

Engine ADF
  title H2O PBE/DZP (all-electron) single point calculation
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZP
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  totalenergy
  xc
    gga PBE
  end
  Relativity
    Level None
  End
EndEngine
eor

# -----
# H2O B3LYP/DZP all-electron
# -----

AMS_JOBNAME=B3LYP $AMSBIN/ams <<eor
System
  atoms
    O      0.00000      0.00000      0.00000
    H      0.00000      -0.68944      -0.57851
    H      0.00000      0.68944      -0.57851
  end
end

Task SinglePoint

Engine ADF
  title H2O B3LYP/DZP (all-electron) single point calculation
  beckegrid
    quality good
  end
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZP

```

(continues on next page)

(continued from previous page)

```

end
noprnt BAS FUNCTIONS
totalenergy
xc
  hybrid B3LYP
end
zlmfit
  quality good
end
Relativity
  Level None
End
EndEngine
eor

# -----
# H2O HARTREEFOCK/DZP all-electron
# -----

AMS_JOBNAME=HF $AMSBIN/ams <<eor
System
  atoms
    O      0.00000      0.00000      0.00000
    H      0.00000     -0.68944     -0.57851
    H      0.00000      0.68944     -0.57851
  end
end

Task SinglePoint

Engine ADF
  title H2O HARTREEFOCK/DZP (all-electron) single point calculation
  beckeGRID
    quality good
  end
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  exactdensity
  basis
    core None
    type DZP
  end
  noprnt BAS FUNCTIONS
  totalenergy
  xc
    hartreefock
  end
  zlmfit
    quality good
  end
  Relativity
    Level None
  End
EndEngine
eor

```

Example: Multiplet States: [Cr(NH3)6]3+

Download SD_CrNH3_6.run

```

#!/bin/sh

# The computation of multiplet states corresponding to an open-shell system can
# be carried out with ADF by first computing the 'Average-of-Configuration'
# (aoc) state, where all orbitals in the open shell are degenerate and equally
# occupied. This computation is spin-restricted and serves as a fragment file
# for the multiplet run, where then different occupation numbers are assigned to
# the various orbitals in the open shell. The corresponding energies are
# computed in the field of the aoc, which is achieved by not iterating the self-
# consistency equations to convergence but only computing the orbitals in the
# initial field.

# Since ADF requires that all symmetry-partners in an irreducible representation
# (irrep) have equal occupations, the multiplet calculation, where such orbitals
# are not equally occupied, must be carried out in a formally lower point group
# symmetry. The point group to select and the appropriate occupation numbers to
# apply must be worked out by the user 'on paper' in advance.
# See the discussion of Multiplet energies in ADF manual.

# The script starts with the 'creation' of the required basic atoms, N, H, Cr
# using a fair basis set quality.

# The next step is the computation of the ammonia fragment NH3. This is not a
# crucial step here: the multiplet state computation can equally well be carried
# out by not using any intermediate compound fragments. However, it illustrates
# once more how a bigger molecule can be built up from smaller, but not trivial
# fragments.

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/Cr.2p
mv TAPE12 t12.rel

AMS_JOBNAME=Cr $AMSBIN/ams <<eor
System
  Atoms
    Cr 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create Cr file=$AMSRESOURCES/ADF/ZORA/TZP/Cr.2p
  corepotentials t12.rel
    Cr 1
  end
EndEngine
eor

AMS_JOBNAME=NH3 $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    N      0      0      0
    H -0.95522523  0      0.3711068

```

(continues on next page)

(continued from previous page)

```

      H      0.477612615    -0.8272493155158333    0.3711068
      H      0.477612615      0.8272493155158333    0.3711068
    end
  end

Task SinglePoint

Engine ADF
  title AMMONIA
  basis
    core Small
    type TZP
    CreateOutput No
  end
  noprint sfo,frag,functions
  symmetry C(3V)
EndEngine
eor

# The input of the atomic coordinates does not use expressions. In this case to
# enforce exact symmetry relations 14-digit input values are required.
# The symmetrization key is used to enforce the symmetry to machine precision,
# and to put the molecule in the right orientation for the symmetry.
# The symmetry specification is redundant: the program would
# also find it by itself.

# == Average-of-Configuration ==

# The next step is to compute the reference state, with respect to which we will
# later compute the multiplet states. The reference state is the so-called
# 'Average-of-configuration' (aoc) state. The result file (TAPE21) of this
# calculation will be used as a fragment file.

AMS_JOBNAME=AOC $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    Cr      0.00000000    0.00000000    0.00000000
    N      0.00000000    1.71464325    1.21243632    adf.f=NH3|1
    H      0.00000000    1.46615142    2.20663314    adf.f=NH3|1
    H     -0.82724932    2.29340040    1.03672570    adf.f=NH3|1
    H      0.82724932    2.29340040    1.03672570    adf.f=NH3|1
    N     -1.48492461   -0.85732162    1.21243632    adf.f=NH3|2
    H     -1.26972438   -0.73307571    2.20663314    adf.f=NH3|2
    H     -1.57251835   -1.86311912    1.03672570    adf.f=NH3|2
    H     -2.39976767   -0.43028128    1.03672570    adf.f=NH3|2
    N      1.48492461   -0.85732162    1.21243632    adf.f=NH3|3
    H      1.26972438   -0.73307571    2.20663314    adf.f=NH3|3
    H      2.39976767   -0.43028128    1.03672570    adf.f=NH3|3
    H      1.57251835   -1.86311912    1.03672570    adf.f=NH3|3
    N      0.00000000   -1.71464325   -1.21243632    adf.f=NH3|4
    H      0.00000000   -1.46615142   -2.20663314    adf.f=NH3|4
    H      0.82724932   -2.29340040   -1.03672570    adf.f=NH3|4
    H     -0.82724932   -2.29340040   -1.03672570    adf.f=NH3|4
    N      1.48492461    0.85732162   -1.21243632    adf.f=NH3|5
    H      1.26972438    0.73307571   -2.20663314    adf.f=NH3|5
    H      1.57251835    1.86311912   -1.03672570    adf.f=NH3|5

```

(continues on next page)

(continued from previous page)

```

      H      2.39976767      0.43028128      -1.03672570      adf.f=NH3|5
      N     -1.48492461      0.85732162      -1.21243632      adf.f=NH3|6
      H     -1.26972438      0.73307571      -2.20663314      adf.f=NH3|6
      H     -2.39976767      0.43028128      -1.03672570      adf.f=NH3|6
      H     -1.57251835      1.86311912      -1.03672570      adf.f=NH3|6
    end
  end

Task SinglePoint

Engine ADF
  title Cr(NH3)6 : Average-of-Configuration run
  comment
    using NH3-fragments
  end
  fragments
    Cr  Cr.results/adf.rkf
    NH3 NH3.results/adf.rkf
  end
  Basis CreateOutput=No
  irreproccupations
    A1.G 8.75
    A2.G 2
    E1.G 16 1.5 0.75
    A1.U 2
    A2.U 8
    E1.U 20
  end
  scf
    iterations 25
    mixing 0.15
  end
  symmetry D(3d)
EndEngine

eor

# Occupation numbers are specified, to make certain what the reference state is
# that we will start from in the subsequent calculations. The result file TAPE21
# is saved to serve as fragment file in the subsequent calculations.

# == One-determinant states ==

# Now, we proceed with the multiplet calculations. In the example they are
# combined in one single run, but they could also be evaluated in separate runs.
# For each calculation it is required to:

# a) Use the aoc TAPE21 file as fragment file
# b) Choose which molecular orbitals in the open shell to occupy: select the
# appropriate point group symmetry and the UnRestricted key if necessary and
# specify the occupation numbers, using the irreducible representations of the
# selected point group.

# The results are one-determinant calculations, which must then, later, be
# combined analytically to obtain the required multiplet energy values.

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=SD $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    Cr      0.00000000    0.00000000    0.00000000  adf.f=CrA6
    N      0.00000000    1.71464325    1.21243632  adf.f=CrA6
    H      0.00000000    1.46615142    2.20663314  adf.f=CrA6
    H     -0.82724932    2.29340040    1.03672570  adf.f=CrA6
    H      0.82724932    2.29340040    1.03672570  adf.f=CrA6
    N     -1.48492461   -0.85732162    1.21243632  adf.f=CrA6
    H     -1.26972438   -0.73307571    2.20663314  adf.f=CrA6
    H     -1.57251835   -1.86311912    1.03672570  adf.f=CrA6
    H     -2.39976767   -0.43028128    1.03672570  adf.f=CrA6
    N      1.48492461   -0.85732162    1.21243632  adf.f=CrA6
    H      1.26972438   -0.73307571    2.20663314  adf.f=CrA6
    H      2.39976767   -0.43028128    1.03672570  adf.f=CrA6
    H      1.57251835   -1.86311912    1.03672570  adf.f=CrA6
    N      0.00000000   -1.71464325   -1.21243632  adf.f=CrA6
    H      0.00000000   -1.46615142   -2.20663314  adf.f=CrA6
    H      0.82724932   -2.29340040   -1.03672570  adf.f=CrA6
    H     -0.82724932   -2.29340040   -1.03672570  adf.f=CrA6
    N      1.48492461    0.85732162   -1.21243632  adf.f=CrA6
    H      1.26972438    0.73307571   -2.20663314  adf.f=CrA6
    H      1.57251835    1.86311912   -1.03672570  adf.f=CrA6
    H      2.39976767    0.43028128   -1.03672570  adf.f=CrA6
    N     -1.48492461    0.85732162   -1.21243632  adf.f=CrA6
    H     -1.26972438    0.73307571   -2.20663314  adf.f=CrA6
    H     -2.39976767    0.43028128   -1.03672570  adf.f=CrA6
    H     -1.57251835    1.86311912   -1.03672570  adf.f=CrA6
  end
end

Task SinglePoint

Engine ADF
  title Cr(NH3)6 : SlaterDeterminants run
  fragments
    CrA6  AOC.results/adf.rkf
  end
  noprint frag
  scf
    iterations 0
  end
  slaterdeterminants
    Check AOC
    A1.g  4 0.375          // 4 0.375
    A2.g  1                // 1
    E1.g:1 4 0.375 0.1875 // 4 0.375 0.1875
    E1.g:2 4 0.375 0.1875 // 4 0.375 0.1875
    A1.u  1//1
    A2.u  4//4
    E1.u:1 5//5
    E1.u:2 5//5
    SUBEND
    State1
    A1.g  4 1              // 4 1
    A2.g  1                // 1

```

(continues on next page)

(continued from previous page)

```

E1.g:1 4 0      0      // 4 0      1
E1.g:2 4 0      0      // 4 0      0
A1.u   1//1
A2.u   4//4
E1.u:1 5//5
E1.u:2 5//5
SUBEND
State2
A1.g   4 1      // 4 1
A2.g   1      // 1
E1.g:1 4 0      0      // 4 1      0
E1.g:2 4 0      0      // 4 0      0
A1.u   1//1
A2.u   4//4
E1.u:1 5//5
E1.u:2 5//5
SUBEND
State3
A1.g   4 1      // 4 1
A2.g   1      // 1
E1.g:1 4 0      1      // 4 0      0
E1.g:2 4 0      0      // 4 0      0
A1.u   1//1
A2.u   4//4
E1.u:1 5//5
E1.u:2 5//5
SUBEND
end
symmetry C(I)
unrestricted
EndEngine
eor

# The SlaterDeterminants block may contain any number of sub blocks, each
# starting with an (arbitrary) title record, followed by a set of occupation
# numbers and closed by a SubEnd record. Each such subkey block specifies a
# single one-determinant-state calculation. All occupation numbers must
# reference the irreps of the specified point group symmetry, C(I) in the
# example, and must be just a reassignment of the electrons that are equally
# distributed over the corresponding degenerate irreps in the reference aoc
# calculation.

# The so-obtained energies of the one-determinant states can now be combined to
# calculate the desired multiplet energies. See the ADF manual.

# Note carefully that in the calculation of the SingleDeterminants, the scf
# procedure is prevented to cycle to convergence by setting the subkey
# Iterations to zero in the SCF data block.

```

Example: Calculation of S2: CuH+

Download CuH+_S-squared.run

```

#!/bin/sh

# Example calculates expectation value of S^2 (<S^2>) of CuH+ in various
# symmetries, using unrestricted density functional theory.

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
  atoms
    Cu    0.0    0.0 0.0
    H     1.463 0.0 0.0
  end
  charge 1.0
end

Task SinglePoint

Engine ADF
  title calculate expectation value of S-squared
  basis
    core Small
    type TZP
  end
  spinpolarization 1.0
  symmetry Nosym
  unrestricted Yes
EndEngine

eor

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
  atoms
    Cu    0.0 0.0 0.0
    H     0.0 0.0 1.463
  end
  charge 1.0
end

Task SinglePoint

Engine ADF
  title calculate expectation value of S-squared
  basis
    core Small
    type TZP
  end
  spinpolarization 1.0
  symmetry C(LIN)
  unrestricted Yes
EndEngine

eor

```

(continues on next page)

(continued from previous page)

```
AMS_JOBNAME=third $AMSBIN/ams <<eor
System
  atoms
    Cu   0.0   0.0 0.0
    H    1.463 0.0 0.0
  end
  charge 1.0
end

Task SinglePoint

Engine ADF
  title calculate expectation value of S-squared
  basis
    core Small
    type TZP
  end
  spinpolarization 1.0
  symmetry C(S)
  unrestricted Yes
EndEngine

eor

AMS_JOBNAME=fourth $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    Cu   0.0   0.0 0.0
    H    1.463 0.0 0.0
  end
  charge 1.0
end

Task SinglePoint

Engine ADF
  title calculate expectation value of S-squared
  basis
    core Small
    type TZP
  end
  spinpolarization -1.0
  unrestricted Yes
EndEngine

eor
```

Example: Localized Hole: N2+

Download ModStPot_N2+.run

```

#!/bin/sh

# This calculation illustrates:

# - How to specify the net total charge on a molecule
# - How to enforce breaking the symmetry that is present in the start-up
#   situation, in this case to localize a hole in the electron density on one of
#   the two equivalent atoms.
# - How to prevent the scf from oscillating back and forth between the two
#   equivalent situations or from even restoring the unwanted symmetry

$AMSBIN/ams <<eor
System
  Atoms
    N 0 0 -2.0
    N 0 0  2.0
  End
  Charge 1
End

Task SinglePoint

Engine ADF
  Title N2+ hole localization
  IrrepOccupations
    sigma 3 // 1 0 1
    pi    2 // 2
  End

  ModifyStartPotential
    N/1 0.5 0.5
    N/2 4 1
  End

  Basis
    Type DZP
    Core Small
    CreateOutput Yes
  End

  SCF
    DIIS
    ok 0.5
  End
End
Unrestricted Yes
SpinPolarization 1

Relativity
  Level None
End

```

(continues on next page)

(continued from previous page)

```

Symmetry C(lin)
EndEngine
eor

# The purpose of this run is to compute the N2+ ion, with the hole localized on
# one of the atoms. In a very small system like N2+ this is a tricky thing to
# do. The program has a tendency towards the symmetric solution, with the hole
# delocalized. A few trial runs, just putting a net +1 charge into the system,
# will reveal that clearly.

# To achieve the desired situation we apply the key modifystartpotential to
# break the symmetry of the initial potential. A potential is generated as if
# the electronic cloud in the second N fragment is spin-polarized in a ratio 4:1
# (this precise value is not very relevant), which achieves that initially a
# non-symmetric solution is obtained. The symmetry must be specified, lest the
# program determine and use the higher symmetry from the nuclear frame. This
# would prevent any symmetry breaking altogether.

# Next, in order to prevent that the system relaxes to the symmetric situation,
# we apply the keeporbitals option of the occupations key. This fixes the
# occupied orbitals in the sense that in each scf cycle the program will try to
# keep the electrons in orbitals that resemble the previously occupied orbitals
# as much as possible.

# The key modifystartpotential here demonstrated has a more relevant and less
# unstable application in larger systems. See the User's Guide for references.

```

Example: Broken spin-symmetry: Fe4S4

Download Fe4S4_BrokenSymm.run

```

#!/bin/sh

# This calculation shows a spin-flip restart feature that allows to exchange
# alpha and beta fit coefficients for selected atoms upon restart. First the
# high spin configuration with 8 more alpha-electrons than beta-electrons is
# calculated (S_z=4). Next the broken spin-symmetry configuration is calculated
# (S_z=0), using the subkey spinflip in the restart key. In this case the spin
# will be flipped for iron atoms 1 and 2. Note that the used symmetry C(2v) is
# lower than the actual symmetry T(d), such that iron atoms 1 and 2 can have a
# different spin than iron atoms 3 and 4.

AMS_JOBNAME=HighSpin $AMSBIN/ams <<eor
System
atoms
  Fe      -0.000000000000      -1.256142548900      0.888226914500
  Fe       0.000000000000       1.256142548900      0.888226914500
  Fe     -1.256142548900      0.000000000000     -0.888226914500
  Fe      1.256142548900     -0.000000000000     -0.888226914500
  S      -1.845393493800      0.000000000000      1.304890253400
  S       1.845393493800     -0.000000000000      1.304890253400
  S     -0.000000000000     -1.845393493800     -1.304890253400
  S       0.000000000000      1.845393493800     -1.304890253400

```

(continues on next page)

(continued from previous page)

```

End
End

Task SinglePoint

Engine ADF
  Title Fe4S4 High-spin configuration

  Unrestricted Yes
  SpinPolarization 8.0

  symmetry C(2v)

  XC
    GGA OPBE
  End

  ! Omit printing of SFOs, populations, etc. since they may change per computer
  ! In real-life calculations you may want to have them
  NoPrint SFO SCF FIT NUMINT MDC DensityAtNucleus
EndEngine
eor

```

```
AMS_JOBNAME=LowSpin $AMSBIN/ams <<eor
```

```

System
  atoms
    Fe      -0.000000000000      -1.256142548900      0.888226914500
    Fe       0.000000000000       1.256142548900      0.888226914500
    Fe      -1.256142548900       0.000000000000     -0.888226914500
    Fe       1.256142548900     -0.000000000000     -0.888226914500
    S       -1.845393493800       0.000000000000      1.304890253400
    S        1.845393493800     -0.000000000000      1.304890253400
    S       -0.000000000000     -1.845393493800     -1.304890253400
    S        0.000000000000       1.845393493800     -1.304890253400
  End
End

```

```

Task SinglePoint

EngineRestart HighSpin.results/adf.rkf

```

```

Engine ADF
  Title Fe4S4 low-spin configuration

  Restart
    SpinFlip 1 2
  End

  Unrestricted Yes
  SpinPolarization 0.0

  symmetry C(2v)

  XC
    GGA OPBE
  End

```

(continues on next page)

(continued from previous page)

```
EndEngine
eor
```

Example: Core-electron binding energies (CEBE): NNO

Download CEBE_NNO.run

```
#!/bin/sh

# ADF is well suited for calculating Core Electron Binding Energies (CEBEs). In
# this example it is shown how one can differentiate between the 1s CEBEs of the
# two non-equivalent nitrogen atoms in N2 O, using a delta-SCF technique. It
# starts with a regular calculation that has the purpose of preparing a
# reference adf.rkf file for the NNO molecule, which will later be useful in the
# energy analysis. The result file is saved to t21.NNO.

# The same GGA functional is specified throughout the run. The amount of output
# is reduced by using some print keys.

# The prepare the nitrogen atom with a core hole (restricted) will be used as a
# fragment later. This enables selection of where the core hole should be.

# prepare the Nitrogen core hole restricted to be used as fragment

AMS_JOBNAME=N_ch $AMSBIN/ams <<eor
System
  atoms
    N   0.0   0.0   0.0
  end
end

Task SinglePoint

Engine ADF
  title N atom core hole
  irreoccupations
    s   1 2
    p   3
  end
  basis
    type TZ2P
    core None
    CreateOutput Yes
  end
  numericalquality good
  xc
    gga pw86x pw91c
  end
EndEngine

eor
```

(continues on next page)

(continued from previous page)

```
# Now perform the restricted ground state molecule for analysis later. The
# adf.rkf result file is saved.
# Remark: In the core hole calculation the 2 N atoms will have different fragments.
# Therefore also in this calculation the 2 N atoms are treated with 2 different
# → fragments,
# which is done here by using 2 different region: 'one' and 'two'
```

```
AMS_JOBNAME=NNO $AMSBIN/ams <<eor
```

```
System
  atoms
    N  0.0    0.0   -1.1284  region=one
    N  0.0    0.0    0.0     region=two
    O  0.0    0.0    1.1841
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
  title NNO
  basis
    type TZ2P
    core None
  end
  noprint sfofragpop fragsfo
  numericalquality good
  xc
    gga pw86x pw91c
  end
EndEngine
```

```
eor
```

```
# Next follow two sets of almost identical calculations in which a 1s electron
# is removed from one or the other N atom (please note that the deepest s level
# is associated with the 1s of the oxygen atom). The molecular NNO result file
# is used as fragment. An unrestricted calculation is done and a positive charge
# is specified. The final result file for the molecule with the core hole is
# saved. Then another calculation is done to conveniently obtain the energy with
# respect to the normal molecule. This is repeated for a core hole on the other
# N atom.
```

```
AMS_JOBNAME=NNO_unr1 $AMSBIN/ams <<eor
```

```
System
  atoms
    N  0.0    0.0   -1.1284  region=one  adf.f=N_ch
    N  0.0    0.0    0.0     region=two
    O  0.0    0.0    1.1841
  end
  charge 1
end
```

```
Task SinglePoint
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title NNO unrestricted core hole
  fragments
    N_ch N_ch.results/adf.rkf
  end
  irreproccupations
    sigma 1 1 1 4 // 1 0 1 4
    pi 4 // 4
  end
  basis
    type TZ2P
    core None
  end
  noprint sfofragpop fragsfo
  numericalquality good
  spinpolarization 1
  unrestricted Yes
  xc
    gga pw86x pw91c
  end
EndEngine

```

```
eor
```

```

# In the second calculation the result file of one of the unrestricted NNO
# calculations is used as restart file, which ensures that the hole stays at its
# place, because the starting density is already correct. The result file
# t21.NNO for the normal NNO calculation is specified as fragment to serve as an
# energy reference. The final Bonding Energy printed by ADF indicates what the
# CEBE is. However, please check Chong, D.P. Accurate DFT Calculation of Core-
# Electron Binding Energies in Reviews in Modern Quantum Chemistry, A
# Celebration of the Contributions of R.G. Parr, edited by K.D. Sen (World
# Scientific Publishing Co., Singapore), 1106-1139 (2002) for more detailed
# information on Core-Electron Binding Energies. This reference also contain
# information on empirical corrections that may have to be made on the final
# numbers.

```

```
AMS_JOBNAME=NNO_unr1_1 $AMSBIN/ams <<eor
```

```

System
  atoms
    N 0.0 0.0 -1.1284 region=one adf.f=NNO
    N 0.0 0.0 0.0 region=two adf.f=NNO
    O 0.0 0.0 1.1841 adf.f=NNO
  end
  charge 1
end

```

```
Task SinglePoint
```

```
EngineRestart NNO_unr1.results/adf.rkf
```

```

Engine ADF
  title NNO unr. core hole
  fragments
    NNO NNO.results/adf.rkf

```

(continues on next page)

(continued from previous page)

```

end
irrepopulations
  sigma 1 1 1 4 // 1 0 1 4
  pi    4      // 4
end
noprnt sfofragpop fragsfo
numericalquality good
spinpolarization 1
unrestricted Yes
xc
  gga pw86x pw91c
end
EndEngine

eor

# core hole nr. 2

AMS_JOBNAME=NNO_unr2 $AMSBIN/ams <<eor
System
atoms
  N  0.0    0.0   -1.1284  region=one
  N  0.0    0.0    0.0     region=two  adf.f=N_ch
  O  0.0    0.0    1.1841
end
charge 1
end

Task SinglePoint

Engine ADF
title NNO unrestricted core hole
fragments
  N_ch N_ch.results/adf.rkf
end
irrepopulations
  sigma 1 1 1 4 // 1 0 1 4
  pi    4      // 4
end
basis
  type TZ2P
  core None
end
noprnt sfofragpop fragsfo
numericalquality good
spinpolarization 1
unrestricted Yes
xc
  gga pw86x pw91c
end
EndEngine

eor

# analysis for core hole 2

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=unr3 $AMSBIN/ams <<eor
System
  atoms
    N   0.0   0.0  -1.1284  region=one  adf.f=NNO
    N   0.0   0.0   0.0     region=two  adf.f=NNO
    O   0.0   0.0   1.1841                adf.f=NNO
  end
  charge 1
end

Task SinglePoint

EngineRestart NNO_unr2.results/adf.rkf

Engine ADF
  title NNO unr. core hole
  fragments
    NNO NNO.results/adf.rkf
  end
  irreproccupations
    sigma 1 1 1 4 // 1 0 1 4
    pi     4      // 4
  end
  noprint sfofragpop fragsfo
  numericalquality good
  spinpolarization 1
  unrestricted Yes
  xc
    gga pw86x pw91c
  end
EndEngine

eor

# Similarly, one could easily have prepared an oxygen with a core hole and
# determined the CEBE of the oxygen 1s atom.

```

Example: CEBE 1s Iodine in HI

Download CEBE_HI.run

```

#!/bin/sh

# Spin-orbit coupled relativistic ZORA, X2C, and RA-X2C
# are compared in this example for the calculation of
# Core Electron Binding Energies (CEBEs).
# In this case the CEBE of the 1s of Iodine in the molecule HI.
# For such calculations X2C or RA-X2C is recommended.
# Note, for more accurate calculations one should increase the basis set.
# In this example the LDA functional is used.

# Results of this example will show that for X2C the CEBE is around 33.211 keV
# and for RA-X2C the CEBE is around 33.202 keV.
# If one increases the basis set (especially in the core region), for example, with a
# QZ4P basis set,

```

(continues on next page)

(continued from previous page)

```

# the results obtained with X2C and RA-X2C will be much closer.

# In case of ZORA, without the scaled ZORA energy correction
# the CEBE in this case is around 34.515 keV, much larger than the results with X2C
↳or RA-X2C.
# If one includes the scaled ZORA energy correction (can be found in the output)
# the CEBE in case of ZORA is around 33.238 keV.

# NOTE: The scaled ZORA energy correction should only be used to compare two
↳calculations
# in which the only difference in the calculation is the electron configuration.
# Then the difference in energy of this term should be added to the difference in
↳energy of
# the two electron configurations.
# This term should not be used otherwise.
# In practice it is useful only for core excitation energy calculations.

for f in "ZORA" "X2C" "RA-X2C"
do

AMS_JOBNAME=HI_ $f $AMSBIN/ams <<eor
System
  atoms
    H 0.0 0.0 0.000
    I 0.0 0.0 1.609
  end
end

Task SinglePoint

Engine ADF
  basis
    core None
    type DZ
  end
  numericalquality good
  relativity
    level spin-orbit
    formalism $f
  end
  nuclearmodel gaussian
EndEngine
eor

AMS_JOBNAME=HI_core_ $f $AMSBIN/ams <<eor
System
  atoms
    H 0.0 0.0 0.000
    I 0.0 0.0 1.609
  end
  charge 1
end

Task SinglePoint

Engine ADF
  basis

```

(continues on next page)

(continued from previous page)

```

    core None
    type DZ
end
numericalquality good
relativity
    level spin-orbit
    formalism $f
    SpinOrbitMagnetization NonCollinear
end
unrestricted
symmetry nosym
irreppoccupations
    A1/2 1 0 52
end
nuclearmodel gaussian
EndEngine
eor
done

```

Example: Constrained DFT: H2O+ ... H2O

Download WaterDimer.run

```

#!/bin/sh

# Example of Constrained Density Functional Theory (CDFT) for the charged Water
# dimer, in which the charge is constrained to be on one of the waters. In this
# case there is one constraint, with a total charge of 1.0 on the atoms 1-3.

$AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000
    H     -0.9358409558      0.2646136961      0.0000000000
    H     -0.0304663436     -0.9828924420      0.0000000000
    O      0.0000000000     -2.9053396088      0.0000000000
    H     -0.4092227596     -3.3374838250     -0.7701260000
    H     -0.4092227596     -3.3374838250      0.7701260000
  end
  charge 1
end

Task SinglePoint

Engine ADF
  title water dimer h2o+ ... h2o

  cdft
    constraints 1.0
    natomserset 3
    nconstraints 1
    theatoms 1 2 3
  end

```

(continues on next page)

(continued from previous page)

```

basis
  core none
  type TZP
end

unrestricted
spinpolarization 1

symmetry NOSYM

xc
  gga PW91
end

noprnt BAS FUNCTIONS
eprint
  sfo NOEIG NOOVL NOORBPOP
end
EndEngine
eor

```

Example: ROKS: O2

Download O2_ROKS.run

```

#!/bin/sh

# Example restricted open shell Kohn-Sham (ROKS, ROSCF) for O2.

# The method implemented in ADF needs integer occupation numbers,
# and a positive spin polarization.
# In this case one can use symmetry, since the calculated occupation numbers
# will be integer, also for the orbitals in the degenerate irreps.
# Orbitals in degenerate irreps for a given spin need to be either fully occupied or
→ zero.
# For example, one of the orbitals in the PI.g irrep will have
# 2 occupied alpha electrons and 0 beta electrons.

"$AMSBIN/ams" << eor
Task SinglePoint
System
  Atoms
    O  0.000 0.000 -0.604
    O  0.000 0.000  0.604
  End
End

Engine ADF
Basis
  Type TZ2P
  Core None
End
Occupations IntegerAufbau
Unrestricted Yes

```

(continues on next page)

(continued from previous page)

```

SpinPolarization 2
Scf
  ROSCF
  End
End
NumericalQuality Good
XC
  Hybrid B3LYP
End
EndEngine
eor

```

Example: ROKS: SF

Download SF_ROKS.run

```

#!/bin/sh

# Example restricted open shell Kohn-Sham (ROKS, ROSCF) for SF.

# The method implemented in ADF needs integer occupation numbers,
# and a positive spin polarization.
# In this case one can not use full C(lin) symmetry, since one of
# the orbitals in one of the degenerate representation might not
# be fully occupied or zero.
# If one would use C(lin) one of the orbitals in the degenerate
# irrep Pi would have 1 beta electron.
# This looks like an integer number, however, 1 beta electron in Pi
# effectively would lead to a fractional 0.5 electron in Pi:x and
# 0.5 electron in Pi:y beta orbital.
# Since this method needs integer occupations, a lower symmetry is
# used, in this case C(2v).
# Note that in this case one needs to use the key Occupations IntegerAufbau
# or explicit integer occupation numbers with the key IrrepOccupations,
# otherwise one could still end up with fractional occupation numbers.

# Note that the ROSCF method is less useful for electron
# configurations with 1 electron in a multidimensional irrep,
# since it will lose orbital degeneracy.

"$AMSBIN/ams" << eor
Task SinglePoint
System
  Atoms
    S  0.0000 0.0000 0.0000
    F  0.0000 0.0000 1.6000
  End
End

Engine ADF
Basis
  Type TZ2P
  Core None
End
SpinPolarization 1

```

(continues on next page)

(continued from previous page)

```

XC
  Hybrid B3LYP
End
Scf
  ROSCF
  End
End
symmetry C(2v)
Unrestricted Yes
Occupations IntegerAufbau
NumericalQuality Good
IrrepOccupations
  A1 7 // 7
  B1 3 // 3
  B2 3 // 2
End
EndEngine
eor

```

15.4 Spectroscopic Properties

15.4.1 IR Frequencies, (resonance) Raman, VROA, VCD

Example: Numerical Frequencies: NH3

Download Freq_NH3.run

```

#!/bin/sh

# Summary:
# - Frequencies with symmetric displacements
# - Frequencies with Cartesian displacements
# - Isotope effects in the frequencies

# == Frequencies with symmetric displacements ==

# Computation of frequencies by symmetric displacements. The assumed equilibrium
# input structure should be given in Cartesian coordinates.

# The symmetry is determined automatically by the program as C(3v), from the
# input coordinates. During the calculation first symmetric atomic displacements
# are constructed. The number of such displacements in each irreducible
# representation corresponds to the number of frequencies with the corresponding
# symmetry. All displaced geometries within one representation have the same
# symmetry, which enables us to use it to speed up the computation
# significantly.

AMS_JOBNAME=NH3_symm $AMSBIN/ams <<eor
System
atoms
  N  0.0000    0.0000    0.0000
  H  0.4729    0.8190    0.3821
  H -0.9457    0.0000    0.3821

```

(continues on next page)

(continued from previous page)

```

      H  0.4729   -0.8190    0.3821
    end
    Symmetrize Yes
  end

Task SinglePoint

Properties
  NormalModes Yes
End

NormalModes
  Displacements Symmetric
End

Thermo
  Temperatures 300:400:10
End

Engine ADF
  title NH3 frequencies in symmetric displacements
  BeckeGrid
    quality good
  End
  Basis
    type TZP
    core Small
  End
EndEngine
eor

# == Frequencies with Cartesian displacements ==

# Computation of frequencies by Cartesian displacements. The assumed equilibrium
# input structure is given in internal coordinates.

AMS_JOBNAME=NH3_cartesian $AMSBIN/ams <<eor
System
  atoms
    N  0.0000    0.0000    0.0000
    H  0.4729    0.8190    0.3821
    H -0.9457    0.0000    0.3821
    H  0.4729   -0.8190    0.3821
  end
  Symmetrize Yes
end

Task SinglePoint

Properties
  NormalModes Yes
End

NormalModes
  Hessian Numerical
  Displacements Cartesian

```

(continues on next page)

(continued from previous page)

```

End

Thermo
  Temperatures 300:400:10
End

Engine ADF
  title NH3 frequencies
  BeckeGrid
    quality good
  End
  Basis
    type TZP
    core Small
  End
EndEngine
eor

# The symmetry is determined automatically by the program as C(3v), from the
# input coordinates. In a Frequencies calculation the symmetry (specified on
# input or computed internally) is used for analysis and in some cases to speed
# up the calculation.

# The equilibrium coordinate values are supplied as identifiers that are
# associated with values in the define block.

# The key thermo addresses the thermodynamical analysis (only available in a
# Frequencies calculation, otherwise ignored). The specification Temperatures_
→ 300:400:10
# means that the thermodynamic properties are printed for the temperature range
# 300-400K using 10 equidistant steps and for a pressure of 1.0 atmosphere
# (default).

# Frequencies calculations suffer easily from numerical inaccuracies. Therefore,
# the default numerical integration precision in a Frequencies calculation is
# higher than in an ordinary single-point or minimization run.

# == Isotope effects in the frequencies ==

# Calculate a different isotope of H, in this case deuterium.

AMS_JOBNAME=Isotope $AMSBIN/ams <<eor
System
  atoms
    N   0.0000    0.0000    0.0000
    H   0.4729    0.8190    0.3821 mass=2.014
    H  -0.9457    0.0000    0.3821 mass=2.014
    H   0.4729   -0.8190    0.3821 mass=2.014
  end
  Symmetrize Yes
end

Task SinglePoint

Properties

```

(continues on next page)

(continued from previous page)

```

    NormalModes Yes
End

NormalModes
    Hessian Numerical
    Displacements Cartesian
End

Thermo
    Temperatures 300:400:10
End

Engine ADF
    title NH3 frequencies
    BeckeGrid
        quality good
    End
    Basis
        type TZP
        core Small
    End
EndEngine
eor

```

Example: Numerical Frequencies, spin-orbit coupled ZORA: UF6Download `Freq_UF6.run`

```

#!/bin/sh

# Optimization and frequencies for scalar relativistic ZORA

AMS_JOBNAME=SR_GO $AMSBIN/ams <<eor
System
    atoms
        U  0.00000  0.00000  0.00000
        F  2.00000  0.00000  0.00000
        F -2.00000  0.00000  0.00000
        F  0.00000  2.00000  0.00000
        F  0.00000 -2.00000  0.00000
        F  0.00000  0.00000  2.00000
        F  0.00000  0.00000 -2.00000
    end
end

Task GeometryOptimization

GeometryOptimization
    Convergence Gradients=1E-4
End

Engine ADF
    title UF6 geometry optimization + freq: scalar ZORA
    beckeGRID quality=good
    basis type=TZP

```

(continues on next page)

(continued from previous page)

```

    relativity
      level scalar
      formalism ZORA
    end
  EndEngine
eor

AMS_JOBNAME=SR_Freq $AMSBIN/ams <<eor
LoadSystem
  File SR_GO.results/adf.rkf
End

Task SinglePoint

Properties
  NormalModes Yes
End

LoadEngine SR_GO.results/adf.rkf
eor

# # Optimization and frequencies for spinorbit ZORA

AMS_JOBNAME=SO_GO $AMSBIN/ams <<eor
System
  atoms
    U  0.00000  0.00000  0.00000
    F  2.00000  0.00000  0.00000
    F -2.00000  0.00000  0.00000
    F  0.00000  2.00000  0.00000
    F  0.00000 -2.00000  0.00000
    F  0.00000  0.00000  2.00000
    F  0.00000  0.00000 -2.00000
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence Gradients=1E-4
End

Engine ADF
  title UF6 geometry optimization + freq: spinorbit ZORA
  beckeGRID quality=good
  basis type=TZP
  relativity
    level spin-orbit
    formalism ZORA
  end
EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=SO_Freq $AMSBIN/ams <<eor
LoadSystem
  File SO_GO.results/adf.rkf
End

Task SinglePoint

Properties
  NormalModes Yes
End

NormalModes
  Displacements Symmetric
End

LoadEngine SO_GO.results/adf.rkf
eor

```

Example: Numerical Frequencies, accurate Hartree-Fock: H2O

Download H2O_HF_freq.run

```

#!/bin/sh

# Example shows a Hartree-Fock frequency calculation with an accurate basis set.
# Note that numerical issues may be present in ADF with large basis sets icw
# Hartree-Fock or (range-separated) (meta-)hybrids.
# An RIHartreeFock VeryGood fit set is recommended in those cases.

# First a geometry optimization is performed.

AMS_JOBNAME=GO $AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000   -0.007124
    H      0.000000    0.751933    0.556531
    H      0.000000   -0.751933    0.556531
  end
end

Task GeometryOptimization

Engine ADF
  title accurate HF geometry optimization with large QZ4P basis set
  basis
    type QZ4P
    core None
  end
  numericalquality Good
  rihartreefock
    quality verygood
  end
  xc
    hartreefock

```

(continues on next page)

(continued from previous page)

```

    end
EndEngine
eor

# Next the frequency calculation is done.

AMS_JOBNAME=Freq $AMSBIN/ams <<eor

LoadSystem
  File GO.results/adf.rkf
End

Task SinglePoint

Properties
  NormalModes Yes
End

Engine ADF
  title accurate HF frequency calculation with large QZ4P basis set
  basis
    type QZ4P
    core None
  end
  numericalquality Good
  rihartreefock
    quality verygood
  end
  xc
    hartreefock
  end
EndEngine
eor

```

Example: Analytic Frequencies: CN

Download CN_SecDeriv.run

```

#!/bin/sh

# Calculation of normal modes is requested by specifying in the AMS input:
# Properties
#   NormalModes Yes
# End
# ADF will compute the Hessian analytically if possible.
# If the Hessian cannot be computed analytically, numerical differentiation
# will automatically be used.

# A good quality is specified for the numerical Becke integration to be sure of
# reliable results. In general, it seems advisable to use high accuracy for
# heavy nuclei at the moment, whereas default integration accuracy is usually
# sufficient for light atoms. The precision of the fit may be improved with the

```

(continues on next page)

(continued from previous page)

```

# ZlmFit block keyword.

$AMSBIN/ams <<eor
System
  Symmetrize
  atoms
    N  -1.3  0.0  0.0
    C   0.0  0.0  0.0
  end
  charge -1
end

Task SinglePoint

Properties
  NormalModes Yes
End

Engine ADF
  title CN
  beckeGRID
  quality good
end
basis
  type DZ
  core None
  CreateOutput Yes
end
xc
  lda Xonly
end
EndEngine

eor

```

Example: Analytic Frequencies: CH4

Download CH4_SecDeriv.run

```

#!/bin/sh

# In this example we perform a geometry optimization immediately followed by
# calculation of frequencies. This is done by setting the task to
# GeometryOptimization and by requesting the normal modes in Properties block

# Note: when using this feature, one might improve the precision if one uses
# NumericalQuality Good. In order to save time this is not done in this example.

$AMSBIN/ams <<eor
System
  atoms
    C  0.0          0.0          0.0
    H  0.6264250420707439  0.6264250420707439  0.6264250420707439

```

(continues on next page)

(continued from previous page)

```

      H  0.6264250420707439 -0.6264250420707439 -0.6264250420707439
      H -0.6264250420707439  0.6264250420707439 -0.6264250420707439
      H -0.6264250420707439 -0.6264250420707439  0.6264250420707439
    end
  end

Task GeometryOptimization

GeometryOptimization
  Convergence
    Gradients 1E-4
  End
End

Properties
  NormalModes Yes
End

Engine ADF
  basis
    type TZP
    core None
  end
EndEngine
eor

```

Example: Analytic Frequencies: HI

Download HI_SecDer_ZORA.run

```

#!/bin/sh

# Analytical frequencies of HI using the scalar ZORA relativistic approximation.
# A good NumericalQuality is used.

$AMSBIN/ams <<eor
System
  atoms
    I 0.0 0.0 0.0
    H 0.0 0.0 1.6090
  end
end

Task SinglePoint

Properties
  NormalModes Yes
End

Engine ADF
  title HI scalar, ZORA,
  basis
    core None

```

(continues on next page)

(continued from previous page)

```

    type DZ
    CreateOutput Yes
end
numericalquality good
relativity
    level scalar
    formalism ZORA
end
symmetry NOSYM
xc
    lda Xonly
end
EndEngine
eor

```

Example: Mobile Block Hessian (MBH): Ethanol

Download MBH_Ethanol.run

```

#!/bin/sh

# A frequency calculation is performed using the mobile block Hessian (MBH)
# method. The coordinates in the ATOMS section can be the partially optimized
# coordinates (or the fully optimized coordinates would work too).

AMS_JOBNAME=Ethanol_MBH $AMSBIN/ams <<eor
System
  atoms
    C      -0.029587   -0.006554    0.008124
    H      -0.087498   -0.025163    1.109913
    H       1.027473   -0.056237   -0.302751
    H      -0.565305   -0.891154   -0.376242
    C      -0.694908    1.238909   -0.501807
    H      -0.670258    1.265092   -1.608847
    O      -2.069894    1.175059   -0.017251
    H      -0.182335    2.138977   -0.109315
    H      -2.586972    1.972802   -0.317216
  end
end

Task SinglePoint
Properties
  NormalModes True
End
NormalModes
  Displacements Block
  BlockDisplacements
    BlockAtoms 1 2 3 4
  End
End

Engine ADF

```

(continues on next page)

(continued from previous page)

```

title ethanol: second derivatives with MBH approach. CH3 is treated as a rigid block
numericalquality good
scf
  converge 1.0e-8
end
symmetry nosym
EndEngine
eor

# For comparison in this example also a calculation is performed without any
# restrictions.

AMS_JOBNAME=Ethanol_full $AMSBIN/ams <<eor
System
  atoms
    C      -0.029587   -0.006554    0.008124
    H      -0.087498   -0.025163    1.109913
    H       1.027473   -0.056237   -0.302751
    H      -0.565305   -0.891154   -0.376242
    C      -0.694908    1.238909   -0.501807
    H      -0.670258    1.265092   -1.608847
    O      -2.069894    1.175059   -0.017251
    H      -0.182335    2.138977   -0.109315
    H      -2.586972    1.972802   -0.317216
  end
end

Task SinglePoint
Properties
  NormalModes True
End

Engine ADF
  title ethanol: complete vibrational spectrum, compare with MBH above
  numericalquality good
EndEngine
eor

```

Example: Mobile Block Hessian: CH4

Download MBH_CH4.run

```

#!/bin/sh

# A frequency calculation is performed using the mobile block Hessian
# (MBH)method. The coordinates in the ATOMS section should be the partially
# optimized coordinates (or the fully optimized coordinates would work too).

# Such geometry optimization will not be discussed here any further. The next
# input for ADF shows how to perform a frequency calculation with MBH.

$AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    C      0.000000    0.000000    0.000000
    H      0.634671    0.634671    0.634671
    H     -0.634671   -0.634671    0.634671
    H     -0.634671    0.634671   -0.634671
    H      0.634671   -0.634671   -0.634671
  end
end

```

```

Task SinglePoint
Properties
  NormalModes True
End

```

```

NormalModes
  Displacements Block
  BlockDisplacements
    BlockAtoms 1 2 3 4
    RadialDisplacement 0.001
  End
End

```

```

Engine ADF
  title Methane
  basis
    core None
    type DZ
    CreateOutput Yes
  end
  numericalquality verygood
  symmetry nosym
EndEngine
eor

```

```

# The quality of the frequencies/modes depends largely on the block choice. Best
# results are obtained when grouping atoms in a block if those atoms are known
# to form rather rigid structures. For instance, grouping the 11 atoms of
# benzene side group into a block, will usually result in representative
# frequencies. In this example the block choice is only illustrative for the
# methodology.

```

Example: Raman: NH3

Download Freq_NH3_RAMAN.run

```

#!/bin/sh

# Summary:
# - Analytical frequencies with subsequent calculation of Raman intensities in a
#   range
# - Numerical frequencies including all Raman intensities

# == Raman Intensities for Selected Frequencies ==

```

(continues on next page)

(continued from previous page)

```
# The VibrationalAnalysis task (type ModeScanning) can be used to calculate Raman
# intensities for a range of frequencies only.
# The Raman intensities are calculated by numerical differentiation of the
# polarizability tensor. Only frequencies frequencies withing the interval
# that are known to be Raman-active will be included.
```

```
AMS_JOBNAME=NH3 $AMSBIN/ams <<eor
```

```
System
  symmetrize
  atoms
    N      0.0000    0.0000    0.0000
    H      0.4729    0.8190    0.3821
    H     -0.9457    0.0000    0.3821
    H      0.4729   -0.8190    0.3821
  end
end
Task SinglePoint
Properties
  NormalModes True
End
thermo
  temperatures 300:400:10
end
Engine ADF
  title NH3 frequencies
  beckegrid
  quality good
end
basis
  core Small
  type TZP
end
EndEngine
eor
```

```
AMS_JOBNAME=RamanRange1 $AMSBIN/ams <<eor
```

```
LoadSystem
  File NH3.results/ams.rkf
End
Task VibrationalAnalysis
VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile NH3.results/adf.rkf
    ModeSelect
      FreqRange 0.0 2000.0
    End
  End
End
Properties
  Raman True
End
thermo
  temperatures 300:400:10
end
```

(continues on next page)

(continued from previous page)

```

EngineRestart NH3.results/adf.rkf

Engine ADF
  title NH3 Raman intensities in the range 0-2000 cm-1
  beckegrid
    quality good
  end
  basis
    core Small
    type TZP
  end
  responseformalism response
EndEngine
eor

AMS_JOBNAME=RamanRange2 $AMSBIN/ams <<eor
LoadSystem
  File NH3.results/ams.rkf
End

Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile NH3.results/adf.rkf
    ModeSelect
      FreqRange 2000.0 5000.0
    End
  End
End

Properties
  Raman True
End

EngineRestart NH3.results/adf.rkf

Engine ADF
  title NH3 Raman intensities in the range 2000-5000 cm-1
  beckegrid
    quality good
  end
  basis
    core Small
    type TZP
  end
  responseformalism response
EndEngine
eor

# == Raman Intensities for All Frequencies ==

# Raman scattering intensities and depolarization ratios for all molecular
# vibrations at a certain laser frequency can be calculated in a single run.

```

(continues on next page)

(continued from previous page)

```
# In this example the static Raman scattering is calculated (omega = 0). This
# type of calculation is very similar to an IR intensity calculation. In fact,
# all IR output is automatically generated as well. At all distorted geometries
# the dipole polarizability tensor is calculated. This is very time-consuming
# and is only feasible for small molecules.
```

```
AMS_JOBNAME=Raman $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    N      0.0000    0.0000    0.0000
    H      0.4729    0.8190    0.3821
    H     -0.9457    0.0000    0.3821
    H      0.4729   -0.8190    0.3821
  end
end
Task SinglePoint
Properties
  NormalModes True
  Raman True
End
thermo
  temperatures 300:400:10
end

Engine ADF
  title NH3 frequencies with Raman intensities
  beckegrid
    quality good
  end
  basis
    core Small
    type TZP
  end
  response
    raman
  end
EndEngine
eor
```

Example: Raman: HI

Download HI_Raman.run

```
#!/bin/sh

# Example shows a calculation of the Raman spectrum of HI
# with a scalar relativistic ZORA and a spin-orbit coupled ZORA Hamiltonian.
# Note that used basis set is too small to get accurate results.

# == scalar relativistic ZORA ==

# 3 calculations are performed.
# First a scalar relativistic geometry optimization is performed
```

(continues on next page)

(continued from previous page)

```

# and analytical frequencies are calculated. This calculation produces a restart file,
# which is used in the second and third calculation as input for the Raman calculation.
# The FreqRange keyword is used to calculate Raman intensities for a range of
↪frequencies only.
# In the second calculation RESPONSE is used and in the third calculation AORESPONSE.

AMS_JOBNAME=SR $AMSBIN/ams <<eor
System
  atoms
    H  0.0000 0.0000 0.0000
    I  0.0000 0.0000 1.6092
  end
end

Task GeometryOptimization
Properties
  NormalModes Yes
End

Engine ADF
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level scalar
    formalism ZORA
  end
EndEngine
eor

AMS_JOBNAME=SR_response $AMSBIN/ams <<eor
Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile SR.results/adf.rkf
    ModeSelect
      FreqRange 0.0 4000.0
    End
  End
End

Properties
  Raman True
End
Raman
  IncidentFrequency 2.0 [eV]
End

LoadSystem
  File SR.results/ams.rkf
End

EngineRestart SR.results/adf.rkf

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  responseformalism response
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level scalar
    formalism ZORA
  end
EndEngine
eor

AMS_JOBNAME=SR_aoresponse $AMSBIN/ams <<eor
Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile SR.results/adf.rkf
    ModeSelect
      FreqRange 0.0 4000.0
    End
  End
End

Properties
  Raman True
End
Raman
  IncidentFrequency 2.0 [eV]
End

LoadSystem
  File SR.results/ams.rkf
End

EngineRestart SR.results/adf.rkf

Engine ADF
  responseformalism aoresponse
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level scalar
    formalism ZORA
  end
EndEngine
eor

# == Relativistic Spinorbit ZORA ==

```

(continues on next page)

(continued from previous page)

```

# 4 calculations are performed.
# First a spin-orbit coupled relativistic geometry optimization is performed.
# This calculation produces a restart file which is used in the second calculation
# to calculate numerical frequencies. This calculation produces a restart file
# which is used in the third and fourth calculation as input for the Raman
↳ calculation.
# The FreqRange keyword is used to calculate Raman intensities for a range of
↳ frequencies only.
# In the third calculation RESPONSE is used and in the fourth calculation AORESPONSE.
# Symmetry NOSYM is needed for AORESPONSE icw spin-orbit coupling.

AMS_JOBNAME=SO $AMSBIN/ams <<eor
System
  atoms
    H  0.0000 0.0000 0.0000
    I  0.0000 0.0000 1.6092
  end
end

Task GeometryOptimization
Properties
  NormalModes Yes
End

Engine ADF
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level spin-orbit
    formalism ZORA
  end
EndEngine
eor

AMS_JOBNAME=SO_response $AMSBIN/ams <<eor
Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile SO.results/adf.rkf
    ModeSelect
      FreqRange 0.0 4000.0
    End
  End
End

Properties
  Raman True
End
Raman
  IncidentFrequency 2.0 [eV]
End

```

(continues on next page)

(continued from previous page)

```

LoadSystem
  File SO.results/ams.rkf
End

EngineRestart SO.results/adf.rkf

Engine ADF
  responseformalism response
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level spin-orbit
    formalism ZORA
  end
EndEngine
eor

AMS_JOBNAME=SO_aoresponse $AMSBIN/ams <<eor
Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile SO.results/adf.rkf
    ModeSelect
      FreqRange 0.0 4000.0
    End
  End
End

Properties
  Raman True
End
Raman
  IncidentFrequency 2.0 [eV]
End

LoadSystem
  File SO.results/ams.rkf
End

EngineRestart SO.results/adf.rkf

Engine ADF
  responseformalism aoresponse
  basis
    core None
    type DZ
  end
  noprint SFO
  relativity
    level spin-orbit
    formalism ZORA
  end
end

```

(continues on next page)

(continued from previous page)

```

    symmetry nosym
EndEngine
eor

```

Example: Resonance Raman, excited state finite lifetime: HFDownload `HF_ResonanceRaman.run`

```

#!/bin/sh

# Example shows a calculation of the Resonance Raman spectrum (RRS) of HF. In
# this example the RRS is calculated from the geometrical derivatives of the
# frequency-dependent polarizability, including a finite lifetime.

# In the AMS input one then needs to request 'Raman' in the 'Properties' block
# and specify 'IncidentFrequency' and 'LifeTime' in the Raman Block

# Note that used basis set is too small to get accurate results.

$AMSBIN/ams <<eor
System
  atoms
    H 0.0000 0.0000 0.0000
    F 0.0000 0.0000 0.9170
  end
end

Task SinglePoint
Properties
  Raman True
End
NormalModes
  Displacements Symmetric
  SymmetricDisplacements
  Type InfraredAndRaman
  End
End
Raman
  IncidentFrequency 0.52362 [Hartree]
  LifeTime 0.0034
  FreqRange 0.0 5000.0
End

Engine ADF
  title HF ao-raman
  basis
    Type DZP
    Core None
    CreateOutput Yes
  end
  noprint SFO
  numericalquality Good
  Relativity
    Level None
  End

```

(continues on next page)

(continued from previous page)

```
EndEngine
eor
```

Example: Vibrational Raman optical activity (VROA): H2O2

Download VROA.run

```
#!/bin/sh

# Example showing a calculation of normal Vibrational Raman Optical Activity (VROA).

# For accuracy reasons 'NumericalQuality Good' and EXACTDENSITY are used.

$AMSBIN/ams <<eor
System
  atoms
    O      -0.750254  -0.034490   0.015133
    O      0.750254   0.034490   0.015133
    H     -0.943532   0.744006   0.580040
    H      0.943532  -0.744006   0.580040
  end
end

Task SinglePoint

Properties
  VROA True
End

Raman
  IncidentFrequency 2.41 [eV]
End

NumericalDifferentiation
  Parallel nGroups=1
End

Engine ADF
  title VROA TEST H2O2

  numericalquality Good

  exactdensity

  basis
    type TZP
    core None
  end

  xc
    gga BLYP
  end
EndEngine
eor
```

(continues on next page)

(continued from previous page)

```
# Note that used basis set is too small to get accurate results. Better is to
# use larger basis sets for such a small molecule, like one of the even
# tempered basis sets (for example Type ET/ET-QZ3P-1DIFFUSE), or use augmented
# basis sets (for example Type AUG/ATZ2P).
```

Example: Resonance VROA: H2O2

Download VROA_RESO.run

```
#!/bin/sh

# Example shows a calculation of resonance vibrational Raman optical activity
# (resonance VROA).

# For accuracy reasons 'NumericalQuality Good' and EXACTDENSITY are used.

$AMSBIN/ams <<eor
System
  atoms
    O      -0.750254  -0.034490   0.015133
    O      0.750254   0.034490   0.015133
    H     -0.943532   0.744006   0.580040
    H      0.943532  -0.744006   0.580040
  End
End

UseSymmetry NO

Task SinglePoint

Properties
  VROA True
End

Raman
  IncidentFrequency 5.15462 [eV]
  Lifetime 0.0037
End

Engine ADF
  Title VROA-RESO TEST H2O2

  NumericalQuality Good

  ExactDensity

  Basis
    Core None
    Type TZP
  End

  SCF
    Converge 1.0e-10
```

(continues on next page)

(continued from previous page)

```

End

XC
  GGA BLYP
End
EndEngine

eor

# Note that used basis set is too small to get accurate results. Better is to
# use larger basis sets for such a small molecule, like one of the even
# tempered basis sets (for example Type ET/ET-QZ3P-1DIFFUSE), or use augmented
# basis sets (for example Type AUG/ATZ2P).

```

Example: Raman and VROA for approximate modes

Download DFTB_modes_ADF_Raman_VROA.run

```

#!/bin/sh

# Example to calculate vibrational modes with an approximate method,
# in this case DFTB (using GFN1-xTB)
# Next scan selected modes with ADF to calculate (resonance) Raman and VROA.

AMS_JOBNAME=dftb $AMSBIN/ams <<eor
System
  atoms
    O      -0.750254  -0.034490   0.015133
    O      0.750254   0.034490   0.015133
    H     -0.943532   0.744006   0.580040
    H      0.943532  -0.744006   0.580040
  end
end
Task SinglePoint
Properties
  NormalModes True
End
Engine DFTB
  Model GFN1-xTB
EndEngine
eor

AMS_JOBNAME=offresonance $AMSBIN/ams <<eor
LoadSystem
  file dftb.results/ams.rkf
End
Task VibrationalAnalysis
VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile dftb.results/dftb.rkf
    ModeSelect
      FreqRange 0.0 1000.0
    End
  End
End

```

(continues on next page)

(continued from previous page)

```
End
Properties
  Raman True
  VROA True
End
Raman
  IncidentFrequency 2.41 [eV]
End
Engine ADF
  basis
    type TZP
    core None
  end
  xc
    gga BLYP
  end
EndEngine
eor

AMS_JOBNAME=resonance $AMSBIN/ams <<eor
LoadSystem
  file dftb.results/ams.rkf
End
Task VibrationalAnalysis
VibrationalAnalysis
  Type ModeScanning
  NormalModes
    ModeFile dftb.results/dftb.rkf
    ModeSelect
      FreqRange 0.0 1000.0
    End
  End
End
Properties
  Raman True
  VROA True
End
Raman
  IncidentFrequency 5.15462 [eV]
  Lifetime 0.0037
End
Engine ADF
  basis
    type TZP
    core None
  end
  xc
    gga BLYP
  end
EndEngine
eor
```


Example: Vibrational Circular Dichroism (VCD): NHDT

Download VCD_COG_NHDT.run

```

#!/bin/sh

# Analytical frequencies with subsequent calculation of vibrational circular
# dichroism (VCD)

# Recommended is use to use high accuracy for the geometry optimization which
# one needs to do before the frequency calculation. This simple example is an
# NHDT molecule, which is NH3 where one hydrogen atom is replaced with deuterium
# and another with tritium.

$AMSBIN/ams <<eor
System
  atoms
    N      0.000000    0.000000    0.010272
    H     -0.471582   -0.816803    0.407861
    H      0.943163    0.000000    0.407861 mass=2.014101778
    H     -0.471582    0.816803    0.407861 mass=3.01604927
  end
end

Task SinglePoint

Properties
  VCD Yes
End

Engine ADF
  basis
    core None
    type TZP
  end
  xc
    gga BP86
  end
  beckegrid
    quality verygood
  end
EndEngine

eor

```

Example: unrestricted VCD: CHFCIBr

Download VCD_CHFCIBr_DZP.run

```

#!/bin/sh

# Analytical frequencies with subsequent calculation of unrestricted
# vibrational circular dichroism (VCD)

# This test is using a small basis set; use of a large basis set for

```

(continues on next page)

(continued from previous page)

```

# chemical application is recommended

$AMSBIN/ams <<eor

Task SinglePoint

System
  Atoms
    C      -1.194957    0.619864    0.018398
    Br     0.712857    0.534545    0.755317
    Cl     -0.705615   -0.120328   -1.557332
    F      -1.636918    1.848290   -0.093005
    H      -1.832068   -0.042181    0.608806
  End
  Charge 1
End

Properties
  VCD Yes
End

Engine ADF
  Basis
    Type DZP
    Core None
  End
  XC
    GGA BLYP
  end
  Unrestricted Yes
  SpinPolarization 1
  LinearScaling
    Overlap_Int 98
  End
EndEngine
eor

```

15.4.2 Excitation energies: UV/Vis spectra, X-ray absorption, CD, MCD

Example: Excitation energies and polarizability: Au₂

Download Au2_Resp.run

```

#!/bin/sh

# A calculation of response properties of the Au2 dimer, with ZORA relativistic
# corrections

# In the response module infinite symmetries cannot be handled (see the User's
# Guide), so we specify a lower subgroup in the input file, here D(8h).

# In this sample run the LB94 potential is used. The implementation implies that
# the XC potential is evaluated from the exact charge density, rather than the

```

(continues on next page)

(continued from previous page)

```

# cheaper and faster fitted density (as is the case for other XC functionals).
# This means that the computation times are longer. In a small molecule like Au2
# this hardly shows, but in larger molecules the differences may be more
# significant. Note that the LB94 is a model potential, thus the calculated bond
# energy has not so much meaning. If the BASIS key is specified and the model
# potential LB94 is used, in the create run of the atoms the BP86 functional is used.

# Excitation energies are computed, in principle the lowest 10 in each irrep of
# the symmetry (see the User's Guide for more details).

$AMSBIN/ams <<eor
System
  atoms
    Au   0.0 0.0 1.236
    Au   0.0 0.0 -1.236
  end
end

Task SinglePoint

Engine ADF
  title Au2, Response Properties
  excitations
    lowest 10
    tolerance 1e-10
  end
  basis
    PerAtomType Symbol=Au File=ZORA/DZ/Au.4d
  end
  response
    allcomponents
  end
  symmetry D(8h)
  xc
    gga LB94
  end
EndEngine

eor

```

Example: Excitation energies open shell molecule: CN

Download CN_unr_exci.run

```

#!/bin/sh

# Calculation of the excitation energies of the open shell molecule CN

# In this example, the lowest 20 excitation energies of CN are calculated in a
# spin-unrestricted TDDFT calculation. In the MO -> MO transitions part for the
# excitations of the output file, the spin of each molecular orbitals are also
# specified to help assign the spin state of the excited states. The transitions
# are always from alpha spin-orbital to alpha spin-orbital or from beta spin-
# orbital to beta spin-orbital.

```

(continues on next page)

(continued from previous page)

```
AMS_JOBNAME=exci $AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

```
  C  0.0000  0.0000  0.0000
```

```
  N  0.0000  0.0000  1.1718
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title excitation energies of CN
```

```
  excitations
```

```
    lowest 20
```

```
    nto
```

```
    sfoanalysis
```

```
end
```

```
basis
```

```
  type AUG/ADZP
```

```
end
```

```
spinpolarization 1
```

```
unrestricted
```

```
EndEngine
```

```
eor
```

```
# Next the same example for CN is given with the Tamm-Dancoff approximation  
# (TDA) approximation (including TDA in the input). Due to this approximation  
# the calculated excitation energies will not be exactly the same as in the  
# first example.
```

```
AMS_JOBNAME=exci_tda $AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

```
  C  0.0000  0.0000  0.0000
```

```
  N  0.0000  0.0000  1.1718
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title excitation energies (TDA) of CN
```

```
  excitations
```

```
    lowest 20
```

```
    nto
```

```
    sfoanalysis
```

```
end
```

```
basis
```

```
  type AUG/ADZP
```

```
end
```

```
spinpolarization 1
```

```
tda
```

```
unrestricted
```

```
EndEngine
```

(continues on next page)

(continued from previous page)

```

eor

# Note that the basis set is still far from complete, the ATZ2P is better. For
# accuracy reasons one may need to increase the numerical quality. If one uses
# the augmented basis sets for accuracy reasons one could use NumericalQuality
# Good.

# The third calculation is the calculation of spin-flip excitation energies for
# CN. Again these energies will not be exactly the same as in the first example.
# For open-shell molecules, spin-flip transition can result in transition to the
# ground state with a different S_z value, while the symmetry of the transition
# density is A1 (Sigma+ for linear molecules). The excitation energy of this
# transition should be zero and this can be used to test the reliability of
# spin-flip TDDFT. Indeed the calculation of the spin-flip excitation energies
# of CN shows one value which is close to zero and has a transition density of
# Sigma+ symmetry.

AMS_JOBNAME=exci_tda_spinflip $AMSBIN/ams <<eor
System
  atoms
    C .0000 .0000 .0000
    N .0000 .0000 1.1718
  end
end

Task SinglePoint

Engine ADF
  title spin-flip excitation energies (TDA) of CN
  excitations
    lowest 20
    nto
    sfoanalysis
  end
  basis
    type AUG/ADZP
  end
  sftddft
  spinpolarization 1
  tda
  unrestricted
EndEngine

eor

```

Example: Spin-flip excitation energies: SiH2

Download SiH2_spinflip.run

```
#!/bin/sh

# Calculation of the spin-flip excitation energies of the open shell molecule SiH2

AMS_JOBNAME=SpinFlip $AMSBIN/ams <<eor
System
  atoms
    Si 0.0 0.0 0.0
    H 0.0 -1.095664024353027 -1.045576810836792
    H 0.0 1.095664024353027 -1.045576810836792
  end
end

Task SinglePoint

Engine ADF
  title spin-flip excitation energies of SiH2
  excitations
    lowest 20
  end
  forcealda
  basis
    type TZ2P
  end
  sftddft
  spinpolarization 2
  tda
  unrestricted
EndEngine
eor

# In this example, the lowest 20 spin-flip excitation energies of SiH2 are
# calculated in a spin-unrestricted TDDFT calculation.

# In this case an excited state is used as reference, which means that there can
# also be a negative excitation energy, which is indeed the case. The electron
# configuration used in the SCF is (a1)^1 (b1)^1, with Sz=1, thus a ^3B_1
# state, which is an excited state. The ^1A_1 state with electron configuration
# (a1)^2 is lower in energy, and is the ground state.

# There is also an excited 1A1 state with electron configuration (b1)^2. The
# transition from the ground 1A1 state to the excited 1A1 state is an excitation
# from the electron configuration (a1)^2 to (b1)^2. This transition is actually
# a double excitation, which means that some double excitations can be reached
# using spin-flip TDDFT with carefully selected reference states.

# In the MO -> MO transitions part for the excitations of the output file, the
# spin of each molecular orbitals are also specified to help assign the spin
# state of the excited states. Note that in these spin-flip calculations the
# transitions are always from alpha spin-orbital to beta or from beta spin-
# orbital to alpha spin-orbital.

# For open-shell molecules, spin-flip transition can result in transition to the
```

(continues on next page)

(continued from previous page)

```

# ground state with a different Sz value, while the symmetry of the transition
# density is A1. The excitation energy of this transition should be zero and
# this can be used to test the reliability of spin-flip TDDFT. Indeed the
# calculation of the spin-flip excitation energies of SiH2 shows one value which
# is close to zero and has a transition density of A1 symmetry.

# The 1A1 state with electron configuration (a1)^2 can also be used in the
# calculation of the excitation energies. This is a closed shell configuration,
# in which case we do not need the spin-flip method.

AMS_JOBNAME=Excitation $AMSBIN/ams <<eor
System
  atoms
    Si 0.0 0.0 0.0
    H 0.0 -1.095664024353027 -1.045576810836792
    H 0.0 1.095664024353027 -1.045576810836792
  end
end

Task SinglePoint

Engine ADF
  title excitation energies of SiH2
  excitations
    lowest 20
  end
  basis
    type TZ2P
  end
EndEngine

eor

# The transition from the ground ^1A_1 state to the excited ^1A_1 state, which
# is an excitation from the electron configuration (a1)^2 to (b1)^2, can not be
# reached in this calculation, since it has mainly double excitation character.
# Of course, other excited ^1A_1 states can be reached.

```

Example: TDHF excitation energies: N2

Download N2_TDHF.run

```

#!/bin/sh

# Calculation of the excitation energies of N2 using time-dependent Hartree-Fock
# (TDHF). It also shows the possibility to use the Tamm-Dancoff approximation
# (TDA). This examples consists of 4 calculations:

# TDHF non-relativistic and spin-orbit coupled
# TDA non-relativistic and spin-orbit coupled (CIS)

# == TDHF non-relativistic ==

```

(continues on next page)

(continued from previous page)

```
AMS_JOBNAME=TDHF_NR $AMSBIN/ams <<eor
```

```
System
  symmetrize
  atoms
    N 0 0 0
    N 0 0 1.0977
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
  beckegrid
    quality Good
  end
  excitations
    lowest 5
  end
  basis
    core None
    type DZ
  end
  xc
    hartreefock
  end
  Relativity
    Level None
  End
EndEngine
eor
```

```
# == TDHF spin-orbit coupled ==
```

```
AMS_JOBNAME=TDHF_SO $AMSBIN/ams <<eor
```

```
System
  symmetrize
  atoms
    N 0 0 0
    N 0 0 1.0977
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
  beckegrid
    quality Good
  end
  excitations
    lowest 20
  end
  basis
```

(continues on next page)

(continued from previous page)

```

    core None
    type DZ
end
relativity
    level spin-orbit
    formalism ZORA
end
xc
    hartreefock
end
EndEngine
eor

# == TDA non-relativistic ==

AMS_JOBNAME=TDA_NR $AMSBIN/ams <<eor
System
    symmetrize
    atoms
        N 0 0 0
        N 0 0 1.0977
    end
end

Task SinglePoint

Engine ADF
    beckegrid
        quality Good
    end
    excitations
        lowest 5
    end
    basis
        core None
        type DZ
    end
    tda
    xc
        hartreefock
    end
    Relativity
        Level None
    End
EndEngine
eor

# == TDA spin-orbit coupled ==

AMS_JOBNAME=TDA_SO $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

symmetrize
atoms
  N 0 0 0
  N 0 0 1.0977
end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality Good
  end
  excitations
    lowest 20
  end
  basis
    core None
    type DZ
  end
  relativity
    level spin-orbit
    formalism ZORA
  end
  tda
  xc
    hartreefock
  end
EndEngine
eor

```

Example: excitation energies CAM-B3LYP: Pyridine

Download Pyridine_CAM-B3LYP.run

```

#!/bin/sh

# Calculation of the excitation energies of Pyridine using the range-separated
# functional CAM-B3LYP. To use this range-separated functional CAM-B3LYP LibXC is
# needed.
# Note that CAM-B3LYP is not the same as CAMY-B3LYP.
# For the LibXC range separated functionals, like CAM-B3LYP, the kernel consists
# of range separated ALDA plus the kernel of the range separated exact exchange part.

$AMSBIN/ams <<eor
System
atoms
  N      0.00000000      0.00000000      1.07112000
  C      0.00000000      0.00000000      3.88763000
  C      0.00000000     -1.14432000      1.77593000
  C      0.00000000      1.14432000      1.77593000
  C      0.00000000      1.19947000      3.17299000
  C      0.00000000     -1.19947000      3.17299000
  H      0.00000000     -2.16297000      3.68508000

```

(continues on next page)

(continued from previous page)

```

      H      0.00000000      -2.06734000      1.18970000
      H      0.00000000      0.00000000      4.97897000
      H      0.00000000      2.16297000      3.68508000
      H      0.00000000      2.06734000      1.18970000
    end
  end

Task SinglePoint

Engine ADF
  excitations
    onlysing
  end
  basis
    type DZP
    core None
  end
  xc
    libxc CAM-B3LYP
  end
EndEngine

eor

```

Example: CAMY-B3LYP excitation energies: H2O

Download CAMY-B3LYP_TDDFT_H2O.run

```

#!/bin/sh

# Example for the range separated functional CAMY-B3LYP for the calculation of
# excitation energies of water. Note that CAMY-B3LYP is not the same as CAM-
# B3LYP.

$AMSBIN/ams <<eor
  Task SinglePoint
  System
    ATOMS
      O      0.000000      0.000000      0.000000
      H      0.000000      0.500000     -0.6
      H      0.000000     -0.500000     -0.6
    END
  END
  Engine ADF
    TITLE  H2O excitations with CAMY-B3LYP functional
    NOPRINT BAS FIT FUNCTIONS SFO
    XC
      HYBRID CAMY-B3LYP
      xcfun
      RANGESEP GAMMA=0.34
    END
    BeckeGrid
      Quality good
  end
EndEngine

```

(continues on next page)

(continued from previous page)

```

End
EXCITATIONS
  LOWEST 10
  ONLYSING
END
basis
  Type DZP
END
EndEngine
eor

```

Example: Full XC kernel in excitation energy calculation: H2O+

Download XCFUN_FULLKERNEL_TDDFT_H2O.run

```

#!/bin/sh

# Example of using the full XC kernel in the calculation of excitation energies,
# in this case for the BP86 functional. Note that SYMMETRY NOSYM is required and
# XCFUN should be added to the XC block key. In this case spin-flip excitations
# are calculated.

$AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000    0.000631
    H      0.000000    0.771769   -0.605006
    H      0.000000   -0.771769   -0.605006
  end
  charge 1
end

Task SinglePoint

Engine ADF
  title H2O+ spin-flip TDDFT with BP and the non-ALDA kernel

  basis
    type DZP
  end

  xc
    gga Becke Perdew
    xcfun
  end

  beckegrid
    quality good
  end

  excitations
    fullkernel
    lowest 5
  end

```

(continues on next page)

(continued from previous page)

```

sftddft
tda

unrestricted
spinpolarization 1

symmetry NOSYM

noprnt BAS FIT FUNCTIONS SFO
EndEngine

eor

```

Example: Use of xcfun in excitation energy calculations: H2O

Download XCFUN_TDDFT_H2O.run

```

#!/bin/sh

# Example for the use of the xcfun library for a calculation of excitation
# energies, in this case for the BP86 functional. Note that for closed shell
# molecules only singlet-singlet can be calculated with xcfun, therefore the
# key 'onlysing' in the 'excitations' block the is used.

$AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000    0.000631
    H      0.000000    0.771769   -0.605006
    H      0.000000   -0.771769   -0.605006
  end
end

Task SinglePoint

Engine ADF
  title H2O TDDFT with XCFUN
  beckegrid
    quality good
  end
  excitations
    lowest 5
    onlysing
  end
  basis
    type DZP
  end
  noprnt BAS FIT FUNCTIONS SFO
  xc
    gga Becke Perdew
    xcfun
  end
EndEngine

eor

```

Example: Core excitation energies: TiCl4

Download TiCl4_CoreExci.run

```

#!/bin/sh

# Calculation of the 2p Ti and 2p Cl core excitation energies of TiCl4

# The state selective method (key SELECTEXCITATION) can be used to calculate
# core excitation energies. The use of the key SELECTEXCITATION is similar as
# the use of the key MODIFYEXCITATION. However, the key SELECTEXCITATION can not
# be used in combination with the key MODIFYEXCITATION. In the state selective
# method (key SELECTEXCITATION) the one-electron excited state configuration
# space remains complete, whereas it is reduced in case the scheme with the
# MODIFYEXCITATION key.

AMS_JOBNAME=SOT $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Ti 0.      0.      0.
    Cl  2.36754  2.36754  2.36754
    Cl -2.36754 -2.36754  2.36754
    Cl  2.36754 -2.36754 -2.36754
    Cl -2.36754  2.36754 -2.36754
  end
end

Task SinglePoint

Engine ADF
  title TiCl4 TD-DFT spinorbit relativistic 2p Cl core excitations single orbital_
  ↪transitions
  beckegrid
    quality good
  end
  eprint
    eigval 1000 1000
  end
  excitations
    allowed
    kfwrite 0
    lowest 40
    singleorbtrans
  end
  basis
    core None
    type DZ
    CreateOutput Yes
  end
  relativity
    level spin-orbit
    formalism ZORA
  end
  selectexcitation
    useoccrange -20.0 -16.0
    usescaledzora
  end

```

(continues on next page)

(continued from previous page)

```

symmetry T(D)
xc
  gga LB94
end
EndEngine

eor

# == An example with the key MODIFYEXCITATION ==

# In this example, the 12 lowest singlet-singlet excitation energies of T2
# symmetry are calculated, the dipole allowed excitations. This can also be
# achieved using the ALLOWED subkey in the key Excitation.

# In this example only excitations from the 2t2 -orbital are included (see the
# key MODIFYEXCITATION), an almost pure 2p core orbital of titanium. The orbital
# energies of the uninteresting other occupied orbitals are artificially changed
# to a large negative value (-1d6 hartree).

AMS_JOBNAME=T2 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Ti 0.      0.      0.
    Cl  2.36754 2.36754 2.36754
    Cl -2.36754 -2.36754 2.36754
    Cl  2.36754 -2.36754 -2.36754
    Cl -2.36754 2.36754 -2.36754
  end
end

Task SinglePoint

Engine ADF
  title TiCl4 TD-DFT scalar relativistic 2p Ti core excitations
  beckegrid
    quality good
  end
  eprint
    eigval 1000 1000
  end
  excitations
    davidson
      T2 12
    end
    onlysing
  end
  modifyexcitation
    useoccupied
      T2 2
    end
    usescaledzora
  end
  basis
    core None
    type DZ
    CreateOutput Yes

```

(continues on next page)

(continued from previous page)

```

end
relativity
  level scalar
  formalism ZORA
end
symmetry T(D)
xc
  gga LB94
end
EndEngine

eor

# In this example the 2p Cl core excitation energies of TiCl4 are calculated.

# In this example only excitations from occupied orbitals are considered which
# have orbital energies between -8 and -6 hartree, namely the 5a1, 1e, 1t1,
# 4t2, and 5t2 orbitals, which are almost pure 2p core orbitals of chlorine.
# The orbital energies of the uninteresting other occupied orbitals are again
# artificially changed to a large negative value (-1d6 hartree).

AMS_JOBNAME=OccRange $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Ti 0.      0.      0.
    Cl  2.36754  2.36754  2.36754
    Cl -2.36754 -2.36754  2.36754
    Cl  2.36754 -2.36754 -2.36754
    Cl -2.36754  2.36754 -2.36754
  end
end

Task SinglePoint

Engine ADF
  title TiCl4 TD-DFT scalar relativistic 2p Cl core excitations
  beckegrid
  quality good
end
eprint
  eigval 1000 1000
end
excitations
  allowed
  lowest 50
end
modifyexcitation
  useoccrange -8.0 -6.0
  usescaledzora
end
basis
  core None
  type DZ
  CreateOutput Yes
end
relativity
  level scalar

```

(continues on next page)

(continued from previous page)

```

    formalism ZORA
end
symmetry T(D)
xc
    gga LB94
end
EndEngine

eor

# Another possibility is the use of the subkey OccVirtRange:
AMS_JOBNAME=OccVirt $AMSBIN/ams <<eor
System
    atoms [Bohr]
        Ti 0.      0.      0.
        Cl  2.36754  2.36754  2.36754
        Cl -2.36754 -2.36754  2.36754
        Cl  2.36754 -2.36754 -2.36754
        Cl -2.36754  2.36754 -2.36754
    end
end

Task SinglePoint

Engine ADF
    title TiCl4 TD-DFT scalar relativistic 2p Cl core excitations
    beckegrid
        quality good
    end
    eprint
        eigval 1000 1000
    end
    excitations
        allowed
        lowest 50
    end
    modifyexcitation
        useoccvirtrange 7.0 100.0
        usescaledzora
    end
    basis
        core None
        type DZ
        CreateOutput Yes
    end
    relativity
        level scalar
        formalism ZORA
    end
    symmetry T(D)
    xc
        gga LB94
    end
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor

AMS_JOBNAME=SelectT2 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Ti 0.      0.      0.
    Cl  2.36754 2.36754 2.36754
    Cl -2.36754 -2.36754 2.36754
    Cl  2.36754 -2.36754 -2.36754
    Cl -2.36754 2.36754 -2.36754
  end
end

Task SinglePoint

Engine ADF
  title TiCl4 TD-DFT scalar relativistic 2p Ti core excitations
  beckegrid
    quality good
  end
  eprint
    eigval 1000 1000
  end
  excitations
    davidson
      T2 12
    end
    onlysing
  end
  basis
    core None
    type DZ
    CreateOutput Yes
  end
  relativity
    level scalar
    formalism ZORA
  end
  selectexcitation
    useoccupied
      T2 2
    end
    usescaledzora
  end
  symmetry T(D)
  xc
    gga LB94
  end
EndEngine

eor

AMS_JOBNAME=SelectOccVir $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Ti 0.      0.      0.

```

(continues on next page)

(continued from previous page)

```

      C1      2.36754      2.36754      2.36754
      C1     -2.36754     -2.36754      2.36754
      C1      2.36754     -2.36754     -2.36754
      C1     -2.36754      2.36754     -2.36754
    end
  end
Task SinglePoint

Engine ADF
  title TiCl4 TD-DFT scalar relativistic 2p Cl core excitations
  beckegrid
    quality good
  end
  eprint
    eigval 1000 1000
  end
  excitations
    allowed
    lowest 25
  end
  basis
    core None
    type DZ
    CreateOutput Yes
  end
  relativity
    level scalar
    formalism ZORA
  end
  selectexcitation
    useoccvirtrange 7.0 100.0
    usescaledzora
  end
  symmetry T(D)
  xc
    gga LB94
  end
EndEngine

eor

```

Example: X-Ray Absorption and Emission Quadrupole Oscillator strengths at the Cl K-edge: TiCl4

Download TiCl4_XASXES.run

```

#!/bin/sh

# Calculation of the 1s Cl core excitation energies of TiCl4. Both X-Ray
# Emission (XES keyword) and X-Ray absorption (XAS keyword in EXCITATION key)
# are calculated. The individual (zeroth and higher order) oscillator strength
# components to the total oscillator strengths will be printed
# (ALLXESQUADRUPOLE, ALLXASQUADRUPOLE).

```

(continues on next page)

(continued from previous page)

```

# In order to calculate a 1s-orbital that is localized on one of the Cl atoms, a
# frozen core approach is used on the other Cl atoms, such that there is only
# one Cl 1s-orbital, which will remain localized in the molecule.

# In order to get information of the population analysis on all core orbitals, a
# large negative value was included as argument for the orbpoper subkey of the
# block key EPRINT. This orbital analysis shows that the 2 A1 orbital is indeed
# the 1s Cl orbital, see subkey corehole of block key XES, and subkey
# useoccupied of block key MODIFYEXCITATION.

AMS_JOBNAME=XASXES $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    Ti  0.0000  0.0000  0.0000
    Cl  0.0000  0.0000  2.2930
    Cl  1.0809 -1.8722 -0.7643  region=Cl.2p
    Cl -2.1618  0.0000 -0.7643  region=Cl.2p
    Cl  1.0809  1.8722 -0.7643  region=Cl.2p
  end
end

Task SinglePoint

Engine ADF
  title TiCl4 X-Ray Absorption and Emission Quadrupole Oscillator strengths at the Cl-
  ↪K-edge
  eprint
    eigval 1000 1000
    orbpoper -10000 100
  end
  excitations
    allxasquadrupole
    davidson
  end
  lowest 10
  onlysing
  xas
end
modifyexcitation
  useoccupied
    A1 2
  end
end
basis
  PerRegion Region=Cl.2p File=$AMSRESOURCES/ADF/TZP/Cl.2p
  core None
  type TZP
end
relativity
  level scalar
  formalism ZORA
end
scf
  iterations 200
end
symmetry C(3V)

```

(continues on next page)

(continued from previous page)

```

xc
  gga Becke Perdew
end
xes
  allxesquadrupole
  corehole A1 2
end
EndEngine

eor

# In the second example, to test gauge dependency, the molecule is shifted 100
# Angstrom in the z-direction.

AMS_JOBNAME=Gauge $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    Ti  0.0000  0.0000  100.0000
    Cl  0.0000  0.0000  102.2930
    Cl  1.0809 -1.8722  99.2357  region=Cl.2p
    Cl -2.1618  0.0000  99.2357  region=Cl.2p
    Cl  1.0809  1.8722  99.2357  region=Cl.2p
  end
end

Task SinglePoint

EngineRestart XASXES.results/adf.rkf

Engine ADF
  title TiCl4 X-Ray Absorption and Emission Quadrupole Oscillator strengths at the Cl-
  ↪K-edge shifted 100Ang in z-direction
  eprint
    eigval 1000 1000
    orbpoper -10000 100
  end
  excitations
    allxasquadrupole
    davidson
  end
  lowest 10
  onlysing
  xas
end
modifyexcitation
  useoccupied
  A1 2
end
end
basis
  PerRegion Region=Cl.2p File=$AMSRESOURCES/ADF/TZP/Cl.2p
  core None
  type TZP
end
relativity

```

(continues on next page)

(continued from previous page)

```

    level scalar
    formalism ZORA
end
scf
    iterations 200
end
symmetry C(3V)
xc
    gga Becke Perdew
end
xes
    allxesquadrupole
    corehole A1 2
end
EndEngine
eor

```

Example: (Core) Excitation energies including spin-orbit coupling: Ne

Download Ne_exciso.run

```

#!/bin/sh

# Calculation of the (core) excitation energies of Ne including spin-orbit
# coupling.

# The state selective method (key SELECTEXCITATION) can be used to reduce the
# computational costs of, for example, core excitation energies. In this scheme
# a guess vector for the orbital transition has to be provided. It should be
# used in combination with the davidson method to calculate excitation energies.
# An overlap criterion is used to follow the wanted eigenvector. This key can
# also be used in case of spin-orbit coupling. The use of the key
# SELECTEXCITATION is similar as the use of the key MODIFYEXCITATION. However,
# the key SELECTEXCITATION can not be used in combination with the key
# MODIFYEXCITATION. In the state selective method (key SELECTEXCITATION) the
# one-electron excited state configuration space remains complete, whereas it is
# reduced in case the scheme with the MODIFYEXCITATION key.

AMS_JOBNAME=Frag $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000
  end
end

Task SinglePoint

Engine ADF
  title Ne
  excitations
    lowest 8
  end

```

(continues on next page)

(continued from previous page)

```

basis
  type QZ4P
  CreateOutput Yes
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
symmetry d(8h)
xc
  model SAOP
end
EndEngine
eor

```

```

AMS_JOBNAME=Excitations $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000 adf.f=Frag
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title Ne spin-orbit
  excitations
    alsorestricted
    lowest 8
  end
  fragments
    Frag Frag.results/adf.rkf
  end
  numericalquality Good
  relativity
    level spin-orbit
    formalism ZORA
  end
  stcontrib
  symmetry d(8h)
  xc
    model SAOP
  end
EndEngine
eor

```

```

# The difference between the core excitation calculation and the standard
# excitation is the extra subkey MODIFYEXCITATION or SELECTEXCITATION in the
# core excitation calculation (in italic).

```

```

# ADF can not handle ATOM and linear symmetries in excitation calculations.
# Therefore a subsymmetry is used, in this case symmetry d(8h).

```

```

# A relatively large QZ4P basis set is used, which is still insufficient for

```

(continues on next page)

(continued from previous page)

```

# excitations to Rydberg-like orbitals, one needs more diffuse functions.

# The key STCONTRIB is used, which will give a composition of the spin-orbit
# coupled excitation in terms of singlet-singlet and singlet-triplet scalar
# relativistic excitations. In order to use the key STCONTRIB the scalar
# relativistic fragment should be the complete molecule.

# In this case the key MODIFYEXCITATION or SELECTEXCITATION takes care that only
# excitations from the occupied 1s-orbital (spinor) are included. In symmetry
# d(8H) the 1s-orbital (spinor) is of A1.g (E1/2.g) symmetry.

```

Download Ne_CoreExci.run

```

#!/bin/sh

AMS_JOBNAME=Fragmod $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000
  end
end

Task SinglePoint

Engine ADF
  title Ne
  excitations
    lowest 8
  end
  modifyexcitation
    useoccupied
      A1.g 1
    end
    usescaledzora
  end
  basis
    type QZ4P
    CreateOutput Yes
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
  symmetry d(8h)
  xc
    model SAOP
  end
EndEngine
eor

AMS_JOBNAME=Excitationsmod $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000 adf.f=Frag

```

(continues on next page)

(continued from previous page)

```

    end
end

Task SinglePoint

Engine ADF
  title Ne spin-orbit
  excitations
    alsorestricted
    lowest 11
  end
  fragments
    Frag Fragmod.results/adf.rkf
  end
  modifyexcitation
    useoccupied
    E1/2.g 1
  end
  usescaledzora
end
numericalquality Good
relativity
  level spin-orbit
  formalism ZORA
end
stcontrib
symmetry d(8h)
xc
  model SAOP
end
EndEngine
eor

AMS_JOBNAME=FragSel $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000
  end
end

Task SinglePoint

Engine ADF
  title Ne
  excitations
    lowest 8
  end
  basis
    type QZ4P
    CreateOutput Yes
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
end

```

(continues on next page)

(continued from previous page)

```
selectexcitation
  useoccupied
    A1.g 1
  end
  usescaledzora
end
symmetry d(8h)
xc
  model SAOP
end
EndEngine
eor

AMS_JOBNAME=Excitationssel $AMSBIN/ams <<eor
System
  atoms
    Ne .0000 .0000 0.0000 adf.f=Frag
  end
end

Task SinglePoint

Engine ADF
  title Ne spin-orbit
  excitations
    alsorestricted
    lowest 11
  end
  fragments
    Frag Fragsel.results/adf.rkf
  end
  numericalquality Good
  relativity
    level spin-orbit
    formalism ZORA
  end
  selectexcitation
    useoccupied
      E1/2.g 1
    end
    usescaledzora
  end
  stcontrib
  symmetry d(8h)
  xc
    model SAOP
  end
EndEngine
eor
```

Example: Excitation energies perturbative spin-orbit coupling: AgI

Download AgI_asoexcit.run

```

#!/bin/sh

# Calculation of the excitation energies of AgI including spin-orbit coupling in
# a perturbative way.

# ADF can not handle ATOM and linear symmetries in excitation calculations.
# In case of linear symmetries ADF will automatically use a
# a subsymmetry, in this case symmetry C(7v).
# In the excitation part of the output the symmetry labels are those of C(LIN) in
→this case.

# For such a small molecule, a relatively small TZ2P basis set is used, which is
# not sufficient for excitations to Rydberg-like orbitals, one needs more
# diffuse functions. For larger molecules a TZ2P basis set is in most cases
# sufficient. In that case one might even consider smaller basis sets.

# The key SOPERT is included in scalar relativistic ZORA calculations of
# excitation energies. First scalar relativistic TDDFT calculations are
# performed to determine the lowest 60 singlet-singlet and singlet-triplet
# excited states and the spin-orbit coupling operator is applied to these
# single-group excited states to obtain the excitation energies with spin-orbit
# coupling effects included.

$AMSBIN/ams <<eor
System
  atoms
    Ag 0.0000 0.0000 2.5446
    I 0.0000 0.0000 0.0000
  end
end

Task SinglePoint

Engine ADF
  title [AgI]
  excitations
    lowest 60
  end
  basis
    type TZ2P
    core None
    CreateOutput Yes
  end
  numericalquality Good
  sopert
  end
EndEngine

eor

```

Example: ROKS-TDA-SOC: Cd+

Download Cdplus_ROKS_TDA_SOC.run

```

#!/bin/sh

# Example excited state calculations of Cd+, which has a doublet ground state.
# Used is spin restricted open shell Kohn-Sham (ROKS, ROSCF) with perturbative
# spin-orbit coupling for this open shell molecule, using the keyword SOPERT.
# Symmetry can not be used.

"$AMSBIN/ams" << eor
Task SinglePoint
System
  Atoms
    Cd 0 0 0
  End
  Charge 1.0
End

Engine ADF
  Basis
    Type QZ4P
    Core None
  End
  Unrestricted Yes
  SpinPolarization 1
  Scf
    ROSCF
    End
  End
  Symmetry NOSYM
  NumericalQuality Good
  TDA
  Excitations
    RoksTddftType
      Calculate SS-SU
    End
    Lowest 17 3
  End
  SOPERT
  End
EndEngine
eor

```

Example: ROKS_TDA_SOC: NpF6

Download NpF6_ROKS_TDA_SOC.run

```

#!/bin/sh

# Example excited state calculations of NpF6, which has a doublet ground state.
# Used is spin restricted open shell Kohn-Sham (ROKS, ROSCF).

# First scalar relativistic excitations are calculated using octahedral symmetry.
→ (O(h)) .

```

(continues on next page)

(continued from previous page)

```

# Note that ADF reports the irreducible representation (irrep) of the transition_
↳density,
# which may not be the symmetry species of the excitation in case of open shell_
↳molecules.
# In this case the unpaired electron in the octahedral NpF6 is an a2.u orbital.
# The lowest excitation has a T1.g irrep transition density,
# which means that the symmetry species of this excited state is T2.u
# (T2.u = direct product A2.u times T1.g).
# In this calculation both excitations with the same spin as the ground state
# (S_excited = S_groundstate, SS) and excitations with a spin 1 higher than the_
↳ground state
# (S_excited = S_groundstate + 1, SU) are calculated.

AMS_JOBNAME=NpF6.sym "$AMSBIN/ams" << eor
Task SinglePoint
System
  Atoms
    Np 0.0  0.0  0.0
    F  0.0  0.0  1.98
    F  0.0  0.0 -1.98
    F  0.0  1.98  0.0
    F  0.0 -1.98  0.0
    F  1.98  0.0  0.0
    F -1.98  0.0  0.0
  End
End

Engine ADF
  Basis
    Type TZP
    Core None
  End
  Unrestricted Yes
  SpinPolarization 1
  Scf
    ROSCF
  End
End
NumericalQuality Good
TDA
Excitations
  RoksTddftType
    Calculate SS-SU
  End
  Lowest 6 2
End
EndEngine
eor

# Next excitations are calculated with perturbative spin-orbit coupling,
# for this open shell molecule, using the keyword SOPERT. Symmetry can not be used.
# In this calculation both excitations with the same spin as the ground state
# (S_excited = S_groundstate) and excitations with a spin 1 higher than the ground_
↳state
# (S_excited = S_groundstate + 1) are calculated.

```

(continues on next page)

(continued from previous page)

```

# With the subkey Excitations%Lowest one can specify the number of wanted excited
↪states.
# If 2 numbers are provided the first number is the wanted excited states with same
↪spin
# and the second number the wanted excited states with higher spin.
# For open shell excitations typically the excited states with higher spin than
# the ground state are higher in energy than those of the excited states with
# the same spin as the ground state.

AMS_JOBNAME=NpF6.soc "$AMSBIN/ams" << eor
Task SinglePoint
System
  Atoms
    Np 0.0  0.0  0.0
    F  0.0  0.0  1.98
    F  0.0  0.0 -1.98
    F  0.0  1.98  0.0
    F  0.0 -1.98  0.0
    F  1.98  0.0  0.0
    F -1.98  0.0  0.0
  End
End

Engine ADF
  Basis
    Type TZP
    Core None
  End
  Unrestricted Yes
  SpinPolarization 1
  Scf
    ROSCF
  End
End
Symmetry NOSYM
NumericalQuality Good
TDA
Excitations
  RoksTddftType
    Calculate SS-SU
  End
  Lowest 6 2
End
SOPERT
End
EndEngine
eor

```

Example: Excitation energies including spin-orbit coupling for open shell: PbF

Download PbF_excisou.run

```
#!/bin/sh

# Application of a spin-orbit coupled relativistic excitation energy calculation
# for an open-shell system. Note that the used method used is highly
# approximate. In this example the effect of spin-orbit coupling is large, in
# which case this method can be of use.

# First a scalar relativistic calculation is performed with symmetry. The
# resulting scalar relativistic adf.rkf file is used as fragment in the spin-orbit
# coupled calculation. Using a scalar relativistic fragment is not necessary,
# but makes the identification of the spin-orbit coupled results easier.

AMS_JOBNAME=PbF_SR $AMSBIN/ams <<eor
System
  atoms
    Pb   0    0    0
    F    0    0    2.06
  end
end

Task SinglePoint

Engine ADF
  basis
    core None
    type TZ2P
  end
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga bp86
  end
EndEngine
eor

# Next the spin-orbit coupled excitation unrestricted calculation is performed.
# The Tamm-Dancoff approximation (TDA) is needed and symmetry NOSYM should be
# used. Best is to use the noncollinear approximation.

AMS_JOBNAME=PbF_SO $AMSBIN/ams <<eor
System
  atoms
    Pb   0    0    0    adf.f=PbF
    F    0    0    2.06 adf.f=PbF
  end
end

Task SinglePoint
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  excitations
    lowest 14
  end
  fragments
    PbF PbF_SR.results/adf.rkf
  end
  relativity
    level spin-orbit
    formalism ZORA
    spinorbitmagnetization noncollinear
  end
  symmetry nosym
  tda
  unrestricted
  xc
    gga bp86
  end
EndEngine
eor

```

Example: Circular Dichroism (CD) spectrum: DMO

Download DMO_CD.run

```

#!/bin/sh

# If the subkey CDSPECTRUM is included in the key EXCITATIONS, the rotatory
# strength is calculated for the calculated excitations, in order to calculate
# the CD (Circular Dichroism) spectrum. Only useful for chiral molecules.

# With the VELOCITY keyword also the dipole-velocity representation of the
# rotatory strength is calculated.

# Note: results will be physically meaningless due to small basis set. purpose
# of this job is to provide a test case for the CD implementation

# Do not use less strict convergence criteria than default, better to use
# tighter criteria. The approximations in the evaluation of the integrals one
# makes with the linear scaling techniques are effectively switched off by
# setting LINEARSCALING 100 (recommended to use this).

$AMSBIN/ams <<eor
System
  atoms
    O  0.0          0.0          1.141417145729065
    C -0.5970248579978943 -0.4282023310661316 -0.09432400763034821
    C  0.5970248579978943  0.4282023310661316 -0.09432400763034821
    H -0.4430356621742249 -1.487679243087769 -0.302562028169632
    H  0.4430356621742249  1.487679243087769 -0.302562028169632
    C -1.97874128818512    0.09404171258211136 -0.3866550326347351
    H -2.723244667053223 -0.4288762211799622    0.2206400185823441
    H -2.043423652648926  1.15996515750885    -0.1578925102949142
  
```

(continues on next page)

(continued from previous page)

```

      H -2.236041307449341 -0.05517048016190529 -1.439977645874023
      C  1.97874128818512 -0.09404171258211136 -0.3866550326347351
      H  2.236041307449341  0.05517048016190529 -1.439977645874023
      H  2.723244667053223  0.4288762211799622  0.2206400185823441
      H  2.043423652648926 -1.15996515750885 -0.1578925102949142
    end
  end
Task SinglePoint

Engine ADF
  title dimethyloxirane excitations + CD
  comment
    results will be physically meaningless due to small basis set.
    purpose of this job is to provide a test case for the CD implementation
  end
  beckegrid
    quality good
  end
  excitations
    cdspectrum
    lowest 10
    onlising
    velocity
  end
  linearscaling 100
  end
  basis
    core Small
    type DZP
  end
  scf
    converge 1e-7
  end
  xc
    gga becke perdew
  end
EndEngine
eor

```

Example: CD spectrum with spin-orbit coupling: C2H3I

Download C2H3I_SOCD.run

```

#!/bin/sh

# Example for the calculation of an electronic CD spectrum including spin-orbit
↪coupling
# for the molecule Iodoethene.
# The lowest 3 excited states have high triplet character, but due to spin-orbit
↪coupling
# have non-negligible singlet character, such that the electronic CD spectrum is non-
↪zero.
# Phosphorescence dissymmetry factors are calculated.

```

(continues on next page)

(continued from previous page)

```

$AMSBIN/ams <<eor
System
  atoms
    C      -0.016815      0.033201      -0.680171
    I      -0.322076      1.796278      -1.883624
    C      -0.019887      0.012368      0.646966
    H      -0.185572     -0.930351      1.163416
    H       0.141293     -0.844352     -1.293414
    H       0.134807      0.889756      1.262747
  end
end

Task SinglePoint

engine ADF
  numericalquality Good
  excitations
    cdspectrum
    fullkernel
    lowest 4
  end
  basis
    PerAtomType Symbol=C File=ZORA/DZP/C
    PerAtomType Symbol=H File=ZORA/DZ/H
    PerAtomType Symbol=I File=ZORA/TZP/I
  end
  relativity
    level spin-orbit
  end
  title iodoethene-socd
  xc
    LibXC BP86
  end
endengine
eor

```

Example: CD spectrum, hybrid functional: Twisted ethene

Download Twist_Ethene_TDDFT.run

```

#!/bin/sh

# If the subkey CDSPECTRUM is included in the key EXCITATIONS, the rotatory
# strength is calculated for the calculated excitations, in order to calculate
# the CD (Circular Dichroism) spectrum. Only useful for chiral molecules. A
# hybrid functional is used in this case.

# With the VELOCITY keyword also the dipole-velocity representation of the
# rotatory strength is calculated.

# Note: results will be physically meaningless due to small basis set. purpose
# of this job is to provide a test case for the CD implementation

# Do not use less strict convergence criteria than default, better to use

```

(continues on next page)

(continued from previous page)

```
# tighter criteria. The approximations in the evaluation of the integrals one
# makes with the linear scaling techniques are effectively switched off by
# setting LINEARSCALING 99 (recommended to use this).
```

```
$AMSBIN/ams <<eor
```

```
System
```

```
  symmetrize
```

```
  atoms
```

```
    C 0.000000 0.000000 0.000000
```

```
    C -0.000000 -0.000000 1.350716
```

```
    H 0.565703 -0.745428 -0.540179
```

```
    H -0.565703 0.745428 -0.540179
```

```
    H 0.035837 -0.935093 1.890895
```

```
    H -0.035837 0.935093 1.890895
```

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title twisted ethene
```

```
  comment
```

```
    purpose of this job is to provide a test case for the CD implementation
```

```
    with hybrid functionals, and to test the "velocity" keyword
```

```
  end
```

```
  excitations
```

```
    cdspectrum
```

```
    lowest 20
```

```
    onlysing
```

```
    velocity
```

```
  end
```

```
  linearscaling 99
```

```
  end
```

```
  basis
```

```
    core Small
```

```
    type TZ2P
```

```
  end
```

```
  numericalquality good
```

```
  rihartreefock
```

```
    fitsetquality Normal
```

```
  end
```

```
  scf
```

```
    converge 1.e-8
```

```
  end
```

```
  xc
```

```
    hybrid PBE0
```

```
  end
```

```
  Relativity
```

```
    Level None
```

```
  End
```

```
EndEngine
```

```
eor
```

Example: MCD: H2O

Download H2O_MCD.run

```
#!/bin/sh

# Example for the calculation of magnetic circular dichroism (MCD). If the
# subkey MCD is included in the key EXCITATIONS the MCD parameters of the
# calculated excitations are calculated (A and B terms). The keys RELATIVISTIC
# ZORA and SOMCD are required for a calculation of temperature-dependent C
# terms. The key ALLPOINTS is required for an MCD calculation (if the molecule
# has symmetry).

$AMSBIN/ams <<eor
System
  atoms
    O          0.0000    0.0000    0.0000
    H          0.0000   -0.7071    0.7071
    H          0.0000    0.7071    0.7071
  end
  charge 1
end

Task SinglePoint

Engine ADF
  title water MCD
  allpoints
  excitations
    lowest 20
    mcd NMCDTERM=5
    onlysing
  end
  basis
    type DZP
  end
  relativity
    level scalar
    formalism ZORA
  end
  somcd
  spinpolarization 1
  unrestricted
EndEngine
eor
```

Example: MCD including zero-field splitting: H2O

Download H2O_MCD_ZFS.run

```

#!/bin/sh

# Example for the calculation of magnetic circular dichroism (MCD) including
# zero-field splitting (ZFS). If the subkey MCD is included in the key
# EXCITATIONS the MCD parameters of the calculated excitations are calculated (A
# and B terms). The keys RELATIVISTIC ZORA and SOMCD are required for a
# calculation of temperature-dependent C terms. The key ALLPOINTS is required
# for an MCD calculation (if the molecule has symmetry). For zero-field
# splitting (ZFS) the electron spin S<=1.

$AMSBIN/ams <<eor
System
  atoms
    O          0.0000    0.0000    0.0000
    H          0.0000   -0.7071    0.7071
    H          0.0000    0.7071    0.7071
  end
  charge 2
end

Task SinglePoint

Engine ADF
  title water MCD with zero-field splitting
  allpoints
  excitations
    lowest 20
    mcd NMCDTERM=5 NODIRECT NTEMP=2 TMIN=1.0 TMAX=300.0 NBFIELD=2 BMIN=1.0 BMAX=8.0
    onlysing
  end
  basis
    type DZP
  end
  relativity
    level scalar
    formalism ZORA
  end
  somcd
  spinpolarization 2
  unrestricted
  zfs
EndEngine
eor

```

Example: CV(n)-DFT excitation energies: Formamide

Download Formamide_CVnDFT.run

```
#!/bin/sh

# Calculation of the excitation energies of Formamide using the CV(n)-DFT
# method. Due to bugs in older versions it is important to use ADF2016.105 or
# later.

# Example of CV(infinity)-DFT where the molecular orbitals for the particular
# excitation are optimized (relaxed), which is called the R-CV(infinity)-DFT method.
# In this case, the transition U-vector is frozen, while the orbitals are
# relaxed. ALLPOINTS should be used in case of a symmetric molecule.
# EXACTDENSITY should be used for precision reasons. Note that the irrep labels
# for C(s) symmetry that are used in the excitation code (A' and A'') differ
# from those that are used during the SCF (AA and AAA). The example contains of
# 2 parts. In the first example singlet-singlet excitations are calculated using
# the subkeyword ONLYSING in the EXCITATIONS block key. In the second example
# singlet-triplet excitations are calculated replacing the subkeyword ONLYSING
# with the subkeyword ONLYTRIP in the EXCITATIONS block key.

AMS_JOBNAME=SS $AMSBIN/ams <<eor
System
  atoms
    H -0.927427 -0.600301 0.000000
    H  1.070498 -1.782390 0.000000
    H  2.024514 -0.325050 0.000000
    C  0.000000  0.000000 0.000000
    O  0.000000  1.225060 0.000000
    N  1.119392 -0.775069 0.000000
  end
end

Task SinglePoint

Engine ADF
  allpoints
  cvndft
    iteration 10
    r_cv_dft &
      damporbrelex 0.2
      relaxalpha 1
      relaxbeta 1
    end
    tolerance 0.001
  end
  exactdensity
  excitations
    analytical
    davidson
      A' 2
      A'' 2
    end
    lowest 4
    onlysing
```

(continues on next page)

(continued from previous page)

```

    tolerance 1e-5
end
basis
  core None
  fittype ZORA/QZ4P
  type DZ
end
numericalquality good
tda
title Formamide
xc
  hybrid B3LYP
end
EndEngine
eor

AMS_JOBNAME=ST $AMSBIN/ams <<eor
System
  atoms
    H -0.927427 -0.600301 0.000000
    H  1.070498 -1.782390 0.000000
    H  2.024514 -0.325050 0.000000
    C  0.000000  0.000000 0.000000
    O  0.000000  1.225060 0.000000
    N  1.119392 -0.775069 0.000000
  end
end

Task SinglePoint

Engine ADF
  allpoints
  cvndft
    iteration 10
    r_cv_dft &
      damporbrelex 0.2
      relaxalpha 1
      relaxbeta 1
    end
    tolerance 0.001
  end
  exactdensity
  excitations
    analytical
    davidson
      A' 2
      A'' 2
    end
    lowest 4
    onlytrip
    tolerance 1e-5
  end
  basis
    core None
    fittype ZORA/QZ4P

```

(continues on next page)

(continued from previous page)

```

    type DZ
  end
  numericalquality good
  tda
  title Formamide
  xc
    hybrid B3LYP
  end
EndEngine
eor

```

Example: HDA excitation energies: NH3

Download NH3_HDA.run

```

#!/bin/sh

# Calculation of the excitation energies of NH3 using the
# Hybrid Diagonal Approximation (HDA).
# Relevant in case hybrid XC functionals are used.
# For speed reasons one should set a (not so large) value for HDA_CutOff.

AMS_JOBNAME=NH3 $AMSBIN/ams << eor
System
  symmetrize
  atoms
    N   0.000000    0.000000    0.000000
    H   0.956305    0.000000    0.292372
    H  -0.478152    0.828184    0.292372
    H  -0.478152   -0.828184    0.292372
  end
end

Task SinglePoint

Engine ADF
  Basis
    Type TZP
  End

  XC
    Hybrid B3LYP
  End

  Excitations
    Allowed
    lowest 21
    HDA
    HDA_CutOff 40.0 [eV]
  End
EndEngine
eor

```


Example: HDA spin-orbit coupled excitation energies: H2O

Download H2O_SO_HDA.run

```
#!/bin/sh

# Calculation of the spin-orbit (SO) coupled excitation energies of H2O using the
# Hybrid Diagonal Approximation (HDA).
# Relevant in case hybrid XC functionals are used.
# For HDA icw SO symmetry NOSYM is required.
# For speed reasons one should not use a too large value for HDA_CutOff.

AMS_JOBNAME=H2O_SO $AMSBIN/ams << eor
System
  atoms
    O   0.000000    0.000000    0.000000
    H   0.000000    0.759062   -0.587729
    H   0.000000   -0.759062   -0.587729
  end
end

Task SinglePoint

Engine ADF
  Basis
    Type TZP
  End

  Symmetry NOSYM

  relativity
    level spin-orbit
    formalism ZORA
  end

  XC
    Hybrid B3LYP
  End

  Excitations
    lowest 50
    HDA
    HDA_CutOff 40.0
  END
EndEngine
eor
```

Example: TD-DFT+TB excitation energies: beta-Carotene

Download TD-DFTB_betacarotene.run

```
#!/bin/sh

# Calculation of the excitation energies of beta-Carotene using the TD-DFT+TB
# method. This method is meant for GGA or LDA functionals. In this example PBE
# is used during the SCF. In the calculation of the excitation energies the
# TD-DFTB+TB method is used in which the required integrals are approximated in
# the same way as in a TD-DFTB calculation. Symmetry NOSYM is required.

# The key MODIFYEXCITATION allows to remove single orbital transitions based on
# certain criteria. For example, for a large calculation, one can combine
# several of the filtering techniques with the key MODIFYEXCITATION. If one uses
# the next input, only the lowest 10000 single orbital transitions are used
# (which have the lowest orbital energy differences). Out of these 10000 the
# single orbital transitions with an oscillator strength smaller than 0.001 are
# removed, and single orbital transitions are removed that have an energy
# difference larger than 1.0 Hartree. In the space of single-orbital transition
# that are left the lowest 1000 eigenvectors are calculated.

#   ModifyExcitation
#   UseOccVirtNumbers 1 10000
#   OscStrength 0.001
#   UseOccVirtRange 0.0 1.0
#   End
#   Excitations
#   TDDFTB
#   OnlySing
#   Lowest 1000
#   End

# In the actual example only single orbital transitions with an oscillator
# strength smaller than 0.001 are removed, which one might do if one is
# interested only in excitation energies with a high oscillator strength.

$AMSBIN/ams <<eor
System
atoms
  C      -1.67096000      1.41980000     -1.15887000
  C      -0.38686000      2.25210000     -1.41391000
  C      -1.74087000      0.49471000     -0.15347000
  C      -2.78739000      1.72912000     -2.05465000
  C       0.64868000      2.05301000     -0.28395000
  C       0.23104000      1.84552000     -2.77135000
  C      -0.70560000      3.76543000     -1.46182000
  C      -0.54745000      0.11313000      0.69574000
  C      -3.00351000     -0.21803000      0.26657000
  C      -3.76926000      0.89738000     -2.51350000
  C       0.78914000      0.59489000      0.13981000
  C      -4.86625000      1.29159000     -3.36539000
  C      -5.83916000      0.35729000     -3.66241000
  C      -4.93554000      2.71910000     -3.84917000
  C      -7.05227000      0.56749000     -4.37867000
  C      -8.05019000     -0.37384000     -4.49171000
```

(continues on next page)

(continued from previous page)

C	-9.34557000	-0.15733000	-5.06205000
C	-10.30909000	-1.14399000	-4.91514000
C	-9.64286000	1.17054000	-5.71730000
C	-11.69180000	-1.05048000	-5.21459000
C	-12.61955000	-2.01468000	-4.87148000
C	-14.02165000	-1.83518000	-4.98190000
C	-15.01934000	-2.67078000	-4.50243000
C	-16.37196000	-2.20132000	-4.51598000
C	-14.71829000	-4.01459000	-3.88235000
C	-17.44392000	-2.81539000	-3.90884000
C	-18.74098000	-2.23505000	-3.81068000
C	-19.81891000	-2.70482000	-3.08600000
C	-21.01079000	-1.89278000	-3.01886000
C	-19.77834000	-4.00300000	-2.31809000
C	-22.11699000	-2.17469000	-2.26831000
C	-23.34229000	-1.38813000	-2.11260000
C	-24.62364000	-2.22792000	-1.86832000
C	-23.37421000	-0.02091000	-2.14864000
C	-25.81771000	-1.33236000	-1.46707000
C	-24.97031000	-3.02505000	-3.14664000
C	-24.41619000	-3.23491000	-0.71197000
C	-24.66206000	0.77221000	-2.09033000
C	-22.15090000	0.86196000	-2.20093000
C	-25.91751000	-0.06612000	-2.31089000
H	-2.80910000	2.75370000	-2.43250000
H	1.61418000	2.46808000	-0.61595000
H	0.33480000	2.64516000	0.59383000
H	-0.50118000	1.95999000	-3.58430000
H	1.10267000	2.47962000	-3.00160000
H	0.55846000	0.79551000	-2.76878000
H	-1.27083000	4.08204000	-0.57268000
H	0.23706000	4.33391000	-1.48690000
H	-1.27659000	4.05053000	-2.35573000
H	-0.69913000	0.51646000	1.71643000
H	-0.54631000	-0.98424000	0.82135000
H	-3.05490000	-1.23815000	-0.15105000
H	-3.01240000	-0.33500000	1.36235000
H	-3.91214000	0.31400000	-0.03789000
H	-3.75416000	-0.15646000	-2.22797000
H	1.07957000	-0.02480000	-0.72369000
H	1.58320000	0.48035000	0.89321000
H	-5.69282000	-0.64720000	-3.25046000
H	-4.00625000	2.99962000	-4.36844000
H	-5.76674000	2.88684000	-4.54145000
H	-5.05424000	3.41602000	-3.00441000
H	-7.22923000	1.55534000	-4.80743000
H	-7.87841000	-1.35648000	-4.03966000
H	-9.98472000	-2.07170000	-4.43134000
H	-8.86494000	1.42343000	-6.45273000
H	-10.60514000	1.16993000	-6.23979000
H	-9.66280000	1.98327000	-4.97344000
H	-12.06891000	-0.12920000	-5.66646000
H	-12.24343000	-2.93190000	-4.41065000
H	-14.35090000	-0.88585000	-5.41809000
H	-16.54169000	-1.22776000	-4.98799000
H	-15.37918000	-4.79019000	-4.29660000
H	-13.68496000	-4.33124000	-4.05827000

(continues on next page)

(continued from previous page)

```

H      -14.88466000      -3.99412000      -2.79324000
H      -17.27327000      -3.77423000      -3.41639000
H      -18.87740000      -1.27545000      -4.32124000
H      -20.99304000      -0.98523000      -3.62576000
H      -19.85755000      -3.82238000      -1.23433000
H      -20.62535000      -4.64779000      -2.59868000
H      -18.85754000      -4.56711000      -2.49752000
H      -22.10976000      -3.13142000      -1.74142000
H      -26.74148000      -1.93003000      -1.53138000
H      -25.70276000      -1.04055000      -0.40816000
H      -24.12173000      -3.65146000      -3.45913000
H      -25.83556000      -3.68339000      -2.96560000
H      -25.21348000      -2.35763000      -3.98638000
H      -24.03490000      -2.73308000       0.18974000
H      -25.38111000      -3.70177000      -0.46026000
H      -23.72534000      -4.04703000      -0.97564000
H      -24.71649000       1.28228000      -1.10831000
H      -24.60164000       1.58888000      -2.83152000
H      -21.95198000       1.22417000      -3.22414000
H      -22.31941000       1.76042000      -1.58543000
H      -21.24680000       0.35543000      -1.84399000
H      -26.00957000      -0.32720000      -3.37736000
H      -26.81690000       0.51083000      -2.04725000
end
end

Task SinglePoint

Engine ADF
  excitations
    onlysing
    td-dftb
  end
  modifyexcitation
    oscstrength 0.001
  end
  symmetry NOSYM
  xc
    gga PBE
  end
EndEngine

eor

```

Example: TDDFT-aas: Singlet excited state geometry optimization

Download Furan-TDDFT-aas.run

```

#!/bin/sh

# Excited state geometry optimization using TDDFT-aas, for the molecule Furan.
# The lowest singlet excited state S1 is optimized.
# This method is meant for GGA or LDA functionals, symmetry NOSYM is required.
#
# For excited state gradients all electron basis sets are required.

```

(continues on next page)

(continued from previous page)

```
# Note that for symmetric systems, one could perturb the coordinates
# to break the symmetry of the system. This can be done, for example,
# by including PerturbCoordinates 0.05 in the System block.
# In this example this is not done, which in practice means that the
# molecule remains symmetric.
```

```
$AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    C      -0.3794795800      0.6253630100      0.0000000000
    C       0.8347990000     -0.1408004800      0.0000000000
    C     -1.4034209400     -0.2770148700      0.0000000000
    O     -0.9123264600     -1.5648407100      0.0000000000
    C       0.4613593600     -1.4534489500      0.0000000000
    H     -0.4753888200      1.7069426000      0.0000000000
    H       1.8524186400      0.2382823200      0.0000000000
    H     -2.4837942800     -0.1874789500      0.0000000000
    H       1.0075920800     -2.3897179700      0.0000000000
  end
end
```

```
Task GeometryOptimization
```

```
Engine ADF
```

```
  excitations
    onlysing
    LOWEST 10
    AAS
  end
  symmetry NOSYM
  EXCITEDGO
  State A 1
End
Basis
  type TZP
  core None
End
xc
  gga PBE
end
EndEngine
eor
```

Example: sTDA excitation energies: Adenine

Download Adenine_sTDA.run

```
#!/bin/sh
```

```
# Calculation of the excitation energies of Adenine using the simplified Tamm-
# Dancoff (sTDA) method by Grimme. This method is meant for hybrid functionals
# or range-separated functionals during the SCF. In this example the hybrid PBE0
# is used during the SCF. In the the calculation of the excitation energies the
```

(continues on next page)

(continued from previous page)

```
# stDA method is used in which the required integrals are approximated. For
# hybrid functionals ADF will automatically set the parameters that are needed
# in this method. For range-separated functional one needs to set the parameters
# manually. Symmetry NOSYM is required. A TZP or TZ2P basis set is recommended
# for this method.
```

```
$AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

N	1.966533	-0.556678	0.000000
C	1.351210	-1.750556	0.000000
N	0.039008	-2.019043	0.000000
C	-0.679938	-0.889685	0.000000
C	-0.192782	0.421840	0.000000
C	1.210298	0.557343	0.000000
N	-2.051805	-0.746568	0.000000
C	-2.311388	0.608600	0.000000
N	-1.225604	1.347025	0.000000
N	1.828584	1.760602	0.000000
H	2.012099	-2.612788	0.000000
H	-2.725918	-1.499744	0.000000
H	-3.323166	0.988113	0.000000
H	1.288936	2.610953	0.000000
H	2.835883	1.795025	0.000000

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
excitations
```

```
onlysing
```

```
stda
```

```
end
```

```
basis
```

```
type DZ
```

```
end
```

```
symmetry nosym
```

```
xc
```

```
hybrid PBE0
```

```
end
```

```
EndEngine
```

```
eor
```

Example: sTDDFT excitation energies: Adenine

Download Adenine_sTDDFT.run

```

#!/bin/sh

# Calculation of the excitation energies of Adenine using the simplified time-
# dependent DFT (sTDDFT) method by Grimme. This method is meant for hybrid
# functionals or range-separated functionals during the SCF. In this example the
# hybrid PBE0 is used during the SCF. In the calculation of the excitation
# energies the sTDDFT method is used in which the required integrals are
# approximated. For hybrid functionals ADF will automatically set the parameters
# that are needed in this method. For range-separated functional one needs to
# set the parameters manually. Symmetry NOSYM is required A TZP or TZ2P basis
# set is recommended for this method.

$AMSBIN/ams <<eor
System
  atoms
    N      1.966533  -0.556678  0.000000
    C      1.351210  -1.750556  0.000000
    N      0.039008  -2.019043  0.000000
    C     -0.679938  -0.889685  0.000000
    C     -0.192782   0.421840  0.000000
    C      1.210298   0.557343  0.000000
    N     -2.051805  -0.746568  0.000000
    C     -2.311388   0.608600  0.000000
    N     -1.225604   1.347025  0.000000
    N      1.828584   1.760602  0.000000
    H      2.012099  -2.612788  0.000000
    H     -2.725918  -1.499744  0.000000
    H     -3.323166   0.988113  0.000000
    H      1.288936   2.610953  0.000000
    H      2.835883   1.795025  0.000000
  end
end

Task SinglePoint

Engine ADF
  excitations
    onlysing
    stddft
  end
  basis
    type DZ
  end
  symmetry nosym
  xc
    hybrid pbe0
  end
EndEngine

eor

```

Example: sTDA excitation energies RS functional: Bimane

Download Bimane_wB97X.run

```

#!/bin/sh

# Calculation of the excitation energies of Bimane using the simplified Tamm-
# Dancoff (sTDA) method by Grimme, for a range-separated function. This method
# is meant for hybrid functionals or range-separated functionals during the SCF.
# In this example the range-separated functional wB97X is used during the SCF.
# In the the calculation of the excitation energies the sTDA method is used
# in which the required integrals are approximated. For range-separated
# functional one needs to set the parameters manually. Note that the alpha and
# beta parameters for sTDA for range separated functionals in the Risthaus paper
# (dx.doi.org/10.1039/C3CP54517B) are mixed up. A TZP or TZ2P basis set is
# recommended for this method.
# To use the wB97X range-separated functional LibXC is needed. Symmetry NOSYM is
# required. The sTDA parameters should be set with the subkeys GRIMMEAEX,
# GRIMMEALPHA, and GRIMMEBETA of the key MODIFYEXCITATION.

$AMSBIN/ams <<eor

Task SinglePoint

System
  Atoms
    C      1.331698   -1.879605   -0.108603
    C      2.132097   -0.654088   -0.003948
    C      1.302873    0.426430   -0.104903
    C     -1.300787    0.433951   -0.101824
    C     -2.136017   -0.641707    0.001280
    C     -1.342993   -1.871870   -0.104659
    N     -0.000534   -0.021248   -0.324354
    N     -0.004568   -1.403598   -0.331622
    O     -1.679176   -3.039253   -0.043168
    O      1.661467   -3.048960   -0.049039
    C     -1.615093    1.891323   -0.058117
    C     -3.618641   -0.678771    0.170347
    C      1.626055    1.881942   -0.064754
    C      3.614962   -0.700043    0.160744
    H     -4.049414    0.325596    0.200326
    H     -3.887430   -1.197656    1.097229
    H     -4.086348   -1.233771   -0.650635
    H     -1.173280    2.374317    0.820379
    H     -2.696603    2.026980   -0.008719
    H     -1.243008    2.407629   -0.949030
    H      2.707594    2.010775   -0.000483
    H      1.174301    2.373283    0.803861
    H      1.270709    2.395192   -0.964373
    H      4.079173   -1.241294   -0.671464
    H      3.883147   -1.237421    1.077108
    H      4.049818    0.301869    0.208419
  End
End

Engine ADF

```

(continues on next page)

(continued from previous page)

```

Basis
  Type DZ
  Core None
End
Symmetry nosym
Excitations
  STDA
  OnlySing
end
XC
  LibXC wB97X
End
ModifyExcitation
  GRIMMEPERTC
  GRIMMEAEX 0.56
  GRIMMEALPHA 4.51
  GRIMMEBETA 8.00
end
EndEngine
eor

```

Example: sTDA excitation energies wB97: TCNE-Benzene

Download TCNE-Benzene_wB97.run

```

#!/bin/sh

# Calculation of the excitation energies of the complex TCNE-Benzene using the
# simplified Tamm-Dancoff (sTDA) method by Grimme, for a range-separated
# function. This method is meant for hybrid functionals or range-separated
# functionals during the SCF. In this example the range-separated functional
# wB97 is used during the SCF. In the the calculation of the excitation
# energies the sTDA method is used in which the required integrals are
# approximated. For range-separated functional one needs to set the parameters
# manually. Note that the alpha and beta parameters for sTDA for range separated
# functionals in the Risthaus paper (dx.doi.org/10.1039/C3CP54517B) are mixed
# up. A TZP or TZ2P basis set is recommended for this method.

# For the excitation energies of the complex TCNE-Benzene, charge
# transfer (CT) states are important. Symmetry NOSYM is required.
# The subkey DESCRIPTORS is added to the key EXCITATIONS such that CT descriptors
# are calculated. The the atomic distance criterion used for the calculation of
# CT_AT was set to 3.0 Angstrom.
# The sTDA parameters should be set with the subkeys GRIMMEAEX, GRIMMEALPHA, and
# GRIMMEBETA of the key MODIFYEXCITATION.

$AMSBIN/ams <<eor
System
atoms
  C      -2.274205   -1.398789   -0.000000
  C      -2.274206    1.398791   -0.000000
  C      -2.274506   -0.699551    1.213150
  C      -2.274505   -0.699551   -1.213150
  C      -2.274506    0.699551    1.213150

```

(continues on next page)

(continued from previous page)

```

C      -2.274505    0.699551   -1.213150
H      -2.278385   -2.491323   -0.000000
H      -2.278386    2.491321   -0.000000
C      1.368996   -0.686302    0.000000
C      1.368996    0.686301    0.000000
C      1.379968   -1.434052   -1.220900
C      1.379968   -1.434052    1.220895
C      1.379968    1.434051   -1.220900
C      1.379967    1.434051    1.220895
N      1.400955   -2.054479   -2.204820
N      1.400955   -2.054479    2.204824
N      1.400955    2.054481   -2.204820
N      1.400954    2.054481    2.204824
H      -2.276046   -1.246672    2.158733
H      -2.276045   -1.246672   -2.158730
H      -2.276045    1.246671   -2.158730
H      -2.276046    1.246671    2.158733
end
end

Task SinglePoint

Engine ADF
  excitations
    descriptors
    descriptors_ct_at_rab 3.0
    onlysing
    stda
  end
  Basis
    Type DZ
    Core None
    CreateOutput yes
  End
  modifyexcitation
    grimmeaex 0.61
    grimmealpha 4.41
    grimmebeta 8.00
    grimmeperc
  end
  symmetry nosym
  xc
    libxc wB97
  end
EndEngine

eor

```

15.4.3 Excited state (geometry) optimizations

Example: Excited state geometry optimization: N2

Download EGO_N2.run

```
#!/bin/sh

# Example for a singlet excited state geometry optimization for N2.

# Needed for such excited state optimizations are the key EXCITATIONS (to
# calculate excitation energies), and the key EXCITEDGO (to select for which
# excitation a geometry optimization should be performed).
# In this case a hybrid functional B3LYP is used.

$AMSBIN/ams <<eor
System
  atoms
    N      0.0      0.0     -0.7
    N      0.0      0.0      0.7
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    gradients 0.0001
  End
End

Engine ADF
  title N2 Excited state geometry
  allpoints
  beckegrid
    quality good
  end
  excitations
    lowest 10
    onlysing
  end
  excitedgo
    output 2
    state S-.u 1
  end
  basis
    type DZ
    core NONE
    CreateOutput Yes
  end
  xc
    hybrid B3LYP
  end
EndEngine
eor
```

Download EGO_N2_EIGENF.run

```
#!/bin/sh

# Example for a singlet excited state geometry optimization with eigenvector
# following (subkeyword EIGENFOLLOW of key EXCITEDGO), GGA functional used.

$AMSBIN/ams <<eor
System
  atoms
    N      0.0      0.0      -0.55
    N      0.0      0.0      0.55
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    gradients 0.0001
  End
End

Engine ADF
  title N2 Eigenvector follow. Lowest state at the starting geometry is not the_
↳lowest at min.
  beckegrid
    quality good
  end
  excitations
    lowest 10
    onlysing
  end
  excitedgo
    eigenfollow
    output 2
    state A 1
  end
  basis
    core NONE
    type DZ
  end
  symmetry NOSYM
  xc
    gga Becke Perdew
  end
EndEngine
eor

echo "StartGeometry"
$AMSBIN/amsreport ams.results/ams.rkf Geometry-Angstrom
echo "EndGeometry"
```

Example: Excited state geometry optimization with a constraint: CH2O

Download EGO_CH2O_trip_constr.run

```
#!/bin/sh

# Example for an excited triplet state geometry optimization with a constraint
# included.

# Needed for such excited state optimizations are the key EXCITATIONS (to
# calculate excitation energies), and the key EXCITEDGO (to select for which
# excitation a geometry optimization should be performed).
# Note that one has to select the state with the irrep name A'', and not with AAA.

$AMSBIN/ams <<eor
System
  atoms
    C  0.0  0.0  0.0
    O  1.2  0.0  0.0
    H -0.5  0.5  0.9
    H -0.5  0.4 -0.9
  end
end

Task GeometryOptimization

Constraints
  Distance 1 2 1.2
end

Engine ADF
  excitations
    davidson
  end
  lowest 5
  onlytrip
end
excitedgo
  output 2
  state A 1
  triplet
end
numericalquality good
basis
  core NONE
  type DZ
end
symmetry nosym
EndEngine
eor
```

Example: Spin-flip excited state geometry optimization: CH2

Download EGO_CH2_sf.run

```
#!/bin/sh

# Example for a spin-flip excited state geometry optimization with a triplet
# reference, and a frequency calculation afterwards.

# Needed for such excited state optimizations are the key EXCITATIONS (to
# calculate excitation energies), and the key EXCITEDGO (to select for which
# excitation a geometry optimization should be performed).
# In this case spin-flip excitations are calculated.

AMS_JOBNAME=CH2 $AMSBIN/ams <<eor
System
  atoms
    C      0.000000    0.000000    0.0
    H      0.7        0.0        0.7
    H     -0.7        0.0        0.7
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    energy      0.0001
    gradients 0.0001
  End
  MaxIterations 50
End

Engine ADF
  title CH2 Excited state geometry with triplet reference and spin-flip excitation
  excitations
    lowest 10
  end
  excitedgo
    output 2
    state B2 1
  end
  forcealda
  basis
    type DZP
    core NONE
  end
  scf
    converge 1.0e-9
  end
  sftddft
  unrestricted
  spinpolarization 2
  symmetry C(2V)
  tda
EndEngine
eor
```

(continues on next page)

(continued from previous page)

```

# Next the frequencies are calculated of the excited state. LoadSystem is used to
# pick up the optimized excited state geometry of the previous calculation.
# Note that in a numerical frequencies calculation symmetry, is turned off except to
↳ reduce the
# number of points calculated. Thus irrespective of the specified point group
# symmetry the symmetry label A of SYMMETRY NOSYM should be used to select the
# excited state. Care should be taken to ensure that the correct state is chosen
# in this frequencies calculation as the excited state number can change when
# the point group is changed. In this case instead of 'B2 1' one needs to select
# 'A 2'.

AMS_JOBNAME=ES_FREQUENCIES $AMSBIN/ams <<eor
LoadSystem
  File CH2.results/adf.rkf
End

Task SinglePoint
Properties
  NormalModes Yes
End

Engine ADF
  title CH2 Excited state frequencies with triplet reference and spin-flip excitation
  excitations
    lowest 10
  end
  symmetry NOSYM
  excitedgo
    output 2
    state A 2
  end
  forcealda
  basis
    core NONE
    type DZP
  end
  scf
    converge 1.0e-9
  end
  sftddft
  unrestricted
  spinpolarization 2
  tda
EndEngine
eor

```

Example: Numerical Frequencies of an excited state: PH2

Download EGO_PH2.run

```
#!/bin/sh

# Example for an excited state geometry optimization and frequency calculation.

# Needed for such excited state optimizations are the key EXCITATIONS (to
# calculate excitation energies), and the key EXCITEDGO (to select for which
# excitation a geometry optimization should be performed).

# The ground state and excited state are openshell.

AMS_JOBNAME=PH2 $AMSBIN/ams <<eor
System
  atoms
    P      0.000000    0.000000    0.0
    H      0.7        0.0        0.7
    H     -0.7        0.0        0.7
  end
end

Task GeometryOptimization

GeometryOptimization
  Convergence
    energy    0.0001
    gradients 0.0001
  End
  MaxIterations 50
End

Engine ADF
  title PH2 Excited state geometry
  beckegrid
    quality good
  end
  exactdensity
  excitations
    lowest 10
    onlysing
  end
  excitedgo
    output 1
    state B2 1
  end
  basis
    core NONE
    type DZ
  end
  scf
    converge 1.0e-9
  end
  unrestricted
  spinpolarization 1
  xc
```

(continues on next page)

(continued from previous page)

```

    gga BP86
  end
EndEngine
eor

# Next the frequencies are calculated of the excited state. LoadSystem is used to
# pick up the optimized excited state geometry of the previous calculation. Note that
# in a
# numerical frequencies calculation symmetry is turned off except to reduce the
# number of points calculated. Thus irrespective of the specified point group
# symmetry the symmetry label A of SYMMETRY NOSYM should be used to select the
# excited state. Care should be taken to ensure that the correct state is chosen
# in this frequencies calculation as the excited state number can change when
# the point group is changed. In this case instead of 'B2 1' one needs to select
# 'A 1'. Accurate SCF convergence parameters are used.

AMS_JOBNAME=PH2_Freq $AMSBIN/ams <<eor
LoadSystem
  File PH2.results/adf.rkf
End

Task SinglePoint
Properties
  NormalModes Yes
End

Engine ADF
  title PH2 Excited state frequencies
  beckegrid
    quality good
  end
  exactdensity
  excitations
    lowest 10
    onlysing
  end
  symmetry nosym
  excitedgo
    cpks
    eps 0.000001
  end
  output 2
  state A 1
end
basis
  type DZ
  core NONE
end
scf
  converge 1.0e-9
end
spinpolarization 1
unrestricted
xc
  gga BP86

```

(continues on next page)

(continued from previous page)

```

end
EndEngine
eor

```

Example: TD-DFT+TB: Singlet excited state geometry optimization

Download EGO_TD-DFTB.run

```

#!/bin/sh

# Excited state geometry optimization using TD-DFT+TB, for the molecule m-Cresol.
# The lowest singlet excited state S1 is optimized.
# This method is meant for GGA or LDA functionals. In this example PBE
# is used during the SCF. In the calculation of the excitation energies the
# TD-DFTB+TB method is used in which the required integrals are approximated in
# the same way as in a TD-DFTB calculation. Symmetry NOSYM is required.
# For excited state gradients all electron basis sets are required.

$AMSBIN/ams <<eor
System
atoms
  C    -1.885    0.511   -0.236
  C    -1.213   -0.724   -0.202
  C     0.201   -0.869   -0.029
  C     1.002    0.345   -0.018
  C     0.289    1.570    0.081
  C    -1.111    1.718    0.028
  C     0.871   -2.198    0.048
  O     0.982    2.797    0.335
  H    -2.954    0.574   -0.397
  H    -1.791   -1.644   -0.345
  H     2.054    0.328   -0.314
  H    -1.578    2.668    0.285
  H     1.958    2.608    0.558
  H     1.664   -2.297   -0.731
  H     0.152   -3.015   -0.093
  H     1.370   -2.341    1.021
end
end

Task GeometryOptimization

Engine ADF
  excitations
    onlysing
    td-dftb
  end
  basis
    core none
  end
  symmetry NOSYM
  xc
    gga PBE
  end

```

(continues on next page)

(continued from previous page)

```

excitedGO
  singlet
  state A 1
end
EndEngine
eor

```

Example: TD-DFT+TB: Triplet excited state geometry optimization

Download EGO_TD-DFTB_triplet.run

```

#!/bin/sh

# Excited state geometry optimization using TD-DFT+TB, for the molecule p-
↪Benzoquinone.
# The triplet excited state T3 is optimized.
# This method is meant for GGA or LDA functionals. In this example PBE
# is used during the SCF. In the calculation of the excitation energies the
# TD-DFTB+TB method is used in which the required integrals are approximated in
# the same way as in a TD-DFTB calculation. Symmetry NOSYM is required.
# For excited state gradients all electron basis sets are required.

# Note that for symmetric systems, one could perturb the coordinates
# to break the symmetry of the system. This can be done, for example,
# by including PerturbCoordinates 0.05 in the System block.
# In this example this is not done, which in practice means that the
# molecule remains symmetric.

$AMSBIN/ams <<eor
System
  atoms
    C    0.00000000    -0.67337000    1.26921000
    C    0.00000000     0.67337000    1.26921000
    C    0.00000000     1.44457000     0.00000000
    C    0.00000000     0.67337000   -1.26921000
    C    0.00000000   -0.67337000   -1.26921000
    C    0.00000000   -1.44457000     0.00000000
    O    0.00000000     2.67997000     0.00000000
    O    0.00000000    -2.67997000     0.00000000
    H    0.00000000     1.26436000    -2.18667000
    H    0.00000000    -1.26436000    -2.18667000
    H    0.00000000     1.26436000     2.18667000
    H    0.00000000    -1.26436000     2.18667000
  end
end

Task GeometryOptimization

Engine ADF
  excitations
    onlytrip
    td-dftb
  end
  basis

```

(continues on next page)

(continued from previous page)

```

    core none
end
symmetry NOSYM
xc
    gga PBE
end
excitedGO
    triplet
    state A 3
end
EndEngine
eor

```

Example: TD-DFT+TB: Open shell excited state geometry optimization

Download EGO_TD-DFTB_unrestricted.run

```

#!/bin/sh

# Excited state geometry optimization using TD-DFT+TB,
# for the radical cation of Pyrazine (open shell doublet).
# The lowest unrestricted excited state is optimized.
# This method is meant for GGA or LDA functionals. In this example LDA functional PW92
# is used during the SCF. In the calculation of the excitation energies the
# TD-DFTB+TB method is used in which the required integrals are approximated in
# the same way as in a TD-DFTB calculation. Symmetry NOSYM is required.
# For excited state gradients all electron basis sets are required.

# Note that for symmetric systems, one could perturb the coordinates
# to break the symmetry of the system. This can be done, for example,
# by including PerturbCoordinates 0.05 in the System block.
# In this example this is not done, which in practice means that the
# molecule remains symmetric.

$AMSBIN/ams <<eor
system
  Atoms
    H 0.000000 2.068464 1.258236
    H 0.000000 -2.068464 1.258236
    H 0.000000 2.068464 -1.258236
    H 0.000000 -2.068464 -1.258236
    C 0.000000 1.135920 0.697884
    C 0.000000 -1.135920 0.697884
    C 0.000000 1.135920 -0.697884
    C 0.000000 -1.135920 -0.697884
    N 0.000000 0.000000 1.417402
    N 0.000000 0.000000 -1.417402
  End
  charge 1
End

Task GeometryOptimization

GeometryOptimization
END

```

(continues on next page)

(continued from previous page)

```

Engine adf
  Basis
    Type DZP
    Core none
  End
  XC
    LDA PW92
  End
  SYMMETRY NOSYM
  numericalquality good
  unrestricted Yes
  SpinPolarization 1.0
  EXCITATIONS
    TD-DFTB
    lowest 10
  END
  EXCITEDGO
    STATE A 1
  END
EndEngine
eor

```

15.4.4 Vibrationally resolved (electronic) spectra

Example: Franck-Condon Factors: NO2

Download `FranckCondon_NO2.run`

```

#!/bin/sh

# As an example of a Franck-Condon calculation, lets look at the transition of
# NO2 to NO2 - . NO2 is a small molecule with only three vibrational modes.
# Putting an extra electron on the molecule will cause a big displacement,
# resulting in large electron-phonon couplings.

# In general, the larger the molecule, the smaller the displacement and hence
# the electron-phonon couplings and Franck-Condon factors. Moreover, larger
# molecules have more vibrational modes, meaning that the already smaller
# displacement will generally be smeared out over more modes, resulting in an
# additional decrease in electron-phonon couplings. This is fortunate, since the
# number of Franck-Condon factors increases factorially with the number of
# vibrational modes, making it prohibitively expensive to take more than a few
# vibrational quanta into account for most molecules.

# In order to calculate the Franck-Condon factors for Nitrite and Nitrogen
# dioxide, the equilibrium positions of the nuclei and the vibrational modes
# have to be obtained:

AMS_JOBNAME=NO2 $AMSBIN/ams <<eor
System
  atoms
    N          0.000000    0.000000    -0.016179

```

(continues on next page)

(continued from previous page)

```

      O      0.000000      1.098646      -0.492918
      O      0.000000      -1.098646      -0.492918
    end
  end

Task GeometryOptimization
GeometryOptimization
  Convergence
    Gradients 1.0e-5
  End
End
Properties
  NormalModes True
End

Engine ADF
  basis
    core NONE
    type DZP
  end
  spinpolarization 1
  title Nitrogen dioxide
  unrestricted
  xc
    lda SCF VWN
  end
EndEngine
eor

# We are using an already optimized geometry for the second calculation but in a
# real experiment one should run geometry optimization first

AMS_JOBNAME=NO2_minus $AMSBIN/ams <<eor
System
  atoms
    N      0.000000      0.000000      0.126041
    O      0.000000      1.070642      -0.555172
    O      0.000000      -1.070642      -0.555172
  end
  charge -1.0
end

Task SinglePoint
Properties
  NormalModes True
End

Engine ADF
  basis
    core NONE
    type DZP
  end
  title Nitrite
  xc
    lda SCF VWN
  end
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor

# This runscript produces two adf.rkf files containing the frequencies and the
# normal modes for both charge states. Lets first look at the ground state to
# ground state overlap:

$AMSBIN/fcf <<eor
  STATE1 NO2.results/adf.rkf
  STATE2 NO2_minus.results/adf.rkf
  TRANSLATE
  ROTATE
eor

rm TAPE61 logfile

```

Example: Vibronic-Structure Tracking: Naphthalene

Download Naphthalene_VST.run

```

#!/bin/sh

# Calculation of a vibrationally resolved electronically excited
# state spectrum with the VG-FC vibronic-structure tracking (VST)
# method of the molecule naphthalene.
# Important is to be at the ground state geometry of naphthalene.
# Note that a geometry optimization of naphthalene is skipped here,
# but we do use optimized coordinates.

# The lowest singlet-singlet excitation of naphthalene and
# its excited state gradient is calculated at the optimized
# ground state geometry of naphthalene.

# In the single point calculation the 'Gradients' are requested in the properties_
↳block
# In addition one needs to include the EXCITATIONS key and the EXCITEDGO key such_
↳that the
# excited state nuclear gradients are calculated.

AMS_JOBNAME=ES $AMSBIN/ams <<eor
System
atoms
  C 0.0  0.705203949620  2.423171793837
  C 0.0  1.398484082024  1.236799665234
  C 0.0 -1.398484082024  1.236799665234
  C 0.0  0.715180917267  0.0
  C 0.0 -0.705203949620  2.423171793837
  C 0.0 -0.715180917267  0.0
  C 0.0  1.398484082024 -1.236799665234
  C 0.0  0.705203949620 -2.423171793837
  C 0.0 -0.705203949620 -2.423171793837
  C 0.0 -1.398484082024 -1.236799665234

```

(continues on next page)

(continued from previous page)

```

      H 0.0  2.493594473281  1.232860022766
      H 0.0  1.244970418595  3.374117886966
      H 0.0 -1.244970418595  3.374117886966
      H 0.0 -2.493594473281  1.232860022766
      H 0.0 -2.493594473281 -1.232860022766
      H 0.0 -1.244970418595 -3.374117886966
      H 0.0  1.244970418595 -3.374117886966
      H 0.0  2.493594473281 -1.232860022766
    end
  end

Task SinglePoint

Properties
  Gradients Yes
End

Engine ADF
  excitations
    lowest 1
    nto
    onlysing
  end
  excitedgo
    allgradients
  end
  basis
    type DZ
    core None
  end
EndEngine
eor

# The calculation of the vibrationally resolved spectrum of the lowest
# singlet excited state of naphthalene is calculated with the VG-FC VST method.
# The excited state gradient is read from the file ES.results/adf.rkf.

AMS_JOBNAME=VibronicStructure "$AMSBIN/ams" <<eor
Task VibrationalAnalysis
System
  Atoms
    C 0.0  0.705203949620  2.423171793837
    C 0.0  1.398484082024  1.236799665234
    C 0.0 -1.398484082024  1.236799665234
    C 0.0  0.715180917267  0.0
    C 0.0 -0.705203949620  2.423171793837
    C 0.0 -0.715180917267  0.0
    C 0.0  1.398484082024 -1.236799665234
    C 0.0  0.705203949620 -2.423171793837
    C 0.0 -0.705203949620 -2.423171793837
    C 0.0 -1.398484082024 -1.236799665234
    H 0.0  2.493594473281  1.232860022766
    H 0.0  1.244970418595  3.374117886966
    H 0.0 -1.244970418595  3.374117886966
    H 0.0 -2.493594473281  1.232860022766
    H 0.0 -2.493594473281 -1.232860022766
    H 0.0 -1.244970418595 -3.374117886966

```

(continues on next page)

(continued from previous page)

```

      H 0.0  1.244970418595 -3.374117886966
      H 0.0  2.493594473281 -1.232860022766
    End
  End
  VibrationalAnalysis
    Type VibronicStructureTracking
    AbsorptionSpectrum
      LineWidth 50.0
      AbsorptionRange -200.0 4000.0
    End
    ExcitationSettings
      ExcitationFile ES.results/adf.rkf
      Singlet
        B2.u 1
      End
    End
  End
End
Engine ADF
  basis
    Type DZ
    Core None
  End
EndEngine
eor

```

Example: Vibronic Density of States

Download DOS_FCF.run

```

#!/bin/bash

# The simplified PLAMS script calculates the density of states (DOS)
# for the transfer between two systems, in this case NO2 radical and NO2 anion
# We start from pre-optimized geometries to save time, though normally the
# geometry optimization should come first, then we calculate the frequencies
# for both systems and finally the absorption and emission FCF spectra
# and finally the DOS is calculated from the FCF spectra using the FCFDOS utility
# implemented in PLAMS

cp $AMSHOME/examples/adf/DOS_FCF/no2_1.xyz no2_1.xyz
cp $AMSHOME/examples/adf/DOS_FCF/no2_2.xyz no2_2.xyz
cp $AMSHOME/examples/adf/DOS_FCF/DOS_FCF.py .

$AMSBIN/plams DOS_FCF.py

# Every time you run a PLAMS script, a uniquely named working directory is
# created (plams.*****). This folder will contain one subdirectory per job. Each
# job directory contains the job's input and results files. In this case there
# will be 1 directory for the ADF calculation of the atomic charges that are
# used for DRF. Next there is a directory which calculates the full system.

```

15.4.5 (Hyper-)Polarizabilities, dispersion coefficients, ORD, magnetizabilities, Verdet constants

Example: Polarizabilities including spin-orbit coupling: AgI

Download `AgI_SO_Pol.run`

```
#!/bin/sh

# Example shows an frequency-dependent ZORA calculation of complex linear
# response of AgI including spin-orbit coupling.

# The polarizability is calculated using the AORESPONSE key, in which spin-orbit
# coupling is taken into account. In this case a spin-restricted calculation is
# required, but, unlike the rest of AORESPONSE, also NOSYM. In this example
# lifetime effects are included.

"$AMSBIN/ams" <<eor

Task SinglePoint

System
  ATOMS
    Ag    0.0 0.0  1.2723
    I     0.0 0.0 -1.2723
  END
End

Engine ADF
  TITLE AgI,SO-ZORA
  basis
    type TZ2P
    core None
  end
  symmetry nosym
  allpoints
  BeckeGrid
  quality good
End
  linearscaling 9.0
End
xc
  lda VWN
end
relativity
  level spin-orbit
end
aoreponse
  scf
  frequencies 0.085 [Hartree]
  lifetime 0.007
  ALDA
  EL_DIPOLE_EL_DIPOLE
end
EndEngine
```

(continues on next page)

(continued from previous page)

eor

Example: damped first hyperpolarizability: LiH

Download LiH_DampedBeta.run

```

#!/bin/sh

# If the subkey lifetime and BETA or QUADRATIC is included in the key
# AORESPONSE, the damped (frequency dependent) first hyperpolarizability is
# calculated. This test example consists of two calculations: one
# with BETA and the other with QUADRATIC.

# The subkey EOPE is used, which means the electro-optical Pockels effect
# beta(-omega;omega,0). This example can easily be modified to calculate the
# static beta(0;0,0), the optical rectification beta(0;omega,-omega), the second
# harmonic generation beta(-2omega;omega,omega), or the general case
# beta(-(omega1+omega2);omega1,omega2).

# Note: results will be physically meaningless due to small basis set. Purpose
# of this job is to provide a test case for the first hyperpolarizability
# implementation

# In the first example the first hyperpolarizability is calculated with the
# subkey BETA, for EOPE, the electro-optical Pockels effect
# beta(-omega;omega,0).

#####
# Damped EOPE, 2n+1
#####

AMS_JOBNAME=EOPE_beta $AMSBIN/ams <<eor
System
  atoms
    Li      0.00000000    0.00000000    3.49467000
    H      0.00000000    0.00000000    1.89402300
  end
end

Task SinglePoint

Engine ADF
  title Damped EOPE of LiH, 2n+1
  allpoints
  aoresponse
    alda
    beta
    eoep
  frequencies 0.1000 0.0000 [Hartree]
  lifetime 0.0034
  scf iterations 50
end
basis
  core None

```

(continues on next page)

(continued from previous page)

```

        type SZ
    end
    numericalquality good
    symmetry nosym
EndEngine
eor

# In the second example the first hyperpolarizability is calculated with the
# subkey QUADRATIC, again for EOPE, the electro-optical Pockels effect
# beta(-omega;omega,0).

#####
# Damped EOPE, Quadratic
#####

AMS_JOBNAME=EOPE_quadratic $AMSBIN/ams <<eor
System
  atoms
    Li    0.00000000    0.00000000    3.49467000
    H     0.00000000    0.00000000    1.89402300
  end
end

Task SinglePoint

Engine ADF
  title Damped EOPE of LiH, Quadratic
  allpoints
  aoresponse
    alda
    eopec
    frequencies 0.1000 0.0000 [Hartree]
    lifetime 0.0034
    quadratic
    scf iterations 50
  end
  basis
    core None
    type SZ
  end
  numericalquality good
  symmetry nosym
EndEngine
eor

# For the static case beta(0;0,0) use the subkey STATIC
#   aoresponse
#   ...
#   frequencies 0.0000 0.0000 [Hartree]
#   static
#   end

# For optical rectification beta(0;omega,-omega) use the subkey OPTICALR.
#   aoresponse
#   ...

```

(continues on next page)

(continued from previous page)

```
# frequencies 0.1000 -0.1000 [Hartree]
# opticalr
# end

# For the second harmonic generation beta(-2omega;omega,omega) use the subkey SHG
# aoresponse
# ...
# frequencies 0.1000 0.1000 [Hartree]
# shg
# end

# Or in the general case for beta(-(omega1+omega2);omega1,omega2) choose two
# input frequencies omega1 and omega2
# aoresponse
# ...
# frequencies omega1 omega2 [Hartree]
# end
```

Example: damped second hyperpolarizability: LiH

Download LiH_DampedGamma.run

```
#!/bin/sh

# If the subkey lifetime and GAMMA or CUBIC is included in the key AORESPONSE,
# the damped (frequency dependent) second hyperpolarizability is calculated.
# This test example consists of three calculations: two with GAMMA
# and one with CUBIC.

# The first two examples subkey EFIOR is used, which means the electric
# field induced optical rectification gamma(0;omega,-omega,0). In the third
# example two-photon absorption (TPA) cross sections are calculated, the reduced
# form of gamma(-omega;omega,omega,-omega). Examples can easily be modified to
# calculate the static case gamma(0;0,0,0), the optical Kerr effect
# gamma(-omega;omega,0,0), the intensity dependent refractive index
# gamma(-omega;omega,omega,-omega), the electric field induced second harmonic
# generation gamma(-2omega;omega,omega,0), the third harmonic generation
# gamma(-3omega;omega,omega,omega) use the subkey THG, or the general case
# gamma(-(omega1+omega2+omega3);omega1,omega2,omega3).

# Note: results will be physically meaningless due to small basis set. Purpose
# of this job is to provide a test case for the second hyperpolarizability
# implementation

# In the first example the second hyperpolarizability is calculated with the
# subkey GAMMA, for EFIOR, the electric field induced optical rectification
# gamma(0;omega,-omega,0).

#####
# Damped EFIOR, 2n+1
#####

AMS_JOBNAME=EFIOR_gamma $AMSBIN/ams <<eor
```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Li    0.00000000    0.00000000    3.49467000
    H     0.00000000    0.00000000    1.89402300
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title Damped EFior of LiH, 2n+1
  allpoints
  aoresponse
    alda
    efior
    frequencies 0.1000 -0.1000 0.0000 [Hartree]
    gamma
    lifetime 0.0034
    scf iterations 50
  end
  basis
    core None
    type SZ
  end
  numericalquality good
  symmetry nosym
EndEngine
eor

```

```

# In the second example the second hyperpolarizability is calculated with the
# subkey CUBIC, again for EFior, the electric field induced optical
# rectification gamma(0;omega,-omega,0).

```

```

#####
# Damped EFior, Cubic
#####

```

```
AMS_JOBNAME=EFOR_cubic $AMSBIN/ams <<eor
```

```

System
  atoms
    Li    0.00000000    0.00000000    3.49467000
    H     0.00000000    0.00000000    1.89402300
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title Damped EFior of LiH, Cubic
  allpoints
  aoresponse
    alda
    cubic
    efior
    frequencies 0.1000 -0.1000 0.0000 [Hartree]
    lifetime 0.0034

```

(continues on next page)

(continued from previous page)

```

    scf iterations 50
end
basis
  core None
  type SZ
end
numericalquality good
symmetry nosym
EndEngine
eor

# In the third example the subkeyword TPA is be used to calculate the gammagamma
# corresponding to the two photon absorption process (i.e., the reduced form of
# gamma(-omega;omega,omega,-omega)), however, TPA can ONLY be used with keyword
# GAMMA.

#####
# Damped TPA, 2n+1
#####

AMS_JOBNAME=TPA_gamma $AMSBIN/ams <<eor
System
  atoms
    Li    0.00000000    0.00000000    3.49467000
    H     0.00000000    0.00000000    1.89402300
  end
end

Task SinglePoint

Engine ADF
  title Damped TPA of LiH, 2n+1
  allpoints
  aoresponse
    alda
    frequencies 0.1000 0.1000 -0.1000 [Hartree]
    gamma
    lifetime 0.0034
    scf iterations 50
    tpa
  end
  basis
    core None
    type SZ
  end
  numericalquality good
  symmetry nosym
EndEngine
eor

# For the static case gamma(0;0,0,0) use the subkey STATIC
# aoresponse
# ...
# frequencies 0.0000 0.0000 0.0000 [Hartree]
# static

```

(continues on next page)

(continued from previous page)

```

# end

# For the optical Kerr effect gamma(-omega;omega,0,0) use the subkey OKE
# aoresponse
# ...
# frequencies 0.1000 0.0000 0.0000 [Hartree]
# oke
# end

# For the intensity dependent refractive index gamma(-omega;omega,omega,-omega)
# use the subkey IDRI
# aoresponse
# ...
# frequencies 0.1000 0.1000 -0.1000 [Hartree]
# idri
# end

# For the electric field induced second harmonic generation
# gamma(-2omega;omega,omega,0) use the subkey EFISHG
# aoresponse
# ...
# frequencies 0.1000 0.1000 0.0000 [Hartree]
# efishg
# end

# For the third harmonic generation gamma(-3omega;omega,omega,omega) use the
# subkey THG
# aoresponse
# ...
# frequencies 0.1000 0.1000 0.1000 [Hartree]
# thg
# end

# Or in the general case for gamma(-(omega1+omega2+omega3);omega1,omega2,omega3)
# choose three input frequencies omega1, omega2, and omega3
# aoresponse
# ...
# frequencies omega1 omega2 omega3 [Hartree]
# end

```

Example: Verdet constants: H2O

Download H2O_Verdet.run

```

#!/bin/sh

# Specify the subkey MAGOPTROT in the AORESPONSE key to calculate the Verdet
# constant.

$AMSBIN/ams <<eor
System
atoms
O          0.000000    0.134692    0.000000

```

(continues on next page)

(continued from previous page)

```

      H      0.869763   -0.538741   0.000000
      H     -0.869763   -0.538794   0.000000
    end
  end

Task SinglePoint

Engine ADF
  allpoints
  aoresponse
  alda
  frequencies 0.088558 [Hartree]
  giao
  magoptrot
  scf converge 1d-6 iterations 25
end
basis
  core None
  type TZP
end
numericalquality Good
symmetry nosym
xc
  gga revPBE
  lda vwn
end
Relativity
  Level None
End
EndEngine
eor

```

Example: Dispersion Coefficients: HF

Download Disper_HF.run

```

#!/bin/sh

# General dispersion coefficients (beyond de dipole-dipole C6 interaction
# coefficient) are computed with the auxiliary program DISPER. It uses two
# output files from previous ADF Response calculations. In the example, the two
# ADF runs are one and the same and the relevant TENSOR output file is used
# twice.

$AMSBIN/ams <<eor
System
  atoms
    H  0 0  -0.8708056087
    F  0 0   0.04619439132
  end
end

Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title Van der Waals coefficients HF
  basis
    core Small
    type DZP
  end
  response
    allcomponents
    alltensor
    maxwaals 8
    vanderwaals 7
  end
  symmetry C(8v)
EndEngine

eor

# Polarizabilities are computed at 7 (imaginary) frequencies between 0 and
# infinity. The program determines internally the actual frequency values in
# this range to use. The user only specifies the number of them, thereby
# determining the precision of, in fact, a numerical integration over the zero-
# infinity frequency range. A value of 7 is rather low.

# MaxWaals determines that not only the C6 but also C7 and C8 coefficients are
# computed. A value higher than 8 would not be recommended, because the
# available basis sets would be inadequate for higher coefficients.

# In DISPER calculations the preparatory Response calculation must use the
# AllTensor and AllComponents subkeys.

# The calculation produces a file TENSOR. The subsequent DISPER run uses two
# such files. In this example, both are taken from the same ADF run, copying the
# TENSOR file to, respectively, tensorA and tensorB. These names are prescribed
# for a DISPER calculation.

cp ams.results/TENSOR tensorA
cp ams.results/TENSOR tensorB

$AMSBIN/disper -n1 <<eor
eor

# The DISPER program needs no other input than just the files tensorA and
# tensorB, which must both be present as local files. Note the '-n1' flag: this
# enforces that a single-node (non-parallel) run is performed. The current
# implementation does not support parallelization of DISPER, because the kid
# processes may not have the (local to the master!) files tensorA and tensorB.

```

Example: Optical Rotation Dispersion (ORD): DMO

Download DMO_ORD.run

```
#!/bin/sh

# If the subkey OPTICALROTATION is included in the key RESPONSE, the (frequency
# dependent) optical rotation is calculated.

# Note: results will be physically meaningless due to small basis set. purpose
# of this job is to provide a test case for the ORD implementation

# Do not use less strict convergence criteria than default, better to use
# tighter criteria. The approximations in the evaluation of the integrals one
# makes with the linear scaling techniques are effectively switched off by
# setting LINEARSCALING 100 (recommended to use this).

$AMSBIN/ams <<eor
System
  atoms
    O  0.0          0.0          1.141417145729065
    C -0.5970248579978943 -0.4282023310661316 -0.09432400763034821
    C  0.5970248579978943  0.4282023310661316 -0.09432400763034821
    H -0.4430356621742249 -1.487679243087769 -0.302562028169632
    H  0.4430356621742249  1.487679243087769 -0.302562028169632
    C -1.97874128818512    0.09404171258211136 -0.3866550326347351
    H -2.723244667053223 -0.4288762211799622    0.2206400185823441
    H -2.043423652648926  1.15996515750885 -0.1578925102949142
    H -2.236041307449341 -0.05517048016190529 -1.439977645874023
    C  1.97874128818512    -0.09404171258211136 -0.3866550326347351
    H  2.236041307449341  0.05517048016190529 -1.439977645874023
    H  2.723244667053223  0.4288762211799622    0.2206400185823441
    H  2.043423652648926 -1.15996515750885 -0.1578925102949142
  end
end

Task SinglePoint

Engine ADF
  title dimethyloxirane, ORD
  comment
    results will be physically meaningless due to small basis set.
    purpose of this job is to provide a test case for the ORD implementation
  end
  beckegrid
    quality good
  end
  linearscaling 100
end
basis
  core Small
  type DZP
end
response
  allcomponents
  opticalrotation
```

(continues on next page)

(continued from previous page)

```

end
xc
  gga becke perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: ORD, lifetime effects (key AORESPONSE): DMO

Download DMO_ORD_aoresponse.run

```

#!/bin/sh

# If the subkey OPTICALROTATION is included in the key AORESPONSE, the
# (frequency dependent) optical rotation is calculated. In this example lifetime
# effects are included. This test example consists of two ORD calculations: one
# with and one without the velocity gauge.

# Note: results will be physically meaningless due to small basis set. purpose
# of this job is to provide a test case for the ORD implementation

AMS_JOBNAME=opticalrotation $AMSBIN/ams <<eor
System
  atoms
    O  0.0          0.0          1.141417145729065
    C -0.5970248579978943 -0.4282023310661316 -0.09432400763034821
    C  0.5970248579978943  0.4282023310661316 -0.09432400763034821
    H -0.4430356621742249 -1.487679243087769 -0.302562028169632
    H  0.4430356621742249  1.487679243087769 -0.302562028169632
    C -1.97874128818512   0.09404171258211136 -0.3866550326347351
    H -2.723244667053223 -0.4288762211799622  0.2206400185823441
    H -2.043423652648926  1.15996515750885 -0.1578925102949142
    H -2.236041307449341 -0.05517048016190529 -1.439977645874023
    C  1.97874128818512   -0.09404171258211136 -0.3866550326347351
    H  2.236041307449341  0.05517048016190529 -1.439977645874023
    H  2.723244667053223  0.4288762211799622  0.2206400185823441
    H  2.043423652648926 -1.15996515750885 -0.1578925102949142
  end
end

Task SinglePoint

Engine ADF
  title dimethyloxirane, ORD
  comment
    results will be physically meaningless due to small basis set.
    You may also want to increase the NumericalQuality to "Good".
    purpose of this job is to provide a test case for the ORD implementation
  end

```

(continues on next page)

(continued from previous page)

```

allpoints
aoresponse
  alda
  frequencies 2.103923139 [eV]
  lifetime 0.007
  opticalrotation
  scf iter 20
end
basis
  core Small
  type DZP
end
numericalquality Normal
xc
  gga becke perdew
end
Relativity
  Level None
End
EndEngine

eor

# In the second example the subkey OPTICALROTATION of the key AORESPONSE is
# changed into VELOCITYORD:

AMS_JOBNAME=velocityord $AMSBIN/ams <<eor
System
  atoms
    O 0.0          0.0          1.141417145729065
    C -0.5970248579978943 -0.4282023310661316 -0.09432400763034821
    C 0.5970248579978943 0.4282023310661316 -0.09432400763034821
    H -0.4430356621742249 -1.487679243087769 -0.302562028169632
    H 0.4430356621742249 1.487679243087769 -0.302562028169632
    C -1.97874128818512 0.09404171258211136 -0.3866550326347351
    H -2.723244667053223 -0.4288762211799622 0.2206400185823441
    H -2.043423652648926 1.15996515750885 -0.1578925102949142
    H -2.236041307449341 -0.05517048016190529 -1.439977645874023
    C 1.97874128818512 -0.09404171258211136 -0.3866550326347351
    H 2.236041307449341 0.05517048016190529 -1.439977645874023
    H 2.723244667053223 0.4288762211799622 0.2206400185823441
    H 2.043423652648926 -1.15996515750885 -0.1578925102949142
  end
end

Task SinglePoint

Engine ADF
  title dimethyloxirane, ORD with velocity gauge
  comment
    results will be physically meaningless due to small basis set.
    You may also want to increase the NumericalQuality to "Good".
    purpose of this job is to provide a test case for the ORD implementation
  end
  allpoints

```

(continues on next page)

(continued from previous page)

```

aoresponse
  alda
  frequencies 2.103923139 [eV]
  lifetime 0.007
  scf iter 20
  velocityord
end
basis
  core Small
  type DZP
end
numericalquality Normal
xc
  gga becke perdw
end
Relativity
  Level None
End
EndEngine
eor

```

Example: Polarizability: first order perturbed density

Download ALPHA_DENSITY.run

```

#!/bin/sh

$AMSBIN/ams <<eor
System
  atoms
    O      0.00000000  -0.06692444  0.00000000
    H      0.76766392   0.53123258  0.00000000
    H     -0.76766392   0.53123258  0.00000000
  end
end

Task SinglePoint

Engine ADF
  aoresponse
    alda
    alpha
    frequencies 2.2489 [eV]
    lifetime 0.0037
    scf iter 200
  end
  beckegrid
    quality verygood
  end
  basis
    core None
    type TZP
  end

```

(continues on next page)

(continued from previous page)

```

symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity Level=None
EndEngine
eor

```

```

$AMSBIN/densf << eor
adffile ams.results/adf.rkf
TAPE16file ams.results/TAPE16

```

```

Grid Inline
-4.0  -3.0  -3.0
-4.0  -3.0  -2.2
-4.0  -3.0  -1.4
-4.0  -3.0  -0.6
-4.0  -3.0   0.2
-4.0  -3.0   1.0
-4.0  -3.0   1.8
-4.0  -3.0   2.6
-4.0  -2.2  -3.0
-4.0  -2.2  -2.2
-4.0  -2.2  -1.4
-4.0  -2.2  -0.6
-4.0  -2.2   0.2
-4.0  -2.2   1.0
-4.0  -2.2   1.8
-4.0  -2.2   2.6
-4.0  -1.4  -3.0
-4.0  -1.4  -2.2
-4.0  -1.4  -1.4
-4.0  -1.4  -0.6
-4.0  -1.4   0.2
-4.0  -1.4   1.0
-4.0  -1.4   1.8
-4.0  -1.4   2.6
-4.0  -0.6  -3.0
-4.0  -0.6  -2.2
-4.0  -0.6  -1.4
-4.0  -0.6  -0.6
-4.0  -0.6   0.2
-4.0  -0.6   1.0
-4.0  -0.6   1.8
-4.0  -0.6   2.6
-4.0   0.2  -3.0
-4.0   0.2  -2.2
-4.0   0.2  -1.4
-4.0   0.2  -0.6
-4.0   0.2   0.2
-4.0   0.2   1.0
-4.0   0.2   1.8
-4.0   0.2   2.6
-4.0   1.0  -3.0
-4.0   1.0  -2.2
-4.0   1.0  -1.4
-4.0   1.0  -0.6

```

(continues on next page)

(continued from previous page)

-4.0	1.0	0.2
-4.0	1.0	1.0
-4.0	1.0	1.8
-4.0	1.0	2.6
-4.0	1.8	-3.0
-4.0	1.8	-2.2
-4.0	1.8	-1.4
-4.0	1.8	-0.6
-4.0	1.8	0.2
-4.0	1.8	1.0
-4.0	1.8	1.8
-4.0	1.8	2.6
-4.0	2.6	-3.0
-4.0	2.6	-2.2
-4.0	2.6	-1.4
-4.0	2.6	-0.6
-4.0	2.6	0.2
-4.0	2.6	1.0
-4.0	2.6	1.8
-4.0	2.6	2.6
-4.0	3.4	-3.0
-4.0	3.4	-2.2
-4.0	3.4	-1.4
-4.0	3.4	-0.6
-4.0	3.4	0.2
-4.0	3.4	1.0
-4.0	3.4	1.8
-4.0	3.4	2.6
-3.2	-3.0	-3.0
-3.2	-3.0	-2.2
-3.2	-3.0	-1.4
-3.2	-3.0	-0.6
-3.2	-3.0	0.2
-3.2	-3.0	1.0
-3.2	-3.0	1.8
-3.2	-3.0	2.6
-3.2	-2.2	-3.0
-3.2	-2.2	-2.2
-3.2	-2.2	-1.4
-3.2	-2.2	-0.6
-3.2	-2.2	0.2
-3.2	-2.2	1.0
-3.2	-2.2	1.8
-3.2	-2.2	2.6
-3.2	-1.4	-3.0
-3.2	-1.4	-2.2
-3.2	-1.4	-1.4
-3.2	-1.4	-0.6
-3.2	-1.4	0.2
-3.2	-1.4	1.0
-3.2	-1.4	1.8
-3.2	-1.4	2.6
-3.2	-0.6	-3.0
-3.2	-0.6	-2.2
-3.2	-0.6	-1.4
-3.2	-0.6	-0.6
-3.2	-0.6	0.2

(continues on next page)

(continued from previous page)

-3.2	-0.6	1.0
-3.2	-0.6	1.8
-3.2	-0.6	2.6
-3.2	0.2	-3.0
-3.2	0.2	-2.2
-3.2	0.2	-1.4
-3.2	0.2	-0.6
-3.2	0.2	0.2
-3.2	0.2	1.0
-3.2	0.2	1.8
-3.2	0.2	2.6
-3.2	1.0	-3.0
-3.2	1.0	-2.2
-3.2	1.0	-1.4
-3.2	1.0	-0.6
-3.2	1.0	0.2
-3.2	1.0	1.0
-3.2	1.0	1.8
-3.2	1.0	2.6
-3.2	1.8	-3.0
-3.2	1.8	-2.2
-3.2	1.8	-1.4
-3.2	1.8	-0.6
-3.2	1.8	0.2
-3.2	1.8	1.0
-3.2	1.8	1.8
-3.2	1.8	2.6
-3.2	2.6	-3.0
-3.2	2.6	-2.2
-3.2	2.6	-1.4
-3.2	2.6	-0.6
-3.2	2.6	0.2
-3.2	2.6	1.0
-3.2	2.6	1.8
-3.2	2.6	2.6
-3.2	3.4	-3.0
-3.2	3.4	-2.2
-3.2	3.4	-1.4
-3.2	3.4	-0.6
-3.2	3.4	0.2
-3.2	3.4	1.0
-3.2	3.4	1.8
-3.2	3.4	2.6
-2.4	-3.0	-3.0
-2.4	-3.0	-2.2
-2.4	-3.0	-1.4
-2.4	-3.0	-0.6
-2.4	-3.0	0.2
-2.4	-3.0	1.0
-2.4	-3.0	1.8
-2.4	-3.0	2.6
-2.4	-2.2	-3.0
-2.4	-2.2	-2.2
-2.4	-2.2	-1.4
-2.4	-2.2	-0.6
-2.4	-2.2	0.2
-2.4	-2.2	1.0

(continues on next page)

(continued from previous page)

-2.4	-2.2	1.8
-2.4	-2.2	2.6
-2.4	-1.4	-3.0
-2.4	-1.4	-2.2
-2.4	-1.4	-1.4
-2.4	-1.4	-0.6
-2.4	-1.4	0.2
-2.4	-1.4	1.0
-2.4	-1.4	1.8
-2.4	-1.4	2.6
-2.4	-0.6	-3.0
-2.4	-0.6	-2.2
-2.4	-0.6	-1.4
-2.4	-0.6	-0.6
-2.4	-0.6	0.2
-2.4	-0.6	1.0
-2.4	-0.6	1.8
-2.4	-0.6	2.6
-2.4	0.2	-3.0
-2.4	0.2	-2.2
-2.4	0.2	-1.4
-2.4	0.2	-0.6
-2.4	0.2	0.2
-2.4	0.2	1.0
-2.4	0.2	1.8
-2.4	0.2	2.6
-2.4	1.0	-3.0
-2.4	1.0	-2.2
-2.4	1.0	-1.4
-2.4	1.0	-0.6
-2.4	1.0	0.2
-2.4	1.0	1.0
-2.4	1.0	1.8
-2.4	1.0	2.6
-2.4	1.8	-3.0
-2.4	1.8	-2.2
-2.4	1.8	-1.4
-2.4	1.8	-0.6
-2.4	1.8	0.2
-2.4	1.8	1.0
-2.4	1.8	1.8
-2.4	1.8	2.6
-2.4	2.6	-3.0
-2.4	2.6	-2.2
-2.4	2.6	-1.4
-2.4	2.6	-0.6
-2.4	2.6	0.2
-2.4	2.6	1.0
-2.4	2.6	1.8
-2.4	2.6	2.6
-2.4	3.4	-3.0
-2.4	3.4	-2.2
-2.4	3.4	-1.4
-2.4	3.4	-0.6
-2.4	3.4	0.2
-2.4	3.4	1.0
-2.4	3.4	1.8

(continues on next page)

(continued from previous page)

-2.4	3.4	2.6
-1.6	-3.0	-3.0
-1.6	-3.0	-2.2
-1.6	-3.0	-1.4
-1.6	-3.0	-0.6
-1.6	-3.0	0.2
-1.6	-3.0	1.0
-1.6	-3.0	1.8
-1.6	-3.0	2.6
-1.6	-2.2	-3.0
-1.6	-2.2	-2.2
-1.6	-2.2	-1.4
-1.6	-2.2	-0.6
-1.6	-2.2	0.2
-1.6	-2.2	1.0
-1.6	-2.2	1.8
-1.6	-2.2	2.6
-1.6	-1.4	-3.0
-1.6	-1.4	-2.2
-1.6	-1.4	-1.4
-1.6	-1.4	-0.6
-1.6	-1.4	0.2
-1.6	-1.4	1.0
-1.6	-1.4	1.8
-1.6	-1.4	2.6
-1.6	-0.6	-3.0
-1.6	-0.6	-2.2
-1.6	-0.6	-1.4
-1.6	-0.6	-0.6
-1.6	-0.6	0.2
-1.6	-0.6	1.0
-1.6	-0.6	1.8
-1.6	-0.6	2.6
-1.6	0.2	-3.0
-1.6	0.2	-2.2
-1.6	0.2	-1.4
-1.6	0.2	-0.6
-1.6	0.2	0.2
-1.6	0.2	1.0
-1.6	0.2	1.8
-1.6	0.2	2.6
-1.6	1.0	-3.0
-1.6	1.0	-2.2
-1.6	1.0	-1.4
-1.6	1.0	-0.6
-1.6	1.0	0.2
-1.6	1.0	1.0
-1.6	1.0	1.8
-1.6	1.0	2.6
-1.6	1.8	-3.0
-1.6	1.8	-2.2
-1.6	1.8	-1.4
-1.6	1.8	-0.6
-1.6	1.8	0.2
-1.6	1.8	1.0
-1.6	1.8	1.8
-1.6	1.8	2.6

(continues on next page)

(continued from previous page)

-1.6	2.6	-3.0
-1.6	2.6	-2.2
-1.6	2.6	-1.4
-1.6	2.6	-0.6
-1.6	2.6	0.2
-1.6	2.6	1.0
-1.6	2.6	1.8
-1.6	2.6	2.6
-1.6	3.4	-3.0
-1.6	3.4	-2.2
-1.6	3.4	-1.4
-1.6	3.4	-0.6
-1.6	3.4	0.2
-1.6	3.4	1.0
-1.6	3.4	1.8
-1.6	3.4	2.6
-0.8	-3.0	-3.0
-0.8	-3.0	-2.2
-0.8	-3.0	-1.4
-0.8	-3.0	-0.6
-0.8	-3.0	0.2
-0.8	-3.0	1.0
-0.8	-3.0	1.8
-0.8	-3.0	2.6
-0.8	-2.2	-3.0
-0.8	-2.2	-2.2
-0.8	-2.2	-1.4
-0.8	-2.2	-0.6
-0.8	-2.2	0.2
-0.8	-2.2	1.0
-0.8	-2.2	1.8
-0.8	-2.2	2.6
-0.8	-1.4	-3.0
-0.8	-1.4	-2.2
-0.8	-1.4	-1.4
-0.8	-1.4	-0.6
-0.8	-1.4	0.2
-0.8	-1.4	1.0
-0.8	-1.4	1.8
-0.8	-1.4	2.6
-0.8	-0.6	-3.0
-0.8	-0.6	-2.2
-0.8	-0.6	-1.4
-0.8	-0.6	-0.6
-0.8	-0.6	0.2
-0.8	-0.6	1.0
-0.8	-0.6	1.8
-0.8	-0.6	2.6
-0.8	0.2	-3.0
-0.8	0.2	-2.2
-0.8	0.2	-1.4
-0.8	0.2	-0.6
-0.8	0.2	0.2
-0.8	0.2	1.0
-0.8	0.2	1.8
-0.8	0.2	2.6
-0.8	1.0	-3.0

(continues on next page)

(continued from previous page)

-0.8	1.0	-2.2
-0.8	1.0	-1.4
-0.8	1.0	-0.6
-0.8	1.0	0.2
-0.8	1.0	1.0
-0.8	1.0	1.8
-0.8	1.0	2.6
-0.8	1.8	-3.0
-0.8	1.8	-2.2
-0.8	1.8	-1.4
-0.8	1.8	-0.6
-0.8	1.8	0.2
-0.8	1.8	1.0
-0.8	1.8	1.8
-0.8	1.8	2.6
-0.8	2.6	-3.0
-0.8	2.6	-2.2
-0.8	2.6	-1.4
-0.8	2.6	-0.6
-0.8	2.6	0.2
-0.8	2.6	1.0
-0.8	2.6	1.8
-0.8	2.6	2.6
-0.8	3.4	-3.0
-0.8	3.4	-2.2
-0.8	3.4	-1.4
-0.8	3.4	-0.6
-0.8	3.4	0.2
-0.8	3.4	1.0
-0.8	3.4	1.8
-0.8	3.4	2.6
0.0	-3.0	-3.0
0.0	-3.0	-2.2
0.0	-3.0	-1.4
0.0	-3.0	-0.6
0.0	-3.0	0.2
0.0	-3.0	1.0
0.0	-3.0	1.8
0.0	-3.0	2.6
0.0	-2.2	-3.0
0.0	-2.2	-2.2
0.0	-2.2	-1.4
0.0	-2.2	-0.6
0.0	-2.2	0.2
0.0	-2.2	1.0
0.0	-2.2	1.8
0.0	-2.2	2.6
0.0	-1.4	-3.0
0.0	-1.4	-2.2
0.0	-1.4	-1.4
0.0	-1.4	-0.6
0.0	-1.4	0.2
0.0	-1.4	1.0
0.0	-1.4	1.8
0.0	-1.4	2.6
0.0	-0.6	-3.0
0.0	-0.6	-2.2

(continues on next page)

(continued from previous page)

0.0	-0.6	-1.4
0.0	-0.6	-0.6
0.0	-0.6	0.2
0.0	-0.6	1.0
0.0	-0.6	1.8
0.0	-0.6	2.6
0.0	0.2	-3.0
0.0	0.2	-2.2
0.0	0.2	-1.4
0.0	0.2	-0.6
0.0	0.2	0.2
0.0	0.2	1.0
0.0	0.2	1.8
0.0	0.2	2.6
0.0	1.0	-3.0
0.0	1.0	-2.2
0.0	1.0	-1.4
0.0	1.0	-0.6
0.0	1.0	0.2
0.0	1.0	1.0
0.0	1.0	1.8
0.0	1.0	2.6
0.0	1.8	-3.0
0.0	1.8	-2.2
0.0	1.8	-1.4
0.0	1.8	-0.6
0.0	1.8	0.2
0.0	1.8	1.0
0.0	1.8	1.8
0.0	1.8	2.6
0.0	2.6	-3.0
0.0	2.6	-2.2
0.0	2.6	-1.4
0.0	2.6	-0.6
0.0	2.6	0.2
0.0	2.6	1.0
0.0	2.6	1.8
0.0	2.6	2.6
0.0	3.4	-3.0
0.0	3.4	-2.2
0.0	3.4	-1.4
0.0	3.4	-0.6
0.0	3.4	0.2
0.0	3.4	1.0
0.0	3.4	1.8
0.0	3.4	2.6
0.8	-3.0	-3.0
0.8	-3.0	-2.2
0.8	-3.0	-1.4
0.8	-3.0	-0.6
0.8	-3.0	0.2
0.8	-3.0	1.0
0.8	-3.0	1.8
0.8	-3.0	2.6
0.8	-2.2	-3.0
0.8	-2.2	-2.2
0.8	-2.2	-1.4

(continues on next page)

(continued from previous page)

0.8	-2.2	-0.6
0.8	-2.2	0.2
0.8	-2.2	1.0
0.8	-2.2	1.8
0.8	-2.2	2.6
0.8	-1.4	-3.0
0.8	-1.4	-2.2
0.8	-1.4	-1.4
0.8	-1.4	-0.6
0.8	-1.4	0.2
0.8	-1.4	1.0
0.8	-1.4	1.8
0.8	-1.4	2.6
0.8	-0.6	-3.0
0.8	-0.6	-2.2
0.8	-0.6	-1.4
0.8	-0.6	-0.6
0.8	-0.6	0.2
0.8	-0.6	1.0
0.8	-0.6	1.8
0.8	-0.6	2.6
0.8	0.2	-3.0
0.8	0.2	-2.2
0.8	0.2	-1.4
0.8	0.2	-0.6
0.8	0.2	0.2
0.8	0.2	1.0
0.8	0.2	1.8
0.8	0.2	2.6
0.8	1.0	-3.0
0.8	1.0	-2.2
0.8	1.0	-1.4
0.8	1.0	-0.6
0.8	1.0	0.2
0.8	1.0	1.0
0.8	1.0	1.8
0.8	1.0	2.6
0.8	1.8	-3.0
0.8	1.8	-2.2
0.8	1.8	-1.4
0.8	1.8	-0.6
0.8	1.8	0.2
0.8	1.8	1.0
0.8	1.8	1.8
0.8	1.8	2.6
0.8	2.6	-3.0
0.8	2.6	-2.2
0.8	2.6	-1.4
0.8	2.6	-0.6
0.8	2.6	0.2
0.8	2.6	1.0
0.8	2.6	1.8
0.8	2.6	2.6
0.8	3.4	-3.0
0.8	3.4	-2.2
0.8	3.4	-1.4
0.8	3.4	-0.6

(continues on next page)

(continued from previous page)

0.8	3.4	0.2
0.8	3.4	1.0
0.8	3.4	1.8
0.8	3.4	2.6
1.6	-3.0	-3.0
1.6	-3.0	-2.2
1.6	-3.0	-1.4
1.6	-3.0	-0.6
1.6	-3.0	0.2
1.6	-3.0	1.0
1.6	-3.0	1.8
1.6	-3.0	2.6
1.6	-2.2	-3.0
1.6	-2.2	-2.2
1.6	-2.2	-1.4
1.6	-2.2	-0.6
1.6	-2.2	0.2
1.6	-2.2	1.0
1.6	-2.2	1.8
1.6	-2.2	2.6
1.6	-1.4	-3.0
1.6	-1.4	-2.2
1.6	-1.4	-1.4
1.6	-1.4	-0.6
1.6	-1.4	0.2
1.6	-1.4	1.0
1.6	-1.4	1.8
1.6	-1.4	2.6
1.6	-0.6	-3.0
1.6	-0.6	-2.2
1.6	-0.6	-1.4
1.6	-0.6	-0.6
1.6	-0.6	0.2
1.6	-0.6	1.0
1.6	-0.6	1.8
1.6	-0.6	2.6
1.6	0.2	-3.0
1.6	0.2	-2.2
1.6	0.2	-1.4
1.6	0.2	-0.6
1.6	0.2	0.2
1.6	0.2	1.0
1.6	0.2	1.8
1.6	0.2	2.6
1.6	1.0	-3.0
1.6	1.0	-2.2
1.6	1.0	-1.4
1.6	1.0	-0.6
1.6	1.0	0.2
1.6	1.0	1.0
1.6	1.0	1.8
1.6	1.0	2.6
1.6	1.8	-3.0
1.6	1.8	-2.2
1.6	1.8	-1.4
1.6	1.8	-0.6
1.6	1.8	0.2

(continues on next page)

(continued from previous page)

1.6	1.8	1.0
1.6	1.8	1.8
1.6	1.8	2.6
1.6	2.6	-3.0
1.6	2.6	-2.2
1.6	2.6	-1.4
1.6	2.6	-0.6
1.6	2.6	0.2
1.6	2.6	1.0
1.6	2.6	1.8
1.6	2.6	2.6
1.6	3.4	-3.0
1.6	3.4	-2.2
1.6	3.4	-1.4
1.6	3.4	-0.6
1.6	3.4	0.2
1.6	3.4	1.0
1.6	3.4	1.8
1.6	3.4	2.6
2.4	-3.0	-3.0
2.4	-3.0	-2.2
2.4	-3.0	-1.4
2.4	-3.0	-0.6
2.4	-3.0	0.2
2.4	-3.0	1.0
2.4	-3.0	1.8
2.4	-3.0	2.6
2.4	-2.2	-3.0
2.4	-2.2	-2.2
2.4	-2.2	-1.4
2.4	-2.2	-0.6
2.4	-2.2	0.2
2.4	-2.2	1.0
2.4	-2.2	1.8
2.4	-2.2	2.6
2.4	-1.4	-3.0
2.4	-1.4	-2.2
2.4	-1.4	-1.4
2.4	-1.4	-0.6
2.4	-1.4	0.2
2.4	-1.4	1.0
2.4	-1.4	1.8
2.4	-1.4	2.6
2.4	-0.6	-3.0
2.4	-0.6	-2.2
2.4	-0.6	-1.4
2.4	-0.6	-0.6
2.4	-0.6	0.2
2.4	-0.6	1.0
2.4	-0.6	1.8
2.4	-0.6	2.6
2.4	0.2	-3.0
2.4	0.2	-2.2
2.4	0.2	-1.4
2.4	0.2	-0.6
2.4	0.2	0.2
2.4	0.2	1.0

(continues on next page)

(continued from previous page)

2.4	0.2	1.8
2.4	0.2	2.6
2.4	1.0	-3.0
2.4	1.0	-2.2
2.4	1.0	-1.4
2.4	1.0	-0.6
2.4	1.0	0.2
2.4	1.0	1.0
2.4	1.0	1.8
2.4	1.0	2.6
2.4	1.8	-3.0
2.4	1.8	-2.2
2.4	1.8	-1.4
2.4	1.8	-0.6
2.4	1.8	0.2
2.4	1.8	1.0
2.4	1.8	1.8
2.4	1.8	2.6
2.4	2.6	-3.0
2.4	2.6	-2.2
2.4	2.6	-1.4
2.4	2.6	-0.6
2.4	2.6	0.2
2.4	2.6	1.0
2.4	2.6	1.8
2.4	2.6	2.6
2.4	3.4	-3.0
2.4	3.4	-2.2
2.4	3.4	-1.4
2.4	3.4	-0.6
2.4	3.4	0.2
2.4	3.4	1.0
2.4	3.4	1.8
2.4	3.4	2.6
3.2	-3.0	-3.0
3.2	-3.0	-2.2
3.2	-3.0	-1.4
3.2	-3.0	-0.6
3.2	-3.0	0.2
3.2	-3.0	1.0
3.2	-3.0	1.8
3.2	-3.0	2.6
3.2	-2.2	-3.0
3.2	-2.2	-2.2
3.2	-2.2	-1.4
3.2	-2.2	-0.6
3.2	-2.2	0.2
3.2	-2.2	1.0
3.2	-2.2	1.8
3.2	-2.2	2.6
3.2	-1.4	-3.0
3.2	-1.4	-2.2
3.2	-1.4	-1.4
3.2	-1.4	-0.6
3.2	-1.4	0.2
3.2	-1.4	1.0
3.2	-1.4	1.8

(continues on next page)

(continued from previous page)

3.2	-1.4	2.6
3.2	-0.6	-3.0
3.2	-0.6	-2.2
3.2	-0.6	-1.4
3.2	-0.6	-0.6
3.2	-0.6	0.2
3.2	-0.6	1.0
3.2	-0.6	1.8
3.2	-0.6	2.6
3.2	0.2	-3.0
3.2	0.2	-2.2
3.2	0.2	-1.4
3.2	0.2	-0.6
3.2	0.2	0.2
3.2	0.2	1.0
3.2	0.2	1.8
3.2	0.2	2.6
3.2	1.0	-3.0
3.2	1.0	-2.2
3.2	1.0	-1.4
3.2	1.0	-0.6
3.2	1.0	0.2
3.2	1.0	1.0
3.2	1.0	1.8
3.2	1.0	2.6
3.2	1.8	-3.0
3.2	1.8	-2.2
3.2	1.8	-1.4
3.2	1.8	-0.6
3.2	1.8	0.2
3.2	1.8	1.0
3.2	1.8	1.8
3.2	1.8	2.6
3.2	2.6	-3.0
3.2	2.6	-2.2
3.2	2.6	-1.4
3.2	2.6	-0.6
3.2	2.6	0.2
3.2	2.6	1.0
3.2	2.6	1.8
3.2	2.6	2.6
3.2	3.4	-3.0
3.2	3.4	-2.2
3.2	3.4	-1.4
3.2	3.4	-0.6
3.2	3.4	0.2
3.2	3.4	1.0
3.2	3.4	1.8
3.2	3.4	2.6
4.0	-3.0	-3.0
4.0	-3.0	-2.2
4.0	-3.0	-1.4
4.0	-3.0	-0.6
4.0	-3.0	0.2
4.0	-3.0	1.0
4.0	-3.0	1.8
4.0	-3.0	2.6

(continues on next page)

(continued from previous page)

4.0	-2.2	-3.0
4.0	-2.2	-2.2
4.0	-2.2	-1.4
4.0	-2.2	-0.6
4.0	-2.2	0.2
4.0	-2.2	1.0
4.0	-2.2	1.8
4.0	-2.2	2.6
4.0	-1.4	-3.0
4.0	-1.4	-2.2
4.0	-1.4	-1.4
4.0	-1.4	-0.6
4.0	-1.4	0.2
4.0	-1.4	1.0
4.0	-1.4	1.8
4.0	-1.4	2.6
4.0	-0.6	-3.0
4.0	-0.6	-2.2
4.0	-0.6	-1.4
4.0	-0.6	-0.6
4.0	-0.6	0.2
4.0	-0.6	1.0
4.0	-0.6	1.8
4.0	-0.6	2.6
4.0	0.2	-3.0
4.0	0.2	-2.2
4.0	0.2	-1.4
4.0	0.2	-0.6
4.0	0.2	0.2
4.0	0.2	1.0
4.0	0.2	1.8
4.0	0.2	2.6
4.0	1.0	-3.0
4.0	1.0	-2.2
4.0	1.0	-1.4
4.0	1.0	-0.6
4.0	1.0	0.2
4.0	1.0	1.0
4.0	1.0	1.8
4.0	1.0	2.6
4.0	1.8	-3.0
4.0	1.8	-2.2
4.0	1.8	-1.4
4.0	1.8	-0.6
4.0	1.8	0.2
4.0	1.8	1.0
4.0	1.8	1.8
4.0	1.8	2.6
4.0	2.6	-3.0
4.0	2.6	-2.2
4.0	2.6	-1.4
4.0	2.6	-0.6
4.0	2.6	0.2
4.0	2.6	1.0
4.0	2.6	1.8
4.0	2.6	2.6
4.0	3.4	-3.0

(continues on next page)

(continued from previous page)

```

4.0    3.4    -2.2
4.0    3.4    -1.4
4.0    3.4    -0.6
4.0    3.4     0.2
4.0    3.4     1.0
4.0    3.4     1.8
4.0    3.4     2.6
End
Density scf
aoresponse alpha lifetime imag
eor

```

Example: Hyperpolarizabilities of He and H2

Download Hyperpol.run

```

#!/bin/sh

# This sample illustrates the computation of (hyper) polarizability tensors for
# the He atom and the H2 molecule.

# The symmetry is specified, because the Response module in ADF cannot yet
# handle the infinite symmetries ATOM, C(lin), D(lin).

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/He
mv TAPE12 t12.rel

AMS_JOBNAME=He8 $AMSBIN/ams <<eor
System
  Atoms
    He 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF
  create He $AMSRESOURCES/ADF/Special/Vdiff/He.2s2p2d2f
  corepotentials t12.rel
  He 1
end
EndEngine
eor

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/H
mv TAPE12 t12.rel

AMS_JOBNAME=H7 $AMSBIN/ams <<eor
System
  Atoms
    H 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine ADF

```

(continues on next page)

(continued from previous page)

```

create H $AMSRESOURCES/ADF/Special/Vdiff/H.2p
corepotentials t12.rel
  H 1
end
EndEngine
eor

```

```

AMS_JOBNAME=H2 $AMSBIN/ams <<eor
System
  atoms
    H 0 0 -0.37305
    H 0 0 0.37305
  end
  ElectrostaticEmbedding
    ElectricField 0 0 0.001 [a.u.]
  End
end

```

```
Task SinglePoint
```

```

Engine ADF
  title expt geometry H2(VII),VWN
  fragments
    H H7.results/adf.rkf
  end
  noprint sfo,frag,functions
  numericalquality Good
  response
    allcomponents
    dynahyp
    hyperpol 0.03 [Hartree]
  end
  symmetry C(8v)
EndEngine
eor

```

```

# The Response data block specifies (AllComponents) that not only the (default)
# zz-dipole polarizability is to be computed, but the complete tensor. The
# subkey HyperPol instructs the program to compute hyper*polarizabilities and
# not only polarizabilities. The DynaHyp subkey implies that the *frequency-
# dependent (hyper)polarizability is calculated. In that case the main laser
# frequency has to be specified, in hartree units, after the HyperPol subkey.

```

```

# Only the first hyperpolarizability has been implemented in ADF. Some
# information on second hyperpolarizabilities can be obtained from the
# calculation of the first one in a finite field (ElectricField).

```

```

# In similar fashion the frequency-dependent hyperpolarizability is computed for
# He, but only the zzz-component because now the AllComponents subkey is
# omitted.

```

```

AMS_JOBNAME=He $AMSBIN/ams <<eor
System
  atoms
    He 0 0 0

```

(continues on next page)

(continued from previous page)

```

end
ElectrostaticEmbedding
  ElectricField 0 0 0.001 [a.u.]
End
end

Task SinglePoint

Engine ADF
  title hyperpolarizability He with the LB94 potential
  fragments
    He He8.results/adf.rkf
  end
  noprint sfo,frag,functions
  numericalquality Good
  response
    dynahyp
    hyperpol 0.07 [Hartree]
  end
  scf
    accelerationmethod LISTi
    converge 1e-8
  end
  symmetry C(8v)
  xc
    gga LB94
  end
EndEngine
eor

```

Example: Damped Verdet constants: Propene

Download DampedVerdet.run

```

#!/bin/sh

# Specify the subkey MAGOPTROT in the AORESPONSE key to calculate the Verdet
# constant. Here it is specified together with the LIFETIME key, such that the
# real and imaginary part of the damped Verdet constant will be calculated.

$AMSBIN/ams <<eor
System
atoms
  C 0.867000 1.441800 3.000000
  C 0.849400 2.777300 3.000000
  C 2.115500 0.591200 3.000000
  H -0.088300 0.909000 3.000000
  H -0.085900 3.336500 3.000000
  H 1.772400 3.363200 3.000000
  H 2.737100 0.793300 2.115200
  H 1.876900 -0.479100 3.000000
  H 2.737100 0.793300 3.884800
end

```

(continues on next page)

(continued from previous page)

```
end

Task SinglePoint

Engine ADF
  title Propene
  allpoints
  aoresponse
    alda
    frequencies 0.2 [Hartree]
    giao
    lifetime 0.007
    magoptrot
    scf converge 1d-5 iterations 25
  end
  beckegrid
    quality good
  end
  basis
    core None
    type DZP
  end
  noprint sfo
  symmetry nosym
  xc
    model SAOP
  end
EndEngine

eor
```

Example: Static magnetizability: H2O

Download `H2O_magnet.run`

```
#!/bin/sh

# Basic example for a magnetizability calculation.

# One should set iterations=0 for STATIC magnetizability. If one does not use
# SYMMETRY NOSYM, one should set use ALLPOINTS for correct results in
# AORESPONSE.

AMS_JOBNAME=Static $AMSBIN/ams <<eor
System
  atoms
    O 0.0 0.0 0.0
    H 0.0 -0.7569504380226135 -0.5858823657035828
    H 0.0 0.7569504380226135 -0.5858823657035828
  end
end

Task SinglePoint
```

(continues on next page)

(continued from previous page)

```

Engine ADF
  allpoints
  aoresponse
    alda
    magneticpert
    scf iterations 0 converge 1e-3
  end
  linearscaling 100
end
basis
  core None
  type DZP
end
xc
  gga revPBE
  lda
end
EndEngine
eor

AMS_JOBNAME=Frequency $AMSBIN/ams <<eor
System
  atoms
    O 0.0 0.0 0.0
    H 0.0 -0.7569504380226135 -0.5858823657035828
    H 0.0 0.7569504380226135 -0.5858823657035828
  end
end

Task SinglePoint

Engine ADF
  allpoints
  aoresponse
    alda
    frequencies 0.182253 0.197012 [Hartree]
    magneticpert
    scf iterations 30 converge 1e-3
  end
  basis
    core None
    type DZP
  end
  linearscaling 100
end
xc
  gga revPBE
  lda
end
EndEngine
eor

```

Example: Dynamic magnetizability: H2O

Download H2O_TD_magnet.run

```
#!/bin/sh

# Example for time-dependent magnetizability with GIAOs (Gauge including atomic
# orbitals).

$AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.134692    0.000000
    H      0.869763   -0.538741    0.000000
    H     -0.869763   -0.538794    0.000000
  end
end

Task SinglePoint

Engine ADF
  title H2O, TD magnetizability
  allpoints
  aoresponse
    alda
    fitaoderiv
    frequencies 2.103923139 [eV]
    gao
    magneticpert
    scf conv 1d-6 iter 25
  end
  comment
    purpose of this job is to calculate time-dependent magnetizability
    with GIAOs
  end
  linearscaling 100
end
basis
  core None
  type TZP
end
numericalquality good
symmetry nosym
xc
  gga revPBE
  lda vwn
end
EndEngine
eor
```

Example: Time-dependent current-density-functional theory: C2H4:

Download C2H4_TDCDFT.run

```
#!/bin/sh

# Calculation of excitation energies and response properties of C2 H4 , with the
# VK functional, thus using time-dependent current-density-functional theory.

AMS_JOBNAME=C2H4_ET-pVQZ $AMSBIN/ams <<eor
Task SinglePoint
System
  Atoms
    C 0.000000    0.000000    0.666318
    C 0.000000    0.000000   -0.666318
    H 0.000000    0.928431    1.239388
    H 0.000000   -0.928431    1.239388
    H 0.000000    0.928431   -1.239388
    H 0.000000   -0.928431   -1.239388
  END
END
Engine ADF
  title C2H4 excitation energy calculation with the VK functional
  basis
    Type ET/ET-pVQZ
  END
  EXCITATIONS
  END
  CURRENTRESPONSE
  END
EndEngine
eor

AMS_JOBNAME=C2H4_TZ2P $AMSBIN/ams <<eor
Task SinglePoint
System
  Atoms
    C 0.000000    0.000000    0.666318
    C 0.000000    0.000000   -0.666318
    H 0.000000    0.928431    1.239388
    H 0.000000   -0.928431    1.239388
    H 0.000000    0.928431   -1.239388
    H 0.000000   -0.928431   -1.239388
  END
End
Engine ADF
  title C2H4 response calculation with the VK functional
  basis
    Type TZ2P
  END
  RESPONSE
  ALLCOMPONENTS
  END
  CURRENTRESPONSE
  END
```

(continues on next page)

(continued from previous page)

```
EndEngine
eor
```

Example: Damped complex polarizabilities with POLTDDFT: Au10

Download Au10_POLTDDFT.run

```
#!/bin/sh

# Calculation of damped complex polarizabilities of Au10
# with POLTDDFT.
# It is very important to use basis sets with specially made
# auxiliary fit sets available in $AMSHOME/atomicdata/ADF/POLTDDFT
#
# Symmetry irreps are chosen which for which the electronic transitions
# are dipole allowed.
# The analysis option is used, which will give an analysis
# of the absorption and CD spectrum in terms of single orbital transitions.
# If the regionsforanalysis option is used, the absorption and CD spectrum
# will be split in region_i -> region_j terms.

$AMSBIN/ams <<eor
System
  atoms
    Au      -1.44000000    0.00000000    2.88000000 region=Au4
    Au       1.44000000   -0.00000000   -2.88000000 region=Au4
    Au      -1.44000000    0.00000000   -2.88000000 region=Au4
    Au       1.44000000   -0.00000000    2.88000000 region=Au4
    Au      -0.00000000   -2.03647000   -1.44000000 region=Au6
    Au       0.00000000    2.03647000   -1.44000000 region=Au6
    Au       1.44000000   -0.00000000    0.00000000 region=Au6
    Au      -0.00000000   -2.03647000    1.44000000 region=Au6
    Au      -1.44000000    0.00000000   -0.00000000 region=Au6
    Au       0.00000000    2.03647000    1.44000000 region=Au6
  end
end

Task SinglePoint

Engine ADF
  title Au10 DZ GGA LB94
  basis
    Type POLTDDFT/DZ
  end
  poltddft
    irrep
      B1.u
      B2.u
      B3.u
    end
    analysis
      regionsforanalysis Au4 Au6
    end
  xc
    gga LB94
```

(continues on next page)

(continued from previous page)

```

end
EndEngine
eor

```

Example: POLTDDFT with hybrid functional: NH3

Download NH3_POLTDDFT.run

```

#!/bin/sh

# Calculation of damped complex polarizabilities of NH3 with POLTDDFT.
# A hybrid XC functionals is used.
# For hybrid functionals POLTDDFT will use HDA (hybrid diagonal approximation).
# For speed reasons one should not use a too large value for CutOff.
# To further speed up HDA one can use the subkey HDA_fitted, as is
# done in the second example.
# It is very important to use basis sets with specially made
# auxiliary fit sets available in $AMSHOME/atomicdata/ADF/POLTDDFT

AMS_JOBNAME=NH3 $AMSBIN/ams << eor
System
  symmetrize
  atoms
    N  0.000000  0.000000  0.000000
    H  0.956305  0.000000  0.292372
    H -0.478152  0.828184  0.292372
    H -0.478152 -0.828184  0.292372
  end
end

Task SinglePoint

Engine ADF
  Basis
    Type POLTDDFT/TZP
  End

  XC
    Hybrid B3LYP
  End

  POLTDDFT
    KGrid 40.
    NGrid 1600
    FreqRange 0.02 20.02
    NFreq 1000
    Lifetime 0.075
    Cutoff 20.
  END
EndEngine
eor

AMS_JOBNAME=NH3_HDA_fited $AMSBIN/ams << eor
System
  symmetrize

```

(continues on next page)

(continued from previous page)

```

atoms
  N   0.000000   0.000000   0.000000
  H   0.956305   0.000000   0.292372
  H  -0.478152   0.828184   0.292372
  H  -0.478152  -0.828184   0.292372
end
end

Task SinglePoint

Engine ADF
  Basis
    Type POLTDDFT/TZP
  End

  XC
    Hybrid B3LYP
  End

  POLTDDFT
    KGrid 40.
    NGrid 1600
    FreqRange 0.02 20.02
    NFreq 1000
    Lifetime 0.075
    Cutoff 20.
    HDA_fitted
  END
EndEngine
eor

```

Example: POLTDDFT with range-separated functional: C2F4-C2H2

Download POLTDDFT_CAMYB3LYP.run

```

#!/bin/sh

# Calculation of damped complex polarizabilities of a C2F4-C2H2 complex with POLTDDFT.
# The range-separated CAMY-B3LYP functional is used.
# Range-separated XC functionals that use XCFUN can be used with PolTDDFT,
# if one includes the subkey HDA_fitted in the PolTDDFT key.
# Range-separated XC functionals that use LibXC can not be used with PolTDDFT.

# For PolTDDFT it is very important to use basis sets with specially made
# auxiliary fit sets available in $AMSHOME/atomicdata/ADF/POLTDDFT

$AMSBIN/ams << eor
System
  symmetrize
  Atoms
    F -1.394866 -1.110938 -1.070259
    F -1.394866  1.110938 -1.070259
    F  1.394866 -1.110938 -1.070259
    F  1.394866  1.110938 -1.070259
    C -0.667784  0.000000 -1.088369
  
```

(continues on next page)

(continued from previous page)

```

C 0.667784 0.000000 -1.088369
H -1.244242 0.935429 3.830123
H -1.244242 -0.935429 3.830123
H 1.244242 0.935429 3.830123
H 1.244242 -0.935429 3.830123
C -0.674558 0.000000 3.833889
C 0.674558 0.000000 3.833889
End
End
Task SinglePoint
Engine ADF
Basis
Type POLTDDFT/TZP
End
Eprint
Eigval 1000 1000
Orbpopper -1000 1000
End
Poltdfft
Irrep
A1
B1
B2
SubEnd
KGrid 100.
NGrid 4000
FreqRange 0.02 10.02
NFreq 500
Lifetime 0.075
Cutoff 50.
HDA_fitted
End
xc
HYBRID CAMY-B3LYP
xcfun
End
EndEngine
eor

```

15.4.6 Ligand Field DFT (LFDFT)

Example: Ligand Field DFT: Co 2+

Download Co_LFDFT.run

```

#!/bin/sh

# Application of the Ligand Field DFT approach for a Co^2+ d^7 electron
# configuration. Here Co is surrounded by 6 Water molecules.

```

(continues on next page)

(continued from previous page)

```
# First an average of configuration calculation (AOC) is performed, where 7
# electrons are equally distributed over the 5 orbitals that have the most
# dominant Co 3d character. Depending on the electron configuration this might
# be a non-trivial task. Symmetry NOSYM should be specified.
```

```
SCM_LFDFT="$AMSHOME/examples/adf/Co_LFDFT/LFDFT"
export SCM_LFDFT
```

```
$AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

Co	0.000000	0.000000	0.000000
O	2.113495	0.000000	0.000000
H	2.687264	-0.787336	0.000000
H	2.687264	0.787336	0.000000
O	0.000000	-2.016255	0.000000
H	0.000000	-2.587300	0.791160
H	0.000000	-2.587300	-0.791160
O	-2.113495	0.000000	0.000000
H	-2.687264	-0.787336	0.000000
H	-2.687264	0.787336	0.000000
O	0.000000	2.016255	0.000000
H	0.000000	2.587300	0.791160
H	0.000000	2.587300	-0.791160
O	0.000000	0.000000	2.124849
H	0.785128	0.000000	2.701737
H	-0.785128	0.000000	2.701737
O	0.000000	0.000000	-2.124849
H	0.785128	0.000000	-2.701737
H	-0.785128	0.000000	-2.701737

```
end
```

```
charge 2
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
irrepoccupations
```

```
A 56 1.4 1.4 1.4 1.4 1.4
```

```
end
```

```
basis
```

```
core small
```

```
type TZP
```

```
end
```

```
relativity
```

```
level scalar
```

```
formalism ZORA
```

```
end
```

```
symmetry nosym
```

```
xc
```

```
gga bp86
```

```
end
```

```
EndEngine
```

```
eor
```

(continues on next page)

(continued from previous page)

```

# When the AOC calculation is ready, you need to make sure that indeed the
# partially occupied orbitals are dominantly d orbitals. In the ADF output you
# can find the character of the MOs in the list of all MOs, ordered by energy,
# with the most significant SFO gross populations.

# Next two LFDFT calculations are performed, first without spin-orbit coupling
# (soc 0), next including spin-orbit coupling (soc 1). In this case there is 1
# shell, and the nlval for 3d is '3 2'. The MO indices should be the
# fractionally occupied levels of the AOC calculation (in this case 29 30 31 32
# 33).

$AMSBIN/lfdft <<eor
  adffile ams.results/adf.rkf
  nshell 1
  nlval1 3 2
  MOind1 29 30 31 32 33
  soc    0
eor

$AMSBIN/lfdft <<eor
  adffile ams.results/adf.rkf
  nshell 1
  nlval1 3 2
  MOind1 29 30 31 32 33
  soc    1
eor

```

Example: Ligand Field DFT: f-d transitions in Pr 3+

Download Pr_LFDFT.run

```

#!/bin/sh

# Application of the Ligand Field DFT approach for the atomic Pr 4f^2 -> Pr 4f^1
# 5d^1 transition.

# First an average of configuration calculation (AOC) is performed for the 4f^2
# electron configuration, where 2 electrons are equally distributed over the 7
# orbitals that have the most dominant Pr 4f character. Depending on the
# electron configuration this might be a non-trivial task.

SCM_LFDFT="$AMSHOME/examples/adf/Pr_LFDFT/LFDFT"
export SCM_LFDFT

AMS_JOBNAME=f2 $AMSBIN/ams <<eor
System
atoms
  Pr      0.000000    0.000000    0.000000
end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  irrepopulations
    A 54 0.2857143 0.2857143 0.2857143 0.2857143 0.2857143 0.2857143 0.2857143
  end
  basis
    core none
    type ZORA/TZ2P+
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  symmetry nosym
EndEngine
eor

# Next the an LFDFT calculation is performed including spin-orbit coupling (soc
# 1). In this case there is 1 shell, and the nlval for 4f is '4 3'. The MO
# indices should be the fractionally occupied levels of the AOC calculation (28
# 29 30 31 32 33 34). Results are added on adf.rkf.

$AMSBIN/lfdft <<eor
  adffile f2.results/adf.rkf
  nshel 1
  nlval 4 3
  MOind 28 29 30 31 32 33 34
  soc 1
eor

rm logfile

# Next an average of configuration calculation (AOC) is performed for the 4f^1
# 5d^1 electron configuration, where 1 electron is equally distributed over the
# 7 orbitals that have the most dominant Pr 4f character, and 1 electron is
# equally distributed over the 7 orbitals that have the most dominant Pr 5d
# character. Depending on the electron configuration this might be a non-trivial
# task.

AMS_JOBNAME=f1d1 $AMSBIN/ams <<eor
System
  atoms
    Pr          0.000000    0.000000    0.000000
  end
end

Task SinglePoint

Engine ADF
  irrepopulations
    A 54 0.1428571 0.1428571 0.1428571 0.1428571 0.1428571 0.1428571 0.1428571 0.2 0.
    ↪ 2 0.2 0.2 0.2
  end
  basis

```

(continues on next page)

(continued from previous page)

```

    core none
    type ZORA/TZ2P+
end
numericalquality good
relativity
    level scalar
    formalism ZORA
end
symmetry nosym
EndEngine
eor

# Next the an LFDFT calculation is performed including spin-orbit coupling for
# both 4f and 5d (soc 1 1). In this case there are 2 shells, and the nlval for
# 4f is '4 3', and for 5d '5 2'. The MO indices should be the fractionally
# occupied levels of the AOC calculation for 4f (28 29 30 31 32 33 34), and for
# 5d (35 36 37 38 39). Results are added on adf.rkf.

$AMSBIN/lfdft <<eor
adffile f1d1.results/adf.rkf
nshel 2
nlval1 4 3
nlval2 5 2
MOind1 28 29 30 31 32 33 34
MOind2 35 36 37 38 39
soc 1 1
eor

rm logfile

# Next excitation energies are calculated for exciting from the ground state of
# the Pr 4f2 -> Pr 4f1 5d1. Input for lfdft_tdm are the 2 .t21 files that were
# calculated previously. Results of the excitation energies are added on the
# adf.rkf file belonging to state2.

$AMSBIN/lfdft_tdm <<eor
state1 f2.results/adf.rkf
state2 f1d1.results/adf.rkf
eor

```

Example: LFDFT: g-tensor of Co(acacen)

Download Co_LFDFT_gtensor.run

```

#!/bin/sh

# Application of the Ligand Field DFT approach for the calculation
# of the g-tensor. The g-tensor is only calculated for Kramer doublet states.
# This example calculates the g-tensor of the ground and excited doublet states
# of Co(acacen) with a Co d7 electron configuration.

# First an average of configuration calculation (AOC) is performed, where 7
# electrons are equally distributed over the 5 orbitals that have the most
# dominant Co 3d character. Depending on the electron configuration this might
# be a non-trivial task. Here the Keeporbitals=0 and Freeze functionality is used,

```

(continues on next page)

(continued from previous page)

```

# such that ADF will on successive SCF cycles assign electrons to the MOs
# that maximally resemble - in spatial form - those that were occupied in 0th
# (in fact 1st) cycle. Note that the orbitals that have the most
# dominant Co 3d character in the 1st cycle are orbitals 71, 72, 73, 74, and 75,
# whereas at the end of the SCF they are 71, 72, 73, 74, and 77.
#
# Symmetry NOSYM should be specified.

SCM_LFDFT="$AMSHOME/examples/adf/Co_LFDFT/LFDFT"
export SCM_LFDFT

$AMSBIN/ams <<eor
System
  Atoms
    Co      0.000000      0.000000      0.000000
    N      1.327385      1.278147      0.000000
    N      1.327385     -1.278147      0.000000
    O     -1.395357      1.224920      0.000000
    O     -1.395357     -1.224920      0.000000
    C      2.704031      0.764453      0.000000
    C      2.704031     -0.764453      0.000000
    C     -1.309408      2.515386      0.000000
    C     -1.309408     -2.515386      0.000000
    C      1.166666      2.611094      0.000000
    C      1.166666     -2.611094      0.000000
    C     -0.103243     -3.216502      0.000000
    C     -0.103243      3.216502      0.000000
    H      3.246281     -1.139682      0.884137
    H      3.246281      1.139682      0.884137
    H      3.246281      1.139682     -0.884137
    H      3.246281     -1.139682     -0.884137
    C     -2.626185      3.259046      0.000000
    C     -2.626185     -3.259046      0.000000
    C      2.374732      3.518898      0.000000
    C      2.374732     -3.518898      0.000000
    H     -3.453721     -2.540862      0.000000
    H     -3.453721      2.540862      0.000000
    H     -0.145492      4.305797      0.000000
    H     -0.145492     -4.305797      0.000000
    H      3.008094      3.350507      0.884680
    H      3.008094     -3.350507      0.884680
    H      3.008094      3.350507     -0.884680
    H      3.008094     -3.350507     -0.884680
    H     -2.710536      3.904463      0.886944
    H     -2.710536     -3.904463      0.886944
    H     -2.710536      3.904463     -0.886944
    H     -2.710536     -3.904463     -0.886944
    H      2.061821     -4.568536      0.000000
    H      2.061821      4.568536      0.000000
  End
  Charge 0
End

task SinglePoint

Engine adf

```

(continues on next page)

(continued from previous page)

```

Symmetry NOSYM
IrrepOccupations
  A 140 1.4 1.4 1.4 1.4 1.4
End
Occupations Keeporbitals=0 Freeze
basis
  Core None
  Type DZ
  PerAtomType Symbol=Co File=ZORA/TZP/Co
End
XC
  GGA PBE
End
EndEngine
eor

# When the AOC calculation is ready, you need to make sure that indeed the
# partially occupied orbitals are dominantly d orbitals. In the ADF output you
# can find the character of the MOs in the list of all MOs, ordered by energy,
# with the most significant SFO gross populations.

# First the LFDFT calculation is performed without spin-orbit coupling (soc 0),
# in which pure spin states are calculated, doublets and quartets in this case.
# Next the LFDFT calculation is performed including spin-orbit coupling (soc 1),
# which is needed for the g-tensor calculation. In this case there is 1
# shell, and the nlval for 3d is '3 2'. The MO indices should be the
# fractionally occupied levels of the AOC calculation (in this case 71 72 73 74 77).

# One should be careful when interpreting the g-tensor for 2 Kramer doublets
# that are close in energy. In the effective Hamiltonian used to interpret ESR
# experiments, an effective spin=3/2 might be used.

$AMSBIN/lfdft << eor
  adffile ams.results/adf.rkf
  nshel 1
  nlval 3 2
  MOind 71 72 73 74 77
  soc 0.0
  DegeneracyThreshold 1.0E-5
eor

$AMSBIN/lfdft << eor
  adffile ams.results/adf.rkf
  nshel 1
  nlval 3 2
  MOind 71 72 73 74 77
  soc 1.0
  DegeneracyThreshold 1.0E-5
eor

```

Example: LFDFT: g-tensor of Cu(H₂O)₆

Download Cu_LFDFT_gtensor.run

```
#!/bin/sh

# Application of the Ligand Field DFT approach for the calculation
# of the g-tensor. The g-tensor is only calculated for doublet states.
# This example calculates the g-tensor of the ground and excited doublet states
# of [Cu(H2O)6]^2+ with a Cu^2+ d^9 electron configuration.

# First an average of configuration calculation (AOC) is performed, where 9
# electrons are equally distributed over the 5 orbitals that have the most
# dominant Cu 3d character. Depending on the electron configuration this might
# be a non-trivial task. Symmetry NOSYM should be specified.

SCM_LFDFT="$AMSHOME/examples/adf/Cu_LFDFT_gtensor/LFDFT"
export SCM_LFDFT

$AMSBIN/ams <<eor
System
  Atoms
    Cu      0.000000    0.000000    0.000000
    O       0.000000    0.000000    2.325873
    O       0.000000    0.000000   -2.325873
    O      -2.004009    0.000000    0.000000
    O       2.004009    0.000000    0.000000
    O       0.000000   -2.004009    0.000000
    O       0.000000    2.004009    0.000000
    H       0.000000    0.773171   -2.924278
    H       0.000000   -0.773171   -2.924278
    H      -0.794410    2.570047    0.000000
    H       0.794410    2.570047    0.000000
    H      -2.570047    0.000000   -0.794410
    H      -2.570047    0.000000    0.794410
    H       0.794410   -2.570047    0.000000
    H      -0.794410   -2.570047    0.000000
    H       2.570047    0.000000   -0.794410
    H       2.570047    0.000000    0.794410
    H       0.000000   -0.773171    2.924278
    H       0.000000    0.773171    2.924278
  End
  Charge 2
End

task SinglePoint

Engine adf
  Symmetry NOSYM
  IrrepOccupations
    A 78 1.8 1.8 1.8 1.8 1.8
  End
  basis
    Core None
    Type TZP
  End
  XC
```

(continues on next page)

(continued from previous page)

```

    GGA PBE
  End
EndEngine
eor

# When the AOC calculation is ready, you need to make sure that indeed the
# partially occupied orbitals are dominantly d orbitals. In the ADF output you
# can find the character of the MOs in the list of all MOs, ordered by energy,
# with the most significant SFO gross populations.

# Next the LFDFT calculation is performed including spin-orbit coupling (soc 1),
# which is needed for the g-tensor calculation. In this case there is 1
# shell, and the nlval for 3d is '3 2'. The MO indices should be the
# fractionally occupied levels of the AOC calculation (in this case 40 41 42 43 44).

$AMSBIN/lfdft << eor
adffile ams.results/adf.rkf
nshel 1
nlval 3 2
MOind 40 41 42 43 44
soc 1.0
DegeneracyThreshold 1.0E-5
eor

```

Example: LFDFT: XMCD 3d-4f transitions in Er 3+

Download Er_LFDFT_MCD.run

```

#!/bin/sh

# Application of the Ligand Field DFT approach for the calculation
# of the X-ray Magnetic Circular Dichroism (XMCD) for lanthanide ion and complexes.
# This example calculates the XMCD spectra of the Er3+ ion
# for an Er 4f11 (ground state) -> Er 3d9 4f12 transition, in which case a 3d core
# electron is promoted to the 4f shell.

# First an average of configuration calculation (AOC) is performed, where 11
# electrons are equally distributed over the 7 orbitals that have the most
# dominant Er 4f character. Depending on the electron configuration this might
# be a non-trivial task.
# Symmetry NOSYM should be specified.

SCM_LFDFT="$AMSHOME/examples/adf/Er_LFDFT_MCD/LFDFT"
export SCM_LFDFT

AMS_JOBNAME=GS $AMSBIN/ams <<eor
System
  Atoms
    Er      0.0000000000      0.0000000000      0.0000000000
  End
  Charge +3
End

task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine adf
  Unrestricted No
  Symmetry NOSYM
  IrrepOccupations
    A 54 1.571428571428571 1.571428571428571 1.571428571428571 1.571428571428571 1.
    ↪ 571428571428571 1.571428571428571 1.571428571428571
  End
  basis
    Core None
    Type TZP
  End
  XC
    GGA PBE
  End
EndEngine
eor

# When the AOC calculation is ready, you need to make sure that indeed the
# partially occupied orbitals are dominantly f orbitals. In the ADF output you
# can find the character of the MOs in the list of all MOs, ordered by energy,
# with the most significant SFO gross populations.

# Next the LFDFT calculation is performed including a magnetic field of 1 Tesla
# in the z-direction (Bfield 0 0 1),
# which is needed for the XMCD calculation. In this case there is 1
# shell, and the nlval for 4f is '4 3'. The MO indices should be the
# fractionally occupied levels of the AOC calculation (in this case 28 29 30 31 32 33 ↪
    ↪ 34).

$AMSBIN/lfdft << eor
adffile GS.results/adf.rkf
nshel 1
nlval 4 3
MOind 28 29 30 31 32 33 34
soc 1.0
Bfield 0.0 0.0 1.0
DegeneracyThreshold 1.0E-8
eor

# Then, we need to calculate the electronic structure corresponding to the Er
# core electron excitation. In this case, we promote 1 electron from 3d orbitals
# to the 4f. Therefore, an average of configuration calculation (AOC) is
# performed, where 9 electrons are equally distributed over the 5 orbitals
# that have the most dominant Er 3d character; and 11+1 electrons are
# equally distributed over the 7 orbitals that have the most dominant Er 4f
# character. Symmetry NOSYM should be specified.

AMS_JOBNAME=ES $AMSBIN/ams <<eor
System
  Atoms
    Er      0.0000000000      0.0000000000      0.0000000000
  End
  Charge +3
End

task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine adf
  Unrestricted No
  Symmetry NOSYM
  IrrepOccupations
    A 18 1.8 1.8 1.8 1.8 1.8 26 1.714285714285714 1.714285714285714 1.714285714285714
    ↪ 1.714285714285714 1.714285714285714 1.714285714285714 1.714285714285714
  End
  basis
    Core None
    Type TZP
  End
  XC
    GGA PBE
  End
EndEngine
eor

# When the AOC calculation is ready, you need to make sure that indeed the
# partially occupied orbitals are dominantly d and f orbitals. In the ADF output you
# can find the character of the MOs in the list of all MOs, ordered by energy,
# with the most significant SFO gross populations.

# Next the LFDFT calculation is performed, again including a magnetic field of 1
↪ Tesla
# in the z-direction (Bfield 0 0 1),
# which is needed for the XMCD calculation. In this case there are 2
# shells, and the nlval for 3d is '3 2' and 4f is '4 3'. The MO indices should be the
# fractionally occupied levels of the AOC calculation
# (in this case 10, 11, 12, 13, and 14 for the 3d; and 28, 29, 30, 31, 32, 33, and 34
↪ for 4f).

$AMSBIN/lfdft << eor
  adffile ES.results/adf.rkf
  nshel 2
  nlval1 3 2
  nlval2 4 3
  MOind1 10 11 12 13 14
  MOind2 28 29 30 31 32 33 34
  soc 1.0 1.0
  Bfield 0.0 0.0 1.0
  DegeneracyThreshold 1.0E-08
eor

# Finally, we use lfdft_tdm to calculate the oscillator strengths for the
# Er 4f11 (ground state) -> 3d9 4f12 transitions.
# Input for lfdft_tdm are the 2 adf.rkf files that were
# calculated previously. Results of the excitation energies are added on the
# adf.rkf file belonging to state2.

$AMSBIN/lfdft_tdm << eor
  STATE1 GS.results/adf.rkf
  STATE2 ES.results/adf.rkf
eor

```

15.4.7 NMR chemical shifts and spin-spin coupling constants

Example: NMR Chemical Shifts: HBr

Download HBr.run

```
#!/bin/sh

# Computation of the NMR chemical shifts for HBr.

# == Non-relativistic ==

AMS_JOBNAME=NR $AMSBIN/ams <<eor
System
  atoms
    H   .0000 .0000 .0000
    Br  .0000 .0000 1.4140
  end
end

Task SinglePoint

Engine ADF
  basis CreateOutput=Yes
  save TAPE10
  title HBr non-relativistic
  xc
    gga Becke Perdew
  end
  zlmfit
    quality good
  end
  Relativity
    Level None
  End
EndEngine
eor

# The TAPE21 result file and TAPE10 of ADF must be present under those names for
# the NMR calculation
# The NMR program uses mostly only one input (block) key NMR. The subkeys
# specify what output is produced (OUT) and for which Nuclei the NMR data are
# computed and printed (NUC). See the ADF manual.

$AMSBIN/nmr <<eor
tape10file NR.results/TAPE10
adffile NR.results/adf.rkf
NMR
  Out  TENS
  Nuc  1  2
End
eor

rm logfile TAPE15
```

(continues on next page)

(continued from previous page)

```

# == Scalar relativistic ZORA (default) ==

AMS_JOBNAME=SR $AMSBIN/ams <<eor
System
  atoms
    H   .0000 .0000 .0000
    Br  .0000 .0000 1.4140
  end
end

Task SinglePoint

Engine ADF
  basis CreateOutput=Yes

  save TAPE10
  title HBr scalar relativistic ZORA
  xc
    gga Becke Perdew
  end
  zlmfit
    quality good
  end
EndEngine
eor

$AMSBIN/nmr <<eor
tape10file SR.results/TAPE10
adffile SR.results/adf.rkf
NMR
  Out  TENS
  Nuc  1  2
End
eor

rm logfile TAPE15

# == Relativistic spin-orbit ZORA ==

# Using Spin-Orbit implies that NOSYM symmetry must be used in the ADF
# calculation: the NMR program cannot handle symmetry calculations in
# combination with spin-orbit terms and will stop with an error message if you
# try to do so.

AMS_JOBNAME=SO $AMSBIN/ams <<eor
System
  atoms
    H   .0000 .0000 .0000
    Br  .0000 .0000 1.4140
  end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  basis CreateOutput=Yes
  relativity
    level spin-orbit
    formalism ZORA
  end
  save TAPE10
  symmetry NoSYM
  title HBr relativistic spinorbit ZORA
  xc
    gga Becke Perdew
  end
  zlmfit
    quality good
  end
EndEngine
eor

$AMSBIN/nmr <<eor
tape10file SO.results/TAPE10
adffile SO.results/adf.rkf
NMR
  UIK BEST
  OUT TENS
  NUC 1 2
End
eor

rm logfile TAPE15

```

Example: NMR Chemical Shifts: HgMeBr

Three examples: a non-relativistic, a ZORA scalar relativistic, and a ZORA Spin-Orbit coupled one.

Download `HgMeBr_pnr.run`

```

#!/bin/sh

# NMR data are computed for the 1st and 3rd nucleus only. The UIK subkey is used
# to indicate that certain terms are to be included in the 'U-matrix', which
# goes into the first-order change of the MO's due to the applied magnetic
# field. See the documentation for more information.

# The 'BEST' specification means the best (recommended) options for each
# relativistic option are included for this sub key. In a non-relativistic run
# it has no meaning. In a spin-orbit run it would include the ZORA Spin-Orbit
# terms for a ZORA calculation.

$AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  Hg  0.0          0.0          0.0
  Br  0.0          0.0         -2.406
  C   0.0          0.0          2.074
  H   1.0289885545161663  0.0      2.4628220089896287
  H  -0.5144942772580832  0.8911302284144289  2.4628220089896287
  H  -0.5144942772580832 -0.8911302284144289  2.4628220089896287
end
end

Task SinglePoint

Engine ADF
  title HgMeBr
  basis
    Core Small
    Type DZ
    PerAtomType Symbol=C Core=None
  end
  noprint SFO, Frag, Functions
  numericalquality Good
  save TAPE10
  xc
    gga PW91
  end
  Relativity
    Level None
  End
EndEngine
eor

$AMSBIN/nmr << eor
tape10file ams.results/TAPE10
adffile ams.results/adf.rkf
NMR
  OUT ISO
  U1K BEST
  NUC 1 3
END
eor

```

Download HgMeBr_zsc.run

```

#!/bin/sh

$AMSBIN/ams <<eor
System
  atoms
    Hg  0.0          0.0          0.0
    Br  0.0          0.0         -2.406
    C   0.0          0.0          2.074
    H   1.0289885545161663  0.0      2.4628220089896287
    H  -0.5144942772580832  0.8911302284144289  2.4628220089896287
    H  -0.5144942772580832 -0.8911302284144289  2.4628220089896287
  end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  title HgMeBr, scalar, ZORA
  basis
    core None
    type DZ
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
  save TAPE10
  xc
    gga PW91
  end
EndEngine
eor

$AMSBIN/nmr <<eor
tape10file ams.results/TAPE10
adffile ams.results/adf.rkf
NMR
  OUT ISO
  U1K BEST
  NUC 1 3
END
eor

```

Download HgMeBr_zso.run

```

#!/bin/sh

$AMSBIN/ams <<eor
System
  atoms
    Hg  0.0          0.0          0.0
    Br  0.0          0.0         -2.406
    C   0.0          0.0          2.074
    H   1.0289885545161663  0.0      2.4628220089896287
    H  -0.5144942772580832  0.8911302284144289  2.4628220089896287
    H  -0.5144942772580832 -0.8911302284144289  2.4628220089896287
  end
end

Task SinglePoint

Engine ADF
  title HgMeBr, spinorbit, ZORA
  basis
    core None
    type DZ
  end
  numericalquality Good

```

(continues on next page)

(continued from previous page)

```

relativity
  level spin-orbit
  formalism ZORA
end
save TAPE10
symmetry NOSYM
xc
  gga PW91
end
EndEngine
eor

$AMSBIN/nmr <<eor
tape10file ams.results/TAPE10
adffile ams.results/adf.rkf
NMR
  OUT ISO
  U1K BEST
  NUC 1 3
END
eor
mv TAPE21 HgMeBr.t21

```

Example: NMR Chemical Shifts, SAOP potential: CH₄

Download CH4_SAOP.run

```

#!/bin/sh

# Computation of the NMR chemical shifts for CH4, with the model potential
# SAOP.

# Important: use SAVE TAPE10. This is necessary for SAOP, since the nmr program
# does not know about SAOP or other model potentials. On TAPE10 the SCF
# potential is written, which is read in by the nmr program.

# Note: For SAOP one needs an all-electron basis set (i.e. Core None)

$AMSBIN/ams <<eor
System
  atoms
    C 0 0 0
    H 0.6264250420707439 0.6264250420707439 0.6264250420707439
    H 0.6264250420707439 -0.6264250420707439 -0.6264250420707439
    H -0.6264250420707439 0.6264250420707439 -0.6264250420707439
    H -0.6264250420707439 -0.6264250420707439 0.6264250420707439
  end
end

Task SinglePoint

Engine ADF
  basis

```

(continues on next page)

(continued from previous page)

```

    type TZ2P
    core None
end
save TAPE10
xc
    model saop
end
EndEngine
eor

$AMSBIN/nmr <<eor
  adffile ams.results/adf.rkf
  tape10file ams.results/TAPE10
  NMR
    Out  TENS
    Nuc  1  2
  End
eor

```

Example: NMR Nucleus-independent chemical shifts (NICS): PF3

Download NMR_NICS.run

```

#!/bin/sh

# The NMR program enables the calculation of so-called nucleus-independent
# chemical shifts (NICS). More details are available in the Properties Programs
# User's Guide.

# In the ADF run, the ElectrostaticEmbedding key is used to define points charges_
↪with zero
# charge. The GHOSTS key in the nmr program then basically copies this block.
# For the interpretation of the results we refer to the literature.

AMS_JOBNAME=NICS $AMSBIN/ams <<eor
System
  atoms
    P      1.000000    0.000000    0.000000
    F      1.813256    1.425667    0.000000
    F      1.813256   -0.712834    1.234664
    F      1.813256   -0.712834   -1.234664
  end
  ElectrostaticEmbedding
    MultipolePotential
      Coordinates
        3.0 4.0 5.0 0.0
        1.0 2.0 3.0 0.0
      end
    end
  end
end
Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title PF3 - scf
  basis
    core Large
    type TZP
    CreateOutput Yes
  end
  numericalquality Good
  save TAPE10
  symmetry NOSYM
  xc
    gga revPBE
  end
  Relativity
    Level None
  End
EndEngine
eor

$AMSBIN/nmr <<eor
adffile NICS.results/adf.rkf
tape10file NICS.results/TAPE10
NMR
  Out Iso Tens
  GHOSTS
    3.0 4.0 5.0
    1.0 2.0 3.0
  END
END
eor

```

Example: NMR with B3LYP: PF3

Download NMR_B3LYP.run

```

#!/bin/sh

# This example shows how to do hybrid calculation of NMR chemical shifts.

# One needs of course a hybrid functional in the XC block key in ADF. One should
# also use SAVE TAPE10, such that it is an input file in the nmr module.

# In the input for the nmr module one can add the key ZSOA02007 to approximate
# the effect of spin on the nucleus in the spin-orbit coupled calculations.

# In the last example spin-orbit coupling is included. Symmetry should be NOSYM.

AMS_JOBNAME=NR $AMSBIN/ams <<eor
System
  atoms
    P      0.00000000      0.00000000      1.00000000
    F     -0.71283358      1.23466398      1.81325568

```

(continues on next page)

(continued from previous page)

```

      F      -0.71283358      -1.23466398      1.81325568
      F      1.42566716       0.00000000      1.81325568
    end
  end

Task SinglePoint

Engine ADF
  title PF3-NMR-B3LYP
  basis
    core None
    type DZP
  end
  noprint sfo
  numericalquality Good
  save TAPE10
  xc
    hybrid B3LYP
  end
  Relativity
    Level None
  End
EndEngine
eor

$AMSBIN/nmr <<eor
adffile NR.results/adf.rkf
tape10file NR.results/TAPE10
NMR
  U1K BEST
  Out TENS
  Nuc 1 2
  SCF 1.0e-4
End
eor

rm logfile

AMS_JOBNAME=SR $AMSBIN/ams <<eor
System
  atoms
    P      0.00000000      0.00000000      1.00000000
    F      -0.71283358      1.23466398      1.81325568
    F      -0.71283358     -1.23466398      1.81325568
    F      1.42566716       0.00000000      1.81325568
  end
end

Task SinglePoint

Engine ADF
  title PF3-NMR-B3LYP ZORA SCALAR
  basis
    core None
    type DZP
  end
  noprint sfo

```

(continues on next page)

(continued from previous page)

```

numericalquality Good
relativity
  level scalar
  formalism ZORA
end
save TAPE10
xc
  hybrid B3LYP
end
EndEngine
eor

$AMSBIN/nmr <<eor
adffile SR.results/adf.rkf
tape10file SR.results/TAPE10
NMR
  U1K BEST
  Out TENS
  Nuc 1 2
  SCF 1.0e-4
End
eor

rm logfile

AMS_JOBNAME=SO $AMSBIN/ams <<eor
System
  atoms
    P      1.000000    0.000000    0.000000
    F      1.813256    1.425667    0.000000
    F      1.813256   -0.712834    1.234664
    F      1.813256   -0.712834   -1.234664
  end
end

Task SinglePoint

Engine ADF
  title PF3-NMR-B3LYP ZORA SPINORBIT
  basis
    core None
    type DZP
  end
  noprint sfo
  numericalquality Good
  relativity
    level spin-orbit
    formalism ZORA
  end
  rihartreefock
    fitsetquality Normal
  end
  save TAPE10
  symmetry nosym
  xc
    hybrid B3LYP
  end

```

(continues on next page)

(continued from previous page)

```

EndEngine
eor

$AMSBIN/nmr <<eor
adffile SO.results/adf.rkf
tape10file SO.results/TAPE10
NMR
  USE   SO1C
  U1K   BEST
  Out   TENS
  Nuc   1  2
  SCF   1.0e-4
End
eor
rm logfile TAPE15

$AMSBIN/nmr <<eor
adffile SO.results/adf.rkf
tape10file SO.results/TAPE10
NMR
  U1K   BEST
  Out   TENS
  Nuc   1  2
  SCF   1.0e-4
End
eor
rm logfile TAPE15

```

Example: Partial ZORA analysis: NMR chemical shift

Download HI_PZora_NMR.run

```

#!/bin/sh

# Example shows the use of the PartialZORA keyword
# in ADF, which lets us selectively turn off the Spin-orbit
# interaction on certain atomic fragments. The NMR code has
# been adapted accordingly.
# Requires ZORA with spin-orbit coupling

# Job 1: Standard PartialZORA mode with all fragments listed.
# This disables all SO effects and results are equivalent to
# a scalar ZORA run with otherwise identical settings

AMS_JOBNAME=SR $AMSBIN/ams <<eor
System
  atoms
    H 0. 0. 0.
    I 0. 0. 1.60916
  end
end
Task SinglePoint
engine ADF
  PartialZORA atom 1 2
  Basis

```

(continues on next page)

(continued from previous page)

```

    core None
    type DZP
end
Relativity
    level spin-orbit
    formalism ZORA
end
Save TAPE10
Symmetry NOSYM
Usespcode
xc
    gga PBE
end
endengine
eor

$AMSBIN/nmr << eor
adffile SR.results/adf.rkf
tape10file SR.results/TAPE10
ALLINONE
NMR
    USE FXC
    U1K BEST
    OUT TENS
    nuc 1
END
eor

rm -f TAPE* logfile

# Job 2: Standard PartialZORA mode with Iodine (frag. 2) SO disabled.
# For the NMR, this recovers the scalar relativistic proton shielding

AMS_JOBNAME=FRAG2 $AMSBIN/ams <<eor
System
    atoms
        H 0. 0. 0.
        I 0. 0. 1.60916
    end
end
Task SinglePoint
engine ADF
    PartialZORA atom 2
    Basis
        core None
        type DZP
    end
    Relativity
        level spin-orbit
        formalism ZORA
    end
    Save TAPE10
    Symmetry NOSYM
    Usespcode
    xc
        gga PBE
    end

```

(continues on next page)

(continued from previous page)

```

endengine
eor

$AMSBIN/nmr << eor
adffile FRAG2.results/adf.rkf
tape10file FRAG2.results/TAPE10
ALLINONE
NMR
  USE FXC
  U1K BEST
  OUT TENS
  nuc 1
END
eor

rm -f TAPE* logfile

```

Example: open shell NMR (pNMR) shielding: O2

Download O2_pNMR.run

```

#!/bin/sh

# Example calculation open shell NMR (pNMR) chemical shielding.

# This can only be done at the scalar relativistic ZORA level,
# symmetry NOSYM, all electron basis sets,
# and one needs to include the key ALLINONE in the input for NMR

# Needed are the ESR g-tensor, the ESR hyperfine interaction on the nuclei,
# and the orbital dependent part of the NMR chemical shielding.
# The calculation of the orbital dependent part of the NMR chemical shielding
# should be done at the end.
# The ESR g-tensor and ESR A-tensor will be written to adf.rkf, and the nmr
# program will use those to calculate a temperature dependent contribution
# to the NMR chemical shielding.
# Effects due to zero-field splitting are neglected (possibly important for S>1/2).

# The temperature dependent part can be huge and is highly dependent on the
# calculated A-tensor (hyperfine interaction), which is highly dependent
# on the used basis set and used XC-functional, especially if the spin-polarization
↪effects
# on the nuclei are important, like this is the case in this example for O2.
# For an accurate evaluation of the spin-polarization density at the nucleus it is
# important to use an all-electron basis set for the nuclei that one is interested in,
# avoiding the frozen core approximation.
# The basis sets in the directories ZORA/TZ2P-J, ZORA/QZ4P-J are
# recommended for accurate hyperfine calculations.
# For heavy elements the incorporation of a Gaussian finite nucleus model can be
↪important.
# However, one should have really large basis sets with tight basis functions to
↪observe this
# effect in calculations.
# The basis sets in the directories ZORA/TZ2P-J, ZORA/QZ4P-J are suitable for finite
↪nucleus calculations.

```

(continues on next page)

(continued from previous page)

```
# Remark: do not use restricted open shell Kohn-Sham (ROKS), since that would
→ (incorrectly) give
# (almost) zero hyperfine interaction.
```

```
AMS_JOBNAME=SR "$AMSBIN/ams" << eor
```

```
Task SinglePoint
```

```
System
```

```
  Atoms
```

```
    O  0.000 0.000 -0.604
```

```
    O  0.000 0.000  0.604
```

```
  End
```

```
End
```

```
Engine ADF
```

```
  Basis
```

```
    Type TZ2P-J
```

```
    Core None
```

```
  End
```

```
  Occupations IntegerAufbau
```

```
  Unrestricted Yes
```

```
  SpinPolarization 2
```

```
  NumericalQuality Good
```

```
  Symmetry NOSYM
```

```
  XC
```

```
    GGA PBE
```

```
  End
```

```
  SAVE TAPE10
```

```
EndEngine
```

```
eor
```

```
# Calculation of the ESR A-tensors, which are written to adf.rkf
```

```
"$AMSBIN/cpl" << eor
```

```
adffile SR.results/adf.rkf
```

```
tape10file SR.results/TAPE10
```

```
hyperfine
```

```
  atoms 1 2
```

```
END
```

```
eor
```

```
rm logfile TAPE15
```

```
# Calculation of the ESR g-tensor, which is written to adf.rkf
```

```
"$AMSBIN/nmr" << eor
```

```
adffile SR.results/adf.rkf
```

```
tape10file SR.results/TAPE10
```

```
NMR
```

```
  gfactors
```

```
  out iso tens
```

```
  ulk best
```

```
  calc all
```

```
END
```

```
eor
```

```
rm logfile TAPE15
```

```
# Calculation of the orbital dependent part of the NMR chemical shielding
```

(continues on next page)

(continued from previous page)

```

# The ESR g-tensor and ESR A-tensors will be read from adf.rkf, and the nmr
# program will use those to calculate a temperature dependent contribution
# to the pNMR chemical shielding.
# ALLINONE is required.

"$AMSBIN/nmr" << eor
adffile SR.results/adf.rkf
tape10file SR.results/TAPE10
ALLINONE
NMR
    out iso tens
    atoms 1 2
    u1k best
    calc all
End
eor
rm logfile TAPE15

```

Example: NMR Spin-spin coupling constants: C2H2

Download CPL_C2H2.run

```

#!/bin/sh

# Non-relativistic calculation
# =====

# A calculation of NMR nuclear spin-spin coupling constants (NSCCs).

# As explained in the ADF manual, the quality of a calculation for spin-spin
# coupling constants, using the program 'CPL', depends largely on the preceding
# ADF calculation, which produces the Kohn-Sham orbitals and orbital energies,
# used as a starting point.

# One of the quality-determining factors is the chosen basis set. It should be
# sufficiently flexible near the nucleus. Although the all-electron basis TZ2P
# is chosen in this example, it is recommendable to add more functions to the
# basis sets near the nucleus in case of heavy elements. One could start from a
# ZORA/QZ4P basis for example.

# The NOSYM symmetry currently needs to be specified in ADF to enable the CPL
# program to work correctly.

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
  atoms
    C 0.0  0.0  0.0
    C 0.0  0.0  1.20692
    H 0.0  0.0  2.26672
    H 0.0  0.0 -1.0598
  end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  title C2H2 nrel
  beckegrid
    quality good
  end
  basis
    type TZ2P
    core None
  end
  save TAPE10
  symmetry NOSYM
  xc
    gga Becke Perdew
  end
  Relativity
    Level None
  End
EndEngine
eor

# The CPL program can run in parallel.

# The specification of what needs to be calculated is given in the nmrcoupling
# block key.

# coupling without the SD term
$AMSBIN/cpl <<eor
  adffile first.results/adf.rkf
  tape10file first.results/TAPE10
  nmrcoupling
    dso
    pso
    scf converge=1e-7
    nuclei 1 2 3 4
    nuclei 3 4
  end
eor
rm logfile

# In this first example, the SD subkey is left out, as this would lead to a very
# strong increase in the required CPU time. The SD subkey is included in the
# second CPL run. That subkey controls the calculation of the so-called spin-
# dipole term.

# The subkeys dso and pso specify that, respectively, the diamagnetic and
# paramagnetic orbital terms will be calculated. The often dominant Fermi
# contact term (FC) is calculated by default and therefore does not have to be
# specified explicitly.

# The scf convergence subkey, in this context, refers to the convergence for the
# solution of the coupled-perturbed Kohn-sham equations which need to be solved
# to obtain to spin-spin couplings.

```

(continues on next page)

(continued from previous page)

```

# The following lines
#   nuclei 1 2 3 4
#   nuclei 3 4
# specify that one coupled-perturbed Kohn-Sham calculation is performed where
# nucleus number 1 (according to the ordering in the ADF output) is the
# perturbing nucleus, and nuclei 2, 3, and 4 are the perturbed nuclei, and
# another coupled-perturbed Kohn-Sham calculation is performed where nucleus 3
# is the perturbing nucleus and nucleus 4 is the perturbed nucleus.

# The second CPL run also includes the spin-dipole (SD) term, through the SD
# subkey.

# The output of the CPL program first contains a lot of general information, a
# summary of the specified input, and then produces the desired numbers:

# It prints separately the different contributions (FC, DSO, PSO, SD) if
# specified in input and sums them up to a total number. Experimental NSCCs
# between two nuclei A and B are usually reported as J(A,B) in Hertz. From a
# computational point of view, the so-called reduced NSCCs K(A,B) are more
# convenient for comparisons. CPL outputs both. In this example, the Fermi-
# contact term is indeed dominant.

# The first part of the output refers to the line
#   nuclei 1 2 3 4
# then the same thing is done for the second similar line where nucleus 3 is the
# perturbing nucleus.

# The output for the second CPL run looks very similar, but now the SD term is
# added to the Fermi contact term, resulting in much longer execution times.

# == Scalar relativistic and spin-orbit calculations ==

# The CPL program also enables calculations using scalar relativistic effects
# (ZORA) and/or spin-orbit effects.

# Schematically, this requires the following changes to the input file with
# respect to a regular spin-orbit calculation and a non-relativistic CPL
# calculation:

# steep (1s) functions may need to be added to the standard basis sets. the
# full-potential option for ZORA is needed in the create runs and all further
# runs: relativistic zora scalar full the molecular ADF calculation should
# contain the line relativistic zora full spinorbit the CPL input is unmodified
# with respect to the example given here. Please check the ADF manual for
# details on relativistic input options.

# coupling including the SD term

$AMSBIN/cpl <<eor
adffile first.results/adf.rkf
tape10file first.results/TAPE10
nmrcoupling
  dso
  pso
  sd

```

(continues on next page)

(continued from previous page)

```

    scf converge=1e-7
    nuclei 1 2 3 4
    nuclei 3 4
  end
eor
rm logfile

# redo the same set of calculations, but with a different orientation
# of the molecule this time. Only the CPL calculation without the SD
# term is carried out in order to keep the execution time for this example
# within reasonable limits

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
  atoms
    C 0.0  0.0    0.0
    C 0.0  1.20692 0.0
    H 0.0  2.26672 0.0
    H 0.0 -1.0598  0.0
  end
end

Task SinglePoint

Engine ADF
  title C2H2 nrel
  beckegrid
  quality good
end
basis
  core None
  type TZ2P
end
save TAPE10
symmetry NOSYM
xc
  gga Becke Perdew
end
Relativity
  Level None
End
EndEngine
eor

# coupling without the SD term

$AMSBIN/cpl <<eor
  adffile second.results/adf.rkf
  tape10file second.results/TAPE10
  nmrcoupling
    dso
    pso
    scf converge=1e-7
    nuclei 1 2 3 4
    nuclei 3 4
  end
eor

```

(continues on next page)

(continued from previous page)

```
rm logfile
```

Example: NMR Spin-spin coupling constants, hybrid PBE0: HF

Download CPL_HF_hybrid.run

```
#!/bin/sh

# A calculation of NMR nuclear spin-spin coupling constants (NSCCs) for the
# hybrid PBE0.

# The hybrid PBE0 is chosen as exchange-correlation potential in the ADF
# calculation. The key 'usespcode' is required for consistency reasons of the
# PBE0 implementation in ADF and the kernel that is used in the 'CPL' program,
# that calculates NMR spin-spin coupling constants. Symmetry should be NOSYM.
# The basis sets used are specially optimized all-electron basis sets for NMR
# spin-spin coupling calculations (in the directory
# $AMSHOME/atomicdata/ZORA/jcpl), which have extra tight functions, compared to
# a default ADF basis set. The integration accuracy is extra high (Quality
# VeryGood).

$AMSBIN/ams <<eor
System
  atoms
    F 0.0000 0.0000 0.0000
    H 0.0000 0.0000 0.9170
  end
end

Task SinglePoint

Engine ADF
  basis
    core None
    type ZORA/jcpl
  end
  beckegrid
    quality verygood
  end
  scf
    converge 1e-8 1e-7
  end
  symmetry nosym
  usespcode
  xc
    hybrid PBE0
  end
EndEngine
eor

# The first call to cpl is as follows.
# The key 'gga' is included to use the first-order GGA potential instead of the
```

(continues on next page)

(continued from previous page)

```
# first-order VWN potential. The Hartree-Fock part of the kernel is included
# automatically if a hybrid potential is used in the ADF calculation.
```

```
$AMSBIN/cpl <<eor
  adffile ams.results/adf.rkf
  gga
  nmrcoupling
  dso
  pso
  scf converge=1e-6 iterations=20
      nuclei 1 2
  End
eor
```

```
# The second CPL run also includes the spin-dipole (SD) term, through the SD
# subkey, which is much more time-consuming.
```

```
$AMSBIN/cpl <<eor
  adffile ams.results/adf.rkf
  gga
  nmrcoupling
  dso
  pso
  sd
  scf converge=1e-6 iterations=20
      nuclei 1 2
  End
eor
```

Example: NMR Spin-spin coupling constants, finite nucleus: PbH4

Download PbH4_finitenuc.run

```
#!/bin/sh

# Example for a finite nucleus calculation and the calculation of NMR spin-spin
# coupling constants.

# One of the quality-determining factors for the calculation of NMR coupling
# constants is the chosen basis set, especially one needs enough tight s
# functions. If one has a large enough basis set in the core region one can see
# an effect of using a finite size of the nucleus instead of a point nucleus,
# especially for heavy nuclei. Such large basis sets can be found for some
# elements in $AMSRESOURCES/ADF/ZORA/jcpl, which are basis sets especially designed
# for NMR spin-spin coupling calculations. In this example first a basis set for
# Pb is made which has many tight s functions. The file can be found in the
# example directory

# The large basis set for Pb is used in ADF calculations on PbH4 and the
```

(continues on next page)

(continued from previous page)

```

# calculation of the NMR spin-spin coupling constants.

AMS_JOBNAME=PbH4 $AMSBIN/ams <<eor
System
  atoms
    Pb      0.000000      0.000000      0.000000
    H      -1.023703      1.023703      1.023703
    H       1.023703     -1.023703      1.023703
    H      -1.023703     -1.023703     -1.023703
    H       1.023703      1.023703     -1.023703
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality verygood
  end
  basis
    Core None
    Type DZP
    PerAtomType Symbol=Pb File=$AMSHOME/examples/adf/PbH4_finitenuc/Pb
    CreateOutput Yes
  end
  nuclearmodel Gaussian
  print Nuclei
  relativity
    level scalar
    formalism ZORA
  end
  save TAPE10
  scf
    converge 1.0e-8 1.0e-6
    iterations 100
  end
  usespcode
  xc
    gga PBE
  end
EndEngine
eor

## end scalar run, now do the coupling constant

$AMSBIN/cpl <<eor
adffile PbH4.results/adf.rkf
tape10file PbH4.results/TAPE10
gga
Print Nuclei
nmrcoupling
  scf converge=1e-5 iterations=25
  nuclei 1 2
end
eor

```

15.4.8 ESR/EPR g-tensor, A-tensor, Q-tensor, ZFS

Example: ESR g-tensor, A-tensor, Q-tensor, D-tensor: HfV

Download ESR_HfV.run

```
#!/bin/sh

# For the ESR g-tensor and D-tensor (zero-field splitting, ZFS) the effect of
# spin-orbit coupling is important. For the ESR A-tensor and Q-tensor (EFG)
# spin-orbit coupling is less important.

# In this example first spin-orbit coupling is taken into account
# perturbatively. Next spin-orbit coupling is taken into account self-
# consistent, using the COLLINEAR keyword.

# Note that an all-electron calculation is carried out. This is relevant for the
# computation of the A-tensor, the nuclear magnetic dipole hyperfine
# interaction, where an accurate value of the spin-polarization density at the
# nucleus is important. For the g-tensor this plays a minor role. However, for
# the g-tensor calculation that includes spin-orbit coupling perturbatively, all
# electron basis sets are necessary.

# In the first ADF calculation the A-tensor (block key ESR) is calculated
# without the effect of spin-orbit coupling included. The zero-field splitting
# (key ZFS) is calculated by including spin-orbit coupling perturbatively.

AMS_JOBNAME=HfV $AMSBIN/ams <<eor
System
  atoms
    Hf  0.0 0.0 0.0
    V   0.0 0.0 2.033
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  esr
  end
  basis
    core None
    type TZ2P
  end
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  save TAPE21 TAPE10
  spinpolarization 3
  symmetry NoSym
```

(continues on next page)

(continued from previous page)

```
unrestricted
zfs
EndEngine
eor

# In the next calculation the module nmr calculates the g-tensor (subkey
# GFACTORS) using spin-orbit coupling and the external magnetic field as
# perturbation.

$AMSBIN/nmr <<eor
  adffile HfV.results/adf.rkf
  tape10file HfV.results/TAPE10
  nmr
    gfactors
    ulk best
    out iso tens
  end
eor

rm logfile TAPE15

# The module cpl can calculate the A-tensor (key HYPERFINE) using spin-orbit
# coupling and the nuclear magnetic field as perturbation. Note that one needs
# to set the SCF convergence criterion to a small value.

$AMSBIN/cpl <<eor
  adffile HfV.results/adf.rkf
  tape10file HfV.results/TAPE10
  hyperfine
    atoms 1 2 :: calculates A-tensor for atom 1 and 2, input order
    SCF Converge=1e-7
  end
eor
rm logfile

# ADF can calculate the g-tensor and A-tensor (block key ESR) using only the
# nuclear or external magnetic field as perturbation, since spin-orbit coupling
# can be taken into account self-consistently. However, in this case, degenerate
# perturbation theory is used. The collinear approximation is used (and symmetry
# NOSYM) to account for spin-polarization effects.

AMS_JOBNAME=HfV_SO $AMSBIN/ams <<eor
System
  atoms
    Hf  0.0 0.0 0.0
    V   0.0 0.0 2.033
  end
end

Task SinglePoint

Engine ADF
  beckegrid
```

(continues on next page)

(continued from previous page)

```

    quality good
end
esr
end
basis
  core None
  type TZ2P
end
qtens
relativity
  level spin-orbit
  formalism ZORA
  spinorbitmagnetization collinear
end
symmetry NoSym
unrestricted
EndEngine
eor

```

Example: ESR g-tensor, A-tensor, self consistent spin-orbit coupling: VO

Download VO_collinear.run

```

#!/bin/sh

# The ESR parameters of VO are calculated with the collinear approximation for
# unrestricted Spin-Orbit coupled calculations. In this example the VO-molecule
# has three unpaired electrons.

# You calculate Electron Spin Resonance properties with the keywords ESR and
# QTENS. ESR is a block-type key and is used to compute the G-tensor or the
# Nuclear Magnetic Dipole Hyperfine interaction. QTENS is a simple key and
# invokes the computation of the Nuclear Electric Quadrupole Hyperfine
# interaction.

# Proper usage of the key ESR requires that you do one of the following:

# A Spin-Orbit calculation, spin-restricted, with exactly one unpaired electron,
# or (b) A Spin-Orbit calculation, spin-unrestricted in the collinear
# approximation, or (c) No Spin-Orbit terms and spin-unrestricted. In case (a)
# and (b) you obtain the G-tensor. In case (b) and (c) you get the Magnetic
# Dipole Hyperfine interaction.

# Note: in case (a) the program also prints a Magnetic Dipole Hyperfine
# interaction data, but these have then been computed without the terms from the
# spin-density at the nucleus. Note: in case (b) and (c) one can have more than
# one unpaired electron. Note: in case (b) one has to use symmetry NOSYM.

# Two calculations are performed:

# Scalar relativistic spin-unrestricted (case c)
# Spin-Orbit relativistic spin-unrestricted collinear (case b)

# We first calculate the Dipole Hyperfine interaction:

```

(continues on next page)

(continued from previous page)

```

# a spin- unrestricted calculation without Spin-Orbit coupling.

# Note that one has to use ALLPOINTS in the calculation for a linear molecule to
# get results for the nuclear magnetic dipole hyperfine interaction. For an
# accurate calculation of the hyperfine interaction the numerical quality is set
# to VeryGood.

AMS_JOBNAME=scalar $AMSBIN/ams <<eor
System
  atoms
    V 0 0 0
    O 0 0 1.589
  End
End

Task SinglePoint

Engine ADF
  AllPoints

  ESR
  End

  QTens

  ZFS

  basis
    core None
    type TZ2P
  End

  numericalquality verygood

  relativity
    level scalar
    formalism ZORA
  end

  Unrestricted
  SpinPolarization 3
  XC
    GGA Becke Perdew
  End
EndEngine

eor

# Then a spin-orbit coupled spin-unrestricted calculation is performed using the
# collinear approximation. Note that symmetry NOSYM is used.

AMS_JOBNAME=so $AMSBIN/ams <<eor
System
  atoms
    V 0 0 0
    O 0 0 1.589
  End

```

(continues on next page)

(continued from previous page)

```

End

Task SinglePoint

Engine ADF
  ESR
  End

  QTens

  basis
    core None
    type TZ2P
  End

  numericalquality verygood

  relativity
    level spin-orbit
    formalism ZORA
    spinorbitmagnetization collinear
  end

  SCF
    AccelerationMethod LISTf
  End

  symmetry nosym

  Unrestricted

  XC
    GGA Becke Perdew
  End
EndEngine

eor

```

Example: ESR g-tensor, A-tensor, perturbative spin-orbit coupling: HgF

Download ESR_HgF_2der.run

```

#!/bin/sh

# This example calculates the ESR g-tensor and A-tensor for HgF. In this example
# first spin-orbit coupling is taken into account perturbatively.

# Note that an all-electron calculation is carried out. This is relevant for the
# computation of the A-tensor, the nuclear magnetic dipole hyperfine
# interaction, where an accurate value of the spin-polarization density at the
# nucleus is important. For the g-tensor this plays a minor role. However, for
# the g-tensor calculation that includes spin-orbit coupling perturbatively, all
# electron basis sets are necessary.

```

(continues on next page)

(continued from previous page)

```

# In the first example the module nmr calculates the g-tensor (subkey GFACTORS)
# using spin-orbit coupling and the external magnetic field as perturbation.

AMS_JOBNAME=HgF $AMSBIN/ams <<eor
System
  atoms
    Hg      0.0 0.0 0.0
    F       0.0 0.0 2.804
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality verygood
  end
  basis
    core None
    type TZ2P
  end
  relativity
    level scalar
    formalism ZORA
  end
  save TAPE21 TAPE10
  scf
    converge 1e-7 1e-7
    iterations 500
  end
  spinpolarization 1
  symmetry NoSym
  unrestricted
  usespcode
  xc
    gga PBE
  end
EndEngine
eor

$AMSBIN/nmr <<eor
  tape10file HgF.results/TAPE10
  adffile HgF.results/adf.rkf
  nmr
    gfactors
    ulk best
    out iso tens
  end
eor

# In the second example the module cpl calculates the A-tensor (key HYPERFINE)
# using spin-orbit coupling and the nuclear magnetic field as perturbation. Note
# that one needs to set the SCF convergence criterion to a small value. For an
# accurate calculation of the A-tensor one needs a very large basis set in the
# core region (especially tight s-functions), especially for heavy nuclei. If
# one has such a large basis set in the core region, one can also see an effect

```

(continues on next page)

(continued from previous page)

```

# of using a finite size of the nucleus instead of a point nucleus. Such large
# basis sets can be found for some elements in $AMSRESOURCES/ADF/ZORA/jcpl, which
# are basis sets especially designed for ESR A-tensor and NMR spin-spin coupling
# calculations.

AMS_JOBNAME=HgF_jcpl $AMSBIN/ams <<eor
System
  atoms
    Hg          0.0 0.0 0.0
    F           0.0 0.0 2.804
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality verygood
  end
  basis
    PerAtomType Symbol=Hg File=ZORA/jcpl/Hg
    PerAtomType Symbol=F  File=ZORA/jcpl/F
  end
  nuclearmodel Gaussian
  relativity
    level scalar
    formalism ZORA
  end
  scf
    converge 1e-7 1e-7
    iterations 500
  end
  spinpolarization 1
  symmetry NoSym
  unrestricted
  usespcode
  xc
    gga PBE
  end
EndEngine
eor

$AMSBIN/cpl <<eor
  adffile HgF_jcpl.results/adf.rkf
  gga
  hyperfine
    atoms 1 2 :: calculates A-tensor for atom 1 and 2, input order
    SCF Converge=1e-7
  end
eor

```

Example: ESR spin-restricted and spin-unrestricted: TiF3

Download ESR_TiF3.run

```
#!/bin/sh

# You calculate Electron Spin Resonance properties with the keywords ESR and
# QTENS. ESR is a block-type key and is used to compute the G-tensor or the
# Nuclear Magnetic Dipole Hyperfine interaction. QTENS is a simple key and
# invokes the computation of the Nuclear Electric Quadrupole Hyperfine
# interaction.

# Proper usage of the key ESR requires that you do one of the following:

# (a) A Spin-Orbit calculation, spin-restricted, with exactly one unpaired
#     electron, or
# (b) A Spin-Orbit calculation, spin-unrestricted in the collinear
#     approximation, or
# (c) No Spin-Orbit terms and spin-unrestricted.

# In case (a) and (b) you obtain the G-tensor. In case (b) and (c) you get the
# Magnetic Dipole Hyperfine interaction.

# Note: in case (a) the program also prints a Magnetic Dipole Hyperfine
# interaction data, but these have then been computed without the terms from the
# spin-density at the nucleus. Note: in case (b) and (c) one can have more than
# one unpaired electron. Note: in case (b) one has to use symmetry NOSYM.

# Five calculations are performed:
# - Scalar relativistic spin-restricted
# - Scalar relativistic open shell spin-restricted
# - Scalar relativistic spin-unrestricted
# - Spin-Orbit relativistic spin-restricted
# - Spin-Orbit relativistic spin-unrestricted collinear

# First a scalar relativistic spin-restricted calculation is performed. The
# results of this calculation are used as a fragment in the next spin-
# unrestricted calculation, using only 0 SCF iterations, which is a way to get
# the scalar relativistic spin-restricted open shell result for the magnetic
# dipole hyperfine interaction.

AMS_JOBNAME=TiF3_SR $AMSBIN/ams <<eor
System
  atoms
    Ti  0      0      0
    F  1.780  0      0
    F -0.89   1.5415252187363007 0
    F -0.89  -1.5415252187363007 0
  end
end

Task SinglePoint

Engine ADF
  title TiF3  scalar relativistic restricted
  basis
```

(continues on next page)

(continued from previous page)

```

    core None
    type TZ2P
    CreateOutput Yes
end
noprnt sfo frag functions
relativity
  level scalar
  formalism ZORA
end
xc
  gga Becke Perdew
end
EndEngine
eor

AMS_JOBNAME=TiF3_SR_0 $AMSBIN/ams <<eor
System
  atoms
    Ti  0      0      0 adf.f=TiF3
    F  1.780  0      0 adf.f=TiF3
    F -0.89   1.5415252187363007 0 adf.f=TiF3
    F -0.89  -1.5415252187363007 0 adf.f=TiF3
  end
end

Task SinglePoint

Engine ADF
  title TiF3  scalar relativistic open shell restricted
  esr
  end
  fragments
    TiF3 TiF3_SR.results/adf.rkf
  end
  noprnt sfo frag functions
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  scf
    iterations 0
  end
  spinpolarization 1
  unrestricted
  xc
    gga Becke Perdew
  end
EndEngine
eor

# Next a spin-unrestricted SCF calculation is performed to get the scalar
# relativistic spin-unrestricted result for the magnetic dipole hyperfine
# interaction.

AMS_JOBNAME=TiF3_SR_unrestricted $AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Ti  0      0      0 adf.f=TiF3
    F   1.780  0      0 adf.f=TiF3
    F  -0.89   1.5415252187363007 0 adf.f=TiF3
    F  -0.89  -1.5415252187363007 0 adf.f=TiF3
  end
end

Task SinglePoint

Engine ADF
  title TiF3 relativistic open shell unrestricted
  esr
  end
  fragments
    TiF3 TiF3_SR.results/adf.rkf
  end
  noprint sfo frag functions
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 1
  unrestricted
  xc
    gga Becke Perdew
  end
EndEngine
eor

# Then, for the same molecule, we compute the G-tensor in a Spin-Orbit run
# (spin-restricted).

# The here-computed and printed Dipole Hyperfine interaction misses the terms
# from the spin-density at the nucleus: compare with the outcomes from the first
# calculation.

# In each of the calculations, the QTENS key invokes the computation of the
# Electric Quadrupole Hyperfine interaction.

# Note that an all-electron calculation is carried out. This is relevant for the
# computation of the A-tensor, the nuclear magnetic dipole hyperfine
# interaction, where an accurate value of the spin-polarization density at the
# nucleus is important. For the G-tensor (and also for the Q-tensor) this plays
# a minor role, but for reasons of consistency both calculations use the same
# basis set and (absence of) frozen core.

AMS_JOBNAME=TiF3_SO $AMSBIN/ams <<eor
System
  atoms
    Ti  0      0      0 adf.f=TiF3
    F   1.780  0      0 adf.f=TiF3
    F  -0.89   1.5415252187363007 0 adf.f=TiF3
    F  -0.89  -1.5415252187363007 0 adf.f=TiF3
  end
end

```

(continues on next page)

(continued from previous page)

```

    end
end

Task SinglePoint

Engine ADF
  title TiF3  relativistic spinorbit open shell restricted
  esr
  end
  fragments
    TiF3  TiF3_SR.results/adf.rkf
  end
  noprint sfo frag functions
  qtens
  relativity
    level spin-orbit
    formalism ZORA
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

# Finally a spin-orbit coupled spin-unrestricted calculation is performed using
# the collinear approximation. Note that symmetry NOSYM is used.

AMS_JOBNAME=TiF3_SO_unrestricted $AMSBIN/ams <<eor
System
  atoms
    Ti  0      0      0 adf.f=TiF3
    F  1.780  0      0 adf.f=TiF3
    F -0.89   1.5415252187363007 0 adf.f=TiF3
    F -0.89  -1.5415252187363007 0 adf.f=TiF3
  end
end

Task SinglePoint

Engine ADF
  title TiF3  relativistic spinorbit open shell unrestricted collinear
  esr
  end
  fragments
    TiF3  TiF3_SR.results/adf.rkf
  end
  noprint sfo frag functions
  qtens
  relativity
    level spin-orbit
    formalism ZORA
    spinorbitmagnetization collinear
  end
  symmetry nosym
  unrestricted
  xc

```

(continues on next page)

(continued from previous page)

```

    gga Becke Perdew
  end
EndEngine
eor

```

Example: ESR, X2C and RA-X2C: PdH

Download PdH_ESR_X2C.run

```

#!/bin/sh

# This example calculates the ESR A-tensor and g-tensor of PdH, using the X2C
# and RA-X2C relativistic methods. Four calculations are performed:
# - Scalar relativistic X2C open shell spin-restricted
# - Scalar relativistic RA-X2C open shell spin-restricted
# - Spin-Orbit relativistic X2C spin-unrestricted collinear
# - Spin-Orbit relativistic RA-X2C spin-unrestricted collinear

# The spin-orbit coupled spin-unrestricted calculation is performed using the
# collinear approximation, symmetry NOSYM is required in that case. A finite
# nucleus is used, which will be important for the calculated A-tensor,
# especially for heavy nuclei.

# == Scalar relativistic X2C open shell spin-restricted ==

AMS_JOBNAME=X2C_SR $AMSBIN/ams <<eor
System
  atoms
    Pd 0 0 0
    H  0 0 1.529
  end
end

Task SinglePoint

Engine ADF
  esr
  end
  basis
    core None
    type QZ4P
  end
  nuclearmodel gaussian
  relativity
    level scalar
    formalism X2C
  end
  spinpolarization 1
  unrestricted
EndEngine
eor

# == Scalar relativistic RA-X2C open shell spin-restricted ==

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=RAX2C_SR $AMSBIN/ams <<eor
System
  atoms
    Pd 0 0 0
    H  0 0 1.529
  end
end

Task SinglePoint

Engine ADF
  esr
  end
  basis
    core None
    type QZ4P
  end
  nuclearmodel gaussian
  relativity
    level scalar
    formalism RA-X2C
  end
  spinpolarization 1
  unrestricted
EndEngine
eor

# == Spin-Orbit relativistic X2C spin-unrestricted collinear ==

AMS_JOBNAME=X2C_SO $AMSBIN/ams <<eor
System
  atoms
    Pd 0 0 0
    H  0 0 1.529
  end
end

Task SinglePoint

Engine ADF
  esr
  end
  basis
    core None
    type QZ4P
  end
  nuclearmodel gaussian
  relativity
    level spin-orbit
    formalism X2C
    SpinOrbitMagnetization collinear
  end
  symmetry nosym
  unrestricted
EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

# == Spin-Orbit relativistic RA-X2C spin-unrestricted collinear ==

AMS_JOBNAME=RAX2C_SO $AMSBIN/ams <<eor
System
  atoms
    Pd 0 0 0
    H  0 0 1.529
  end
end

Task SinglePoint

Engine ADF
  esr
  end
  basis
    core None
    type QZ4P
  end
  nuclearmodel gaussian
  relativity
    level spin-orbit
    formalism RA-X2C
    SpinOrbitMagnetization collinear
  end
  symmetry nosym
  unrestricted
EndEngine
eor

```

Example: Zero-field splitting (ZFS), ESR D-tensor: NH

Download NH_ZFS.run

```

#!/bin/sh

# The zero-field splitting (ZFS) can be calculated for open shell molecules with
# electron spin S<=1, using the key ZFS.

# Only the spin-orbit contribution to ZFS is evaluated. Can be used in
# combination with LDA and GGAs. RELATIVISTIC ZORA is also required.

$AMSBIN/ams <<eor
System
  atoms
    N      0.000000    0.000000    0.007767
    H      0.000000    0.000000   -1.043445
  end
end

Task SinglePoint

Engine ADF

```

(continues on next page)

(continued from previous page)

```

basis
  type DZP
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
spinpolarization 2.0
title NH Zero-field splitting
unrestricted
xc
  gga BECKE PERDEW
end
zfs
EndEngine
eor

```

Example: ZFS D tensor, including direct electron spin-spin part: Phenylnitrene

Download Phenylnitrene_ZFS.run

```

#!/bin/sh

# The zero-field splitting (ZFS) can be calculated for open shell molecules with
# electron spin  $S \leq 1$ , using the key ZFS.

# The direct electron spin-spin part and the spin-orbit contribution to ZFS is
# evaluated. Can be used in combination with LDA and GGAs. RELATIVISTIC ZORA is
# also required. The direct electron spin-spin part is calculated if HARTREEFOCK
# is included as separate keyword. Both Coulomb and (Hartree-Fock like) exchange
# contributions to the direct electron spin-spin term are calculated. In the
# spin-orbit coupling no Hartree-Fock like exchange contributions are included.

$AMSBIN/ams <<eor
System
atoms
  C 0.000000 0.000000 1.072671
  C 0.000000 1.232517 0.336828
  C 0.000000 1.216609 -1.046705
  C 0.000000 0.000000 -1.747681
  C 0.000000 -1.216609 -1.046705
  C 0.000000 -1.232517 0.336828
  N 0.000000 0.000000 2.400797
  H 0.000000 2.164354 0.892961
  H 0.000000 2.155064 -1.594614
  H 0.000000 0.000000 -2.833691
  H 0.000000 -2.155064 -1.594614
  H 0.000000 -2.164354 0.892961
end
end
Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  hartreefock
  basis
    core None
    type TZ2P
  end
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 2.0
  unrestricted
  xc
    gga blyp
  end
  zfs
EndEngine
eor

```

15.4.9 EFG, Mössbauer

Example: Mössbauer spectroscopy: Ferrocene

Download Mossbauer.run

```

#!/bin/sh

# By default in ADF the electron density at the nuclei is calculated, no input
# key is required. The electron density at the nuclei could be used for the
# interpretation of isomer shifts in Mossbauer spectroscopy. The absolute
# electron density at a nucleus heavily depends on the accuracy of the basis set
# in the core region of this nucleus, especially if relativistic effects are
# included. Important is to use the same basis set, same exchange correlation
# functional, same numerical accuracy, if electron densities at nuclei in
# different molecules are compared. For the calculation of Mossbauer quadrupole
# splittings the key QTENS is required For 57 Fe quadrupole splittings will be
# written in units of mm/s, used in Mossbauer spectroscopy Example shows a
# calculation on ferrocene with anon-relativistic, and two with a scalar
# relativistic ZORA Hamiltonian using a different all electron basis set.

# First a non-relativistic calculation.

AMS_JOBNAME=NR $AMSBIN/ams <<eor
System
  symmetrize Yes
  atoms
    Fe      0.000000    0.000000    0.000000
    C      1.215650    0.000000    1.600813
    C      0.375656   -1.156152    1.600813
    C     -0.983481   -0.714541    1.600813
    C     -0.983481    0.714541    1.600813
    C      0.375656    1.156152    1.600813
    C      1.215650    0.000000   -1.600813

```

(continues on next page)

(continued from previous page)

```

      C      0.375656      1.156152     -1.600813
      C     -0.983481      0.714541     -1.600813
      C     -0.983481     -0.714541     -1.600813
      C      0.375656     -1.156152     -1.600813
      H      2.310827      0.000000      1.629796
      H      0.714085     -2.197727      1.629796
      H     -1.869498     -1.358270      1.629796
      H     -1.869498      1.358270      1.629796
      H      0.714085      2.197727      1.629796
      H      2.310827      0.000000     -1.629796
      H      0.714085      2.197727     -1.629796
      H     -1.869498      1.358270     -1.629796
      H     -1.869498     -1.358270     -1.629796
      H      0.714085     -2.197727     -1.629796
    end
  end
end

```

```
Task SinglePoint
```

```
Engine ADF
```

```

  title ferrocene
  exactdensity
  basis
    core none
    type TZP
  end
  numericalquality Good
  qtens
  xc
    gga blyp
  end
  Relativity
    Level None
  End

```

```
EndEngine
```

```
eor
```

```

# Next the scalar relativistic ZORA calculations. ADF will also calculate the
# quadrupole splittings including the small component density, also called SR
# ZORA-4.

```

```
AMS_JOBNAME=SR $AMSBIN/ams <<eor
```

```
System
```

```

  symmetrize
  atoms
    FE      0.000000      0.000000      0.000000
    C      1.215650      0.000000      1.600813
    C      0.375656     -1.156152      1.600813
    C     -0.983481     -0.714541      1.600813
    C     -0.983481      0.714541      1.600813
    C      0.375656      1.156152      1.600813
    C      1.215650      0.000000     -1.600813
    C      0.375656      1.156152     -1.600813
    C     -0.983481      0.714541     -1.600813
    C     -0.983481     -0.714541     -1.600813
  
```

(continues on next page)

(continued from previous page)

```

      C      0.375656   -1.156152   -1.600813
      H      2.310827    0.000000    1.629796
      H      0.714085   -2.197727    1.629796
      H     -1.869498   -1.358270    1.629796
      H     -1.869498    1.358270    1.629796
      H      0.714085    2.197727    1.629796
      H      2.310827    0.000000   -1.629796
      H      0.714085    2.197727   -1.629796
      H     -1.869498    1.358270   -1.629796
      H     -1.869498   -1.358270   -1.629796
      H      0.714085   -2.197727   -1.629796
    end
  end
Task SinglePoint

Engine ADF
  title ferrocene
  exactdensity
  basis
    core none
    type TZP
  end
  numericalquality Good
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga blyp
  end
EndEngine
eor

# Next a scalar relativistic calculation is performed with a much larger basis
# set (QZ4P) in the core region. Changing the basis set will have a large effect
# on the electron density at the nucleus and a noticeable effect on the
# calculated quadrupole splittings.

AMS_JOBNAME=SR_QZ4P $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    FE      0.000000    0.000000    0.000000
    C      1.215650    0.000000    1.600813
    C      0.375656   -1.156152    1.600813
    C     -0.983481   -0.714541    1.600813
    C     -0.983481    0.714541    1.600813
    C      0.375656    1.156152    1.600813
    C      1.215650    0.000000   -1.600813
    C      0.375656    1.156152   -1.600813
    C     -0.983481    0.714541   -1.600813
    C     -0.983481   -0.714541   -1.600813
    C      0.375656   -1.156152   -1.600813

```

(continues on next page)

(continued from previous page)

```

      H      2.310827      0.000000      1.629796
      H      0.714085     -2.197727      1.629796
      H     -1.869498     -1.358270      1.629796
      H     -1.869498      1.358270      1.629796
      H      0.714085      2.197727      1.629796
      H      2.310827      0.000000     -1.629796
      H      0.714085      2.197727     -1.629796
      H     -1.869498      1.358270     -1.629796
      H     -1.869498     -1.358270     -1.629796
      H      0.714085     -2.197727     -1.629796
    end
  end
Task SinglePoint

Engine ADF
  title ferrocene
  exactdensity
  basis
    core none
    type QZ4P
  end
  numericalquality Good
  qtens
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga blyp
  end
EndEngine
eor

```

Example: Mössbauer with X2C: Hg compounds

Download Hg_Mossbauer_X2C.run

```

#!/bin/sh

# This example uses the relativistic spin-orbit coupled X2C method. By default
# in ADF the electron density at the nuclei is calculated, no input key is
# required. The electron density at the nuclei could be used for the
# interpretation of isomer shifts in Mossbauer spectroscopy. Typically one needs
# to perform a fit of the experimentally measured isomer shifts versus the
# calculated electron densities. The absolute electron density at a nucleus
# heavily depends on the accuracy of the basis set in the core region of this
# nucleus, especially if relativistic effects are included. Important is to use
# the same basis set, same exchange correlation functional, same numerical
# accuracy, if electron densities at nuclei in different molecules are compared.
# For the calculation of Mossbauer quadrupole splittings the key QTENS is
# required This example calculates the compounds Hg, HgF, HgF2, HgF4, and HgCl2.

```

(continues on next page)

(continued from previous page)

```
AMS_JOBNAME=Hg_X2C $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
```

```
    Hg 0 0 0
```

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  exactdensity
```

```
  basis
```

```
    core None
```

```
    type ZORA/DZ
```

```
  end
```

```
  nuclearmodel gaussian
```

```
  numericalquality good
```

```
  relativity
```

```
    level spin-orbit
```

```
    formalism X2C
```

```
  end
```

```
EndEngine
```

```
eor
```

```
AMS_JOBNAME=HgF_X2C $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
```

```
    Hg 0 0 0
```

```
    F  0 0 2.007
```

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  exactdensity
```

```
  basis
```

```
    core None
```

```
    type ZORA/DZ
```

```
  end
```

```
  nuclearmodel gaussian
```

```
  numericalquality good
```

```
  qtens
```

```
  relativity
```

```
    Level spin-orbit
```

```
    Formalism X2C
```

```
    SpinOrbitMagnetization NonCollinear
```

```
  end
```

```
  symmetry nosym
```

```
  unrestricted
```

```
EndEngine
```

```
eor
```

```
AMS_JOBNAME=HgF2_X2C $AMSBIN/ams <<eor
```

```
System
```

(continues on next page)

(continued from previous page)

```

atoms
  Hg 0 0 0
  F 0 0 1.914
  F 0 0 -1.914
end
end

Task SinglePoint

Engine ADF
  exactdensity
  basis
    core None
    type ZORA/DZ
  end
  nuclearmodel gaussian
  numericalquality good
  qtens
  relativity
    level spin-orbit
    formalism X2C
  end
EndEngine
eor

AMS_JOBNAME=HgF4_X2C $AMSBIN/ams <<eor
System
  atoms
    Hg 0 0 0
    F 0 -1.885 0
    F 0 1.885 0
    F -1.885 0 0
    F 1.885 0 0
  end
end

Task SinglePoint

Engine ADF
  exactdensity
  basis
    core None
    type ZORA/DZ
  end
  nuclearmodel gaussian
  numericalquality good
  qtens
  relativity
    level spin-orbit
    formalism X2C
  end
EndEngine
eor

AMS_JOBNAME=HgCl2_X2C $AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Hg 0 0 0
    Cl 0 0 2.252
    Cl 0 0 -2.252
  end
end

Task SinglePoint

Engine ADF
  exactdensity
  basis
    core None
    type ZORA/DZ
  end
  nuclearmodel gaussian
  numericalquality good
  qtens
  relativity
    level spin-orbit
    formalism X2C
  end
EndEngine
eor

```

15.4.10 GW

Example: G_0W_0 @PBE calculation: H₂O

Download GW_H2O.run

```

#!/bin/sh

# GW calculation for Water. By default. The highest 5 occupied and lowest 5
# unoccupied states are calculated.

# We use an all-electron basis set since core-correlation effects are important

# For H2O, PBE will be a suitable reference since it is only weakly correlated and
# the
# KS HOMO-LUMO gap will be reasonably large.

# RECOMMENDED: Good numerical quality

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    O 2.220871067 0.026716792 0.000620476
    H 2.597492682 -0.411663274 0.766744858

```

(continues on next page)

(continued from previous page)

```

      H      2.593135384   -0.449496183   -0.744782026
    End
    Symmetrize Yes
  End

task SinglePoint

Engine adf
  Basis
    Core None
    Type TZ2P
  end

  NumericalQuality GOOD
  RIHartreeFock fitsetQuality=Normal dependencyThreshold=1e-3
  Dependency bas=1e-4

  XC
    GGA PBE
  end

  GW
    nstates 3
  END
EndEngine
eor

```

Example: G_0W_0 @PBE0 calculation: O3

Download GW_O3.run

```

#!/bin/sh

# GW calculation on Ozone. By default. The highest 5 occupied and lowest 5
# unoccupied states are calculated.

# We use an all-electron basis set since core-correlation effects are important
# to capture all screening effects.

# Since for a GGA reference poles of the self-energy will be close to the highest
# (particle )QP solution, we use a hybrid reference. This shifts away the poles
# from the QP solution. We also use large imaginary time and imaginary frequency
# grids to ensure convergence of the QP energies despite the small HOMO-LUMO gap.

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    O      0.000000      0.000000      0.000000
    O      1.086900      0.000000      0.660000
    O     -1.086900      0.000000      0.660000
  End

```

(continues on next page)

(continued from previous page)

```

    Symmetrize Yes
End

task SinglePoint

Engine adf
  Basis
    Core None
    Type TZ2P
  end

  NumericalQuality GOOD

  RIHartreeFock
    fitsetQuality Normal
  end

  MBPT
    nFrequency 18
    nTime 18
  end

  XC
    Hybrid PBE0
  end

  GW
    nstates 2
  END
EndEngine
eor

```

Example: G_0W_0 @PBE0 calculation: Phenol

Download GW_Phenol.run

```

#!/bin/sh

# GW calculation of Toluene. By default, the highest occupied and lowest
# unoccupied state are calculated. We use an all-electron basis set
# since core-correlation effects are important to capture all screening effects.

# Since we are interested in an accurate QP HOMO-LUMO gap, we use the aug-TZ2P
# basis set. To ensure numerical stability, we switch on the dependency key.

# We also use imaginary time and imaginary frequency grids of 16 points each.
# Note, that PBE is not a recommended starting point (better hybrid PBE0).
# Also note, that Good fitsetQuality is recommended

$AMSBIN/ams << eor

System
  Atoms
    C 4.555420 5.661760 4.489060
    C 4.584960 2.843420 4.498910

```

(continues on next page)

(continued from previous page)

```
C 3.378760 3.548270 4.498890
C 3.359200 4.943960 4.500070
C 5.758650 4.948670 4.502800
C 5.789840 3.550210 4.500330
H 4.622340 1.760920 4.495600
H 3.631910 7.321310 4.523190
H 2.474610 2.963630 4.498170
H 2.384290 5.419790 4.496670
H 6.695040 5.492670 4.498160
H 6.727200 3.021210 4.497160
O 4.537700 7.024010 4.500450

End
Symmetrize Yes
End

task SinglePoint

Engine adf
  Basis
    Core None
    Type AUG/ATZ2P
  end

  NumericalQuality Good
  Dependency bas=1e-03

  MBPT
    FitsetQuality Normal
    nFrequency 16
    nTime 16
    Dependency
  end

  XC
    GGA PBE
  end

  GW
  END

  Relativity
    Level None
  End
EndEngine
eor
```

Example: evGW@M06-2X calculation: H2O

Download evGW_H2O.run

```

#!/bin/sh

# eigenvalue-only self-consistent GW calculation for Water.

# We change here several options in the GW block to illustrate how this works

# We chose M06-2X as starting point
# We chose good numerical quality. This implies that 20 imaginary time and frequency_
↳points each are used

# nStates 3
# ==> We want to print out the 3 highest occupied, and the 3 lowest unoccupied quasi-
↳particle states

# nDIIS 5
# ==> We use DIIS to converge the quasi-particle energies (linear mixing is possible_
↳as well, but it is not recommended)
# ==> Per default, the DIIS algorithm in evGW considers the last 10 iterations. We_
↳only want 5 here. If for some reason
# ==> your evGW calculation should not converge, this is the first parameter to look_
↳into

# Converge HOMO=5e-3
# ==> We consider the procedure to be converged when the HOMO quasi-particle energy_
↳between 2 iterations does not change
# ==> by more than 5 meV

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    O  0.0000 0.0000 0.0000
    H  0.7571 0.0000 0.5861
    H -0.7571 0.0000 0.5861
  End
  Symmetrize Yes
End

task SinglePoint

Engine adf
  Basis
    Core None
    Type TZ2P
  End
  XC
    libxc M06-2X
  end
  MBPT
    nTime 20

```

(continues on next page)

(continued from previous page)

```

    nFrequency 20
End
numericalQuality Good

GW
  DIIS 5
  nStates 3
  Converge HOMO=5e-3
  selfconsistency evGW
END

EndEngine
eor

```

Example: qsGW calculation: N2Download `qsGW_N2.run`

```

#!/bin/sh

# Like in evGW in qsGW the quasi-particle energies are updated
# until self-consistency is reached.
# In qsGW, the density is updated as well, however, the self-energy is
# mapped to a static effective potential and the Dyson equation is
# solved by diagonalization instead of inversion.
# The results of a qsGW are independent of the choice of the underlying
# exchange-correlation functional and are usually the most accurate ones.
# The same is done in qsGW0, but the screened interaction is not updated.

for k in 'qsGW' 'qsGW0' ; do

rm -r ams.results

$AMSBIN/ams << eor
Symmetry
  SymmetrizeTolerance 0.001
End

System
  Atoms
    N 0.0000 0.0000 0.0000
    N 0.0000 0.0000 1.0977
  End
  Symmetrize Yes
End

task SinglePoint

Engine adf
Basis
  Core None
  Type TZ2P
End
symmetry nosym
XC

```

(continues on next page)

(continued from previous page)

```

    hartreefock
end
MBPT
    nTime 12
    nFrequency 12
End
numericalQuality Good
GW
    DIIS 3
    nStates 3
    selfconsistency $k
END

EndEngine
eor

done

```

Example: qsGW with frozen core: Br2Download `qsGW_Br2_frozenCore.run`

```

#!/bin/sh

# Standard qsGW calculation using the frozen core approximation in the
# correlation part. An all electron basis set is required.
# The execution time will roughly stay the same, but numerical convergence
# is better since problems with analytical continuation of core states
# are completely avoided. The frozen core approximation only affects the
# correlation part of the self-energy.
# The number of core states are being chosen using a default scheme.
# For Br, the frozen core is Argon.
# Symmetry NOSYM is required in case of MBPT%frozenscore

# Note that the used DZ basis set is too small to get accurate results.
# Recommended is to use at least TZ2P.

$AMSBIN/ams << eor
System
  Atoms
    Br 0.0000 0.0000 0.0000
    Br 0.0000 0.0000 2.2811
  End
  Symmetrize Yes
End

task SinglePoint

Engine adf
  Basis
    Core None
    Type DZ
  End
  symmetry nosym
  XC

```

(continues on next page)

(continued from previous page)

```

    hartreefock
end
MBPT
    frozenCore True
End
numericalQuality Good
GW
    selfconsistency qsGW
END
EndEngine
eor

```

Example: G3W2 calculation: H2O

Download G3W2_H2O.run

```

#!/bin/sh

# G3W2 calculation H2O.
# G3W2 is a GW calculation plus a perturbative second-order statically
# screened exchange correction (second order expansion in the self-energy).
# Note, that there the self-energy is always static.
# Only a second-order screened exchange correction
# is evaluated after the GW calculation is completed.

$AMSBIN/ams << eor
Symmetry
    SymmetrizeTolerance 0.001
End

System
    Atoms
        O    2.220871067    0.026716792    0.000620476
        H    2.597492682   -0.411663274    0.766744858
        H    2.593135384   -0.449496183   -0.744782026
    End
    Symmetrize Yes
End

task SinglePoint

Engine adf
    Basis
        Core None
        Type TZ2P
    end

    NumericalQuality GOOD

    XC
        hartreefock
    end

    GW
        selfenergy G3W2

```

(continues on next page)

(continued from previous page)

```

        nstates 1
    END
EndEngine
eor

```

Example: GW with DRF: CH₂O in Water

Download GW_CH2O_Embed.run

```

#!/bin/sh

# GW calculation on formaldehyde in water.
# In this example a single formaldehyde molecule and its first solvation shell
# which includes water molecules within 4 Angstroms, is simulated

# We use the G0W0 approximation for the QM system, and the DRF model for water.

$AMSBIN/ams << eor
System
  Atoms
    C      2.39264728      2.11086646      -3.70673394
    O      1.47987901      1.52348369      -4.24811419
    H      2.99243915      1.67294268      -2.84396986
    H      2.59427915      3.15468783      -4.03620406
  End
  Symmetrize No
End

UseSymmetry No

Task SinglePoint

Engine ADF
  Basis
    Core None
    Type TZP
  End
  XC
    GGA PBE
  End
  GW
    SelfConsistency G0W0
  End
  MBPT
    formalism RI
  End
  DimQM
    DRF2
  End
  DimPar
    O
      Rad 0.90
      Char 0.6
      Static
    SubEnd

```

(continues on next page)

(continued from previous page)

```

H
  Rad 0.45
  Char -0.3
  Static
SubEnd
XYZ
  51
  H      3.54666213      5.35725337      -7.02041452
  O      2.04645779      7.07368154      -3.27252710
  H      1.78764102      7.78765869      -3.90371649
  H      1.71058215      6.30711583      -3.76280361
  O      4.88286035      4.00451983      -3.28588077
  H      5.38597457      3.44394310      -3.92640544
  H      5.19077667      4.91657693      -3.44227986
  O      0.18656256      4.23618795      -7.03761368
  H      0.89075012      4.62333203      -7.62947059
  H      0.40727875      3.22970332      -7.13319119
  O      -1.14702326      4.47659905      -2.16966035
  H      -1.81501249      3.71212364      -2.27877436
  H      -0.43286915      4.20138660      -2.75613800
  O      7.07024867      0.36614784      -2.04440869
  H      6.46762805      -0.30965402      -1.61572595
  H      6.70719633      1.14126953      -1.55520987
  O      3.57962906      3.67314699      -6.98526274
  H      3.10205286      2.94694403      -7.48923062
  H      4.25784146      3.17526726      -6.41592139
  O      3.13082943      -1.64764804      -5.76593595
  H      2.41673557      -1.74073399      -5.04455583
  H      3.81476755      -2.36835657      -5.73215731
  O      0.74188261      1.82800852      -6.78436630
  H      0.96547395      1.58943581      -5.85019084
  H      -0.03919267      1.19371203      -6.97282629
  O      4.12013607      0.69721169      -6.79199940
  H      3.82718856      -0.16106544      -6.36689761
  H      4.70919651      1.13524018      -6.22423015
  O      3.63633475      1.77306085      0.08634103
  H      3.18738933      0.91138923      -0.17852169
  H      4.08266799      1.46290305      0.89402583
  O      1.57983242      3.47984534      -0.72435642
  H      2.40873386      3.14297655      -0.32712375
  H      1.59962298      4.49653225      -0.66765510
  O      5.92317302      2.67946724      -0.90296232
  H      5.13809949      2.26177170      -0.43308957
  H      5.56497636      3.33063271      -1.61014140
  O      0.38976232      5.05565287      -4.27026257
  H      0.57556838      4.43609806      -5.05893278
  H      -0.20875330      5.77787276      -4.64583021
  O      2.59583614      -0.59253360      -0.56623965
  H      1.68195751      -0.43168111      -0.15029539
  H      2.50988463      -1.59868716      -0.85813667
  O      0.59002147      -1.21174296      -4.24462128
  H      0.26277112      -0.97994479      -3.36169700
  H      0.84085343      -0.34198086      -4.42412382
  O      6.02045233      3.02011606      -5.80000628
  H      6.39638420      3.30267104      -6.68275756
  H      6.73263271      2.47966314      -5.34640323
  O      3.75450136      6.39026611      -7.12258679

```

(continues on next page)

(continued from previous page)

```

      H      2.78990713      6.75181501      -7.10199835
    SubEnd
  End
EndEngine
eor

```

15.5 Transport properties

15.5.1 Charge and exciton transfer integrals

Example: Charge transfer integrals: AT base pair

Download AT_transferintegrals.run

```

#!/bin/sh

# ADF can calculate charge transfer integrals, that are needed in
# approximate methods that model charge transport properties. The molecular
# system typically should be build from 2 fragments. In this example charge
# transfer integrals are calculated between Adenine and Thymine. First these two
# molecules are calculated. In the fragment calculation full symmetry can be
# used. For precision reasons the ZlmFit quality is set to good.

AMS_JOBNAME=Adenine $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    N      0.000000000000      0.656191000000      4.473450000000
    C      0.000000000000      1.850911000000      5.098850000000
    N      0.000000000000      2.094911000000      6.411070000000
    C      0.000000000000      0.951291000000      7.115010000000
    C      0.000000000000     -0.355699000000      6.611740000000
    C      0.000000000000     -0.487619000000      5.203330000000
    N      0.000000000000      0.791131000000      8.484350000000
    C      0.000000000000     -0.567649000000      8.729290000000
    N      0.000000000000     -1.292469000000      7.631450000000
    N      0.000000000000     -1.672349000000      4.572610000000
    H      0.000000000000      2.715551000000      4.433920000000
    H      0.000000000000      1.540301000000      9.166150000000
    H      0.000000000000     -0.961519000000      9.739820000000
    H      0.000000000000     -2.515699000000      5.129900000000
    H      0.000000000000     -1.718459000000      3.541030000000
  end
end

Task SinglePoint

Engine ADF
  title Adenine fragment
  basis
    core None
    type DZ

```

(continues on next page)

(continued from previous page)

```

end
  zlmfit
    quality good
  end
EndEngine
eor

AMS_JOBNAME=Thymine $AMSBIN/ams <<eor
System
  symmetrize
    atoms
      N      0.000000000000      0.617991000000      1.666040000000
      C      0.000000000000      1.851251000000      1.046260000000
      N      0.000000000000      1.768641000000      -0.347380000000
      C      0.000000000000      0.582611000000      -1.042160000000
      C      0.000000000000      -0.621999000000      -0.417040000000
      C      0.000000000000      -0.627269000000      1.045880000000
      O      0.000000000000      -1.670479000000      1.720780000000
      O      0.000000000000      2.924531000000      1.636600000000
      C      0.000000000000      -1.937039000000      -1.138130000000
      H      0.000000000000      0.635221000000      2.733380000000
      H      0.000000000000      2.660141000000      -0.830100000000
      H      0.000000000000      0.676731000000      -2.127100000000
      H      0.880180000000      -2.533409000000      -0.860650000000
      H      0.000000000000      -1.793509000000      -2.225780000000
      H      -0.880180000000      -2.533409000000      -0.860650000000
    end
  end
end

Task SinglePoint

Engine ADF
  title Thymine fragment
  basis
    core None
    type DZ
  end
  zlmfit
    quality good
  end
EndEngine
eor

# Next the the base pair is calculated that consists of Adenine and Thymine. To
# calculate the charge transfer integrals, spatial overlap integrals and site
# energies, include the key TRANSFERINTEGRALS in the input for ADF. Symmetry
# NOSYM should be used.

$AMSBIN/ams <<eor
System
  atoms
    N      0.000000000000      0.656191000000      4.473450000000      adf.f=Adenine
    C      0.000000000000      1.850911000000      5.098850000000      adf.f=Adenine
    N      0.000000000000      2.094911000000      6.411070000000      adf.f=Adenine

```

(continues on next page)

(continued from previous page)

```

C      0.000000000000      0.951291000000      7.115010000000      adf.f=Adenine
C      0.000000000000     -0.355699000000      6.611740000000      adf.f=Adenine
C      0.000000000000     -0.487619000000      5.203330000000      adf.f=Adenine
N      0.000000000000      0.791131000000      8.484350000000      adf.f=Adenine
C      0.000000000000     -0.567649000000      8.729290000000      adf.f=Adenine
N      0.000000000000     -1.292469000000      7.631450000000      adf.f=Adenine
N      0.000000000000     -1.672349000000      4.572610000000      adf.f=Adenine
H      0.000000000000      2.715551000000      4.433920000000      adf.f=Adenine
H      0.000000000000      1.540301000000      9.166150000000      adf.f=Adenine
H      0.000000000000     -0.961519000000      9.739820000000      adf.f=Adenine
H      0.000000000000     -2.515699000000      5.129900000000      adf.f=Adenine
H      0.000000000000     -1.718459000000      3.541030000000      adf.f=Adenine
N      0.000000000000      0.617991000000      1.666040000000      adf.f=Thymine
C      0.000000000000      1.851251000000      1.046260000000      adf.f=Thymine
N      0.000000000000      1.768641000000     -0.347380000000      adf.f=Thymine
C      0.000000000000      0.582611000000     -1.042160000000      adf.f=Thymine
C      0.000000000000     -0.621999000000     -0.417040000000      adf.f=Thymine
C      0.000000000000     -0.627269000000      1.045880000000      adf.f=Thymine
O      0.000000000000     -1.670479000000      1.720780000000      adf.f=Thymine
O      0.000000000000      2.924531000000      1.636600000000      adf.f=Thymine
C      0.000000000000     -1.937039000000     -1.138130000000      adf.f=Thymine
H      0.000000000000      0.635221000000      2.733380000000      adf.f=Thymine
H      0.000000000000      2.660141000000     -0.830100000000      adf.f=Thymine
H      0.000000000000      0.676731000000     -2.127100000000      adf.f=Thymine
H      0.880180000000     -2.533409000000     -0.860650000000      adf.f=Thymine
H      0.000000000000     -1.793509000000     -2.225780000000      adf.f=Thymine
H      -0.880180000000     -2.533409000000     -0.860650000000      adf.f=Thymine

```

end

end

Task SinglePoint

Engine ADF

title AT

fragments

Adenine Adenine.results/adf.rkf

Thymine Thymine.results/adf.rkf

end

symmetry NOSYM

TransferIntegrals

zlmfit

quality good

end

EndEngine

eor

```

# After the calculation has finished in the output one will find the charge
# transfer (overlap integrals and site energies) that are needed to calculate
# hole mobility or electron mobility calculations:

```

#_

```

→ =====

```

```

# Electronic coupling V (also known as effective (generalized) transfer integrals J_
→ eff)

```

```

# V = (J-S(e1+e2)/2)/(1-S^2)

```

#

```

# V for hole transfer:          0.000 eV

```

(continues on next page)

(continued from previous page)

```

# V for electron transfer:      -0.036 eV
#
# The effective transfer integral, or electronic coupling, is calculated from these
# components:
#
# e1(hole) Site energy HOMO fragment 1:      -6.88 eV
# e2(hole) Site energy HOMO fragment 2:      -6.46 eV
# J(hole) Charge transfer integral HOMO fragment 1 - HOMO fragment 2:      0.000 eV
# S(hole) Overlap integral HOMO fragment 1 - HOMO fragment 2:      0.000
#
# e1(electron) Site energy LUMO fragment 1:      -2.24 eV
# e2(electron) Site energy LUMO fragment 2:      -2.62 eV
# J(electron) Charge transfer integral LUMO fragment 1 - LUMO fragment 2:      -0.046
# eV
# S(electron) Overlap integral LUMO fragment 1 - LUMO fragment 2:      0.004
#
# =====

```

Example: Charge transfer integrals with FDE: water dimer

Download `ElectronTransfer_FDE_H2O.run`

```

#!/bin/sh

# == Expert Option ==

# The electron transfer calculation of a water dimer radical cation in this
# example is aimed at:

# - calculate site energies and couplings of FDE-derived charge-localized states
# - calculate the charge-transfer excitation energy from a two-state model that
#   includes the two charge-localized states involved in the calculation
# - the output also includes a rough evaluation of the error introduced by the
#   density fitting on the site energies and coupling

# First the isolated neutral fragments are obtained. Symmetry NOSYM is used.
# Next in the first FDE calculation the localized state D+A is calculated, which
# means that the first water molecule has charge +1, and the second water
# molecule is neutral. The resulting adf.rkf files must be renamed to fragA1.t21
# and fragA2.t21. In the second FDE calculation the localized state DA+ is
# calculated, now the second water molecule has charge +1, and the first water
# molecule is neutral. The resulting adf.rkf files must be renamed to fragB1.t21
# and fragB2.t21. The FDE freeze and thaw cycle is done manually, and a spin-
# unrestricted calculation is performed.

# The electron transfer calculation is next. The files fragA1.t21, fragA2.t21,
# fragB1.t21, and fragB2.t21 must exist and must have these names. The program
# must be executed in serial mode. Hybrids are not supported. NumericalQuality
# good is needed for accuracy.

# == The output of this example is discussed here ==

```

(continues on next page)

(continued from previous page)

```

# ===== Electron Transfer RESULTS =====

# Electronic Coupling =          0.000000 eV
# Electronic Coupling =        -0.000006 cm-1
# H11-H22              =        -1.396836 eV
# Excitation Energy    =         1.396836 eV
# Overlap              =         0.000000
# H11 H22 H12 =   -152.443044906236   -152.391712133030   -151.743951196449 Eh
# S11 S22 S12 =     0.981761438554       0.980941502465       -0.000000000038

# ===== END Electron Transfer RESULTS =====

# Due to symmetry, the overlap is almost diagonal (Overlap = 0.00), thus the
# transition density is evaluated with one less electron as explained in Ref.
# [JCP 138 (2013) 054101, https://doi.org/10.1063/1.4789418].

# The electronic coupling between the state with a positive charge localized on
# one water molecule and another with the charge localized on the other water
# molecule is given by 'Electronic Coupling' and is reported in eV and cm-1.

# 'H11-H22' is the difference of the site energies in eV. Values of the site
# energies are given by the first two values of 'H11 H22 H12' in atomic units.

# 'Excitation Energy' reports the value of the transfer excitation energy as
# calculated by diagonalization of the 2X2 generalized eigenvalue problem in
# the basis of the charge-localized states, see Refs.
# [JCP 135 (2011) 234103, https://doi.org/10.1063/1.3666005] and
# [JCP 138 (2013) 054101, https://doi.org/10.1063/1.4789418].

# 'S11 S22 S12' are the values of the non-normalized overlaps.

# =====
#          OBTAIN ISOLATED FRAGMENTS
# =====

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System
  atoms
    O          0.0000000000          0.0000000000          0.0000000000
    H          -0.9358409558          .2646136961          0.0000000000
    H          -0.0304663436         -0.9828924420          0.0000000000
  end
end

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type TZP

```

(continues on next page)

(continued from previous page)

```

end
noprnt BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
  iterations 90
end
symmetry NOSYM
title Isolated water molecule 1
xc
  gga PW91
end
EndEngine
eor

mv Iso1.results/adf.rkf t21.iso.rho1

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
atoms
  O          0.0000000000      -2.9053396088      0.0000000000
  H          -0.4092227596      -3.3374838250     -0.7701260000
  H          -0.4092227596      -3.3374838250      0.7701260000
end
end

Task SinglePoint

Engine ADF
eprint
  sfo NOEIG NOOVL NOORBPOP
end
basis
  core None
  type TZP
end
noprnt BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
  iterations 90
end
symmetry NOSYM
title isolated water molecule 2
xc
  gga PW91
end
EndEngine
eor
mv ams.results prev.results

mv Iso2.results/adf.rkf t21.iso.rho2

# =====
#  FIRST FDE CALCULATION: STATE D+A
#  note: the freeze and thaw is done manually
#  as we have open-shell fragments

```

(continues on next page)

(continued from previous page)

```
# =====

AMS_JOBNAME=Emb1 $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H      -0.0304663436      -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000      -2.9053396088      0.0000000000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      -0.7701260000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      0.7701260000      adf.f=rho2
  end
  charge 1
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho2 type=fde
  end
  noprint BAS FUNCTIONS
  Relativity Level=None
  numericalquality good
  scf
    iterations 90
  end
  spinpolarization 1
  symmetry NOSYM
  title MODCO: Fragment no.      1; (polarized)
  unrestricted
  xc
    gga PW91
  end
EndEngine
eor

mv Emb1.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2 $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
```

(continues on next page)

(continued from previous page)

```

      H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
      H      -0.0304663436      -0.9828924420      0.0000000000      adf.f=rho1
      O      0.0000000000      -2.9053396088      0.0000000000      adf.f=rho2
      H      -0.4092227596      -3.3374838250      -0.7701260000      adf.f=rho2
      H      -0.4092227596      -3.3374838250      0.7701260000      adf.f=rho2
    end
  end
Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  Relativity Level=None
  numericalquality good
  scf
    iterations 90
  end
  symmetry NOSYM
  title MODCO: Fragment no.          2; (polarized)
  xc
    gga PW91
  end
EndEngine
eor

mv Emb2.results/adf.rkf t21.emb.rho2

AMS_JOBNAME=Emb1r $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H      -0.0304663436      -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000      -2.9053396088      0.0000000000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      -0.7701260000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      0.7701260000      adf.f=rho2
  end
  charge 1
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

EngineRestart t21.emb.rho1

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho2 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  Relativity Level=None
  numericalquality good
  scf
    iterations 90
  end
  spinpolarization 1
  symmetry NOSYM
  title MODCO: Fragment no.          1; relaxed
  unrestricted
  xc
    gga PW91
  end
EndEngine
eor

mv Emb1r.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2r $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H      -0.0304663436      -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000      -2.9053396088      0.0000000000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      -0.7701260000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      0.7701260000      adf.f=rho2
  end
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP

```

(continues on next page)

(continued from previous page)

```

end
fde
  ggapotcfd pw91c
  ggapotxfd pw91x
  pw91k
end
fragments
  rho1 t21.emb.rho1
  rho2 t21.emb.rho2
end
fdefragments
  rho1 subfrag=active type=fde
  rho2 subfrag=active
end
noprnt BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
  iterations 90
end
symmetry NOSYM
title MODCO: Fragment no.          2; relaxed
xc
  gga PW91
end
EndEngine
eor

mv Emb2.results/adf.rkf t21.emb.rho2

mv t21.emb.rho1 fragA1.t21
mv t21.emb.rho2 fragA2.t21

# =====
#  SECOND FDE CALCULATION: STATE DA+
#  note: the freeze and thaw is done manually
#        as we have open-shell fragments
#  note: now rho1 is the second fragment
#        as rho2 is the cation
# =====

AMS_JOBNAME=Emb2p $AMSBIN/ams <<eor
System
atoms
  O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
  H     -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
  H     -0.0304663436     -0.9828924420      0.0000000000      adf.f=rho1
  O      0.0000000000     -2.9053396088      0.0000000000      adf.f=rho2
  H     -0.4092227596     -3.3374838250     -0.7701260000      adf.f=rho2
  H     -0.4092227596     -3.3374838250      0.7701260000      adf.f=rho2
end
charge 1
end

Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 type=fde
  end
  noprint BAS FUNCTIONS
  Relativity Level=None
  numericalquality good
  scf
    iterations 90
  end
  spinpolarization 1
  symmetry NOSYM
  title MODCO: Fragment no.          2; (polarized)
  unrestricted
  xc
    gga PW91
  end
EndEngine
eor

mv Emb2p.results/adf.rkf t21.emb.rho2

AMS_JOBNAME=Emb1p $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H      -0.0304663436     -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000     -2.9053396088      0.0000000000      adf.f=rho2
    H      -0.4092227596     -3.3374838250     -0.7701260000      adf.f=rho2
    H      -0.4092227596     -3.3374838250      0.7701260000      adf.f=rho2
  end
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde

```

(continues on next page)

(continued from previous page)

```

    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
end
fragments
    rho1 t21.iso.rho1
    rho2 t21.emb.rho2
end
fdefragments
    rho2 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
    iterations 90
end
symmetry NOSYM
title MODCO: Fragment no.          1; (polarized)
xc
    gga PW91
end
EndEngine
eor

mv Emb1p.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2pr $AMSBIN/ams <<eor
System
atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H      -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H      -0.0304663436      -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000      -2.9053396088      0.0000000000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      -0.7701260000      adf.f=rho2
    H      -0.4092227596      -3.3374838250      0.7701260000      adf.f=rho2
end
charge 1
end

Task SinglePoint

EngineRestart t21.emb.rho2

Engine ADF
    allow PARTIALSUPERFRAGS
    eprint
        sfo NOEIG NOOVL NOORBPOP
    end
    fde
        ggapotcfd pw91c
        ggapotxfd pw91x
        pw91k
    end
    fragments
        rho1 t21.emb.rho1
        rho2 t21.iso.rho2

```

(continues on next page)

(continued from previous page)

```

end
fdefragments
  rho1 subfrag=active type=fde
end
noprint BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
  iterations 90
end
spinpolarization 1
symmetry NOSYM
title MODCO: Fragment no.          2; relaxed
unrestricted
xc
  gga PW91
end
EndEngine
eor

mv Emb2pr.results/adf.rkf t21.emb.rho2

AMS_JOBNAME=Embp1r $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H     -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H     -0.0304663436     -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000     -2.9053396088      0.0000000000      adf.f=rho2
    H     -0.4092227596     -3.3374838250     -0.7701260000      adf.f=rho2
    H     -0.4092227596     -3.3374838250      0.7701260000      adf.f=rho2
  end
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho1 subfrag=active
    rho2 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  Relativity Level=None
  numericalquality good

```

(continues on next page)

(continued from previous page)

```

scf
  iterations 90
end
symmetry NOSYM
title MODCO: Fragment no.          1; relaxed
xc
  gga PW91
end
EndEngine
eor

mv Embp1r.results/adf.rkf t21.emb.rho1

# =====
# NOW THE adf.rkf FILES MUST BE RENAMED
#
# TO: fragA1.t21, fragA2.t21
# .... up to a max of fragA999.t21
# AND: fragB1.t21, fragB2.t21
# .... up to a max of fragB999.t21
# =====

mv t21.emb.rho1 fragB1.t21
mv t21.emb.rho2 fragB2.t21

# =====
# Electron Transfer calculation is next
#
# 1) note the ELECTRONTRANSFER block keyword
# 2) the program must be execute in
#    serial mode (parallel mode not
#    supported)
# 3) hybrids not supported
# 4) NumericalQuality good is
#    needed for accuracy
# =====

AMS_JOBNAME=ET $AMSBIN/ams <<eor
System
  atoms
    O      0.0000000000      0.0000000000      0.0000000000      adf.f=rho1
    H     -0.9358409558      .2646136961      0.0000000000      adf.f=rho1
    H     -0.0304663436     -0.9828924420      0.0000000000      adf.f=rho1
    O      0.0000000000     -2.9053396088      0.0000000000      adf.f=rho2
    H     -0.4092227596     -3.3374838250     -0.7701260000      adf.f=rho2
    H     -0.4092227596     -3.3374838250      0.7701260000      adf.f=rho2
  end
  charge 1
end

Task SinglePoint

Engine ADF
  electrontransfer
    numfrag 2
  end
  eprint

```

(continues on next page)

(continued from previous page)

```

    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
end
fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
end
noprnt BAS FUNCTIONS
Relativity Level=None
numericalquality good
scf
    iterations 0
end
spinpolarization 1
symmetry nosym
title ElectronTransfer calculation
unrestricted
xc
    gga PW91
end
EndEngine
eor

```

Example: Charge transfer integrals with FOCDFT

Download Ethylene_FOCDFT.run

```

#!/bin/sh

# FOCDFT is used to calculate charge transfer integrals
# for the ethylene dimer using PBE and an all electron DZ basis set.
# The influence of other ethylenes in the environment is investigated.

# FOCDFT is a fragment orbital based method for constraining (integer) charges and
↳ spins on fragments.
# It uses the (localized) Lowdins that ADF makes to to constrain charges and spins on
↳ fragments.
# This method can be used to specify 2 different electron configurations of the same
↳ complex,
# such that a charge on the first fragment in the first calculation is transferred
# to the second fragment in the second calculation.

# Because in the final complexes the ethylene molecules are the same,
# only one fragment needs to be calculated.

AMS_JOBNAME=Frag $AMSBIN/ams <<eor
System
symmetrize
atoms
  C      0.000000    0.000000    0.000000
  C      1.332000    0.000000    0.000000
  H     -0.574301    0.000000   -0.928785
  H     -0.574301    0.000000    0.928785
  H      1.906301    0.000000    0.928785
  H      1.906301    0.000000   -0.928785

```

(continues on next page)

(continued from previous page)

```

    end
end

Task SinglePoint

Engine ADF
  basis
    Type DZ
    core none
  end
  xc
    gga pbe
  end
EndEngine
eor

# Charge transfer integrals for the ethylene dimer at a distance of 4 Angstrom.

AMS_JOBNAME=ET2_4 $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    C      0.000000    0.000000    0.000000 adf.f=Frag1
    C      1.332000    0.000000    0.000000 adf.f=Frag1
    H     -0.574301    0.000000   -0.928785 adf.f=Frag1
    H     -0.574301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000   -0.928785 adf.f=Frag1
    C     -0.000000    4.000000    0.000000 adf.f=Frag2
    C      1.332000    4.000000   -0.000000 adf.f=Frag2
    H     -0.574301    4.000000    0.928785 adf.f=Frag2
    H     -0.574301    4.000000   -0.928785 adf.f=Frag2
    H      1.906301    4.000000   -0.928785 adf.f=Frag2
    H      1.906301    4.000000    0.928785 adf.f=Frag2
  end
  charge 1
end

Task SinglePoint

Engine ADF
  fragments
    Frag1 Frag.results/adf.rkf
    Frag2 Frag.results/adf.rkf
  end
  spinpolarization 1
  unrestricted
  xc
    gga pbe
  end
  FOCDFT
    charge 1 0
    spinpolarization 1 0
    electrontransfer
      charge 0 1
      spinpolarization 0 1
    end

```

(continues on next page)

(continued from previous page)

```

    end
EndEngine
eor

# Charge transfer integrals for the ethylene dimer at a distance of 8 Angstrom.
# The calculated charge transfer integral will be much smaller than that of the
↳previous calculation
# where the two ethylene molecules were at a distance of 4 Angstrom.

AMS_JOBNAME=ET2_8 $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    C      0.000000    0.000000    0.000000 adf.f=Frag1
    C      1.332000    0.000000    0.000000 adf.f=Frag1
    H     -0.574301    0.000000   -0.928785 adf.f=Frag1
    H     -0.574301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000   -0.928785 adf.f=Frag1
    C     -0.000000    8.000000    0.000000 adf.f=Frag3
    C      1.332000    8.000000   -0.000000 adf.f=Frag3
    H     -0.574301    8.000000    0.928785 adf.f=Frag3
    H     -0.574301    8.000000   -0.928785 adf.f=Frag3
    H      1.906301    8.000000   -0.928785 adf.f=Frag3
    H      1.906301    8.000000    0.928785 adf.f=Frag3
  end
  charge 1
end

Task SinglePoint

Engine ADF
  fragments
    Frag1 Frag.results/adf.rkf
    Frag3 Frag.results/adf.rkf
  end
  spinpolarization 1
  unrestricted
  xc
    gga pbe
  end
  FOCDFT
    charge 1 0
    spinpolarization 1 0
    electrontransfer
      charge 0 1
      spinpolarization 0 1
    end
  end
EndEngine
eor

# Charge transfer integrals for the ethylene dimer at a distance of 8 Angstrom,
# with another ethylene molecule exactly in between.
# The calculated charge transfer integral will be significant larger than that of the
↳previous calculation
# where there was no other ethylene molecule in between.

```

(continues on next page)

(continued from previous page)

AMS_JOBNAME=ET3 \$AMSBIN/ams <<eor

System

symmetrize

atoms

C	0.000000	0.000000	0.000000	adf.f=Frag1
C	1.332000	0.000000	0.000000	adf.f=Frag1
H	-0.574301	0.000000	-0.928785	adf.f=Frag1
H	-0.574301	0.000000	0.928785	adf.f=Frag1
H	1.906301	0.000000	0.928785	adf.f=Frag1
H	1.906301	0.000000	-0.928785	adf.f=Frag1
C	-0.000000	4.000000	0.000000	adf.f=Frag2
C	1.332000	4.000000	-0.000000	adf.f=Frag2
H	-0.574301	4.000000	0.928785	adf.f=Frag2
H	-0.574301	4.000000	-0.928785	adf.f=Frag2
H	1.906301	4.000000	-0.928785	adf.f=Frag2
H	1.906301	4.000000	0.928785	adf.f=Frag2
C	0.000000	8.000000	0.000000	adf.f=Frag3
C	1.332000	8.000000	0.000000	adf.f=Frag3
H	-0.574301	8.000000	-0.928785	adf.f=Frag3
H	-0.574301	8.000000	0.928785	adf.f=Frag3
H	1.906301	8.000000	0.928785	adf.f=Frag3
H	1.906301	8.000000	-0.928785	adf.f=Frag3

end

charge 1

end

Task SinglePoint

Engine ADF

fragments

Frag1 Frag.results/adf.rkf

Frag2 Frag.results/adf.rkf

Frag3 Frag.results/adf.rkf

end

spinpolarization 1

unrestricted

xc

gga pbe

end

FOCDFT

charge 1 0 0

spinpolarization 1 0 0

electrontransfer

charge 0 0 1

spinpolarization 0 0 1

end

end

EndEngine

eor

Charge transfer integrals for the ethylene dimer at a distance of 4 Angstrom,
 # with 2 ethylene molecules on either side of the dimer.
 # In this case the calculated charge transfer integral will not be very different
 # than that for the isolated dimer at 4 Angstrom.

AMS_JOBNAME=ET4 \$AMSBIN/ams <<eor

(continues on next page)

(continued from previous page)

```

System
  symmetrize
  atoms
    C      -0.000000   -4.000000    0.000000  adf.f=Frag0
    C      1.332000   -4.000000   -0.000000  adf.f=Frag0
    H     -0.574301   -4.000000    0.928785  adf.f=Frag0
    H     -0.574301   -4.000000   -0.928785  adf.f=Frag0
    H      1.906301   -4.000000   -0.928785  adf.f=Frag0
    H      1.906301   -4.000000    0.928785  adf.f=Frag0
    C      0.000000    0.000000    0.000000  adf.f=Frag1
    C      1.332000    0.000000    0.000000  adf.f=Frag1
    H     -0.574301    0.000000   -0.928785  adf.f=Frag1
    H     -0.574301    0.000000    0.928785  adf.f=Frag1
    H      1.906301    0.000000    0.928785  adf.f=Frag1
    H      1.906301    0.000000   -0.928785  adf.f=Frag1
    C     -0.000000    4.000000    0.000000  adf.f=Frag2
    C      1.332000    4.000000   -0.000000  adf.f=Frag2
    H     -0.574301    4.000000    0.928785  adf.f=Frag2
    H     -0.574301    4.000000   -0.928785  adf.f=Frag2
    H      1.906301    4.000000   -0.928785  adf.f=Frag2
    H      1.906301    4.000000    0.928785  adf.f=Frag2
    C      0.000000    8.000000    0.000000  adf.f=Frag3
    C      1.332000    8.000000    0.000000  adf.f=Frag3
    H     -0.574301    8.000000   -0.928785  adf.f=Frag3
    H     -0.574301    8.000000    0.928785  adf.f=Frag3
    H      1.906301    8.000000    0.928785  adf.f=Frag3
    H      1.906301    8.000000   -0.928785  adf.f=Frag3
  end
  charge 1
end

Task SinglePoint

Engine ADF
  fragments
    Frag0 Frag.results/adf.rkf
    Frag1 Frag.results/adf.rkf
    Frag2 Frag.results/adf.rkf
    Frag3 Frag.results/adf.rkf
  end
  spinpolarization 1
  unrestricted
  xc
    gga pbe
  end
  FOCDFT
    charge 0 1 0 0
    spinpolarization 0 1 0 0
    electrontransfer
      charge 0 0 1 0
      spinpolarization 0 0 1 0
    end
  end
EndEngine
eor

```


Example: Charge Recombination Calculation of Toluene and TCNE

Download ChargeSeparation_Toluene_TCNE.run

```
#!/bin/sh

# Charge Recombination Calculation of Toluene and TCNE
# tol + TCNE ==> tol+ + TCNE-
# aimed at:

# 1) calculate site energies and couplings of fde-derived neutral states
#    (Diabat 1) and charge-localized states (Diabat 2)
# 2) calculate the charge-transfer excitation energy from a two-state model that
#    includes the two Diabatic states involved in the calculation

# First the isolated neutral fragments are obtained. Symmetry NOSYM is used.
# Resulting files: t21.iso.rho1 and t21.iso.rho2. Next in the first FDE
# calculations: state Toluene (neutral) and TCNE (neutral), resulting files:
# fragA1.t21 and fragA2.t21. The freeze and thaw cycles are done manually since
# open-shell fragments were used. Next in the second FDE calculations: state
# Toluene+ and TCNE-, resulting files fragB1.t21 and fragB2.t21. Again freeze
# and thaw cycles are done manually since open-shell fragments were used.

# In the final charge separation calculation the ELECTRONTRANSFER block keyword
# The program must be executed in serial mode.

# NOTE: For production-quality results use a larger basis set

# =====
#          OBTAIN ISOLATED FRAGMENTS
# =====

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System
  atoms
    C      -1.070970000000000    -2.321680000000000    0.000000000000000
    C      -1.395990000000000    -1.695110000000000    1.208637000000000
    C      -1.395990000000000    -1.695110000000000    -1.208640000000000
    H      -0.573940000000000    -3.294470000000000    0.000000000000000
    C      -2.042420000000000    -0.455960000000000    1.205797000000000
    H      -1.145390000000000    -2.174110000000000    2.157975000000000
    C      -2.042420000000000    -0.455960000000000    -1.205800000000000
    H      -1.145390000000000    -2.174110000000000    -2.157980000000000
    C      -2.381860000000000    0.182208000000000    0.000000000000000
    H      -2.290060000000000    0.025693000000000    2.155299000000000
    H      -2.290060000000000    0.025693000000000    -2.155300000000000
    C      -3.120570000000000    1.499082000000000    0.000000000000000
    H      -2.883370000000000    2.099627000000000    0.891903000000000
    H      -2.883370000000000    2.099627000000000    -0.891900000000000
    H      -4.212730000000000    1.335415000000000    0.000000000000000
  end
end

Task SinglePoint

Engine ADF
```

(continues on next page)

(continued from previous page)

```

eprint
  sfo NOEIG NOOVL NOORBPOP
end
basis
  core none
  type DZ
end
noprnt BAS FUNCTIONS
symmetry NOSYM
title Isolated Toluene
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Iso1.results/adf.rkf t21.iso.rho1

AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
System
  atoms
    C      1.83245600000000    -0.14587000000000    0.00000000000000
    C      1.20994900000000     1.07690800000000    0.00000000000000
    C      2.18809800000000    -0.80630000000000   -1.21971000000000
    C      2.18809800000000    -0.80630000000000    1.21971000000000
    C      0.88208300000000     1.75218800000000   -1.21935000000000
    C      0.88208300000000     1.75218800000000    1.21934500000000
    N      2.50290100000000    -1.35237000000000   -2.19775000000000
    N      2.50290100000000    -1.35237000000000    2.19774900000000
    N      0.61754300000000     2.32819700000000   -2.19523000000000
    N      0.61754300000000     2.32819700000000    2.19522600000000
  end
end

Task SinglePoint

Engine ADF
eprint
  sfo NOEIG NOOVL NOORBPOP
end
basis
  core none
  type DZ
end
noprnt BAS FUNCTIONS
symmetry NOSYM
title Isolated TCNE
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Iso2.results/adf.rkf t21.iso.rho2

```

(continues on next page)

(continued from previous page)

```
# =====
# FIRST FDE CALCULATION: STATE tol(neutral) and TCNE (neutral)
# note: the freeze and thaw is done manually
# as we have open-shell fragments
# =====

AMS_JOBNAME=Emb1 $AMSBIN/ams <<eor
System
atoms
  C      -1.07097000000000    -2.32168000000000    0.00000000000000    adf.
↪f=rho1
  C      -1.39599000000000    -1.69511000000000    1.20863700000000    adf.
↪f=rho1
  C      -1.39599000000000    -1.69511000000000    -1.20864000000000    adf.
↪f=rho1
  H      -0.57394000000000    -3.29447000000000    0.00000000000000    adf.
↪f=rho1
  C      -2.04242000000000    -0.45596000000000    1.20579700000000    adf.
↪f=rho1
  H      -1.14539000000000    -2.17411000000000    2.15797500000000    adf.
↪f=rho1
  C      -2.04242000000000    -0.45596000000000    -1.20580000000000    adf.
↪f=rho1
  H      -1.14539000000000    -2.17411000000000    -2.15798000000000    adf.
↪f=rho1
  C      -2.38186000000000    0.18220800000000    0.00000000000000    adf.
↪f=rho1
  H      -2.29006000000000    0.02569300000000    2.15529900000000    adf.
↪f=rho1
  H      -2.29006000000000    0.02569300000000    -2.15530000000000    adf.
↪f=rho1
  C      -3.12057000000000    1.49908200000000    0.00000000000000    adf.
↪f=rho1
  H      -2.88337000000000    2.09962700000000    0.89190300000000    adf.
↪f=rho1
  H      -2.88337000000000    2.09962700000000    -0.89190000000000    adf.
↪f=rho1
  H      -4.21273000000000    1.33541500000000    0.00000000000000    adf.
↪f=rho1
  C      1.83245600000000    -0.14587000000000    0.00000000000000    adf.
↪f=rho2
  C      1.20994900000000    1.07690800000000    0.00000000000000    adf.
↪f=rho2
  C      2.18809800000000    -0.80630000000000    -1.21971000000000    adf.
↪f=rho2
  C      2.18809800000000    -0.80630000000000    1.21971000000000    adf.
↪f=rho2
  C      0.88208300000000    1.75218800000000    -1.21935000000000    adf.
↪f=rho2
  C      0.88208300000000    1.75218800000000    1.21934500000000    adf.
↪f=rho2
  N      2.50290100000000    -1.35237000000000    -2.19775000000000    adf.
↪f=rho2
  N      2.50290100000000    -1.35237000000000    2.19774900000000    adf.
↪f=rho2
  N      0.61754300000000    2.32819700000000    -2.19523000000000    adf.
↪f=rho2
```

(continues on next page)

(continued from previous page)

```

      N      0.617543000000000      2.328197000000000      2.195226000000000      adf.
↪f=rho2
end
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
    xcnadd PW91
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho2 type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization 0
  symmetry NOSYM
  title tol(neutral), First freeze--and--thaw cycle
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

mv Emb1.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2 $AMSBIN/ams <<eor
System
  atoms
    C      -1.070970000000000      -2.321680000000000      0.000000000000000      adf.
↪f=rho1
    C      -1.395990000000000      -1.695110000000000      1.208637000000000      adf.
↪f=rho1
    C      -1.395990000000000      -1.695110000000000      -1.208640000000000      adf.
↪f=rho1
    H      -0.573940000000000      -3.294470000000000      0.000000000000000      adf.
↪f=rho1
    C      -2.042420000000000      -0.455960000000000      1.205797000000000      adf.
↪f=rho1
    H      -1.145390000000000      -2.174110000000000      2.157975000000000      adf.
↪f=rho1
    C      -2.042420000000000      -0.455960000000000      -1.205800000000000      adf.
↪f=rho1
    H      -1.145390000000000      -2.174110000000000      -2.157980000000000      adf.
↪f=rho1
    C      -2.381860000000000      0.182208000000000      0.000000000000000      adf.

```

(continues on next page)

(continued from previous page)

```

→f=rho1
  H      -2.290060000000000    0.025693000000000    2.155299000000000    adf.
→f=rho1
  H      -2.290060000000000    0.025693000000000   -2.155300000000000    adf.
→f=rho1
  C      -3.120570000000000    1.499082000000000    0.000000000000000    adf.
→f=rho1
  H      -2.883370000000000    2.099627000000000    0.891903000000000    adf.
→f=rho1
  H      -2.883370000000000    2.099627000000000   -0.891900000000000    adf.
→f=rho1
  H      -4.212730000000000    1.335415000000000    0.000000000000000    adf.
→f=rho1
  C      1.832456000000000   -0.145870000000000    0.000000000000000    adf.
→f=rho2
  C      1.209949000000000    1.076908000000000    0.000000000000000    adf.
→f=rho2
  C      2.188098000000000   -0.806300000000000   -1.219710000000000    adf.
→f=rho2
  C      2.188098000000000   -0.806300000000000    1.219710000000000    adf.
→f=rho2
  C      0.882083000000000    1.752188000000000   -1.219350000000000    adf.
→f=rho2
  C      0.882083000000000    1.752188000000000    1.219345000000000    adf.
→f=rho2
  N      2.502901000000000   -1.352370000000000   -2.197750000000000    adf.
→f=rho2
  N      2.502901000000000   -1.352370000000000    2.197749000000000    adf.
→f=rho2
  N      0.617543000000000    2.328197000000000   -2.195230000000000    adf.
→f=rho2
  N      0.617543000000000    2.328197000000000    2.195226000000000    adf.
→f=rho2
  end
end

```

Task SinglePoint

Engine ADF

```

allow PARTIALSUPERFRAGS
eprint
  sfo NOEIG NOOVL NOORBPOP
end
fde
  pw91k
  xcnadd PW91
end
fragments
  rho1 t21.emb.rho1
  rho2 t21.iso.rho2
end
fdefragments
  rho1 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
spinpolarization 0
symmetry NOSYM

```

(continues on next page)

(continued from previous page)

```

title TCNE(neutral), First freeze--and--thaw cycle
unrestricted
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb2.results/adf.rkf t21.emb.rho2

it=1
while [ $it -le 2 ]; do

AMS_JOBNAME=Emb1.$it $AMSBIN/ams <<eor
System
  atoms
    C      -1.07097000000000    -2.32168000000000    0.00000000000000    adf.
↪f=rho1
    C      -1.39599000000000    -1.69511000000000    1.20863700000000    adf.
↪f=rho1
    C      -1.39599000000000    -1.69511000000000    -1.20864000000000    adf.
↪f=rho1
    H      -0.57394000000000    -3.29447000000000    0.00000000000000    adf.
↪f=rho1
    C      -2.04242000000000    -0.45596000000000    1.20579700000000    adf.
↪f=rho1
    H      -1.14539000000000    -2.17411000000000    2.15797500000000    adf.
↪f=rho1
    C      -2.04242000000000    -0.45596000000000    -1.20580000000000    adf.
↪f=rho1
    H      -1.14539000000000    -2.17411000000000    -2.15798000000000    adf.
↪f=rho1
    C      -2.38186000000000    0.18220800000000    0.00000000000000    adf.
↪f=rho1
    H      -2.29006000000000    0.02569300000000    2.15529900000000    adf.
↪f=rho1
    H      -2.29006000000000    0.02569300000000    -2.15530000000000    adf.
↪f=rho1
    C      -3.12057000000000    1.49908200000000    0.00000000000000    adf.
↪f=rho1
    H      -2.88337000000000    2.09962700000000    0.89190300000000    adf.
↪f=rho1
    H      -2.88337000000000    2.09962700000000    -0.89190000000000    adf.
↪f=rho1
    H      -4.21273000000000    1.33541500000000    0.00000000000000    adf.
↪f=rho1
    C      1.83245600000000    -0.14587000000000    0.00000000000000    adf.
↪f=rho2
    C      1.20994900000000    1.07690800000000    0.00000000000000    adf.
↪f=rho2
    C      2.18809800000000    -0.80630000000000    -1.21971000000000    adf.
↪f=rho2
    C      2.18809800000000    -0.80630000000000    1.21971000000000    adf.
↪f=rho2
    C      0.88208300000000    1.75218800000000    -1.21935000000000    adf.

```

(continues on next page)

(continued from previous page)

```

↪f=rho2
  C      0.88208300000000    1.75218800000000    1.21934500000000    adf.
↪f=rho2
  N      2.50290100000000   -1.35237000000000   -2.19775000000000    adf.
↪f=rho2
  N      2.50290100000000   -1.35237000000000    2.19774900000000    adf.
↪f=rho2
  N      0.61754300000000    2.32819700000000   -2.19523000000000    adf.
↪f=rho2
  N      0.61754300000000    2.32819700000000    2.19522600000000    adf.
↪f=rho2
  end
end

Task SinglePoint

EngineRestart t21.emb.rho1

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
    xcnadd PW91
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho2 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization 0
  symmetry NOSYM
  title tol(neutral), Relaxation cycles
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

mv Emb1.$it.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2.$it $AMSBIN/ams <<eor
System
  atoms
    C      -1.07097000000000   -2.32168000000000    0.00000000000000    adf.
↪f=rho1
    C      -1.39599000000000   -1.69511000000000    1.20863700000000    adf.
↪f=rho1
    C      -1.39599000000000   -1.69511000000000   -1.20864000000000    adf.
↪f=rho1

```

(continues on next page)

(continued from previous page)

```

      H      -0.573940000000000    -3.294470000000000    0.000000000000000    adf.
↪ f=rho1
      C      -2.042420000000000    -0.455960000000000    1.205797000000000    adf.
↪ f=rho1
      H      -1.145390000000000    -2.174110000000000    2.157975000000000    adf.
↪ f=rho1
      C      -2.042420000000000    -0.455960000000000    -1.205800000000000    adf.
↪ f=rho1
      H      -1.145390000000000    -2.174110000000000    -2.157980000000000    adf.
↪ f=rho1
      C      -2.381860000000000     0.182208000000000     0.000000000000000    adf.
↪ f=rho1
      H      -2.290060000000000     0.025693000000000     2.155299000000000    adf.
↪ f=rho1
      H      -2.290060000000000     0.025693000000000    -2.155300000000000    adf.
↪ f=rho1
      C      -3.120570000000000     1.499082000000000     0.000000000000000    adf.
↪ f=rho1
      H      -2.883370000000000     2.099627000000000     0.891903000000000    adf.
↪ f=rho1
      H      -2.883370000000000     2.099627000000000    -0.891900000000000    adf.
↪ f=rho1
      H      -4.212730000000000     1.335415000000000     0.000000000000000    adf.
↪ f=rho1
      C      1.832456000000000    -0.145870000000000     0.000000000000000    adf.
↪ f=rho2
      C      1.209949000000000     1.076908000000000     0.000000000000000    adf.
↪ f=rho2
      C      2.188098000000000    -0.806300000000000    -1.219710000000000    adf.
↪ f=rho2
      C      2.188098000000000    -0.806300000000000     1.219710000000000    adf.
↪ f=rho2
      C      0.882083000000000     1.752188000000000    -1.219350000000000    adf.
↪ f=rho2
      C      0.882083000000000     1.752188000000000     1.219345000000000    adf.
↪ f=rho2
      N      2.502901000000000    -1.352370000000000    -2.197750000000000    adf.
↪ f=rho2
      N      2.502901000000000    -1.352370000000000     2.197749000000000    adf.
↪ f=rho2
      N      0.617543000000000     2.328197000000000    -2.195230000000000    adf.
↪ f=rho2
      N      0.617543000000000     2.328197000000000     2.195226000000000    adf.
↪ f=rho2
end
end

Task SinglePoint

EngineRestart t21.emb.rho2

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
  sfo NOEIG NOOVL NOORBPOP
end
fde

```

(continues on next page)

(continued from previous page)

```

    pw91k
    xcnadd PW91
end
fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
end
fdefragments
    rho1 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
spinpolarization 0
symmetry NOSYM
title TCNE(neutral), Relaxation cycles
unrestricted
xc
    model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb2.$it.results/adf.rkf t21.emb.rho2

it=$((it+1))
done

mv t21.emb.rho1 fragA1.t21
mv t21.emb.rho2 fragA2.t21

# =====
#  SECOND FDE CALCULATION: STATE tol+ TCNE-
#  note: the freeze and thaw is done manually
#      as we have open-shell fragments
#  =====

AMS_JOBNAME=Emb1p $AMSBIN/ams <<eor
System
atoms
    C      -1.07097000000000    -2.32168000000000    0.00000000000000    adf.
↪f=rho1
    C      -1.39599000000000    -1.69511000000000    1.20863700000000    adf.
↪f=rho1
    C      -1.39599000000000    -1.69511000000000    -1.20864000000000    adf.
↪f=rho1
    H      -0.57394000000000    -3.29447000000000    0.00000000000000    adf.
↪f=rho1
    C      -2.04242000000000    -0.45596000000000    1.20579700000000    adf.
↪f=rho1
    H      -1.14539000000000    -2.17411000000000    2.15797500000000    adf.
↪f=rho1
    C      -2.04242000000000    -0.45596000000000    -1.20580000000000    adf.
↪f=rho1
    H      -1.14539000000000    -2.17411000000000    -2.15798000000000    adf.
↪f=rho1

```

(continues on next page)

(continued from previous page)

```

      C      -2.381860000000000      0.182208000000000      0.000000000000000      adf.
    ↪ f=rho1
      H      -2.290060000000000      0.025693000000000      2.155299000000000      adf.
    ↪ f=rho1
      H      -2.290060000000000      0.025693000000000      -2.155300000000000      adf.
    ↪ f=rho1
      C      -3.120570000000000      1.499082000000000      0.000000000000000      adf.
    ↪ f=rho1
      H      -2.883370000000000      2.099627000000000      0.891903000000000      adf.
    ↪ f=rho1
      H      -2.883370000000000      2.099627000000000      -0.891900000000000      adf.
    ↪ f=rho1
      H      -4.212730000000000      1.335415000000000      0.000000000000000      adf.
    ↪ f=rho1
      C      1.832456000000000      -0.145870000000000      0.000000000000000      adf.
    ↪ f=rho2
      C      1.209949000000000      1.076908000000000      0.000000000000000      adf.
    ↪ f=rho2
      C      2.188098000000000      -0.806300000000000      -1.219710000000000      adf.
    ↪ f=rho2
      C      2.188098000000000      -0.806300000000000      1.219710000000000      adf.
    ↪ f=rho2
      C      0.882083000000000      1.752188000000000      -1.219350000000000      adf.
    ↪ f=rho2
      C      0.882083000000000      1.752188000000000      1.219345000000000      adf.
    ↪ f=rho2
      N      2.502901000000000      -1.352370000000000      -2.197750000000000      adf.
    ↪ f=rho2
      N      2.502901000000000      -1.352370000000000      2.197749000000000      adf.
    ↪ f=rho2
      N      0.617543000000000      2.328197000000000      -2.195230000000000      adf.
    ↪ f=rho2
      N      0.617543000000000      2.328197000000000      2.195226000000000      adf.
    ↪ f=rho2
      end
      charge 1
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
    xcnadd PW91
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho2 type=fde
  end
  noprint BAS FUNCTIONS

```

(continues on next page)

(continued from previous page)

```

spinpolarization 1
symmetry NOSYM
title tol+, First freeze--and--thaw cycle
unrestricted
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb1p.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2p $AMSBIN/ams <<eor
System
atoms
  C      -1.070970000000000    -2.321680000000000    0.000000000000000    adf.
↪ f=rho1
  C      -1.395990000000000    -1.695110000000000    1.208637000000000    adf.
↪ f=rho1
  C      -1.395990000000000    -1.695110000000000    -1.208640000000000    adf.
↪ f=rho1
  H      -0.573940000000000    -3.294470000000000    0.000000000000000    adf.
↪ f=rho1
  C      -2.042420000000000    -0.455960000000000    1.205797000000000    adf.
↪ f=rho1
  H      -1.145390000000000    -2.174110000000000    2.157975000000000    adf.
↪ f=rho1
  C      -2.042420000000000    -0.455960000000000    -1.205800000000000    adf.
↪ f=rho1
  H      -1.145390000000000    -2.174110000000000    -2.157980000000000    adf.
↪ f=rho1
  C      -2.381860000000000    0.182208000000000    0.000000000000000    adf.
↪ f=rho1
  H      -2.290060000000000    0.025693000000000    2.155299000000000    adf.
↪ f=rho1
  H      -2.290060000000000    0.025693000000000    -2.155300000000000    adf.
↪ f=rho1
  C      -3.120570000000000    1.499082000000000    0.000000000000000    adf.
↪ f=rho1
  H      -2.883370000000000    2.099627000000000    0.891903000000000    adf.
↪ f=rho1
  H      -2.883370000000000    2.099627000000000    -0.891900000000000    adf.
↪ f=rho1
  H      -4.212730000000000    1.335415000000000    0.000000000000000    adf.
↪ f=rho1
  C      1.832456000000000    -0.145870000000000    0.000000000000000    adf.
↪ f=rho2
  C      1.209949000000000    1.076908000000000    0.000000000000000    adf.
↪ f=rho2
  C      2.188098000000000    -0.806300000000000    -1.219710000000000    adf.
↪ f=rho2
  C      2.188098000000000    -0.806300000000000    1.219710000000000    adf.
↪ f=rho2
  C      0.882083000000000    1.752188000000000    -1.219350000000000    adf.
↪ f=rho2
  C      0.882083000000000    1.752188000000000    1.219345000000000    adf.

```

(continues on next page)

(continued from previous page)

```

↪f=rho2
  N      2.502901000000000    -1.352370000000000    -2.197750000000000    adf.
↪f=rho2
  N      2.502901000000000    -1.352370000000000     2.197749000000000    adf.
↪f=rho2
  N      0.617543000000000     2.328197000000000    -2.195230000000000    adf.
↪f=rho2
  N      0.617543000000000     2.328197000000000     2.195226000000000    adf.
↪f=rho2
end
charge -1
end

```

Task SinglePoint

```

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
    xcnadd PW91
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization -1
  symmetry NOSYM
  title TCNE-, First freeze--and--thaw cycle
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

```

```
mv Emb2p.results/adf.rkf t21.emb.rho2
```

```

it=1
while [ $it -le 2 ]; do

AMS_JOBNAME=Emb1p.$it $AMSBIN/ams <<eor
System
  atoms
    C      -1.070970000000000    -2.321680000000000     0.000000000000000    adf.
↪f=rho1
    C      -1.395990000000000    -1.695110000000000     1.208637000000000    adf.
↪f=rho1
    C      -1.395990000000000    -1.695110000000000    -1.208640000000000    adf.

```

(continues on next page)

(continued from previous page)

```

→f=rho1
  H      -0.573940000000000    -3.294470000000000    0.000000000000000    adf.
→f=rho1
  C      -2.042420000000000    -0.455960000000000    1.205797000000000    adf.
→f=rho1
  H      -1.145390000000000    -2.174110000000000    2.157975000000000    adf.
→f=rho1
  C      -2.042420000000000    -0.455960000000000    -1.205800000000000    adf.
→f=rho1
  H      -1.145390000000000    -2.174110000000000    -2.157980000000000    adf.
→f=rho1
  C      -2.381860000000000     0.182208000000000     0.000000000000000    adf.
→f=rho1
  H      -2.290060000000000     0.025693000000000     2.155299000000000    adf.
→f=rho1
  H      -2.290060000000000     0.025693000000000    -2.155300000000000    adf.
→f=rho1
  C      -3.120570000000000     1.499082000000000     0.000000000000000    adf.
→f=rho1
  H      -2.883370000000000     2.099627000000000     0.891903000000000    adf.
→f=rho1
  H      -2.883370000000000     2.099627000000000    -0.891900000000000    adf.
→f=rho1
  H      -4.212730000000000     1.335415000000000     0.000000000000000    adf.
→f=rho1
  C      1.832456000000000    -0.145870000000000     0.000000000000000    adf.
→f=rho2
  C      1.209949000000000     1.076908000000000     0.000000000000000    adf.
→f=rho2
  C      2.188098000000000    -0.806300000000000    -1.219710000000000    adf.
→f=rho2
  C      2.188098000000000    -0.806300000000000     1.219710000000000    adf.
→f=rho2
  C      0.882083000000000     1.752188000000000    -1.219350000000000    adf.
→f=rho2
  C      0.882083000000000     1.752188000000000     1.219345000000000    adf.
→f=rho2
  N      2.502901000000000    -1.352370000000000    -2.197750000000000    adf.
→f=rho2
  N      2.502901000000000    -1.352370000000000     2.197749000000000    adf.
→f=rho2
  N      0.617543000000000     2.328197000000000    -2.195230000000000    adf.
→f=rho2
  N      0.617543000000000     2.328197000000000     2.195226000000000    adf.
  end
  charge 1
end

Task SinglePoint

EngineRestart t21.emb.rho1

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
  sfo NOEIG NOOVL NOORBPOP

```

(continues on next page)

(continued from previous page)

```

end
fde
  pw91k
  xcnadd PW91
end
fragments
  rho1 t21.iso.rho1
  rho2 t21.emb.rho2
end
fdefragments
  rho2 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
spinpolarization 1
symmetry NOSYM
title tol+, Relaxation cycles
unrestricted
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb1p.$it.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2p.$it $AMSBIN/ams <<eor
System
  atoms
    C      -1.07097000000000    -2.32168000000000    0.00000000000000    adf.
    ↪f=rho1
    C      -1.39599000000000    -1.69511000000000    1.20863700000000    adf.
    ↪f=rho1
    C      -1.39599000000000    -1.69511000000000    -1.20864000000000    adf.
    ↪f=rho1
    H      -0.57394000000000    -3.29447000000000    0.00000000000000    adf.
    ↪f=rho1
    C      -2.04242000000000    -0.45596000000000    1.20579700000000    adf.
    ↪f=rho1
    H      -1.14539000000000    -2.17411000000000    2.15797500000000    adf.
    ↪f=rho1
    C      -2.04242000000000    -0.45596000000000    -1.20580000000000    adf.
    ↪f=rho1
    H      -1.14539000000000    -2.17411000000000    -2.15798000000000    adf.
    ↪f=rho1
    C      -2.38186000000000    0.18220800000000    0.00000000000000    adf.
    ↪f=rho1
    H      -2.29006000000000    0.02569300000000    2.15529900000000    adf.
    ↪f=rho1
    H      -2.29006000000000    0.02569300000000    -2.15530000000000    adf.
    ↪f=rho1
    C      -3.12057000000000    1.49908200000000    0.00000000000000    adf.
    ↪f=rho1
    H      -2.88337000000000    2.09962700000000    0.89190300000000    adf.
    ↪f=rho1
    H      -2.88337000000000    2.09962700000000    -0.89190000000000    adf.
    ↪f=rho1

```

(continues on next page)

(continued from previous page)

```

      H      -4.212730000000000      1.335415000000000      0.000000000000000      adf.
↪f=rho1
      C      1.832456000000000      -0.145870000000000      0.000000000000000      adf.
↪f=rho2
      C      1.209949000000000      1.076908000000000      0.000000000000000      adf.
↪f=rho2
      C      2.188098000000000      -0.806300000000000      -1.219710000000000      adf.
↪f=rho2
      C      2.188098000000000      -0.806300000000000      1.219710000000000      adf.
↪f=rho2
      C      0.882083000000000      1.752188000000000      -1.219350000000000      adf.
↪f=rho2
      C      0.882083000000000      1.752188000000000      1.219345000000000      adf.
↪f=rho2
      N      2.502901000000000      -1.352370000000000      -2.197750000000000      adf.
↪f=rho2
      N      2.502901000000000      -1.352370000000000      2.197749000000000      adf.
↪f=rho2
      N      0.617543000000000      2.328197000000000      -2.195230000000000      adf.
↪f=rho2
      N      0.617543000000000      2.328197000000000      2.195226000000000      adf.
↪f=rho2
      end
      charge -1
end

Task SinglePoint

EngineRestart t21.emb.rho2

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    pw91k
    xcnadd PW91
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization -1
  symmetry NOSYM
  title TCNE-, Relaxation cycles
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

mv Emb2p.$it.results/adf.rkf t21.emb.rho2

it=$((it+1))
done

mv t21.emb.rho1 fragB1.t21
mv t21.emb.rho2 fragB2.t21

# =====
# Charge Separation calculation is next
#
# 1) note the ELECTRONTRANSFER block keyword
# 2) the program must be execute in
#    serial mode (parallel mode not
#    supported)
# 3) hybrids not supported
# =====

AMS_JOBNAME=ET $AMSBIN/ams <<eor
System
atoms
  C      -1.070970000000000    -2.321680000000000    0.000000000000000    adf.
↪f=rho1
  C      -1.395990000000000    -1.695110000000000    1.208637000000000    adf.
↪f=rho1
  C      -1.395990000000000    -1.695110000000000    -1.208640000000000    adf.
↪f=rho1
  H      -0.573940000000000    -3.294470000000000    0.000000000000000    adf.
↪f=rho1
  C      -2.042420000000000    -0.455960000000000    1.205797000000000    adf.
↪f=rho1
  H      -1.145390000000000    -2.174110000000000    2.157975000000000    adf.
↪f=rho1
  C      -2.042420000000000    -0.455960000000000    -1.205800000000000    adf.
↪f=rho1
  H      -1.145390000000000    -2.174110000000000    -2.157980000000000    adf.
↪f=rho1
  C      -2.381860000000000    0.182208000000000    0.000000000000000    adf.
↪f=rho1
  H      -2.290060000000000    0.025693000000000    2.155299000000000    adf.
↪f=rho1
  H      -2.290060000000000    0.025693000000000    -2.155300000000000    adf.
↪f=rho1
  C      -3.120570000000000    1.499082000000000    0.000000000000000    adf.
↪f=rho1
  H      -2.883370000000000    2.099627000000000    0.891903000000000    adf.
↪f=rho1
  H      -2.883370000000000    2.099627000000000    -0.891900000000000    adf.
↪f=rho1
  H      -4.212730000000000    1.335415000000000    0.000000000000000    adf.
↪f=rho1
  C      1.832456000000000    -0.145870000000000    0.000000000000000    adf.
↪f=rho2

```

(continues on next page)

(continued from previous page)

```

      C      1.209949000000000      1.076908000000000      0.000000000000000      adf.
↪ f=rho2
      C      2.188098000000000     -0.806300000000000     -1.219710000000000      adf.
↪ f=rho2
      C      2.188098000000000     -0.806300000000000      1.219710000000000      adf.
↪ f=rho2
      C      0.882083000000000      1.752188000000000     -1.219350000000000      adf.
↪ f=rho2
      C      0.882083000000000      1.752188000000000      1.219345000000000      adf.
↪ f=rho2
      N      2.502901000000000     -1.352370000000000     -2.197750000000000      adf.
↪ f=rho2
      N      2.502901000000000     -1.352370000000000      2.197749000000000      adf.
↪ f=rho2
      N      0.617543000000000      2.328197000000000     -2.195230000000000      adf.
↪ f=rho2
      N      0.617543000000000      2.328197000000000      2.195226000000000      adf.
↪ f=rho2
      end
end

```

Task SinglePoint

```

Engine ADF
  electrontransfer
    debug
    numfrag 2
  end
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  noprint BAS FUNCTIONS
  scf
    iterations 0
  end
  spinpolarization 0
  symmetry NOSYM
  title ChargeSeparation Calculation
  unrestricted
  xc
    gga PW91
  end
  Relativity Level=None
EndEngine
eor

```

Example: XCDFE: Charge Separation of an ethylene dimer

Download XCDFE_FDE_ET_ethylene.run

```
#!/bin/sh

#
# =====
#
# Charge Separation Calculation of a ethylene dimer:
# C2H4* + C2H4 --> C2H4+ + C2H4-
# aimed at:
#
# 1) calculate site energies and couplings of fde-derived of a localized exciton
# (Diabat 1) and charge-separated state (Diabat 2). The exciton is obtained by
# using
# XCDFE method.
#
# 2) calculate the charge-transfer excitation energy from a two-state model that
# includes the two charge-localized states involved in the calculation
#
# First the isolated (restricted) neutral fragments are obtained. Symmetry NOSYM is
# used.
# In addition, an isolated unrestricted neutral calculation of the fragment to be
# excited is performed.
# Resulting files: t21.iso.rho1, t21.iso.rho2 and gs.t21. Next in the first FDE
# calculation:
# state C2H4* (neutral-XCDFE excitation) and C2H4(neutral), resulting files:
# fragA1.t21 and fragA2.t21. The freeze and thaw cycles are done manually since
# open-shell fragments were used. Next in the second FDE calculation: state C2H4+
# and C2H4-,
# resulting files fragB1.t21 and fragB2.t21. Again freeze and thaw cycles are done
# manually since
# open-shell fragments were used.
#
# In the final charge separation calculation the ELECTRONTRANSFER block keyword is
# used.
# The files fragA1.t21, fragA2.t21, fragB1.t21, and fragB2.t21 must exist and must
# have these names.
#
# =====

# =====
# OBTAIN ISOLATED FRAGMENTS
# =====

AMS_JOBNAME=Iso1 $AMSBIN/ams <<eor
System
atoms
  H      0.930241    1.239503    0.000000
  H     -0.930241    1.239503    0.000000
  C      0.000000    0.667450    0.000000
  C      0.000000   -0.667450    0.000000
  H      0.930241   -1.239503    0.000000
  H     -0.930241   -1.239503    0.000000
end
end
```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type TZP
  end
  noprint BAS FUNCTIONS
  symmetry NOSYM
  title MODCO: Fragment no.          1; (isolated)
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

```

```
mv Iso1.results/adf.rkf t21.iso.rho1
```

```
AMS_JOBNAME=Iso2 $AMSBIN/ams <<eor
```

```

System
  atoms
    H      0.930241    1.239503    8.000000
    H     -0.930241    1.239503    8.000000
    C      0.000000    0.667450    8.000000
    C      0.000000   -0.667450    8.000000
    H      0.930241   -1.239503    8.000000
    H     -0.930241   -1.239503    8.000000
  end
end

```

```

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type TZP
  end
  noprint BAS FUNCTIONS
  symmetry NOSYM
  title MODCO: Fragment no.          2; (isolated)
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

```

```
mv Iso2.results/adf.rkf t21.iso.rho2
```

(continues on next page)

(continued from previous page)

```

# =====
#      OBTAIN ISOLATED UNRESTRICTED FRAGMENT
# =====
AMS_JOBNAME=Iso1u $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000
    H     -0.930241    1.239503    0.000000
    C      0.000000    0.667450    0.000000
    C      0.000000   -0.667450    0.000000
    H      0.930241   -1.239503    0.000000
    H     -0.930241   -1.239503    0.000000
  end
end

Task SinglePoint

Engine ADF
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type TZP
  end
  noprint BAS FUNCTIONS
  spinpolarization 0
  symmetry NOSYM
  title Fragment 1; (isolated_unrestricted)
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

# =====
#      RENAME TAPE21 file as gs.t21, as required in
#      XCDFE methodology.
# =====
mv Iso1u.results/adf.rkf gs.t21

# =====
#      FIRST FDE CALCULATION: STATE D* (XCDFE) + A
#      note: the freeze and thaw is done manually
#      as we have open-shell fragments
# =====

AMS_JOBNAME=Emb1 $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1

```

(continues on next page)

(continued from previous page)

```

      H      0.930241   -1.239503   0.000000   adf.f=rho1
      H     -0.930241   -1.239503   0.000000   adf.f=rho1
      H      0.930241    1.239503   8.000000   adf.f=rho2
      H     -0.930241    1.239503   8.000000   adf.f=rho2
      C      0.000000    0.667450   8.000000   adf.f=rho2
      C      0.000000   -0.667450   8.000000   adf.f=rho2
      H      0.930241   -1.239503   8.000000   adf.f=rho2
      H     -0.930241   -1.239503   8.000000   adf.f=rho2
    end
  end
Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  cdft
    allatoms
    constraints 1.0
    excitedcdft
    initialmultipliers 0.0
    maxiter 250
    metric
    natomsperset 36
    nconstraints 1
    print LOW
    stepsize 0.4
    threshold 1.0e-9
  end
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho2 type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization 0
  symmetry NOSYM
  title MODCO: Fragment no.          1; (polarized)
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

mv Emb1.results/adf.rkf t21.emb.rho1

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=Emb2 $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1
    H      0.930241   -1.239503    0.000000    adf.f=rho1
    H     -0.930241   -1.239503    0.000000    adf.f=rho1
    H      0.930241    1.239503    8.000000    adf.f=rho2
    H     -0.930241    1.239503    8.000000    adf.f=rho2
    C      0.000000    0.667450    8.000000    adf.f=rho2
    C      0.000000   -0.667450    8.000000    adf.f=rho2
    H      0.930241   -1.239503    8.000000    adf.f=rho2
    H     -0.930241   -1.239503    8.000000    adf.f=rho2
  end
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  spinpolarization 0
  symmetry NOSYM
  title MODCO: Fragment no.          2; (polarized)
  unrestricted
  xc
    model SAOP
  end
  Relativity Level=None
EndEngine
eor

mv Emb2.results/adf.rkf t21.emb.rho2

it=1
while [ $it -le 2 ]; do

AMS_JOBNAME=Emb1.$it $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  H      0.930241   1.239503   0.000000   adf.f=rho1
  H     -0.930241   1.239503   0.000000   adf.f=rho1
  C      0.000000   0.667450   0.000000   adf.f=rho1
  C      0.000000  -0.667450   0.000000   adf.f=rho1
  H      0.930241  -1.239503   0.000000   adf.f=rho1
  H     -0.930241  -1.239503   0.000000   adf.f=rho1
  H      0.930241   1.239503   8.000000   adf.f=rho2
  H     -0.930241   1.239503   8.000000   adf.f=rho2
  C      0.000000   0.667450   8.000000   adf.f=rho2
  C      0.000000  -0.667450   8.000000   adf.f=rho2
  H      0.930241  -1.239503   8.000000   adf.f=rho2
  H     -0.930241  -1.239503   8.000000   adf.f=rho2
end
end

Task SinglePoint

EngineRestart t21.emb.rho1

Engine ADF
  allow PARTIALSUPERFRAGS
  cdft
    allatoms
    constraints 1.0
    excitedcdft
    initialmultipliers 0.0
    maxiter 250
    metric
    natomsperset 36
    nconstraints 1
    print LOW
    stepsize 0.4
    threshold 1.0e-9
  end
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    energy
    fullgrid
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.emb.rho2
  end
  fdefragments
    rho2 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  spinpolarization 0
  symmetry NOSYM
  title MODCO: Fragment no.          1; relaxed

```

(continues on next page)

(continued from previous page)

```

unrestricted
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb1.$it.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2.$it $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1
    H      0.930241   -1.239503    0.000000    adf.f=rho1
    H     -0.930241   -1.239503    0.000000    adf.f=rho1
    H      0.930241    1.239503    8.000000    adf.f=rho2
    H     -0.930241    1.239503    8.000000    adf.f=rho2
    C      0.000000    0.667450    8.000000    adf.f=rho2
    C      0.000000   -0.667450    8.000000    adf.f=rho2
    H      0.930241   -1.239503    8.000000    adf.f=rho2
    H     -0.930241   -1.239503    8.000000    adf.f=rho2
  end
end

Task SinglePoint

EngineRestart t21.emb.rho2

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    energy
    fullgrid
    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
  end
  fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
  end
  fdefragments
    rho1 subfrag=active type=fde
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  spinpolarization 0
  symmetry NOSYM
  title MODCO: Fragment no.      2; relaxed
  unrestricted

```

(continues on next page)

(continued from previous page)

```

xc
  model SAOP
end
  Relativity Level=None
EndEngine
eor

mv Emb2.$it.results/adf.rkf t21.emb.rho2

it=$((it+1))
done

# =====
# NOW THE TAPE21 FILES MUST BE RENAMED
#
# TO: fragA1.t21, fragA2.t21
# .... up to a max of fragA999.t21
# AND: fragB1.t21, fragB2.t21
# .... up to a max of fragB999.t21
# =====

mv t21.emb.rho1 fragA1.t21
mv t21.emb.rho2 fragA2.t21

# =====
# SECOND FDE CALCULATION: STATE D+ + A-
# note: the freeze and thaw is done manually
# as we have open-shell fragments
# =====

AMS_JOBNAME=Emb1p $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1
    H      0.930241   -1.239503    0.000000    adf.f=rho1
    H     -0.930241   -1.239503    0.000000    adf.f=rho1
    H      0.930241    1.239503    8.000000    adf.f=rho2
    H     -0.930241    1.239503    8.000000    adf.f=rho2
    C      0.000000    0.667450    8.000000    adf.f=rho2
    C      0.000000   -0.667450    8.000000    adf.f=rho2
    H      0.930241   -1.239503    8.000000    adf.f=rho2
    H     -0.930241   -1.239503    8.000000    adf.f=rho2
  end
  charge 1
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint

```

(continues on next page)

(continued from previous page)

```

    sfo NOEIG NOOVL NOORBPOP
end
fde
  ggapotcfd pw91c
  ggapotxfd pw91x
  pw91k
end
fragments
  rho1 t21.iso.rho1
  rho2 t21.iso.rho2
end
fdefragments
  rho2 type=fde
end
noprnt BAS FUNCTIONS
spinpolarization -1
symmetry NOSYM
title MODCO: Fragment no.          1; (polarized)
unrestricted
xc
  model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb1p.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2p $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1
    H      0.930241   -1.239503    0.000000    adf.f=rho1
    H     -0.930241   -1.239503    0.000000    adf.f=rho1
    H      0.930241    1.239503    8.000000    adf.f=rho2
    H     -0.930241    1.239503    8.000000    adf.f=rho2
    C      0.000000    0.667450    8.000000    adf.f=rho2
    C      0.000000   -0.667450    8.000000    adf.f=rho2
    H      0.930241   -1.239503    8.000000    adf.f=rho2
    H     -0.930241   -1.239503    8.000000    adf.f=rho2
  end
  charge -1
end

Task SinglePoint

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    ggapotcfd pw91c
    ggapotxfd pw91x

```

(continues on next page)

(continued from previous page)

```

    pw91k
end
fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
end
fdefragments
    rho1 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
spinpolarization 1
symmetry NOSYM
title MODCO: Fragment no.          2; (polarized)
unrestricted
xc
    model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb2p.results/adf.rkf t21.emb.rho2

it=1
while [ $it -le 2 ]; do

AMS_JOBNAME=Emb1p.$it $AMSBIN/ams <<eor
System
    atoms
        H      0.930241    1.239503    0.000000    adf.f=rho1
        H     -0.930241    1.239503    0.000000    adf.f=rho1
        C      0.000000    0.667450    0.000000    adf.f=rho1
        C      0.000000   -0.667450    0.000000    adf.f=rho1
        H      0.930241   -1.239503    0.000000    adf.f=rho1
        H     -0.930241   -1.239503    0.000000    adf.f=rho1
        H      0.930241    1.239503    8.000000    adf.f=rho2
        H     -0.930241    1.239503    8.000000    adf.f=rho2
        C      0.000000    0.667450    8.000000    adf.f=rho2
        C      0.000000   -0.667450    8.000000    adf.f=rho2
        H      0.930241   -1.239503    8.000000    adf.f=rho2
        H     -0.930241   -1.239503    8.000000    adf.f=rho2
    end
    charge 1
end

Task SinglePoint

EngineRestart t21.emb.rho1

Engine ADF
    allow PARTIALSUPERFRAGS
    eprint
        sfo NOEIG NOOVL NOORBPOP
    end
    fde
        energy
        fullgrid

```

(continues on next page)

(continued from previous page)

```

    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
end
fragments
    rho1 t21.iso.rho1
    rho2 t21.emb.rho2
end
fdefragments
    rho2 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
numericalquality Good
spinpolarization -1
symmetry NOSYM
title MODCO: Fragment no.          1; relaxed
unrestricted
xc
    model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb1p.$it.results/adf.rkf t21.emb.rho1

AMS_JOBNAME=Emb2p.$it $AMSBIN/ams <<eor
System
  atoms
    H      0.930241    1.239503    0.000000    adf.f=rho1
    H     -0.930241    1.239503    0.000000    adf.f=rho1
    C      0.000000    0.667450    0.000000    adf.f=rho1
    C      0.000000   -0.667450    0.000000    adf.f=rho1
    H      0.930241   -1.239503    0.000000    adf.f=rho1
    H     -0.930241   -1.239503    0.000000    adf.f=rho1
    H      0.930241    1.239503    8.000000    adf.f=rho2
    H     -0.930241    1.239503    8.000000    adf.f=rho2
    C      0.000000    0.667450    8.000000    adf.f=rho2
    C      0.000000   -0.667450    8.000000    adf.f=rho2
    H      0.930241   -1.239503    8.000000    adf.f=rho2
    H     -0.930241   -1.239503    8.000000    adf.f=rho2
  end
  charge -1
end

Task SinglePoint

EngineRestart t21.emb.rho2

Engine ADF
  allow PARTIALSUPERFRAGS
  eprint
    sfo NOEIG NOOVL NOORBPOP
  end
  fde
    energy
    fullgrid

```

(continues on next page)

(continued from previous page)

```

    ggapotcfd pw91c
    ggapotxfd pw91x
    pw91k
end
fragments
    rho1 t21.emb.rho1
    rho2 t21.iso.rho2
end
fdefragments
    rho1 subfrag=active type=fde
end
noprnt BAS FUNCTIONS
numericalquality Good
spinpolarization 1
symmetry NOSYM
title MODCO: Fragment no.          2; relaxed
unrestricted
xc
    model SAOP
end
Relativity Level=None
EndEngine
eor

mv Emb2p.$it.results/adf.rkf t21.emb.rho2

it=$((it+1))
done
# =====
# NOW THE TAPE21 FILES MUST BE RENAMED
#
# TO: fragA1.t21, fragA2.t21
# .... up to a max of fragA999.t21
# AND: fragB1.t21, fragB2.t21
# .... up to a max of fragB999.t21
# =====

mv t21.emb.rho1 fragB1.t21
mv t21.emb.rho2 fragB2.t21

# =====
# Electron Transfer calculation is next
#
# 1) note the ELECTRONTRANSFER block keyword
# 2) hybrids not supported
# 3) NumericalQuality GOOD is needed for accuracy
# =====

AMS_JOBNAME=ET $AMSBIN/ams <<eor
System
atoms
    H          0.930241    1.239503    0.000000 adf.f=rho1
    H         -0.930241    1.239503    0.000000 adf.f=rho1
    C          0.000000    0.667450    0.000000 adf.f=rho1
    C          0.000000   -0.667450    0.000000 adf.f=rho1
    H          0.930241   -1.239503    0.000000 adf.f=rho1
    H         -0.930241   -1.239503    0.000000 adf.f=rho1

```

(continues on next page)

(continued from previous page)

```

      H      0.930241      1.239503      8.000000 adf.f=rho2
      H     -0.930241      1.239503      8.000000 adf.f=rho2
      C      0.000000      0.667450      8.000000 adf.f=rho2
      C      0.000000     -0.667450      8.000000 adf.f=rho2
      H      0.930241     -1.239503      8.000000 adf.f=rho2
      H     -0.930241     -1.239503      8.000000 adf.f=rho2
    end
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality Good
  end
  electrontransfer
    numfrag 2
  end
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  fragments
    rho1 t21.iso.rho1
    rho2 t21.iso.rho2
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  scf
    iterations 0
  end
  spinpolarization 0
  symmetry nosym
  title ET calculation at R=0.0 Angstrom
  unrestricted
  xc
    gga PW91
  end
  Relativity Level=None
EndEngine

eor

```

Example: Exciton transfer integrals with FOCDFT

Download ExcitonTransfer_FOCDFT.run

```

#!/bin/sh

# FOCDFT is used to calculate exciton transfer integrals
# for the ethylene dimer and trimer using CIS (HartreeFock with TDA).

# First the isolated fragments are calculated.
# Because in the final complexes the 2 or 3 ethylene molecules are the same,
# only one fragment needs to be calculated.

```

(continues on next page)

(continued from previous page)

```

# For such a small molecule, a relatively small TZP basis set is used, which is
# not sufficient for excitations to Rydberg-like orbitals.
# For larger molecules a TZ2P basis set is in most cases
# sufficient. In that case one might even consider smaller basis sets.
# In a real application one also probably wants to calculate a higher number
# of excitations than that are calculated in this example.
# Next the choice of XC functional is important.
# If FOCDFT is used for the calculation of exciton transfer
# best is to use an XC functional that can reasonably well
# calculate both local excitations as well as charge-transfer excitations,
# like long range-separated functionals.

# For analysis reasons we also do a CIS calculation
# on the ethylene fragment.
# In the calculation D(2h) symmetry is used.
# The B1.u excitation will be a valence excitation, and
# the B3.u excitation will be a Rydberg excitation.
# Note that in D(2h) symmetry the orientation of the molecule
# matters in what is called a B1.u or B3.u excitation, for example.

```

```
AMS_JOBNAME=Frag $AMSBIN/ams <<eor
```

```
System
```

```
  symmetrize
```

```
  atoms
```

C	0.00000000	0.00000000	-0.66600000
C	0.00000000	0.00000000	0.66600000
H	0.00000000	0.92878500	-1.24030100
H	0.00000000	-0.92878500	-1.24030100
H	0.00000000	-0.92878500	1.24030100
H	0.00000000	0.92878500	1.24030100

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  basis
```

```
    Type TZP
```

```
    core none
```

```
  end
```

```
  xc
```

```
    hartreefock
```

```
  end
```

```
  TDA
```

```
  Excitations
```

```
    Davidson
```

```
      B1.u 1
```

```
      B3.u 1
```

```
    End
```

```
      Tolerance 1e-5
```

```
  End
```

```
EndEngine
```

```
eor
```

```
# Next we calculate the full complex of the dimer.
```

(continues on next page)

(continued from previous page)

```

# The key ExcitonTransfer is used such that electronic couplings between diabatic_
↳states
# are calculated.
# Note that one should not use symmetry-equivalent fragments in the final complex,
# because we want to localize orbitals on a fragment, which breaks this symmetry.
# In the calculation C(2v) symmetry can still be used.

# 'Localize OccupiedOnly' is used, which means that the calculated excitations
# are linear combinations of single-orbital transitions from occupied orbitals
# on one fragment to virtual orbitals on all fragments.
# The subkey descriptors of the block key Excitations is used
# such that the output gives information on the local or charge transfer
# character of these excitations.
# The two lowest localized B1 excitations will be close to the two local B1.u valence_
↳excitations
# on either fragment. Likewise the two lowest localized A1 excitations will be close_
↳to the
# two local B3.u Rydberg excitations on either fragment.
# The calculated electronic couplings between states of different symmetry will be_
↳zero.

AMS_JOBNAME=ET2_excitontransfer $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    C      0.000000    0.000000    0.000000 adf.f=Frag1
    C      1.332000    0.000000    0.000000 adf.f=Frag1
    H     -0.574301    0.000000   -0.928785 adf.f=Frag1
    H     -0.574301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000   -0.928785 adf.f=Frag1
    C     -0.000000    4.000000    0.000000 adf.f=Frag2
    C      1.332000    4.000000   -0.000000 adf.f=Frag2
    H     -0.574301    4.000000    0.928785 adf.f=Frag2
    H     -0.574301    4.000000   -0.928785 adf.f=Frag2
    H      1.906301    4.000000   -0.928785 adf.f=Frag2
    H      1.906301    4.000000    0.928785 adf.f=Frag2
  end
end

Task SinglePoint

Engine ADF
  fragments
    Frag1 Frag.results/adf.rkf
    Frag2 Frag.results/adf.rkf
  end
  xc
    hartreefock
  end
  TDA
  Excitations
    Davidson
      A1 2
      B1 2
    End

```

(continues on next page)

(continued from previous page)

```

    Tolerance 1e-5
    descriptors
End
FOCDFT
End
ExcitonTransfer
    Localize OccupiedOnly
    fullrun false
End
EndEngine
eor

# In the output one can find the excitonic couplings between the diabatic states.
# The calculated electronic couplings between the 2 singlet excited states
# of A1 symmetry is approximately: 0.15 eV.
# of B1 symmetry is approximately: 0.38 eV.
# The calculated excitonic couplings between the 2 triplet excited states
# of A1 symmetry is approximately: 0.10 eV.
# of B1 symmetry is approximately: 0.027 eV.
# Note that these states may also couple with other higher lying excited states,
# but the most important ones are given above.

# Exciton transfer integrals can also be calculated from the energetic splitting
# of excitation energies in the dimer, also called 'Davydov splitting',
# where the effective excitonic coupling equals half the splitting observed.
# This method is used in the final calculation of this example,
# in which a standard CIS calculation is performed on the dimer.
# For convenience the same fragments and symmetry are used as in the previous
↪ calculation.

# If one performs the calculation
# the calculated effective excitonic couplings between the 2 lowest singlet excited
↪ states
# of A1 symmetry is approximately: 0.15 eV (=0.5*(7.82-7.52)).
# of B1 symmetry is approximately: 0.36 eV (=0.5*(8.20-7.48)).
# The calculated effective excitonic couplings between the 2 lowest triplet excited
↪ states
# of A1 symmetry is approximately: 0.10 eV (=0.5*(7.45-7.25)).
# of B1 symmetry is approximately: 0.026 eV (=0.5*(3.556-3.505)).
# In this case the effective excitonic couplings are close to the
# excitonic couplings calculated with FOCDFT. Note that with FOCDFT it is also easy
# to calculate excitonic couplings between diabatic states of different molecules,
# which would be more difficult if one only knows the excitations of the full complex.

AMS_JOBNAME=ET2 $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    C      0.000000    0.000000    0.000000 adf.f=Frag1
    C      1.332000    0.000000    0.000000 adf.f=Frag1
    H     -0.574301    0.000000   -0.928785 adf.f=Frag1
    H     -0.574301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000    0.928785 adf.f=Frag1
    H      1.906301    0.000000   -0.928785 adf.f=Frag1
    C     -0.000000    4.000000    0.000000 adf.f=Frag2
    C      1.332000    4.000000   -0.000000 adf.f=Frag2
    H     -0.574301    4.000000    0.928785 adf.f=Frag2

```

(continues on next page)

(continued from previous page)

```

      H      -0.574301      4.000000      -0.928785 adf.f=Frag2
      H      1.906301      4.000000      -0.928785 adf.f=Frag2
      H      1.906301      4.000000      0.928785 adf.f=Frag2
    end
  end

Task SinglePoint

Engine ADF
  fragments
    Frag1 Frag.results/adf.rkf
    Frag2 Frag.results/adf.rkf
  end
  xc
    hartreefock
  end
  TDA
  Excitations
    Davidson
      A1 2
      B1 2
    End
    Tolerance 1e-5
    descriptors
  End
EndEngine
eor

# As a final example a stacked trimer is calculated, where the distance between
# 2 ethylene molecules is the same as in the dimer.
# In this case only singlet-singlet excitations are calculated,
# where the excited states have B1 symmetry.
# The three lowest localized B1 excitations (diabetic states).
# will be close to the three local B1.u valence excitations on each fragment.
# The calculated excitonic coupling between two neighboring ethylenes will be close to
# that of the dimer, whereas the excitonic coupling between the ethylenes that are
# → furthest
# apart are, as expected, much smaller.

AMS_JOBNAME=ET3_excitontransfer $AMSBIN/ams <<eor
System
  symmetrize
  atoms
    C      0.000000      0.000000      0.000000 adf.f=Frag1
    C      1.332000      0.000000      0.000000 adf.f=Frag1
    H     -0.574301      0.000000     -0.928785 adf.f=Frag1
    H     -0.574301      0.000000      0.928785 adf.f=Frag1
    H      1.906301      0.000000      0.928785 adf.f=Frag1
    H      1.906301      0.000000     -0.928785 adf.f=Frag1
    C     -0.000000      4.000000      0.000000 adf.f=Frag2
    C      1.332000      4.000000     -0.000000 adf.f=Frag2
    H     -0.574301      4.000000      0.928785 adf.f=Frag2
    H     -0.574301      4.000000     -0.928785 adf.f=Frag2
    H      1.906301      4.000000     -0.928785 adf.f=Frag2
    H      1.906301      4.000000      0.928785 adf.f=Frag2
    C      0.000000      8.000000      0.000000 adf.f=Frag3
    C      1.332000      8.000000      0.000000 adf.f=Frag3

```

(continues on next page)

(continued from previous page)

```

      H      -0.574301      8.000000      -0.928785 adf.f=Frag3
      H      -0.574301      8.000000      0.928785 adf.f=Frag3
      H      1.906301      8.000000      0.928785 adf.f=Frag3
      H      1.906301      8.000000      -0.928785 adf.f=Frag3
    end
  end

Task SinglePoint

Engine ADF
  fragments
    Frag1 Frag.results/adf.rkf
    Frag2 Frag.results/adf.rkf
    Frag3 Frag.results/adf.rkf
  end
  xc
    hartreefock
  end
  TDA
  Excitations
    onlysing
    Davidson
    B1 1
  End
  Tolerance 1e-6
  descriptors
End
FOCDFT
End
ExcitonTransfer
  Localize OccupiedOnly
  fullrun false
End
EndEngine
eor

```

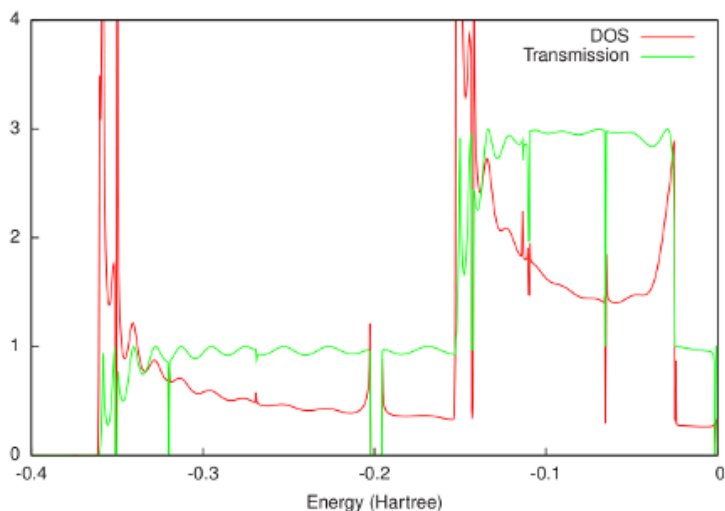
15.5.2 Non-self-consistent Green's function calculation

Example: DOS and transmission: Aluminium

Download `green_Al.run`

As an example of a non-self-consistent Green's function calculation, we will look at the density of states (DOS) and transmission of an infinite 1D chain of Aluminum atoms.

The final resulting DOS and transmission are shown in the following figure:



As would be expected for a 1D system, the DOS shows Van Hove singularities at the band edges. Apart from oscillations due to the finite size of the system in ADF, the transmission only reaches integer values. Between approximately -0.35 and -0.15 Hartree, only the sigma channel contributes to the transmission. Above -0.15 Hartree also the two pi channels start to contribute.

```
#!/bin/sh

# As an example of a non-self-consistent Green's function calculation, we will
# look at the density of states (DOS) and transmission of an infinite 1D chain
# of Aluminum atoms.

# First we need to perform a single-point calculation with ADF on a principal
# layer, consisting, in this case, of four atoms. Since bulk Aluminum has an FCC
# structure with a lattice constant of 4.05 Angstrom, the nearest neighbor
# distance is approximately 2.83 Angstrom. green requires SYMMETRY NOSYM, so we
# have the following input file for the principal layer:

AMS_JOBNAME=layer $AMSBIN/ams <<eor
System
  atoms
    Al      -4.290000    0.000000    0.000000
    Al      -1.430000    0.000000    0.000000
    Al       1.430000    0.000000    0.000000
    Al       4.290000    0.000000    0.000000
  end
end

Task SinglePoint

Engine ADF
  basis
    core Large
    type DZP
  end
  scf
    converge 1.0e-8
  end
  symmetry NOSYM
  title Principal layer
```

(continues on next page)

(continued from previous page)

```

xc
  lda SCF VWN
end
EndEngine
eor

# The bulk contact geometry consists of three principal layers:

AMS_JOBNAME=bulk $AMSBIN/ams <<eor
System
atoms
  Al      -15.730000    0.000000    0.000000 adf.f=left
  Al      -12.870000    0.000000    0.000000 adf.f=left
  Al      -10.010000    0.000000    0.000000 adf.f=left
  Al       -7.150000    0.000000    0.000000 adf.f=left
  Al       -4.290000    0.000000    0.000000 adf.f=center
  Al       -1.430000    0.000000    0.000000 adf.f=center
  Al        1.430000    0.000000    0.000000 adf.f=center
  Al        4.290000    0.000000    0.000000 adf.f=center
  Al        7.150000    0.000000    0.000000 adf.f=right
  Al       10.010000    0.000000    0.000000 adf.f=right
  Al       12.870000    0.000000    0.000000 adf.f=right
  Al       15.730000    0.000000    0.000000 adf.f=right
end
end

Task SinglePoint

Engine ADF
fragments
  left    layer.results/adf.rkf
  center  layer.results/adf.rkf
  right   layer.results/adf.rkf
end
scf
  accelerationmethod LISTi
  converge 1.0e-10
end
symmetry NOSYM
title Bulk
xc
  lda SCF VWN
end
EndEngine
eor

# Notice that we have increased the number of SCF iterations. The combination of
# SYMMETRY NOSYM with a 1D chain of metal atoms generally leads to convergence
# problems. This is the main reason why the principal layer consists of only
# four atoms. Fortunately, for larger 3D contacts, the convergence is generally
# better.

# From the bulk TAPE21 file green can calculate the self-energies of the left
# and right contacts. As discussed in the introduction, the self-energy of the
# left contact needs the center and right fragments of the bulk calculation, and
# the self-energy of the right contact needs the center and left fragments.

```

(continues on next page)

(continued from previous page)

```

# Since we need a self-energy matrix for every energy for which we want to
# calculate the DOS and transmission, already here we have to specify the energy
# range. We take 1000 points between -0.4 and 0 Hartree.

$AMSBIN/green <<eor
SURFACE bulk.results/adf.rkf
    FRAGMENTS center right
END
EPS -0.4 0 1000
ETA 1e-6
eor

mv SURFACE left.kf

$AMSBIN/green <<eor
SURFACE bulk.results/adf.rkf
    FRAGMENTS center left
END
EPS -0.4 0 1000
ETA 1e-6
eor

mv SURFACE right.kf

# Since we want to calculate the DOS and transmission of bare aluminum, we can
# reuse the bulk.t21 file for the extended molecule. We couple the left self-
# energy to the 'left' fragment and the right self-energy to the 'right'
# fragment in bulk.t21. Since we performed restricted ADF calculations, there is
# no difference between spin-A and spin-B and we can omit spin-B from the
# calculation.

$AMSBIN/green <<eor
DOS bulk.results/adf.rkf
TRANS bulk.results/adf.rkf
EPS -0.4 0 1000
ETA 1e-6
LEFT left.kf
    FRAGMENT left
END
RIGHT right.kf
    FRAGMENT right
END
NOSAVE DOS_B, TRANS_B
eor

# As would be expected for a 1D system, the DOS shows Van Hove singularities at
# the band edges. Apart from oscillations due to the finite size of the system
# in ADF, the transmission only reaches integer values. Between approximately
# -0.35 and -0.15 Hartree, only the sigma channel contributes to the
# transmission. Above -0.15 Hartree also the two pi channels start to
# contribute.

echo ""
echo "Contents of DOS_A:"
cat DOS_A
echo "END"
echo ""

```

(continues on next page)

(continued from previous page)

```
echo "Contents of TRANS_A:"
cat TRANS_A
echo "END"
```

Example: Gold electrodes

Download `green_Au.run`

In this example of *green*, the self-energies are calculated of gold electrodes, the material most often used in molecular electronics. In *the example for the Benzenedithiol junction* (page 1100) these self-energies will be used to calculate the DOS and transmission of a benzenedithiol junction. The geometry of the electrodes is shown in Fig. 1.

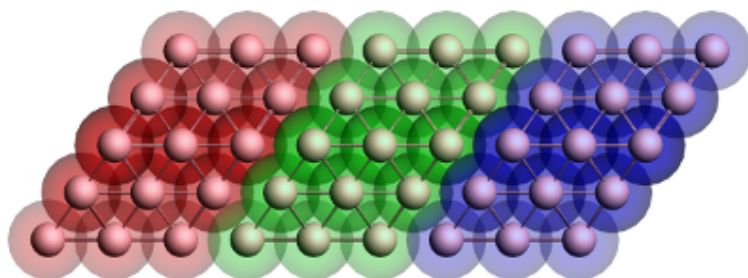
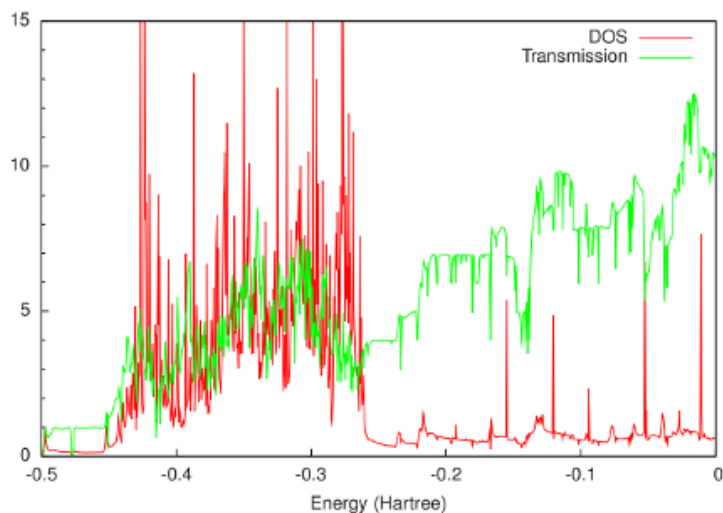


Figure 1: Geometry of the gold contact used in the calculation of the self-energy. The lead consists of two surface layers, left (red) and right (blue), and a bulk layer (green). Each principal layer in turn consists of three atomic layers. This should be sufficient to ensure that the Hamiltonian of the central (green) layer is a bulk Hamiltonian.

The final results are shown in the following figure:



From this figure it can be seen that around the Fermi energy (-0.2 Hartree), both the DOS and the transmission of gold are relatively constant. This feature makes gold an attractive material for electrodes, since one can expect that the transmission of a molecular junction will be dominated by the molecular properties.

```
#!/bin/sh

# In this example of green, the self-energies are calculated of gold electrodes,
# the material most often used in molecular electronics.
# In the example for the Benzenedithiol junction, green_BDT.run, these self-energies
```

(continues on next page)

(continued from previous page)

```

# will be used to calculate the DOS and transmission of a benzenedithiol junction.

# Each principal layer contains 3x3x3=27 gold atoms.
# For the calculation of the self-energies three principal layers are needed,
# and therefore 81 gold atoms in total.
# To keep the runtimes manageable it is therefore important to choose the basis set
# as small as possible.
# For transport calculations, a DZ basis with a large frozen core is generally
↳sufficient.
# Unfortunately, even with the largest frozen core (Au.4f),
# the basis set for Au still contains 19 electrons.
# A significant speedup can be obtained by limiting this to 11 electrons
# (only the outer *d* and *s* shells).
# Be advised that even with this reduction the total runtime of calculation can be
↳long.

# To facilitate the calculation of the electrodes,
# first a gold atom fragment will be calculated with the smallest possible basis.
# The sample directory contains the required Au.5p and Au.5p.dirac files.
# Note that for gold relativistic effects are important.
# Therefore Scalar ZORA will be used throughout this example.

cp $AMSHOME/examples/adf/green_Al/Au.5p .
cp $AMSHOME/examples/adf/green_Al/Au.5p.dirac .

$AMSBIN/dirac < Au.5p.dirac
mv TAPE12 t12.rel

AMS_JOBNAME=Au $AMSBIN/ams <<eor
System
  Atoms
    Au 0.0 0.0 0.0
  End
end
Task SinglePoint
Engine ADF
  corepotentials t12.rel
end
  create Au    file=Au.5p
  relativity
    level scalar
    formalism ZORA
  end
  xc
    lda SCF VWN
  end
EndEngine
eor

# A principal layer of gold consists of three atomic layers,
# which should be sufficient due to the small screening length.
# An atomic layer contains 3x3=9 atoms in a (111) FCC configuration.
# This allows one to use the top-, bridge-, and hollow-site binding configurations for
↳a molecule.
# For the following calculations it is necessary to first construct a fragment
# of a principal layer.

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=layer $AMSBIN/ams <<eor
System
  atoms
    Au      -2.355588   -6.662612    0.000000
    Au      -2.355589   -4.164133   -1.442498
    Au      -2.355589   -4.164133    1.442498
    Au      -2.355589   -1.665653   -2.884996
    Au      -2.355589   -1.665653    0.000000
    Au      -2.355589   -1.665653    2.884996
    Au      -2.355589    0.832826   -1.442498
    Au      -2.355589    0.832826    1.442498
    Au      -2.355589    3.331306    0.000000
    Au      0.000000   -4.996959    0.000000
    Au      0.000000   -2.498480   -1.442498
    Au      0.000000   -2.498480    1.442498
    Au      0.000000    0.000000   -2.884996
    Au      0.000000    0.000000    0.000000
    Au      0.000000    0.000000    2.884996
    Au      0.000000    2.498480   -1.442498
    Au      0.000000    2.498480    1.442498
    Au      0.000000    4.996959    0.000000
    Au      2.355589   -3.331306    0.000000
    Au      2.355589   -0.832826   -1.442498
    Au      2.355589   -0.832826    1.442498
    Au      2.355589    1.665653   -2.884996
    Au      2.355589    1.665653    0.000000
    Au      2.355589    1.665653    2.884996
    Au      2.355589    4.164133   -1.442498
    Au      2.355589    4.164133    1.442498
    Au      2.355588    6.662612    0.000000
  end
end

Task SinglePoint

Engine ADF
  fragments
    Au Au.results/adf.rkf
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Principal layer
  xc
    lda SCF VWN
  end
EndEngine
eor

# Three principal layers are stacked together to calculate the self-energies (see Fig.
# ↪ 1).
# The names of the fragments are significant, since one needs to refer to them by_
# ↪ name in
# the calculation of the self-energies.

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=bulk $AMSBIN/ams <<eor
System
  atoms
    Au      -9.422355  -11.659571    0.000000  adf.f=left
    Au      -9.422356  -9.161092   -1.442498  adf.f=left
    Au      -9.422356  -9.161092    1.442498  adf.f=left
    Au      -9.422356  -6.662612   -2.884996  adf.f=left
    Au      -9.422356  -6.662612    0.000000  adf.f=left
    Au      -9.422356  -6.662612    2.884996  adf.f=left
    Au      -9.422356  -4.164133   -1.442498  adf.f=left
    Au      -9.422356  -4.164133    1.442498  adf.f=left
    Au      -9.422356  -1.665653    0.000000  adf.f=left
    Au      -7.066767  -9.993918    0.000000  adf.f=left
    Au      -7.066767  -7.495439   -1.442498  adf.f=left
    Au      -7.066767  -7.495439    1.442498  adf.f=left
    Au      -7.066767  -4.996959   -2.884996  adf.f=left
    Au      -7.066767  -4.996959    0.000000  adf.f=left
    Au      -7.066767  -4.996959    2.884996  adf.f=left
    Au      -7.066767  -2.498479   -1.442498  adf.f=left
    Au      -7.066767  -2.498479    1.442498  adf.f=left
    Au      -7.066767    0.000000    0.000000  adf.f=left
    Au      -4.711178  -8.328265    0.000000  adf.f=left
    Au      -4.711178  -5.829785   -1.442498  adf.f=left
    Au      -4.711178  -5.829785    1.442498  adf.f=left
    Au      -4.711178  -3.331306   -2.884996  adf.f=left
    Au      -4.711178  -3.331306    0.000000  adf.f=left
    Au      -4.711178  -3.331306    2.884996  adf.f=left
    Au      -4.711178  -0.832826   -1.442498  adf.f=left
    Au      -4.711178  -0.832826    1.442498  adf.f=left
    Au      -4.711179    1.665653    0.000000  adf.f=left
    Au      -2.355588  -6.662612    0.000000  adf.f=center
    Au      -2.355588  -4.164133   -1.442498  adf.f=center
    Au      -2.355588  -4.164133    1.442498  adf.f=center
    Au      -2.355588  -1.665653   -2.884996  adf.f=center
    Au      -2.355588  -1.665653    0.000000  adf.f=center
    Au      -2.355588  -1.665653    2.884996  adf.f=center
    Au      -2.355588    0.832826   -1.442498  adf.f=center
    Au      -2.355588    0.832826    1.442498  adf.f=center
    Au      -2.355588    3.331306    0.000000  adf.f=center
    Au      0.000000   -4.996959    0.000000  adf.f=center
    Au      0.000000   -2.498480   -1.442498  adf.f=center
    Au      0.000000   -2.498480    1.442498  adf.f=center
    Au      0.000000    0.000000   -2.884996  adf.f=center
    Au      0.000000    0.000000    0.000000  adf.f=center
    Au      0.000000    0.000000    2.884996  adf.f=center
    Au      0.000000    2.498480   -1.442498  adf.f=center
    Au      0.000000    2.498480    1.442498  adf.f=center
    Au      0.000000    4.996959    0.000000  adf.f=center
    Au      2.355588   -3.331306    0.000000  adf.f=center
    Au      2.355588   -0.832826   -1.442498  adf.f=center
    Au      2.355588   -0.832826    1.442498  adf.f=center
    Au      2.355588    1.665653   -2.884996  adf.f=center
    Au      2.355588    1.665653    0.000000  adf.f=center
    Au      2.355588    1.665653    2.884996  adf.f=center
    Au      2.355588    4.164133   -1.442498  adf.f=center
    Au      2.355588    4.164133    1.442498  adf.f=center
    Au      2.355588    6.662612    0.000000  adf.f=center

```

(continues on next page)

(continued from previous page)

```

Au      4.711179   -1.665653   0.000000 adf.f=right
Au      4.711178   0.832826  -1.442498 adf.f=right
Au      4.711178   0.832826   1.442498 adf.f=right
Au      4.711178   3.331306  -2.884996 adf.f=right
Au      4.711178   3.331306   0.000000 adf.f=right
Au      4.711178   3.331306   2.884996 adf.f=right
Au      4.711178   5.829785  -1.442498 adf.f=right
Au      4.711178   5.829785   1.442498 adf.f=right
Au      4.711178   8.328265   0.000000 adf.f=right
Au      7.066767   0.000000   0.000000 adf.f=right
Au      7.066767   2.498479  -1.442498 adf.f=right
Au      7.066767   2.498479   1.442498 adf.f=right
Au      7.066767   4.996959  -2.884996 adf.f=right
Au      7.066767   4.996959   0.000000 adf.f=right
Au      7.066767   4.996959   2.884996 adf.f=right
Au      7.066767   7.495439  -1.442498 adf.f=right
Au      7.066767   7.495439   1.442498 adf.f=right
Au      7.066767   9.993918   0.000000 adf.f=right
Au      9.422356   1.665653   0.000000 adf.f=right
Au      9.422356   4.164133  -1.442498 adf.f=right
Au      9.422356   4.164133   1.442498 adf.f=right
Au      9.422356   6.662612  -2.884996 adf.f=right
Au      9.422356   6.662612   0.000000 adf.f=right
Au      9.422356   6.662612   2.884996 adf.f=right
Au      9.422356   9.161092  -1.442498 adf.f=right
Au      9.422356   9.161092   1.442498 adf.f=right
Au      9.422355  11.659571   0.000000 adf.f=right
end
end

Task SinglePoint

Engine ADF
  fragments
    left   layer.results/adf.rkf
    center layer.results/adf.rkf
    right  layer.results/adf.rkf
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Bulk gold
  xc
    lda SCF VWN
  end
EndEngine
eor

# Similar to the other examples, the self-energies of the left and right contacts
# is calculated for 1000 energy points between -0.5 and 0 Hartree.
# This results in two keyfiles of approximately 2.5 GB each.
# Since the self-energies are independent of whatever is placed between the contacts,
# they can be reused many times.

$AMSBIN/green << eor

```

(continues on next page)

(continued from previous page)

```

SURFACE bulk.results/adf.rkf
    FRAGMENTS center right
END
EPS -0.5 0 1000
ETA 1e-6
eor
mv SURFACE left.kf

$AMSBIN/green << eor
SURFACE bulk.results/adf.rkf
    FRAGMENTS center left
END
EPS -0.5 0 1000
ETA 1e-6
eor
mv SURFACE right.kf

# In order to interpret transmissions calculated with these self-energies,
# it is necessary to know the location of the Fermi energy.
# An estimate for the Fermi energy can be obtained from the bulk SCF calculation
# by taking the average of the HOMO and LUMO energies, which in this case equals -0.
# →195 Hartree.

# Usually the self-energies will be used to calculate the transmission of a molecular
# →junction.
# However, it is instructive to use a principal layer of gold as the "molecule" and
# →study
# the DOS and transmission of bulk gold.

$AMSBIN/green << eor
DOS bulk.results/adf.rkf
TRANS bulk.results/adf.rkf
EPS -0.5 0 1000
ETA 1e-6
LEFT left.kf
    FRAGMENT left
END
RIGHT right.kf
    FRAGMENT right
END
NOSAVE DOS_B, TRANS_B
eor

echo ""
echo "Contents of DOS_A:"
cat DOS_A
echo "END"
echo ""
echo "Contents of TRANS_A:"
cat TRANS_A
echo "END"

```

Example: Benzenedithiol junction: Wide-Band-Limit

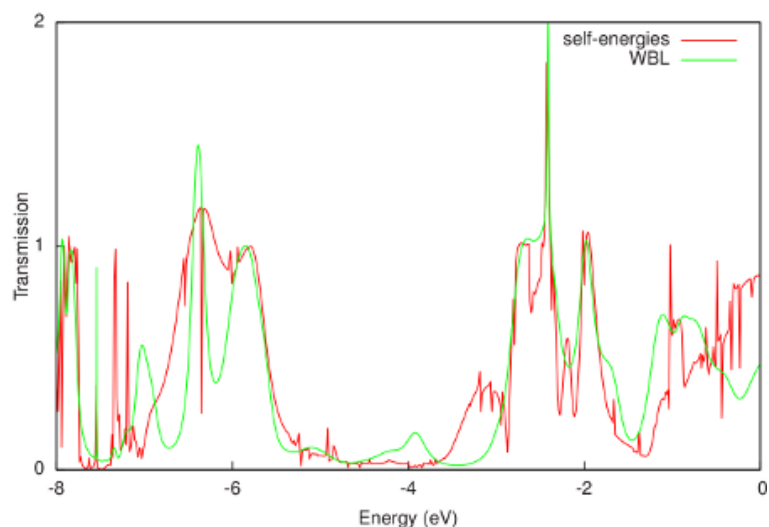
Download `green_WBL.run`

In the wide-band limit (WBL) the coupling to the leads is assumed to be independent of energy. Therefore one does not need to calculate any self-energies. This also means that the eigenspace of the Green's function is independent of energy. It can therefore be diagonalized in advance, greatly speeding up the calculation of the DOS and the transmission.

In the example `$AMSHOME/examples/adf/green_Al/green_WBL/green_WBL.run` of *green*, the transmission of *benzenedithiol junction* (page 1100) in the wide-band limit (WBL) is calculated. In order to model the molecule-metal interface, we do need to include a few gold layers in the calculation. However, unlike *before* (page 1089), only a single atomic layer as the principal layer is used.

Because a single atomic layer is an unnatural configuration for gold, a minor amount of smearing is necessary to make the calculation converge. The molecule is sandwiched in between the electrodes just like before (see Fig. 2 in *the example for benzenedithiol* (page 1100)). However, this time each atomic layer of gold gets its own fragment. The reason for this configuration is that if the WBL is used on the entire gold contact the result is an unphysical coupling to the leads; even the gold atoms contacting the molecule would have a direct coupling to the environment. A much better result can be obtained by only using the WBL on the back-most atomic layer and letting the electrons propagate naturally through the rest of the contact. Because the WBL is computationally so inexpensive, we can easily calculate the DOS and transmission for 10,000 points instead of 1000.

A comparison of the resulting transmission with the calculation with self-energies is shown in the following figure:



The WBL shows good agreement with the non-WBL transmission around the Fermi energy (-0.195 Hartree or -5.306 eV). Note that the quality of the WBL depends on the choice of the coupling (ETA). For this particular contact geometry we obtain good agreement for $\text{ETA} = 0.02$ Hartree, but a better value may be found for other electrodes. Finally, the WBL can be incrementally improved by adding more gold layers to the extended molecule. For many layers it converges to the calculation with full self-energies.

```
#!/bin/sh

# In the wide-band limit (WBL) the coupling to the leads is assumed to be independent_
↪ of energy.
# Therefore one does not need to calculate any self-energies.
# This also means that the eigenspace of the Green's function is independent of_
↪ energy.
# It can therefore be diagonalized in advance,
# greatly speeding up the calculation of the DOS and the transmission.
```

(continues on next page)

(continued from previous page)

```

# In the example $AMSHOME/examples/adf/green_Al/green_WBL.run of green,
# the transmission of benzenedithiol junction, example green_BDT.run,
# in the wide-band limit (WBL) is calculated.
# In order to model the molecule-metal interface, we do need to include a few gold_
↳layers
# in the calculation.
# However, unlike in green_Au.run, only a single atomic layer as the principal layer_
↳is used.

# In green_BDT.run 3 layers of gold atoms from 1 fragment.
# In this example green_WBL.run each layer of gold atoms has its own fragment.
# Because a single atomic layer is an unnatural configuration for gold,
# a minor amount of smearing is necessary to make the calculation converge.
# The molecule is sandwiched in between the electrodes just like before
# (see the example for benzenedithiol, example green_BDT.run).
# However, this time each atomic layer of gold gets its own fragment.
# The reason for this configuration is that if the WBL is used on the
# entire gold contact the result is an an unphysical coupling to the leads;
# even the gold atoms contacting the molecule would have a direct coupling to the_
↳environment.
# A much better result can be obtained by only using the WBL on the back-most atomic_
↳layer
# and letting the electrons propagate naturally through the rest of the contact.
# Because the WBL is computationally so inexpensive, we can easily calculate
# the DOS and transmission for 10,000 points instead of 1000.

cp $AMSHOME/examples/adf/green_Al/Au.5p .
cp $AMSHOME/examples/adf/green_Al/Au.5p.dirac .

$AMSBIN/dirac < Au.5p.dirac
mv TAPE12 t12.rel

AMS_JOBNAME=Au $AMSBIN/ams <<eor
System
  Atoms
    Au 0.0 0.0 0.0
  End
end
Task SinglePoint
Engine ADF
  corepotentials t12.rel
end
  create Au file=Au.5p
  relativity
    level scalar
    formalism ZORA
  end
  xc
    lda SCF VWN
  end
EndEngine
eor

AMS_JOBNAME=layer $AMSBIN/ams <<eor
System
  atoms
    Au          0.000000   -4.996959   0.000000

```

(continues on next page)

(continued from previous page)

```

    Au      0.000000   -2.498480   -1.442498
    Au      0.000000   -2.498480    1.442498
    Au      0.000000    0.000000   -2.884996
    Au      0.000000    0.000000    0.000000
    Au      0.000000    0.000000    2.884996
    Au      0.000000    2.498480   -1.442498
    Au      0.000000    2.498480    1.442498
    Au      0.000000    4.996959    0.000000
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  fragments
    Au Au.t21
  end
  occupations Smearq=0.001
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Principal layer
  xc
    lda SCF VWN
  end
EndEngine
eor

```

```
AMS_JOBNAME=molecule $AMSBIN/ams <<eor
```

```

System
  atoms
    C      -1.400000    0.000000    0.000000
    C      -0.700000    0.000000   -1.200000
    C      -0.700000    0.000000    1.200000
    C      0.700000    0.000000   -1.200000
    C      0.700000    0.000000    1.200000
    C      1.400000    0.000000    0.000000
    H      -1.200000    0.000000   -2.200000
    H      -1.200000    0.000000    2.200000
    H      1.200000    0.000000   -2.200000
    H      1.200000    0.000000    2.200000
    S      -3.200000    0.000000    0.000000
    S      3.200000    0.000000    0.000000
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  basis
    type DZP
    core Large
    createOutput None
  end
  relativity

```

(continues on next page)

(continued from previous page)

```

    level scalar
    formalism ZORA
end
symmetry NOSYM
title Benzenedithiol
xc
    lda SCF VWN
end
EndEngine
eor

AMS_JOBNAME=fock $AMSBIN/ams <<eor
System
atoms
  Au      -9.911177   -6.662612    0.000000 adf.f=left
  Au      -9.911178   -4.164133   -1.442498 adf.f=left
  Au      -9.911178   -4.164133    1.442498 adf.f=left
  Au      -9.911178   -1.665653   -2.884996 adf.f=left
  Au      -9.911178   -1.665653    0.000000 adf.f=left
  Au      -9.911178   -1.665653    2.884996 adf.f=left
  Au      -9.911178    0.832826   -1.442498 adf.f=left
  Au      -9.911178    0.832826    1.442498 adf.f=left
  Au      -9.911178    3.331306    0.000000 adf.f=left
  Au      -7.555589   -4.996959    0.000000 adf.f=left.2
  Au      -7.555589   -2.498480   -1.442498 adf.f=left.2
  Au      -7.555589   -2.498480    1.442498 adf.f=left.2
  Au      -7.555589    0.000000   -2.884996 adf.f=left.2
  Au      -7.555589    0.000000    0.000000 adf.f=left.2
  Au      -7.555589    0.000000    2.884996 adf.f=left.2
  Au      -7.555589    2.498480   -1.442498 adf.f=left.2
  Au      -7.555589    2.498480    1.442498 adf.f=left.2
  Au      -7.555589    4.996959    0.000000 adf.f=left.2
  Au      -5.200000   -3.331306    0.000000 adf.f=left.3
  Au      -5.200000   -0.832826   -1.442498 adf.f=left.3
  Au      -5.200000   -0.832826    1.442498 adf.f=left.3
  Au      -5.200000    1.665653   -2.884996 adf.f=left.3
  Au      -5.200000    1.665653    0.000000 adf.f=left.3
  Au      -5.200000    1.665653    2.884996 adf.f=left.3
  Au      -5.200000    4.164133   -1.442498 adf.f=left.3
  Au      -5.200000    4.164133    1.442498 adf.f=left.3
  Au      -5.200001    6.662612    0.000000 adf.f=left.3
  C       -1.400000    0.000000    0.000000 adf.f=molecule
  C       -0.700000    0.000000   -1.200000 adf.f=molecule
  C       -0.700000    0.000000    1.200000 adf.f=molecule
  C        0.700000    0.000000   -1.200000 adf.f=molecule
  C        0.700000    0.000000    1.200000 adf.f=molecule
  C        1.400000    0.000000    0.000000 adf.f=molecule
  H       -1.200000    0.000000   -2.200000 adf.f=molecule
  H       -1.200000    0.000000    2.200000 adf.f=molecule
  H        1.200000    0.000000   -2.200000 adf.f=molecule
  H        1.200000    0.000000    2.200000 adf.f=molecule
  S       -3.200000    0.000000    0.000000 adf.f=molecule
  S        3.200000    0.000000    0.000000 adf.f=molecule
  Au       5.200001   -6.662612    0.000000 adf.f=right.3
  Au       5.200000   -4.164133   -1.442498 adf.f=right.3
  Au       5.200000   -4.164133    1.442498 adf.f=right.3
  Au       5.200000   -1.665653   -2.884996 adf.f=right.3

```

(continues on next page)

(continued from previous page)

```

    Au      5.200000   -1.665653    0.000000  adf.f=right.3
    Au      5.200000   -1.665653    2.884996  adf.f=right.3
    Au      5.200000    0.832826   -1.442498  adf.f=right.3
    Au      5.200000    0.832826    1.442498  adf.f=right.3
    Au      5.200000    3.331306    0.000000  adf.f=right.3
    Au      7.555589   -4.996959    0.000000  adf.f=right.2
    Au      7.555589   -2.498480   -1.442498  adf.f=right.2
    Au      7.555589   -2.498480    1.442498  adf.f=right.2
    Au      7.555589    0.000000   -2.884996  adf.f=right.2
    Au      7.555589    0.000000    0.000000  adf.f=right.2
    Au      7.555589    0.000000    2.884996  adf.f=right.2
    Au      7.555589    2.498480   -1.442498  adf.f=right.2
    Au      7.555589    2.498480    1.442498  adf.f=right.2
    Au      7.555589    4.996959    0.000000  adf.f=right.2
    Au      9.911178   -3.331306    0.000000  adf.f=right
    Au      9.911178   -0.832826   -1.442498  adf.f=right
    Au      9.911178   -0.832826    1.442498  adf.f=right
    Au      9.911178    1.665653   -2.884996  adf.f=right
    Au      9.911178    1.665653    0.000000  adf.f=right
    Au      9.911178    1.665653    2.884996  adf.f=right
    Au      9.911178    4.164133   -1.442498  adf.f=right
    Au      9.911178    4.164133    1.442498  adf.f=right
    Au      9.911177    6.662612    0.000000  adf.f=right
  end
end

Task SinglePoint

Engine ADF
  fragments
    left      layer.t21
    left.2    layer.t21
    left.3    layer.t21
    molecule  molecule.t21
    right.3   layer.t21
    right.2   layer.t21
    right     layer.t21
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Benzenedithiol
  xc
    lda SCF VWN
  end
EndEngine
eor

$AMSBIN/green << eor
DOS fock.results/adf.rkf
TRANS fock.results/adf.rkf
EPS -0.5 0 10000
ETA 1e-6
LEFT
  FRAGMENT left

```

(continues on next page)

(continued from previous page)

```

    ETA 2e-2
END
RIGHT
    FRAGMENT right
    ETA 2e-2
END
NOSAVE DOS_B, TRANS_B
eor

echo ""
echo "Contents of DOS_A:"
cat DOS_A
echo "END"
echo ""
echo "Contents of TRANS_A:"
cat TRANS_A
echo "END"

```

Example: Benzenedithiol junction

Download `green_BDT.run`

In this example of *green*, the DOS and transmission of a benzenedithiol molecule between gold electrodes is calculated. The calculation uses the self-energies obtained in *the example for the gold electrodes* (page 1089). Note that this is a relatively expensive calculation.

First a fragment of the isolated molecule is constructed. Next the molecule is sandwiched between the electrodes in the configuration of Fig. 2. For this the fragment of the principal layer obtained in *the example for the gold electrodes* (page 1089) is needed.

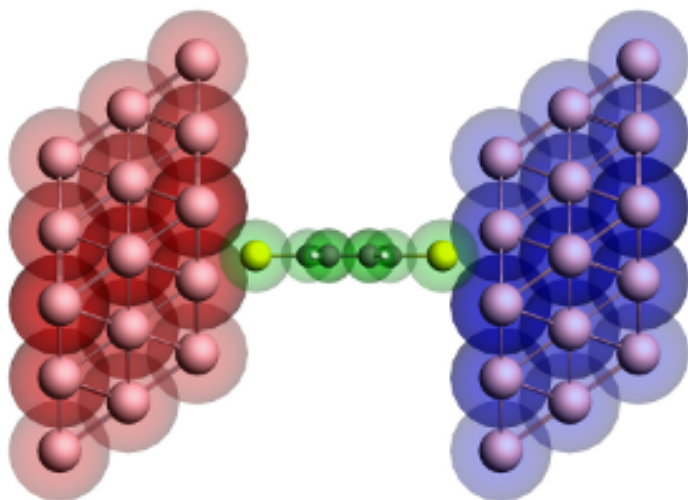
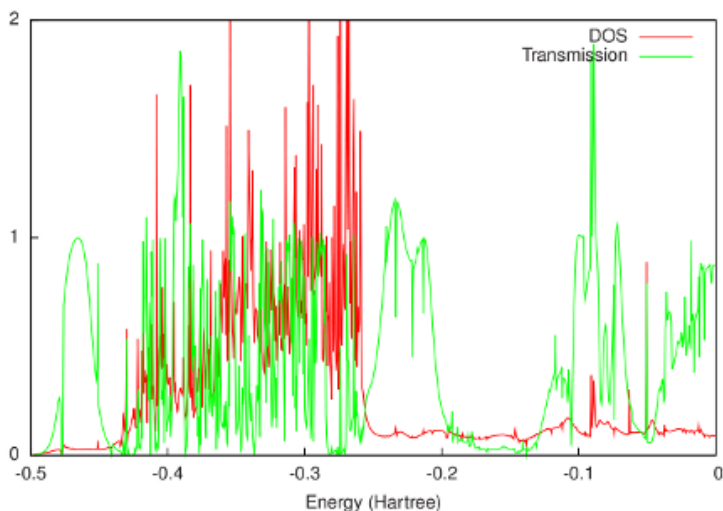


Figure 2: Geometry of the extended molecule used in the calculation of a benzenedithiol junction. The molecule is shown in green, while the left and right contact regions are shown in red and blue, respectively. Note that the red region corresponds to the blue surface layer in Figure 1 of *the example for the gold electrodes* (page 1089) and vice versa.

The final results are shown in the following figure:



The Fermi energy of the electrodes is -0.2 Hartree (see [the example for the gold electrodes](#) (page 1089)). This is just above the HOMO of the molecular junction. Consistent with literature, the HOMO and lower orbitals are combined into a broad peak just below the Fermi energy, while the LUMO is much sharper and situated about 2 eV above the Fermi energy.

The current can be calculated by integrating the transmission around the Fermi energy. At low temperatures this means that the differential conductance is equal to the transmission times the quantum of conductance.

```
#!/bin/sh

# In this example of green, the DOS and transmission of a benzenedithiol molecule
# between gold electrodes is calculated.
# The calculation uses the self-energies obtained in the example for the gold_
↪electrodes,
# green_Au.run.
# Note that this is a relatively expensive calculation.

cp $AMSHOME/examples/adf/green_A1/Au.5p .
cp $AMSHOME/examples/adf/green_A1/Au.5p.dirac .

$AMSBIN/dirac < Au.5p.dirac
mv TAPE12 t12.rel

AMS_JOBNAME=Au $AMSBIN/ams <<eor
System
  Atoms
    Au 0.0 0.0 0.0
  End
end
Task SinglePoint
Engine ADF
  corepotentials t12.rel
end
create Au file=Au.5p
relativity
  level scalar
  formalism ZORA
end
xc
  lda SCF VWN
```

(continues on next page)

(continued from previous page)

```

    end
EndEngine
eor

AMS_JOBNAME=layer $AMSBIN/ams <<eor
System
  atoms
    Au      -2.355588   -6.662612    0.000000
    Au      -2.355589   -4.164133   -1.442498
    Au      -2.355589   -4.164133    1.442498
    Au      -2.355589   -1.665653   -2.884996
    Au      -2.355589   -1.665653    0.000000
    Au      -2.355589   -1.665653    2.884996
    Au      -2.355589    0.832826   -1.442498
    Au      -2.355589    0.832826    1.442498
    Au      -2.355589    3.331306    0.000000
    Au       0.000000   -4.996959    0.000000
    Au       0.000000   -2.498480   -1.442498
    Au       0.000000   -2.498480    1.442498
    Au       0.000000    0.000000   -2.884996
    Au       0.000000    0.000000    0.000000
    Au       0.000000    0.000000    2.884996
    Au       0.000000    2.498480   -1.442498
    Au       0.000000    2.498480    1.442498
    Au       0.000000    4.996959    0.000000
    Au       2.355589   -3.331306    0.000000
    Au       2.355589   -0.832826   -1.442498
    Au       2.355589   -0.832826    1.442498
    Au       2.355589    1.665653   -2.884996
    Au       2.355589    1.665653    0.000000
    Au       2.355589    1.665653    2.884996
    Au       2.355589    4.164133   -1.442498
    Au       2.355589    4.164133    1.442498
    Au       2.355588    6.662612    0.000000
  end
end

Task SinglePoint

Engine ADF
  fragments
    Au Au.results/adf.rkf
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Principal layer
  xc
    lda SCF VWN
  end
EndEngine
eor

AMS_JOBNAME=bulk $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
Au      -9.422355 -11.659571  0.000000 adf.f=left
Au      -9.422356 -9.161092  -1.442498 adf.f=left
Au      -9.422356 -9.161092  1.442498 adf.f=left
Au      -9.422356 -6.662612  -2.884996 adf.f=left
Au      -9.422356 -6.662612  0.000000 adf.f=left
Au      -9.422356 -6.662612  2.884996 adf.f=left
Au      -9.422356 -4.164133  -1.442498 adf.f=left
Au      -9.422356 -4.164133  1.442498 adf.f=left
Au      -9.422356 -1.665653  0.000000 adf.f=left
Au      -7.066767 -9.993918  0.000000 adf.f=left
Au      -7.066767 -7.495439  -1.442498 adf.f=left
Au      -7.066767 -7.495439  1.442498 adf.f=left
Au      -7.066767 -4.996959  -2.884996 adf.f=left
Au      -7.066767 -4.996959  0.000000 adf.f=left
Au      -7.066767 -4.996959  2.884996 adf.f=left
Au      -7.066767 -2.498479  -1.442498 adf.f=left
Au      -7.066767 -2.498479  1.442498 adf.f=left
Au      -7.066767  0.000000  0.000000 adf.f=left
Au      -4.711178 -8.328265  0.000000 adf.f=left
Au      -4.711178 -5.829785  -1.442498 adf.f=left
Au      -4.711178 -5.829785  1.442498 adf.f=left
Au      -4.711178 -3.331306  -2.884996 adf.f=left
Au      -4.711178 -3.331306  0.000000 adf.f=left
Au      -4.711178 -3.331306  2.884996 adf.f=left
Au      -4.711178 -0.832826  -1.442498 adf.f=left
Au      -4.711178 -0.832826  1.442498 adf.f=left
Au      -4.711179  1.665653  0.000000 adf.f=left
Au      -2.355588 -6.662612  0.000000 adf.f=center
Au      -2.355589 -4.164133  -1.442498 adf.f=center
Au      -2.355589 -4.164133  1.442498 adf.f=center
Au      -2.355589 -1.665653  -2.884996 adf.f=center
Au      -2.355589 -1.665653  0.000000 adf.f=center
Au      -2.355589 -1.665653  2.884996 adf.f=center
Au      -2.355589  0.832826  -1.442498 adf.f=center
Au      -2.355589  0.832826  1.442498 adf.f=center
Au      -2.355589  3.331306  0.000000 adf.f=center
Au      0.000000 -4.996959  0.000000 adf.f=center
Au      0.000000 -2.498480  -1.442498 adf.f=center
Au      0.000000 -2.498480  1.442498 adf.f=center
Au      0.000000  0.000000  -2.884996 adf.f=center
Au      0.000000  0.000000  0.000000 adf.f=center
Au      0.000000  0.000000  2.884996 adf.f=center
Au      0.000000  2.498480  -1.442498 adf.f=center
Au      0.000000  2.498480  1.442498 adf.f=center
Au      0.000000  4.996959  0.000000 adf.f=center
Au      2.355589 -3.331306  0.000000 adf.f=center
Au      2.355589 -0.832826  -1.442498 adf.f=center
Au      2.355589 -0.832826  1.442498 adf.f=center
Au      2.355589  1.665653  -2.884996 adf.f=center
Au      2.355589  1.665653  0.000000 adf.f=center
Au      2.355589  1.665653  2.884996 adf.f=center
Au      2.355589  4.164133  -1.442498 adf.f=center
Au      2.355589  4.164133  1.442498 adf.f=center
Au      2.355588  6.662612  0.000000 adf.f=center
Au      4.711179 -1.665653  0.000000 adf.f=right
Au      4.711178  0.832826  -1.442498 adf.f=right

```

(continues on next page)

(continued from previous page)

```

    Au      4.711178    0.832826    1.442498 adf.f=right
    Au      4.711178    3.331306   -2.884996 adf.f=right
    Au      4.711178    3.331306    0.000000 adf.f=right
    Au      4.711178    3.331306    2.884996 adf.f=right
    Au      4.711178    5.829785   -1.442498 adf.f=right
    Au      4.711178    5.829785    1.442498 adf.f=right
    Au      4.711178    8.328265    0.000000 adf.f=right
    Au      7.066767    0.000000    0.000000 adf.f=right
    Au      7.066767    2.498479   -1.442498 adf.f=right
    Au      7.066767    2.498479    1.442498 adf.f=right
    Au      7.066767    4.996959   -2.884996 adf.f=right
    Au      7.066767    4.996959    0.000000 adf.f=right
    Au      7.066767    4.996959    2.884996 adf.f=right
    Au      7.066767    7.495439   -1.442498 adf.f=right
    Au      7.066767    7.495439    1.442498 adf.f=right
    Au      7.066767    9.993918    0.000000 adf.f=right
    Au      9.422356    1.665653    0.000000 adf.f=right
    Au      9.422356    4.164133   -1.442498 adf.f=right
    Au      9.422356    4.164133    1.442498 adf.f=right
    Au      9.422356    6.662612   -2.884996 adf.f=right
    Au      9.422356    6.662612    0.000000 adf.f=right
    Au      9.422356    6.662612    2.884996 adf.f=right
    Au      9.422356    9.161092   -1.442498 adf.f=right
    Au      9.422356    9.161092    1.442498 adf.f=right
    Au      9.422355   11.659571    0.000000 adf.f=right
end
end

Task SinglePoint

Engine ADF
  fragments
    left    layer.results/adf.rkf
    center  layer.results/adf.rkf
    right   layer.results/adf.rkf
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Bulk gold
  xc
    lda SCF VWN
  end
EndEngine
eor

$AMSBIN/green << eor
SURFACE bulk.results/adf.rkf
  FRAGMENTS center right
END
EPS -0.5 0 1000
ETA 1e-6
eor
mv SURFACE left.kf

```

(continues on next page)

(continued from previous page)

```

$AMSBIN/green << eor
SURFACE bulk.results/adf.rkf
  FRAGMENTS center left
END
EPS -0.5 0 1000
ETA 1e-6
eor
mv SURFACE right.kf

# A fragment of the isolated molecule is constructed:

AMS_JOBNAME=molecule $AMSBIN/ams <<eor
System
  atoms
    C      -1.400000    0.000000    0.000000
    C      -0.700000    0.000000   -1.200000
    C      -0.700000    0.000000    1.200000
    C       0.700000    0.000000   -1.200000
    C       0.700000    0.000000    1.200000
    C      1.400000    0.000000    0.000000
    H      -1.200000    0.000000   -2.200000
    H      -1.200000    0.000000    2.200000
    H       1.200000    0.000000   -2.200000
    H       1.200000    0.000000    2.200000
    S      -3.200000    0.000000    0.000000
    S       3.200000    0.000000    0.000000
  end
end

Task SinglePoint

Engine ADF
  basis
    type DZP
    core Large
    createOutput None
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Benzenedithiol
  xc
    lda SCF VWN
  end
EndEngine
eor

# Next the molecule is sandwiched between the electrodes:

AMS_JOBNAME=fock $AMSBIN/ams <<eor
System
  atoms
    Au      -9.911177   -6.662612    0.000000 adf.f=left
    Au      -9.911178   -4.164133   -1.442498 adf.f=left
    Au      -9.911178   -4.164133    1.442498 adf.f=left

```

(continues on next page)

(continued from previous page)

Au	-9.911178	-1.665653	-2.884996	adf.f=left
Au	-9.911178	-1.665653	0.000000	adf.f=left
Au	-9.911178	-1.665653	2.884996	adf.f=left
Au	-9.911178	0.832826	-1.442498	adf.f=left
Au	-9.911178	0.832826	1.442498	adf.f=left
Au	-9.911178	3.331306	0.000000	adf.f=left
Au	-7.555589	-4.996959	0.000000	adf.f=left
Au	-7.555589	-2.498480	-1.442498	adf.f=left
Au	-7.555589	-2.498480	1.442498	adf.f=left
Au	-7.555589	0.000000	-2.884996	adf.f=left
Au	-7.555589	0.000000	0.000000	adf.f=left
Au	-7.555589	0.000000	2.884996	adf.f=left
Au	-7.555589	2.498480	-1.442498	adf.f=left
Au	-7.555589	2.498480	1.442498	adf.f=left
Au	-7.555589	4.996959	0.000000	adf.f=left
Au	-5.200000	-3.331306	0.000000	adf.f=left
Au	-5.200000	-0.832826	-1.442498	adf.f=left
Au	-5.200000	-0.832826	1.442498	adf.f=left
Au	-5.200000	1.665653	-2.884996	adf.f=left
Au	-5.200000	1.665653	0.000000	adf.f=left
Au	-5.200000	1.665653	2.884996	adf.f=left
Au	-5.200000	4.164133	-1.442498	adf.f=left
Au	-5.200000	4.164133	1.442498	adf.f=left
Au	-5.200001	6.662612	0.000000	adf.f=left
C	-1.400000	0.000000	0.000000	adf.f=molecule
C	-0.700000	0.000000	-1.200000	adf.f=molecule
C	-0.700000	0.000000	1.200000	adf.f=molecule
C	0.700000	0.000000	-1.200000	adf.f=molecule
C	0.700000	0.000000	1.200000	adf.f=molecule
C	1.400000	0.000000	0.000000	adf.f=molecule
H	-1.200000	0.000000	-2.200000	adf.f=molecule
H	-1.200000	0.000000	2.200000	adf.f=molecule
H	1.200000	0.000000	-2.200000	adf.f=molecule
H	1.200000	0.000000	2.200000	adf.f=molecule
S	-3.200000	0.000000	0.000000	adf.f=molecule
S	3.200000	0.000000	0.000000	adf.f=molecule
Au	5.200001	-6.662612	0.000000	adf.f=right
Au	5.200000	-4.164133	-1.442498	adf.f=right
Au	5.200000	-4.164133	1.442498	adf.f=right
Au	5.200000	-1.665653	-2.884996	adf.f=right
Au	5.200000	-1.665653	0.000000	adf.f=right
Au	5.200000	-1.665653	2.884996	adf.f=right
Au	5.200000	0.832826	-1.442498	adf.f=right
Au	5.200000	0.832826	1.442498	adf.f=right
Au	5.200000	3.331306	0.000000	adf.f=right
Au	7.555589	-4.996959	0.000000	adf.f=right
Au	7.555589	-2.498480	-1.442498	adf.f=right
Au	7.555589	-2.498480	1.442498	adf.f=right
Au	7.555589	0.000000	-2.884996	adf.f=right
Au	7.555589	0.000000	0.000000	adf.f=right
Au	7.555589	0.000000	2.884996	adf.f=right
Au	7.555589	2.498480	-1.442498	adf.f=right
Au	7.555589	2.498480	1.442498	adf.f=right
Au	7.555589	4.996959	0.000000	adf.f=right
Au	9.911178	-3.331306	0.000000	adf.f=right
Au	9.911178	-0.832826	-1.442498	adf.f=right
Au	9.911178	-0.832826	1.442498	adf.f=right

(continues on next page)

(continued from previous page)

```

    Au      9.911178    1.665653   -2.884996  adf.f=right
    Au      9.911178    1.665653    0.000000  adf.f=right
    Au      9.911178    1.665653    2.884996  adf.f=right
    Au      9.911178    4.164133   -1.442498  adf.f=right
    Au      9.911178    4.164133    1.442498  adf.f=right
    Au      9.911177    6.662612    0.000000  adf.f=right
  end
end

Task SinglePoint

Engine ADF
  fragments
    left      layer.results/adf.rkf
    molecule   molecule.results/adf.rkf
    right      layer.results/adf.rkf
  end
  relativity
    level scalar
    formalism ZORA
  end
  symmetry NOSYM
  title Benzenedithiol
  xc
    lda SCF VWN
  end
EndEngine
eor

# The DOS and transmission can now be calculated:

$AMSBIN/green << eor
DOS fock.results/adf.rkf
TRANS fock.results/adf.rkf
EPS -0.5 0 1000
ETA 1e-6
LEFT left.kf
  FRAGMENT left
END
RIGHT right.kf
  FRAGMENT right
END
NOSAVE DOS_B, TRANS_B
eor

echo ""
echo "Contents of DOS_A:"
cat DOS_A
echo "END"
echo ""
echo "Contents of TRANS_A:"
cat TRANS_A
echo "END"

```

15.6 Analysis

15.6.1 Fragment orbitals, bond energy decomposition

Example: Compound Fragments: Ni(CO)₄

Download Frags_NiCO4.run

```
#!/bin/sh

# An illustration of the fragment feature of ADF.

# A transition metal complex is built from a Nickel atom and four CO fragments.
# The outcomes allows for an analysis (of molecular orbitals and the Bonding
# energy) in terms of the fragment properties. It is a Single Point calculation.
# Geometry optimization would not have been possible in this set-up because an
# optimization requires that only single-atom fragments are used.

# == CO ==

# The CO molecule, to serve as a fragment template in Ni(CO)4 , is computed from
# the atomic fragments C and O. The coordinate values (atoms) are in bohr,
# rather than in Angstrom because the unit-of-length is redefined by the key
# units with subkey length.

# The key scf is used to specify a somewhat tighter convergence criterion than
# the default, just to illustrate how to do this (normal settings are quite
# adequate).

AMS_JOBNAME=CO $AMSBIN/ams <<eor
System
  atoms [bohr]
    C   0   0   0
    O   0   0  2.15617844
  end
end

Task SinglePoint

Engine ADF
  title CO (as fragment for NiCO4)
  eprint
    sfo eig ovl
  end
  basis
    core Small
    type DZ
  end
  scf
    converge 1e-8
  end
EndEngine
eor
```

(continues on next page)

(continued from previous page)

```

# One needs to include the subkey SFO of the key EPRINT with arguments eig and
# ovl in order to get the SFO MO coefficients and SFO overlap matrix printed on
# standard output.

# == Main calculation ==

# Apart from the title, the input contains comment. This does not specify
# computational parameters but is only echoed in the output header, similar to
# the title. Contrary to the title, however, such comments are not preserved,
# apart from their echo in output and they are not written to adf.rkf or any
# other result file.

# The atomic coordinates (atoms) are given in bohr (Units).

# The Atoms records contain also a specification of the fragments to which the
# respective atoms belong: four different CO fragments. The Basis key is used
# for the Ni atom, which implies that it is a fragment on its own.

AMS_JOBNAME=NiCO4 $AMSBIN/ams <<eor
System
  atoms [bohr]
    Ni   0.0          0.0          0.0
    C    2.0053211    2.0053211    2.0053211    adf.f=CO|1
    C   -2.0053211   -2.0053211    2.0053211    adf.f=CO|2
    C    2.0053211   -2.0053211   -2.0053211    adf.f=CO|3
    C   -2.0053211    2.0053211   -2.0053211    adf.f=CO|4
    O    3.2501913    3.2501913    3.2501913    adf.f=CO|1
    O   -3.2501913   -3.2501913    3.2501913    adf.f=CO|2
    O    3.2501913   -3.2501913   -3.2501913    adf.f=CO|3
    O   -3.2501913    3.2501913   -3.2501913    adf.f=CO|4
  end
end

Task SinglePoint

Engine ADF
  title Ni(CO)4,  from fragments Ni and CO
  eprint
    sfo eig ovl
  end
  Basis
    PerAtomType Symbol=Ni File=$AMSRESOURCES/ADF/ZORA/TZP/Ni.2p
  End
  fragments
    CO CO.results/adf.rkf
  end
EndEngine
eor

```

Example: Fragments: PtCl₄H₂ 2-Download Frags_PtCl₄H₂.run

```

#!/bin/sh

# The (scalar) ZORA relativistic option formalism) is used because of the
# presence of the heavy Pt atom. The complex is built from fragments H2 and
# PtCl42- .

# The calculations of the molecule and larger fragments are performed with
# GGA's.

# == fragments H2 and PtCl42- ==

# The two fragments H2 and PtCl42- are first calculated, from which we are
# going to build the final complex.

AMS_JOBNAME=H2 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    H      0.0      0.0      0.84
    H      0.0      0.0     -0.84
  end
end

Task SinglePoint

Engine ADF
  title H2
  basis
    type DZP
    CreateOutput Yes
  end
  noprint sfo,frag,functions
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine
eor

AMS_JOBNAME=PtCl4 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Pt      0      0      0
    Cl     4.361580  0.000000  0
    Cl      0.000000  4.361580  0
    Cl     -4.361580  0.000000  0
    Cl      0.000000 -4.361580  0
  end
  charge -2
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  title PtCl4 (2-)
  basis
    PerAtomType Symbol=Pt File=ZORA/DZ/Pt.4d
    type DZP
    CreateOutput Yes
  end
  noprint sfo,frag,functions
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga becke perdew
  end
EndEngine
eor

# The key charge is used to specify the net total charge. The default for the
# net total charge is the sum-of-fragment-charges. The fragments (Pt and Cl
# atoms) have been computed neutrally, but we want to calculate the PtCl4
# complex as a 2- ion.

# == Main calculation ==

# Finally we compute PtCl4 H2 2- from the fragments PtCl4^2- and H2/

AMS_JOBNAME=PtCl4H2 $AMSBIN/ams <<eor
System
  atoms [Bohr]
    Pt  0          0          0          adf.f=PtCl4
    Cl  0.000000   -4.361580   0.00000000   adf.f=PtCl4
    Cl  0.000000    4.361580   0.00000000   adf.f=PtCl4
    Cl -4.361580    0.000000   0.00000000   adf.f=PtCl4
    Cl  4.361580    0.000000   0.00000000   adf.f=PtCl4
    H   0.0         0.0         5.58        adf.f=H2
    H   0.0         0.0         7.26        adf.f=H2
  end
  charge -2
end

Task SinglePoint

Engine ADF
  title PtCl4 H2
  eprint
    sfo eig ovl
  end
  fragments
    PtCl4  PtCl4.results/adf.rkf
    H2     H2.results/adf.rkf

```

(continues on next page)

(continued from previous page)

```

end
relativity
  level scalar
  formalism ZORA
end
xc
  gga becke perdew
end
EndEngine
eor

# Note the adf.f=fragment specification in the Atoms block. No fragment-numbering
# suffix (/n) is required because there is only one fragment of each fragment
# type.

```

Example: Spin-unrestricted Fragments: H2

Download UnrFrag_H2.run

```

#!/bin/sh

# This is a small but important example to illustrate what goes into an accurate
# calculation of the 'true' bond energy of a molecule. The (ADF-specific)
# problem is that in a straightforward molecular calculation, the bond energy is
# computed as the energy difference between at the one hand the molecule, and at
# the other hand the isolated spherically symmetric spin-restricted atoms.
# This spherically symmetric spin-restricted reference (comparison) state is usually
# not the physical ground state of the reference system (isolated atoms) and
# hence the computed energy difference has no direct relation to experimental
# data. To account for the true atomic ground states, one has to add correction
# terms. Study this sample carefully to make sure that you fully understand the
# steps to take and consult the User's Guide for details. See also the this
# document for a discussion of multiplet states.

# See also the example, SD_Cr(NH3)6.

# The H2 case consists of a sequence of simple calculations to demonstrate the
# Unrestricted Fragments options.
# In the first part real spin-unrestricted fragments are used.
# In the second part simulate spin-unrestricted fragments are used.

# Unrestricted fragments
# =====

# If one uses unrestricted fragments one needs to calculate the unrestricted
# H atom twice, one in which the 1s alpha orbital is occupied, and one in which
# the 1s beta orbital is occupied.

AMS_JOBNAME=H_A $AMSBIN/ams <<eor
System
  atoms
    H  0.0 0.0 0.0
  end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  eprint
    sfo eig ovl
  end
  basis
    type DZP
  end
  spinpolarization 1
  unrestricted
EndEngine
eor

AMS_JOBNAME=H_B $AMSBIN/ams <<eor
System
  atoms
    H  0.0 0.0 0.0
  end
end

Task SinglePoint

Engine ADF
  eprint
    sfo eig ovl
  end
  basis
    type DZP
  end
  spinpolarization -1
  unrestricted
EndEngine
eor

AMS_JOBNAME=H2_AB $AMSBIN/ams <<eor
System
  atoms
    H  0  0  0.375  adf.f=H_A
    H  0  0 -0.375  adf.f=H_B
  end
end

Task SinglePoint

Engine ADF
  title H2 from unrestricted fragments
  eprint
    sfo eig ovl
  end
  fragments
    H_A  H_A.results/adf.rkf
    H_B  H_B.results/adf.rkf
  end
  spinpolarization 0
  unrestricted

```

(continues on next page)

(continued from previous page)

```

    unrestrictedfragments
EndEngine
eor

# In the unrestricted fragment different numbers of spin-alpha and spin-beta
↳electrons usually
# result in different spatial orbitals and different energy eigenvalues for
# spin-alpha and spin-beta when you go to self-consistency.
# For H2 calculated from real unrestricted fragments this will mean that the SFO
↳analysis of
# the H2 molecular orbitals looks a bit unsymmetric.
# However, if one simulates the unrestricted fragments with the key FRAGOCCUPATIONS
# the SFO analysis for H2 will be symmetric.

# Simulated unrestricted fragments with the key FRAGOCCUPATIONS
# =====

# In this approach spin-restricted fragments are used, in which
# one has the same spatial orbitals and energy eigenvalues for
# spin-alpha and spin-beta.
# The energy difference between an unrestricted
# fragment as it is used with the key FRAGOCCUPATIONS and a self-consistent
# unrestricted fragment is computed. This turns out to be quite small,
# confirming that this approach with simulated unrestricted fragments,
# although not formally exact, is also adequate for practical purposes.

$AMSBIN/dirac -n1 < $AMSRESOURCES/Dirac/H
mv TAPE12 t12.rel

AMS_JOBNAME=H_R $AMSBIN/ams <<eor
System
  Atoms
    H 0.0 0.0 0.0
  End
end
Task SinglePoint
Engine ADF
  create H      file=$AMSRESOURCES/ADF/ZORA/DZP/H
  corepotentials t12.rel
    H 1
  end
EndEngine
eor

AMS_JOBNAME=H_U_noscf $AMSBIN/ams <<eor
System
  atoms
    H 0 0 0
  end
end

Task SinglePoint

Engine ADF
  title H unrestr., not self-consistent (as used in unr.frag. calcs)
  eprint

```

(continues on next page)

(continued from previous page)

```

    sfo eig ovl
end
fragments
    H  H_R.results/adf.rkf
end
scf
    iterations 0
end
spinpolarization 1
unrestricted
EndEngine

eor

# By setting the scf iterations to zero (a value of one (1) would give the same
# result) we prevent cycling to self-consistency. The energy of the 'final' one-
# electron orbitals is consequently computed in the start-up potential, i.e. the
# field of the restricted (basic) atom, where spin-alpha and spin-beta are equally
# occupied, in this case by 0.5 electron each. The not-self-consistent,
# unrestricted H atom is precisely the 'unrestricted' fragment as it can be used
# in an adf calculation with the FRAGOCCUPATIONS key. The fragment file must be
# the TAPE21 result file from a restricted run, but at start-up you can specify
# that the Fragment Orbitals are, for purposes of reference and comparison,
# occupied in an unrestricted way in the final molecule.

# A calculation that uses restricted fragments right away computes the bonding
# energy relative to the restricted fragments. The difference between using
# restricted and unrestricted fragments is the 'bonding' energy computed in the
# run above.

AMS_JOBNAME=H_U_scf $AMSBIN/ams <<eor
System
    atoms
        H  0 0 0
    end
end

Task SinglePoint

Engine ADF
    title H  unr. self-consistent from unr.0
    eprint
        sfo eig ovl
    end
    fragments
        H  H_R.results/adf.rkf
    end
    fragoccupations
        H
        s  1 // 0
        subend
    end
    spinpolarization 1
    unrestricted
EndEngine

eor

```

(continues on next page)

(continued from previous page)

```
# Here we start with the unrestricted fragment and relax to self-consistency.
# The 'bonding energy', i.e. the relaxation energy, is very small, demonstrating
# that using non-self-consistent unrestricted fragments involves only a small
# error (which, moreover, can be computed as shown here).
```

```
# The key UnRestricted sets the spin-unrestricted mode. The key Charge is used
# to specify a net total charge of zero and a net total spin polarization by an
# excess of 1.0 spin-alpha electrons over spin-beta.
```

```
AMS_JOBNAME=H2_R $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
```

```
    H   0   0   0.375
```

```
    H   0   0  -0.375
```

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title H2 restricted, from restricted fragments
```

```
  eprint
```

```
    sfo eig ovl
```

```
  end
```

```
  fragments
```

```
    H   H_R.results/adf.rkf
```

```
  end
```

```
EndEngine
```

```
eor
```

```
# This is the simplest approach, using restricted fragments. The bonding energy
# must be corrected because the reference (restricted H atoms, with 0.5
# electrons in spin-alpha and 0.5 in spin-beta) is far from the true H-atom
# ground state: see the previous runs on the single H atom.
```

```
AMS_JOBNAME=H2_U $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
```

```
    H   0   0   0.375 adf.f=H.1
```

```
    H   0   0  -0.375 adf.f=H.2
```

```
  end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title H2 from simulated unrestricted fragments using the FRAGOCCUPATIONS key
```

```
  eprint
```

```
    sfo eig ovl
```

```
  end
```

```
  fragments
```

```
    H.1 H_R.results/adf.rkf
```

```
    H.2 H_R.results/adf.rkf
```

```
  end
```

```
  fragoccupations
```

(continues on next page)

(continued from previous page)

```

      H.1
      s 1 // 0
      subend
      H.2
      s 0 // 1
      subend
    end
    irrepopulations
      sigma 2
    end
    modifystartpotential
      H.1 1 // 0
      H.2 0 // 1
    end
  EndEngine

eor

# This should be a fair approximation (in the LDA model) to the bonding energy
# of H2 with respect to the unrestricted H atoms. The difference between the
# bonding energies of this and the previous run should be very close to the
# energy of the not-self-consistent unrestricted H-atom with respect to the
# restricted basic atom.

# == Excited state ==

AMS_JOBNAME=H2_excited $AMSBIN/ams <<eor
System
  atoms
    H 0 .0 0.375
    H 0 .0 -0.375
  end
end

Task SinglePoint

Engine ADF
  title H2 excited
  eprint
  sfo eig ovl
end
fragments
  H H_R.results/adf.rkf
end
fragoccupations
  H
    s 1 // 0
    subend
  end
  irrepopulations
    sigma.g 1 // 0
    sigma.u 1 // 0
  end
  spinpolarization 2
  unrestricted
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor

# Finally the calculation of an excited state, with respect to unrestricted
# fragments. The excitation energy is obtained by comparing the energy with the
# energy of the ground state calculation. This difference compares reasonably,
# but not accurately, to the difference in one-electron ground state energies of
# the involved orbitals (Koopman's theorem).

# Note that excitation energies can also be calculated with Time-Dependent DFT,
# using the EXCITATIONS key of ADF. See related sample runs.

```

Example: Bond Energy analysis open-shell fragments: PCCP

Download PCCP_Unr_BondEnergy.run

```

#!/bin/sh

# This example illustrates advanced usage of the bond energy decomposition
# scheme used in ADF.

# Remark: this calculation simulates unrestricted fragments using the FRAGOCCUPATIONS
# key. Real unrestricted fragments can also be used in ADF.

# A proper decomposition of an electron-pair bond energy requires specifying
# opposite spins for the unpaired electrons of the respective radical fragments,
# which can be done with the input key FragOccupations. The specified alpha- and
# beta-spin configurations of the radical fragments are shown in the output
# section B U I L D.

# Please note that if one neglects explicitly specifying opposite spins for the
# unpaired electrons of the fragments, each of them is treated as being half an
# alpha and half a beta electron and consequently, they enter into a spurious
# Pauli repulsive interaction. This results, among others, into the Pauli
# repulsion term being too repulsive and the orbital interaction term being too
# much stabilizing.

# The example consists of an analysis of the C-C single bond between two CP
# radicals in the four-atomic molecule PCCP. The CP fragment calculations used
# to provide the adf.rkf for the overall PCCP calculation are done here in
# the restricted mode ('cp_fpccp_asr'). The proper spins
# are then specified in the calculation of the overall molecule using the
# FragOccupations key ('pccp_fa1_as'). Note that this implies a slight
# approximation because the bond energy computed in this way refers to the
# energy difference between closed-shell PCCP and two CP radicals that are
# described by orbitals from a spin-restricted SCF calculation, which have been
# given an unrestricted occupation. In other words, the set of alpha- and beta-
# spin orbitals are identical and the effect of spin polarization is missing. In
# practice, this leads to minor energy differences with respect to the correct
# bond energy, that is, the energy difference between closed-shell PCCP and two
# CP radicals treated in the unrestricted mode, i.e., for which the set of
# alpha- and beta-spin orbitals are allowed to relax toward different solutions
# in the SCF procedure. This correction term can be computed directly by
# carrying out an unrestricted computation of the CP radical ('cp_fpccp_asu') using
→the

```

(continues on next page)

(continued from previous page)

```

# restricted CP radical ('cp_fpccp_asr') as a fragment.

# The pure orbital interaction effect of forming the electron bonding combination
# of the two radicals can be isolated from the full orbital interaction by carrying_
↳out a
# separate calculation. In this calculation (pccp_fa1_pb) the bond energy analysis is_
↳performed in
# the absence of any virtual CP fragment orbitals, using the key REMOVEFRAGORBITALS.

AMS_JOBNAME=CP $AMSBIN/ams <<eor
System
  atoms
    C      .0000   .0000   .6681
    P      .0000   .0000   2.2555
  end
end

Task SinglePoint

Engine ADF
  title cp_fpccp_asr
  eprint
    sfo eig ovl
  end
  basis
    core Large
    type TZ2P
  end
  numericalquality Good
  xc
    gga BECKE PERDEW
  end
EndEngine
eor

AMS_JOBNAME=CP_Unrestricted $AMSBIN/ams <<eor
System
  atoms
    C      .0000   .0000   .6681   adf.f=CP
    P      .0000   .0000   2.2555   adf.f=CP
  end
end

Task SinglePoint

Engine ADF
  title cp_fpccp_asu
  eprint
    sfo eig ovl
  end
  fragments
    CP    CP.results/adf.rkf
  end
  fragoccupations
    CP
    SIGMA 3//2

```

(continues on next page)

(continued from previous page)

```

        PI      2//2
        SUBEND
    end
    numericalquality Good
    spinpolarization 1
    unrestricted
    xc
        gga BECKE PERDEW
    end
EndEngine
eor

AMS_JOBNAME=PCCP_pb $AMSBIN/ams <<eor
System
    atoms
        P          .0000      .0000      2.2555  adf.f=CP_A
        C          .0000      .0000      .6681  adf.f=CP_A
        C          .0000      .0000     -.6681  adf.f=CP_B
        P          .0000      .0000     -2.2555  adf.f=CP_B
    end
end

Task SinglePoint

Engine ADF
    title pccp_fa1_pb
    eprint
        orbpop 20 20
    end
    sfo eig ovl
end
fragments
    CP_A  CP.results/adf.rkf
    CP_B  CP.results/adf.rkf
end
fragoccupations
    CP_A
    SIGMA 3//2
    PI      2//2
    SUBEND
    CP_B
    SIGMA 2//3
    PI      2//2
    SUBEND
end
    numericalquality Good
    removeallfragvirtals
    symmetry C(LIN)
    xc
        gga BECKE PERDEW
    end
    print VDDanalysis
EndEngine
eor

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=PCCP $AMSBIN/ams <<eor
System
  atoms
    P      .0000   .0000   2.2555   adf.f=CP_A
    C      .0000   .0000   .6681   adf.f=CP_A
    C      .0000   .0000  -.6681   adf.f=CP_B
    P      .0000   .0000  -2.2555   adf.f=CP_B
  end
end

Task SinglePoint

Engine ADF
  title pccp_fa1_as
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  CP_A    CP.results/adf.rkf
  CP_B    CP.results/adf.rkf
end
fragoccupations
  CP_A
  SIGMA 3//2
  PI    2//2
  SUBEND
  CP_B
  SIGMA 2//3
  PI    2//2
  SUBEND
end
numericalquality Good
symmetry C(LIN)
xc
  gga BECKE PERDEW
end
print VDDanalysis
EndEngine
eor

AMS_JOBNAME=CP_B3LYP $AMSBIN/ams <<eor
System
  atoms
    C      .0000   .0000   .6681
    P      .0000   .0000   2.2555
  end
end

Task SinglePoint

Engine ADF
  title B3LYP restricted
  basis
    core None
    type TZ2P

```

(continues on next page)

(continued from previous page)

```

end
numericalquality Good
xc
  hybrid B3LYP
end
EndEngine
eor

AMS_JOBNAME=CP_B3LYP_Unrestricted $AMSBIN/ams <<eor
System
  atoms
    C      .0000   .0000   .6681  adf.f=CP
    P      .0000   .0000   2.2555  adf.f=CP
  end
end

Task SinglePoint

Engine ADF
  title B3LYP unrestricted
  fragments
    CP    CP_B3LYP.results/adf.rkf
  end
  fragoccupations
    CP
    SIGMA 7//6
    PI    4//4
    Subend
  end
  numericalquality Good
  spinpolarization 1
  unrestricted
  xc
    hybrid B3LYP
  end
EndEngine
eor

AMS_JOBNAME=PCCP_B3LYP_pb $AMSBIN/ams <<eor
System
  atoms
    P      .0000   .0000   2.2555  adf.f=CP_A
    C      .0000   .0000   .6681  adf.f=CP_A
    C      .0000   .0000  -.6681  adf.f=CP_B
    P      .0000   .0000  -2.2555  adf.f=CP_B
  end
end

Task SinglePoint

Engine ADF
  title PCCP B3LYP PAIRBONDING
  fragments
    CP_A    CP_B3LYP.results/adf.rkf
    CP_B    CP_B3LYP.results/adf.rkf
  end
  fragoccupations

```

(continues on next page)

(continued from previous page)

```

    CP_A
    SIGMA 7//6
    PI 4//4
    Subend
    CP_B
    SIGMA 6//7
    PI 4//4
    Subend
end
numericalquality Good
removeallfragvirtals
xc
    hybrid B3LYP
end
print VDDanalysis
EndEngine
eor

AMS_JOBNAME=PCCP_B3LYP $AMSBIN/ams <<eor
System
atoms
    P .0000 .0000 2.2555 adf.f=CP_A
    C .0000 .0000 .6681 adf.f=CP_A
    C .0000 .0000 -.6681 adf.f=CP_B
    P .0000 .0000 -2.2555 adf.f=CP_B
end
end

Task SinglePoint

Engine ADF
title PCCP B3LYP
fragments
    CP_A CP_B3LYP.results/adf.rkf
    CP_B CP_B3LYP.results/adf.rkf
end
fragoccupations
    CP_A
    SIGMA 7//6
    PI 4//4
    Subend
    CP_B
    SIGMA 6//7
    PI 4//4
    Subend
end
numericalquality Good
xc
    hybrid B3LYP
end
print VDDanalysis
EndEngine
eor

```

Example: Analysis of NaCl using ionic fragments: Na⁺ and Cl⁻

Download NaCl_ionicbonding.run

```

#!/bin/sh

# This example illustrates advanced usage of the bond energy decomposition
# scheme used in ADF.

# This example shows the energy decomposition analysis of NaCl with
# ionic fragments: Na+ and Cl-
# See also the example with neutral fragments: Na and Cl, both open shell atoms
#
# If the key REMOVEALLFRAGORBITALS is used one can approximately
# see what the electrostatic effect is on the fragment orbitals if one places
# the two ions together.
#
# Another way to see what the electrostatic effect is on the fragment orbitals is
# to use the key 'PRINT FMATSFO' in the full molecule calculation, where one can
# look at the expectation value of the Fock matrix of a fragment orbital in the
# presence of the other fragment.

AMS_JOBNAME=Cl_min $AMSBIN/ams <<eor
System
  atoms
    Cl  0.0 0.0 0.0
  end
  charge -1
end

Task SinglePoint

Engine ADF
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga BECKE PERDEW
  end
EndEngine
eor

AMS_JOBNAME=Na_plus $AMSBIN/ams <<eor
System
  atoms
    Na 0.0 0.0 0.0
  end
  charge 1
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga BECKE PERDEW
  end
EndEngine
eor

AMS_JOBNAME=NaCl_es $AMSBIN/ams <<eor
System
  atoms
    Na  0.0 0.0 0.0  adf.f=Na
    Cl  0.0 0.0 2.361 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na  Na_plus.results/adf.rkf
  Cl  Cl_min.results/adf.rkf
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
removeallfragvirtals
title ionic bonding
xc
  gga BECKE PERDEW
end
EndEngine
eor

AMS_JOBNAME=NaCl $AMSBIN/ams <<eor
System
  atoms

```

(continues on next page)

(continued from previous page)

```

    Na 0.0 0.0 0.0 adf.f=Na
    Cl 0.0 0.0 2.361 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na Na_plus.results/adf.rkf
  Cl Cl_min.results/adf.rkf
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
title ionic bonding
xc
  gga BECKE PERDEW
end
EndEngine
eor

```

Example: Electron Pair bonding in NaCl: open shell fragments

Download NaCl_pairbonding.run

```

#!/bin/sh

# This example illustrates advanced usage of the bond energy decomposition
# scheme used in ADF.

# This example shows the energy decomposition analysis of NaCl with
# neutral fragments: Na and Cl, both open shell atoms
# See also the example with ionic fragments: Na+ and Cl-.

# A proper decomposition of an electron-pair bond energy requires specifying
# opposite spins for the unpaired electrons of the respective radical fragments,
# which can be done with the input key FragOccupations. The specified alpha- and
# beta-spin configurations of the radical fragments are shown in the output
# section B U I L D.

# Please note that if one neglects explicitly specifying opposite spins for the
# unpaired electrons of the fragments, each of them is treated as being half an
# alpha and half a beta electron and consequently, they enter into a spurious
# Pauli repulsive interaction. This results, among others, into the Pauli
# repulsion term being too repulsive and the orbital interaction term being too
# much stabilizing.

```

(continues on next page)

(continued from previous page)

```

# The example consists of an analysis of the Na-Cl single bond between two
# open shell atoms. Two methods are described here.
# The first method uses spin-restricted fragments but simulates unrestricted fragments
# with the use of the FRAGOCCUPATIONS key.
# The second method uses real unrestricted atoms.

# Unrestricted fragments with fragoccuaptions
# -----

# The proper spins in this method are specified in the calculation of the overall
# molecule using the FragOccupations key. Note that this implies a slight
# approximation because the bond energy computed in this way refers to the
# energy difference between closed-shell NaCl and two open shell atoms that are
# described by orbitals from a spin-restricted SCF calculation, which have been
# given an unrestricted occupation. In other words, the set of alpha- and beta-
# spin orbitals are identical and the effect of spin polarization is missing. In
# practice, this leads to minor energy differences with respect to the correct
# bond energy, that is, the energy difference between closed-shell NaCl and the two
# open shell atoms treated in the unrestricted mode, i.e., for which the set of
# alpha- and beta-spin orbitals are allowed to relax toward different solutions
# in the SCF procedure. This correction term can be computed directly by
# carrying out an unrestricted computation of the Na and Cl atom using the spin
# restricted atoms as a fragment.

# Real unrestricted fragments
# -----

# The unrestricted calculated Na and Cl atom are used as fragments.

# Prepared for bonding
# -----

# Note that the Cl atom that is used as fragment is given an electron
# configuration that is so called 'prepared for bonding' in order to minimize
# the Pauli repulsion in the electron pair bond.
# In this case it means that there is a hole in the valence Cl p_z orbital,
# that will later form an electron pair bond with the valence s orbital of Na.

# Pair bonding
# -----

# The pure orbital interaction effect of forming the electron bonding combination
# of the two radicals can be isolated from the full orbital interaction by carrying_
↳ out a
# separate calculation. In this calculation the bond energy analysis is performed in
# the absence of (almost) all virtual fragment orbitals, using the key_
↳ REMOVEALLFRAGVIRTUALS.
# Note that in the calculation there is a slight orbital relaxation term in addition_
↳ to the
# pure orbital interaction, because not only the bonding combination of the singly_
↳ occupied
# orbitals of the fragments are included, but also the anti-bonding combination.

AMS_JOBNAME=Na_r $AMSBIN/ams <<eor
System
atoms

```

(continues on next page)

(continued from previous page)

```
        Na 0.0 0.0 0.0
    end
end

Task SinglePoint

Engine ADF
    basis
        core None
        type TZ2P
        CreateOutput Yes
    end
    numericalquality Good
    relativity
        level scalar
        formalism ZORA
    end
    xc
        gga BECKE PERDEW
    end
EndEngine
eor

AMS_JOBNAME=Cl_r $AMSBIN/ams <<eor
System
    atoms
        Cl 0.0 0.0 0.0
    end
end

Task SinglePoint

Engine ADF
    irreppoccupations
        SIGMA.g 6
        SIGMA.u 2 1
        PI.u 8
    end
    basis
        core None
        type TZ2P
        CreateOutput Yes
    end
    numericalquality Good
    relativity
        level scalar
        formalism ZORA
    end
    symmetry D(LIN)
    xc
        gga BECKE PERDEW
    end
EndEngine
eor
```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=Na_u $AMSBIN/ams <<eor
System
  atoms
    Na 0.0 0.0 0.0 adf.f=Na
  end
end

Task SinglePoint

Engine ADF
  fragments
    Na Na_r.results/adf.rkf
  end
  fragoccupations
    Na
    S 3 // 2
    P 3 // 3
    SubEnd
  end
  irrepopulations
    S 3 // 2
    P 3 // 3
  end
  numericalquality Good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 1
  title unrestricted Na
  unrestricted
  xc
    gga BECKE PERDEW
  end
EndEngine
eor

```

```

AMS_JOBNAME=Cl_u $AMSBIN/ams <<eor
System
  atoms
    Cl 0.0 0.0 0.0 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  fragments
    Cl Cl_r.results/adf.rkf
  end
  fragoccupations
    Cl
    SIGMA.g 3 // 3
    SIGMA.u 1 // 2
    PI.u 4 // 4
    SubEnd

```

(continues on next page)

(continued from previous page)

```

end
irrepopulations
  SIGMA.g 3 // 3
  SIGMA.u 1 // 2
  PI.u    4 // 4
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
spinpolarization -1
symmetry D(LIN)
title unrestricted Cl
unrestricted
xc
  gga BECKE PERDEW
end
EndEngine
eor

AMS_JOBNAME=NaCl_pb $AMSBIN/ams <<eor
System
  atoms
    Na 0.0 0.0 0.0  adf.f=Na
    Cl 0.0 0.0 2.361 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na Na_r.results/adf.rkf
  Cl Cl_r.results/adf.rkf
end
fragoccupations
  Na
    S 3 // 2
    P 3 // 3
  SubEnd
  Cl
    SIGMA.g 3 // 3
    SIGMA.u 1 // 2
    PI.u    4 // 4
  SubEnd
end
numericalquality Good
relativity
  level scalar
  formalism ZORA

```

(continues on next page)

(continued from previous page)

```

end
removeallfragvirtals
title fragoccupations pair bonding
xc
  gga BECKE PERDEW
end
EndEngine
eor

AMS_JOBNAME=NaCl $AMSBIN/ams <<eor
System
  atoms
    Na 0.0 0.0 0.0  adf.f=Na
    Cl 0.0 0.0 2.361 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na Na_r.results/adf.rkf
  Cl Cl_r.results/adf.rkf
end
fragoccupations
  Na
    S 3 // 2
    P 3 // 3
  SubEnd
  Cl
    SIGMA.g 3 // 3
    SIGMA.u 1 // 2
    PI.u    4 // 4
  SubEnd
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
title fragoccupations
xc
  gga BECKE PERDEW
end
EndEngine
eor

AMS_JOBNAME=NaCl_unrfrag_pb $AMSBIN/ams <<eor
System
  atoms

```

(continues on next page)

(continued from previous page)

```

        Na 0.0 0.0 0.0   adf.f=Na
        Cl 0.0 0.0 2.361 adf.f=Cl
    end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na Na_u.results/adf.rkf
  Cl Cl_u.results/adf.rkf
end
numericalquality Good
relativity
  level scalar
  formalism ZORA
end
removeallfragvirtals
spinpolarization 0
title unrestricted fragments pair bonding
unrestricted
unrestrictedfragments
xc
  gga BECKE PERDEW
end
EndEngine
eor

AMS_JOBNAME=NaCl_unrfrag $AMSBIN/ams <<eor
System
  atoms
    Na 0.0 0.0 0.0   adf.f=Na
    Cl 0.0 0.0 2.361 adf.f=Cl
  end
end

Task SinglePoint

Engine ADF
  eprint
    orbpop 20 20
  end
  sfo eig ovl
end
fragments
  Na Na_u.results/adf.rkf
  Cl Cl_u.results/adf.rkf
end
numericalquality Good
relativity
  level scalar

```

(continues on next page)

(continued from previous page)

```

    formalism ZORA
end
spinpolarization 0
title unrestricted fragments
unrestricted
unrestrictedfragments
xc
    gga BECKE PERDEW
end
EndEngine
eor

```

Example: Bond Energy analysis meta-GGA, (meta-)hybrids: Zn2, Cr2, CrH

Download EDA_meta_gga_hybrid.run

```

#!/bin/sh

# This example illustrates the bond energy decomposition scheme using metaGGA or
# metahybrid or hybrid functionals in ADF.

# The first example is straightforward with closed shell atomic fragments: Zn_2.
# The second example has open shell atomic fragments: Cr_2, and the extra
# complication that spin symmetry breaking lowers the energy of the molecule,
# although the total S_z-value is zero. The third example has open shell atomic
# fragments, and the molecule is open shell: CrH.

# == Zn2 ==

# In the first example for Zn_2 the metahybrid TPSSh is used. In the bond energy
# analysis, the bond energy is split in a Pauli repulsion term, a steric
# interaction, and an orbital interaction.

AMS_JOBNAME=Zn2 $AMSBIN/ams <<eor
System
  atoms
    Zn 0.0 0.0 -1.6
    Zn 0.0 0.0 1.6
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type TZ2P
  end
  xc
    metahybrid TPSSh
  end

```

(continues on next page)

(continued from previous page)

```

EndEngine

eor

# == Cr2 ==

# In the second example for Cr2 the metaGGA TPSS is used. You can use
# spin-unrestricted fragments in ADF. However, here simulated unrestricted
# fragments are used. A fair approximation to a computation with unrestricted
# fragments can be achieved with the key FRAGOCCUPATIONS. You tell ADF that you
# want to treat the fragments as if they were unrestricted; this causes the
# program to duplicate the one-electron orbitals of the fragment: one set for
# spin-alpha and one set for spin-beta. You can then specify occupation numbers
# for these spin-unrestricted fragments, and occupy spin-alpha orbitals
# differently from spin-beta orbitals. Especially for the Pauli-repulsion it is
# important that one chooses the spin-occupations on the different fragments
# such that they are 'prepared for bonding'.

# Of course, the unrestricted fragments that you use in this way, are not self-
# consistent: different numbers of spin-alpha and spin-beta electrons usually
# result in different spatial orbitals and different energy eigenvalues for
# spin-alpha and spin-beta when you go to self-consistency, while here you have
# spatially identical fragment orbitals. Nevertheless it is often a fair
# approximation which gives you a considerable extension of analysis
# possibilities.

# Spin-symmetry breaking is enforced by the use of the key ModifyStartPotential
# in combination with the key key UNRESTRICTED. In the ADF output one can find
# that there is spin-density on both of the atoms.

# Cr atom fragment:

AMS_JOBNAME=Cr $AMSBIN/ams <<eor > Cr_create_run.out
System
  atoms
    Cr 0.0 0.0 0.0
  end
end

Task SinglePoint

Engine ADF
  NumericalQuality VeryGood
  IrrepOccupations
    S 7
    P 12
    D 5
  end
  basis
    core None
    type TZ2P
  end
  xc
    metagga TPSS
  end
EndEngine

```

(continues on next page)

(continued from previous page)

```

eor

AMS_JOBNAME=Cr2 $AMSBIN/ams <<eor
System
  atoms
    Cr 0.0 0.0 -0.9 adf.f=Cr.1
    Cr 0.0 0.0 0.9 adf.f=Cr.2
  end
end

Task SinglePoint

Engine ADF
  Fragments
    Cr.1 Cr.results/adf.rkf
    Cr.2 Cr.results/adf.rkf
  End
  beckegrid
    quality good
  end
  fragoccupations
    Cr.1
    S 4 // 3
    P 6 // 6
    D 5 // 0
    SubEnd
    Cr.2
    S 3 // 4
    P 6 // 6
    D 0 // 5
    SubEnd
  end
  modifystartpotential
    Cr.1 1 // 0
    Cr.2 0 // 1
  end
  spinpolarization 0
  unrestricted
  xc
    metagga TPSS
  end
EndEngine

eor

# In order to calculate the effect of self-consistency one should calculate the
# Cr atom spin-unrestrictedly.

AMS_JOBNAME=Cr $AMSBIN/ams <<eor
System
  atoms
    Cr 0.0 0.0 0.0

```

(continues on next page)

(continued from previous page)

```

    end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  fragoccupations
    Cr
      S 4 // 3
      P 6 // 6
      D 5 // 0
    SubEnd
  end
  basis
    core None
    type TZ2P
  end
  spinpolarization 6
  unrestricted
  xc
    metagga TPSS
  end
EndEngine

eor

# == CrH ==

# In this example for CrH the hybrid B3LYP is used.

AMS_JOBNAME=CrH $AMSBIN/ams <<eor
System
  atoms
    Cr 0.0 0.0 0.0
    H  0.0 0.0 1.65
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  fragoccupations
    Cr
      S 4 // 3
      P 6 // 6
      D 5 // 0
    SubEnd
    H
      S 0 // 1
    SubEnd

```

(continues on next page)

(continued from previous page)

```

end
basis
  core None
  type TZ2P
end
spinpolarization 5
unrestricted
xc
  hybrid B3LYP
end
EndEngine

eor

# In order to calculate the effect of self-consistency of spin-polarization on
# the atoms one should calculate the Cr and H atom spin-unrestrictedly.

AMS_JOBNAME=Cr_B3LYP $AMSBIN/ams <<eor
System
  atoms
    Cr 0.0 0.0 0.0
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  fragoccupations
    Cr
      S 4 // 3
      P 6 // 6
      D 5 // 0
    SubEnd
  end
basis
  core None
  type TZ2P
end
spinpolarization 6
unrestricted
xc
  hybrid B3LYP
end
EndEngine

eor

AMS_JOBNAME=H $AMSBIN/ams <<eor
System
  atoms
    H 0.0 0.0 0.0

```

(continues on next page)

(continued from previous page)

```
end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  fragoccupations
    H
    S 1 // 0
  SubEnd
end
basis
  core None
  type TZ2P
end
spinpolarization 1
unrestricted
xc
  hybrid B3LYP
end
EndEngine

eor
```

Example: unrestricted EDA: Cu(C₂H₄)₂

Download EDA_Unr_C2H4_Cu_C2H4.run

```
#!/bin/sh

# An illustration of an unrestricted energy decomposition analysis (unrestricted EDA).
# The open shell Cu atom forms a complex with 2 ethylene molecules.

AMS_JOBNAME=Cu_A $AMSBIN/ams <<eor
System
  atoms
    Cu  0.0 0.0 0.0
  end
end

Task SinglePoint

Engine ADF
  basis
    type DZ
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
```

(continues on next page)

(continued from previous page)

```

end
spinpolarization 1
unrestricted
xc
  dispersion GRIMME4
  gga BP86
end
EndEngine

eor

AMS_JOBNAME=Ethylene $AMSBIN/ams <<eor
System
  atoms
    C      0.000000000000      0.708069500374      1.888278754032
    C      0.000000000000     -0.708069500374      1.888278754032
    H      0.924242618139      1.263978729882      2.061097077561
    H      0.924242618139     -1.263978729882      2.061097077561
    H     -0.924242618139      1.263978729882      2.061097077561
    H     -0.924242618139     -1.263978729882      2.061097077561
  end
end

Task SinglePoint

Engine ADF
  basis
    type DZ
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  xc
    dispersion GRIMME4
    gga BP86
  end
EndEngine

eor

$AMSBIN/ams <<eor
System
  atoms
    C      0.000000000000      0.708069500374      1.888278754032      adf.
    ↪f=Ethylene|1
    C      0.000000000000     -0.708069500374      1.888278754032      adf.
    ↪f=Ethylene|1
    H      0.924242618139      1.263978729882      2.061097077561      adf.
    ↪f=Ethylene|1
    H      0.924242618139     -1.263978729882      2.061097077561      adf.
    ↪f=Ethylene|1
    H     -0.924242618139      1.263978729882      2.061097077561      adf.
    ↪f=Ethylene|1

```

(continues on next page)

(continued from previous page)

```

      H      -0.924242618139      -1.263978729882      2.061097077561      adf.
↪f=Ethylene|1
      Cu      0.000000000000      0.000000000000      0.000000000000      adf.f=Cu_A
      C      0.000000000000      0.708069500374      -1.888278754032      adf.
↪f=Ethylene|2
      C      0.000000000000      -0.708069500374      -1.888278754032      adf.
↪f=Ethylene|2
      H      0.924242618139      1.263978729882      -2.061097077561      adf.
↪f=Ethylene|2
      H      0.924242618139      -1.263978729882      -2.061097077561      adf.
↪f=Ethylene|2
      H      -0.924242618139      1.263978729882      -2.061097077561      adf.
↪f=Ethylene|2
      H      -0.924242618139      -1.263978729882      -2.061097077561      adf.
↪f=Ethylene|2
      end
end
Task SinglePoint

Engine ADF
  fragments
    Ethylene Ethylene.results/adf.rkf
    Cu_A Cu_A.results/adf.rkf
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 1
  unrestricted
  unrestrictedfragments
  xc
    dispersion GRIMME4
    gga BP86
  end
EndEngine

eor

```

Example: unrestricted fragments: CH3I

Download EDA_Unr_CH3I.run

```

#!/bin/sh

# An illustration of an unrestricted energy decomposition analysis (unrestricted EDA).

# Prepared for bonding
# -----

# The electron configuration of the fragments is chosen such that the valence I p_z
↪orbital

```

(continues on next page)

(continued from previous page)

```
# has 1 alpha electron, and the highest occupied Methyl orbital has 1 beta electron.
# Note that this electron configuration of the fragments means that they
# are so called 'prepared for bonding' in order to minimize the Pauli repulsion in
# the electron pair bond.
```

```
AMS_JOBNAME=I_A $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    I   0.0 0.0 0.0
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  irreoccupations
    Sigma.g 2 // 2
    Sigma.u 1 // 0
    Pi.g    2 // 2
    Pi.u    2 // 2
    Delta.g 2 // 2
  end
  basis
    core Small
    type TZ2P
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 1
  symmetry D(lin)
  unrestricted
  xc
    gga BP86
  end
EndEngine
```

```
eor
```

```
AMS_JOBNAME=Methyl_B $AMSBIN/ams <<eor
```

```
System
```

```
  atoms
    C      0.000000000000      0.000000000000      -0.239316000000
    H      -0.521322100000     -0.902956360000     -0.562716000000
    H      -0.521322100000      0.902956360000     -0.562716000000
    H       1.042644200000     -0.000000000000     -0.562716000000
  end
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  basis
    core Small
```

(continues on next page)

(continued from previous page)

```

    type TZ2P
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization -1
  unrestricted
  xc
    gga BP86
  end
EndEngine

eor

# The fragments are prepared. Next the unrestricted EDA is performed,
# in which symmetry can be used.

AMS_JOBNAME=ch3i $AMSBIN/ams <<eor
System
  atoms
    C      0.000000000000      0.000000000000      -0.239316000000  adf.f=Methyl_B
    H      -0.521322100000     -0.902956360000     -0.562716000000  adf.f=Methyl_B
    H      -0.521322100000      0.902956360000     -0.562716000000  adf.f=Methyl_B
    H       1.042644200000     -0.000000000000     -0.562716000000  adf.f=Methyl_B
    I       0.000000000000      0.000000000000      1.927464000000  adf.f=I_A
  end
end

Task SinglePoint

Engine ADF
  fragments
    I_A I_A.results/adf.rkf
    Methyl_B Methyl_B.results/adf.rkf
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 0
  unrestricted
  unrestrictedfragments
  xc
    gga BP86
  end
EndEngine

eor

# Same calculation but now using ETS-NOCV.
# ETS-NOCV: energy analysis using the Natural Orbitals for Chemical Valence.
# In ETS-NOCV symmetry NOSYM is required.

AMS_JOBNAME=etsnocv $AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    C      0.000000000000      0.000000000000      -0.239316000000  adf.f=Methyl_B
    H     -0.521322100000     -0.902956360000     -0.562716000000  adf.f=Methyl_B
    H     -0.521322100000      0.902956360000     -0.562716000000  adf.f=Methyl_B
    H      1.042644200000     -0.000000000000     -0.562716000000  adf.f=Methyl_B
    I      0.000000000000      0.000000000000      1.927464000000  adf.f=I_A
  end
end

Task SinglePoint

Engine ADF
  etsnocv
  end
  fragments
    I_A I_A.results/adf.rkf
    Methyl_B Methyl_B.results/adf.rkf
  end
  numericalquality good
  relativity
    level scalar
    formalism ZORA
  end
  spinpolarization 0
  symmetry nosym
  unrestricted
  unrestrictedfragments
  xc
    gga BP86
  end
EndEngine

eor

```

Example: Spin-Orbit SFO analysis: TIH

Download TIH_SO_analysis.run

```

#!/bin/sh

# Application of the Spin-Orbit relativistic option (using double-group
# symmetry) to TIH with a detailed analysis of the spinors in terms of SFOs
# (Symmetrized Fragment Orbitals).

# In order to get the population analysis, one should have one scalar
# relativistic fragment, which is the whole molecule. The SFOs in this case are
# the scalar relativistic orbitals, which are already orthonormal, because one
# has only one fragment which is the whole molecule.

AMS_JOBNAME=Scalar $AMSBIN/ams <<eor
System
  atoms
    Tl      0.0      0.0      0.0

```

(continues on next page)

(continued from previous page)

```

      H      0.0      0.0      1.870
    end
  end
Task SinglePoint

Engine ADF
  title TlH, scalar relativistic zora
  beckegrid
    quality good
  end
  eprint
    sfo eig ovl
  end
  basis
    core None
    type TZ2P
    CreateOutput Yes
  end
  print SFO
  relativity
    level scalar
    formalism ZORA
  end
  xc
    gga BP86
  end
EndEngine

eor

# In order to get the population analysis, one should have one scalar
# relativistic fragment, which is the whole molecule, which is TlH in this case.

AMS_JOBNAME=SpinOrbit $AMSBIN/ams <<eor
System
  atoms
    Tl      0.0      0.0      0.0    adf.f=TlH
    H      0.0      0.0      1.870  adf.f=TlH
  end
end

Task SinglePoint

Engine ADF
  title TlH from fragment TlH, with SpinOrbit coupling
  beckegrid
    quality good
  end
  eprint
    sfo eig ovl
  end
  fragments
    TlH Scalar.results/adf.rkf
  end
  print SFO
  relativity

```

(continues on next page)

(continued from previous page)

```

    level spin-orbit
    formalism ZORA
end
xc
    gga BP86
end
EndEngine

eor

# The output gives something like:
# =====
#
# =====
# Double group symmetry : *   J1/2   *
# =====
#
#                               === J1/2:1 ===
# Spinors expanded in SFOs
# Spinor:           21           22           23           24
# occup:           1.00           1.00           1.00           0.00
# -----
# SFO SIGMA
# 13.alpha:  0.7614+0.0000i  0.0096+0.0000i  0.0052+0.0000i  -0.0006+0.0000i
# 14.alpha:  0.0154+0.0000i -0.9996+0.0000i  0.0208+0.0000i  -0.0077+0.0000i
# 15.alpha: -0.0146+0.0000i  0.0185+0.0000i  0.9849+0.0000i  0.1625+0.0000i
# SFO PI:x
# 8.beta :  0.4578+0.0000i  0.0091+0.0000i  0.0112+0.0000i  0.0030+0.0000i
# 9.beta :  0.0005+0.0000i -0.0074+0.0000i -0.1119+0.0000i  0.6910+0.0000i
# SFO PI:y
# 8.beta :  0.0000+0.4578i  0.0000+0.0091i  0.0000+0.0112i  0.0000+0.0030i
# 9.beta :  0.0000+0.0005i  0.0000-0.0074i  0.0000-0.1119i  0.0000+0.6910i
#
# =====

# Left out are a lot of small numbers. The meaning is that a spinor of J_z=1/2
# symmetry can have SIGMA and PI character, for example, the 21st spinor with
# occupation number 1.0, is approximately (21 J_z=1/2) = 0.76 (13 SIGMA alpha) +
# 0.46 (8 PI:x beta) + i 0.46 (8 PI:y beta)

# Next in the SFO contributions per spinor the real and imaginary spin alpha
# part and real and imaginary spin beta part are all summed together to give a
# percentage of a certain SFO. are summed. For example the 21st spinor has
# almost 60% (13 SIGMA) character.

# =====
#
# SFO contributions (%) per spinor
# Spinor:      21      22      23      24
# occup:      1.00      1.00      1.00      0.00
# -----
# SFO SIGMA
# 13:      57.97      0.01      0.00      0.00
# 14:      0.02      99.92      0.04      0.01
# 15:      0.02      0.03      97.01      2.64
# SFO PI:x

```

(continues on next page)

(continued from previous page)

```
#      8:      20.96      0.01      0.01      0.00
#      9:       0.00      0.01      1.25     47.75
# SFO PI:y
#      8:      20.96      0.01      0.01      0.00
#      9:       0.00      0.01      1.25     47.75
#
# =====
```

Example: Activation Strain Model Analysis using PyFrag

Download pyfrag.run

```
#!/bin/bash

# The trajectory is a concatenated xyz-file:

cat << eor > coords.xyz
C      -1.741968    -2.220880     0.000000
Pd     -2.137509    -0.237843     0.000000
H      -2.809570    -2.499547     0.000000
H      -1.265288    -2.629932     0.895677
H      -1.265288    -2.629932    -0.895677
H      -0.755099    -0.885698     0.000000

C      -1.741968    -2.220880     0.000000
Pd     -2.137509    -0.250000     0.000000
H      -2.809570    -2.499547     0.000000
H      -1.265288    -2.629932     0.895677
H      -1.265288    -2.629932    -0.895677
H      -0.755099    -0.885698     0.000000
eor

# Input options for ADF:

# One should generally symmetrize the coordinates by setting AMS.System.
↪Symmetrize=Yes

cat << eor > adfinputfile
AMS.Task=SinglePoint
AMS.System.Charge=0
AMS.System.Symmetrize=Yes
ADF.NumericalQuality=VeryGood
ADF.XC.GGA=OPBE
ADF.basis.core=None
ADF.Symmetry=AUTO
ADF.Relativity.Level=Scalar
ADF.Relativity.Formalism=ZORA
ADF.eprint.sfo=eig ovl
eor

# Here we call the PyFrag script.

# PyFrag conducts a total of six single point calculations, one for each fragment and ↪
↪the
```

(continues on next page)

(continued from previous page)

```

# whole system for each of the two geometries in the trajectory, respectively.
# The intermediate results for each geometry are printed during the calculation.
# At the end of its run PyFrag summarizes all results in a table which is also
↪written
# to an output file PyFrag<SystemName>.txt

$AMSBIN/amspython $AMSHOME/scripting/standalone/pyfrag/PyFrag.py \
--xyzpath coords.xyz \
--fragment 2 --fragment 1 3 4 5 6 --strain 0 --strain -554.1 \
--bondlength 1 6 1.093 \
--angle 2 1 6 180 \
--VDD 2 1 6 \
--hirshfeld frag1 \
--irrepOI AA \
--irrepOI AAA \
--orbitalenergy frag1 HOMO \
--orbitalenergy frag2 LUMO \
--orbitalenergy AA frag2 5 \
--population frag1 HOMO \
--population AA frag2 5 \
--overlap frag1 HOMO frag2 LUMO \
--overlap S frag1 5 AA frag2 4 \
--adfininput ADF.basis.type=DZP \
--adfinputfile adfinputfile

```

15.6.2 Localized orbitals, bond orders, charge analysis

Example: (Perturbed) localized molecular orbitals in twisted Ethene

Download LocMO_Resp.run

```

#!/bin/sh

# This is example for the calculation of localized molecular orbitals, and
# perturbed localized molecular orbitals. This example uses the Pipek-Mezey
# localization method (criterion PM in the LOCORB block key). With the
# AORESPONSE block key and the subkey opticalrotation the optical rotation
# dispersion is calculated. The PERTLOC key is specified in order to calculate
# perturbed localized molecular orbitals. The subkey gprime and beta of the key
# PERTLOC are needed to analyze the optical rotation. Note that PERTLOC only
# makes sense in combination with AORESPONSE and LOCORB.

$AMSBIN/ams <<eor
System
atoms
  C 0.000000 0.000000 0.020000
  C 1.350716 0.000000 -0.000000
  H -0.540179 -0.745428 -0.565703
  H -0.540179 0.745428 0.565703
  H 1.890895 -0.935093 -0.035837
  H 1.890895 0.935093 0.035837
end
end

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint

Engine ADF
  title twisted ethene PM localization and response prop analysis
  aoresponse
    frequencies .05 [Hartree]
    giao
    opticalrotation
  end
  locorb
    criterion PM
  end
  basis
    core None
    type DZP
  end
  pertloc
    alfa
    beta
    dynamic
    efield
    fulltens
    gprime
  end
  symmetry nosym
  Relativity
    Level None
  End
EndEngine
eor

```

Example: Rose localization and TD-DFT: C2F4-C2H4

Download Rose_TDDFT.run

```

#!/bin/sh

# This is an example for running ROSE with two non-overlapping fragments

# C2F4 PBE/DZP

AMS_JOBNAME=C2F4 $AMSBIN/ams <<eor
System
  atoms
    C      0.00000000      0.00000000      0.66676000
    C      0.00000000      0.00000000     -0.66676000
    F      0.00000000      1.10881000      1.39667000
    F      0.00000000     -1.10881000      1.39667000
    F      0.00000000     -1.10881000     -1.39667000
    F      0.00000000      1.10881000     -1.39667000
  end
end

Task SinglePoint

```

(continues on next page)

(continued from previous page)

```

Engine ADF
  title C2F4 PBE/DZP single point
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type DZP
  end
  xc
    gga PBE
  end
  symmetry nosym
  noprint BAS FUNCTIONS
EndEngine
eor

# C2H4 PBE/DZP

AMS_JOBNAME=C2H4 $AMSBIN/ams <<eor
System
  atoms
    C      4.00000000    0.00000000    0.66634000
    C      4.00000000    0.00000000   -0.66634000
    H      4.00000000    0.92873000    1.24070000
    H      4.00000000   -0.92873000    1.24070000
    H      4.00000000   -0.92873000   -1.24070000
    H      4.00000000    0.92873000   -1.24070000
  end
end

Task SinglePoint

Engine ADF
  title C2H4 PBE/DZP single point
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type DZP
  end
  xc
    gga PBE
  end
  symmetry nosym
  noprint BAS FUNCTIONS
EndEngine
eor

# C2F4-C2H4: Supermolecular calculation

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=ROSE $AMSBIN/ams <<eor
System
  atoms
    C      4.00000000      0.00000000      0.66634000
    C      4.00000000      0.00000000     -0.66634000
    H      4.00000000      0.92873000      1.24070000
    H      4.00000000     -0.92873000      1.24070000
    H      4.00000000     -0.92873000     -1.24070000
    H      4.00000000      0.92873000     -1.24070000
    C      0.00000000      0.00000000      0.66676000
    C      0.00000000      0.00000000     -0.66676000
    F      0.00000000      1.10881000      1.39667000
    F      0.00000000     -1.10881000      1.39667000
    F      0.00000000     -1.10881000     -1.39667000
    F      0.00000000      1.10881000     -1.39667000
  end
end

Task SinglePoint

Engine ADF
  title C2F4-C2H4 PBE/DZP ROSE orbital localization
  eprint
    scf NOPOP
    sfo NOEIG NOOVL NOORBPOP
  end
  basis
    core None
    type DZP
  end
  xc
    gga PBE
  end
  rose
    FragmentFile C2F4.results/adf.rkf
    FragmentFile C2H4.results/adf.rkf
  end
  noprint BAS FUNCTIONS
  numericalquality Good
  tda
  excitations
    Lowest 10
    OnlySing
    descriptors
  end
  ExcitonTransfer
    Localize OccupiedAndVirtual
    FullRun
    Output AllAndFilteredCouplings
    Lowest 3 3
    LowestCT 1 1
    CoupleFinalStates
  end
  symmetry nosym
EndEngine
eor

```

Example: Charge model 5 (CM5)

Download CM5_chargemodel.run

```
#!/bin/sh

# With the key CM5 charge model 5 (CM5) atomic charges are calculated. The CM5
# model is especially designed such that one can reasonably accurately predict
# dipole moments with only atomic CM5 charges.

AMS_JOBNAME=Acetone $AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000    1.396962
    C      0.000000    0.000000    0.188800
    H      0.871902    1.314824   -1.265092
    C      0.000000   -1.275657   -0.611044
    H      0.000000    2.142271    0.042196
    H      0.000000   -2.142271    0.042196
    H      0.871902   -1.314824   -1.265092
    C      0.000000    1.275657   -0.611044
    H     -0.871902    1.314824   -1.265092
    H     -0.871902   -1.314824   -1.265092
  end
end

Task SinglePoint

Engine ADF
  title Acetone
  AtomicChargesTypeForAMS CM5
  basis
    type TZP
    core none
  end
  numericalquality good
  xc
    metagga M06-L
  end
EndEngine

eor

AMS_JOBNAME=Nitrobenzene $AMSBIN/ams <<eor
System
  atoms
    C      0.000000    0.000000   -2.503225
    C      0.000000    1.205864   -1.812565
    C      0.000000    1.214022   -0.427327
    C      0.000000    0.000000    0.239613
    C      0.000000   -1.214022   -0.427327
    C      0.000000   -1.205864   -1.812565
    H      0.000000   -2.131001    0.143627
    H      0.000000   -2.142362   -2.354096
    H      0.000000    2.142362   -2.354096
```

(continues on next page)

(continued from previous page)

```

      H      0.000000      2.131001      0.143627
      H      0.000000      0.000000     -3.585546
      N      0.000000      0.000000      1.715151
      O      0.000000     -1.084613      2.278800
      O      0.000000      1.084613      2.278800
    end
  end

Task SinglePoint

Engine ADF
  title Nitrobenzene
  AtomicChargesTypeForAMS cm5
  basis
    type TZP
    core none
  end
  numericalquality good
  xc
    metagga M06-L
  end
EndEngine

eor

```

Example: Bond Orders

Download `BondOrder.run`

```

#!/bin/sh

# With the key BONDORDER a bond order analysis is performed based on SFOs. Note
# that symmetry used in the calculation should be NOSYM.

AMS_JOBNAME=benzene $AMSBIN/ams <<eor
Task SinglePoint

System
atoms
  C 0.0      0.0      0.0
  C 1.384765863418579 0.0      0.0
  C 2.077148675918579 1.199242353439331 0.0
  C 1.384765863418579 2.398484706878662 0.0
  C 0.0      2.398484706878662 0.0
  C -0.6923829317092896 1.199242353439331 0.0
  H 1.920830130577087 -0.9284905791282654 0.0
  H 3.149277210235596 1.199242353439331 0.0
  H 1.920830130577087 3.326975345611572 0.0
  H -0.5360642671585083 3.326975345611572 0.0
  H -1.764511466026306 1.199242353439331 0.0
  H -0.5360642671585083 -0.9284905791282654 0.0
end
end

```

(continues on next page)

(continued from previous page)

```

Properties
  BondOrders Yes
End

Engine ADF
  title benzene BP/SZ bondorders PrintTolerance=0.05
  basis
    Type SZ
    Core None
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  BondOrders
    PrintAll Yes
    PrintTolerance 0.05
  End
  noprint sfo
EndEngine
eor

```

```

AMS_JOBNAME=ethylene $AMSBIN/ams <<eor
Task SinglePoint

```

```

System
  atoms
    C      0.0000    0.0000    0.0000
    C      1.3319    0.0000    0.0000
    H     -0.5723    0.9299    0.0000
    H     -0.5725   -0.9297    0.0000
    H      1.9043    0.9298    0.0000
    H      1.9042   -0.9298    0.0000
  end
end

```

```

Properties
  BondOrders Yes
End

```

```

Engine ADF
  title ethylene BP/SZ bondorders-standard output
  basis
    Type SZ
    Core None
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  noprint sfo
EndEngine
eor

```

```

AMS_JOBNAME=Cr2 $AMSBIN/ams <<eor
Task GeometryOptimization

```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Cr 0.0 0.0 -0.8
    Cr 0.0 0.0 0.8
  end
end

GeometryOptimization
  Convergence
    Gradients 0.0001
  End
End

Properties
  BondOrders Yes
End

Engine ADF
  title Cr2 BP/TZP - bondorder - standard printout
  basis
    Type TZP
    Core None
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  noprint sfo
EndEngine
eor

```

```

AMS_JOBNAME=Mo2 $AMSBIN/ams <<eor
Task GeometryOptimization

```

```

System
  atoms
    Mo 0.0 0.0 -1.0
    Mo 0.0 0.0 1.0
  end
end

Properties
  BondOrders Yes
End

Engine ADF
  title Mo2 BP/TZP - bondorder - standard printout
  basis
    Type TZP
    Core Small
  end
  symmetry NOSYM
  relativity
    level scalar
    formalism ZORA
  end

```

(continues on next page)

(continued from previous page)

```

end
xc
  gga becke perdew
end
noprnt sfo
EndEngine
eor

AMS_JOBNAME=NaCl $AMSBIN/ams <<eor
Task SinglePoint

System
atoms
  Na 0.0 0.0 0.0
  Cl 0.0 0.0 2.377
end
end

Properties
  BondOrders Yes
End

Engine ADF
  title NaCl BP/TZP - bondorder - standard printout
  basis
    Type DZP
    Core None
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  BondOrders
    PrintAll Yes
  End
  noprnt sfo
EndEngine
eor

```

15.6.3 ETS-NOCV

Example: NOCV: ethylene – Ni-diimina

Download Diimina_NOCV.run

```

#!/bin/sh

# Example for calculation of ETS-NOCV for spin-restricted fragments. ETS-NOCV:
# energy analysis using the Natural Orbitals for Chemical Valence. The ethylene
# molecule and a Ni-diimina form a complex together. This example will be
# discussed first. The other example is H+ and CO form together HCO+ , this
# example is similar to the discussed example. All electron basis sets are

```

(continues on next page)

(continued from previous page)

```

# required.

# First the two fragments are calculated.

AMS_JOBNAME=etfrag $AMSBIN/ams <<eor
System
  atoms
    C   -0.430177075 -1.815433265  0.860288229
    C   -0.363705637 -1.910722338 -0.515633302
    H    0.533109934 -2.284970854 -1.016904201
    H   -1.279922499 -1.884673940 -1.115144723
    H   -1.389295819 -1.753589602  1.377541080
    H    0.440296224 -2.041861443  1.484489314
  end
end

Task SinglePoint

Engine ADF
  title et-----Ni-diimina: ethylene run
  basis
    core Small
    type DZP
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  Relativity
    Level None
  End
EndEngine

eor

AMS_JOBNAME=Nifrag $AMSBIN/ams <<eor
System
  atoms
    Ni   0.022615419  0.037783871  0.025751533
    N    0.386170317  1.871072585  0.306265538
    C    1.612863056  2.248007643  0.148716016
    C    2.540686607  1.163409862 -0.183603690
    N    1.976290003  0.008161589 -0.301176178
    H   -0.288333328  2.609667211  0.546869047
    H    1.942601454  3.283060847  0.269249237
    H    3.613259273  1.338293482 -0.302134814
    H    2.621707427 -0.766258151 -0.517479818
    H   -1.351756655  0.253389698  0.386197419
  end
  charge 1
end

Task SinglePoint

Engine ADF

```

(continues on next page)

(continued from previous page)

```

title et-----Ni-diimina: Ni-diimina run
basis
  core Small
  type DZP
end
symmetry NOSYM
xc
  gga scf becke perdew
end
Relativity
  Level None
End
EndEngine

eor

# Next these fragments are used in the calculation of the full complex. The block
# ETSNOCV is used to analyze the bonding in the molecule with respect to the
# →fragments.
# The symmetry must be NOSYM.

$AMSBIN/ams <<eor
System
atoms
  Ni  0.022615419  0.037783871  0.025751533  adf.f=k
  N   0.386170317  1.871072585  0.306265538  adf.f=k
  C   1.612863056  2.248007643  0.148716016  adf.f=k
  C   2.540686607  1.163409862  -0.183603690  adf.f=k
  N   1.976290003  0.008161589  -0.301176178  adf.f=k
  H   -0.288333328  2.609667211  0.546869047  adf.f=k
  H   1.942601454  3.283060847  0.269249237  adf.f=k
  H   3.613259273  1.338293482  -0.302134814  adf.f=k
  H   2.621707427  -0.766258151  -0.517479818  adf.f=k
  H   -1.351756655  0.253389698  0.386197419  adf.f=k
  C   -0.430177075  -1.815433265  0.860288229  adf.f=m
  C   -0.363705637  -1.910722338  -0.515633302  adf.f=m
  H   0.533109934  -2.284970854  -1.016904201  adf.f=m
  H   -1.279922499  -1.884673940  -1.115144723  adf.f=m
  H   -1.389295819  -1.753589602  1.377541080  adf.f=m
  H   0.440296224  -2.041861443  1.484489314  adf.f=m
end
charge 1
end

Task SinglePoint

Engine ADF
  title et-----Ni-diimina run

  ETSNOCV
  End

  fragments
    m etfrag.results/adf.rkf
    k Nifrag.results/adf.rkf
  end
  symmetry NOSYM

```

(continues on next page)

(continued from previous page)

```

xc
  gga scf becke perdew
end
Relativity
  Level None
End
EndEngine
eor

```

Example: NOCV: H+ - CO

Download Hplus_CO_etsnocv.run

```

#!/bin/sh

AMS_JOBNAME=Hplus $AMSBIN/ams <<eor
System
  atoms
    H      -0.010992    0.000002    0.148581
  end
  charge 1
end

Task SinglePoint

Engine ADF
  title [H]+-----[CO] run from H+ and CO fragments, FULL electron calc.!
  Basis Type=SZ Core=None
  numericalquality Good
  scf
    converge 1E-6
    iterations 2500
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
EndEngine
eor

AMS_JOBNAME=CO $AMSBIN/ams <<eor
System
  atoms
    C      0.005191    0.000001    1.248610
    O      0.021536    0.000000    2.359675
  end
end

Task SinglePoint

Engine ADF
  title [CO] run
  Basis Type=SZ Core=None

```

(continues on next page)

(continued from previous page)

```

numericalquality Good
scf
  converge 1E-6
  iterations 2500
end
symmetry NOSYM
xc
  gga becke perdew
end
EndEngine
eor

AMS_JOBNAME=HCO $AMSBIN/ams <<eor
System
  atoms
    H      -0.010992    0.000002    0.148581 adf.f=f1
    C      0.005191    0.000001    1.248610 adf.f=f2
    O      0.021536    0.000000    2.359675 adf.f=f2
  end
  charge 1
end

Task SinglePoint

Engine ADF
  title [H]---[CO], etsnocv activated by etsnocv and print etslowdin
  etsnocv
    ekmin 1.5
    enocv 0.05
    rhokmin 1.e-3
  end
  fragments
    f1 Hplus.results/adf.rkf
    f2 CO.results/adf.rkf
  end
  numericalquality Good
  print etslowdin
  scf
    converge 1E-6
    iterations 800
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
EndEngine
eor

$AMSBIN/densf <<eor
adffile HCO.results/adf.rkf
Grid Medium
End
NOCV
  1
  11
  2

```

(continues on next page)

(continued from previous page)

```

3
9
10
END
eor
mv TAPE41 nocv1.t41

$AMSBIN/densf <<eor
adffile HCO.results/adf.rkf
Grid Medium
End
NOCV
  THRESH 0.01
END
eor
mv TAPE41 nocv2.t41

$AMSBIN/densf <<eor
adffile HCO.results/adf.rkf
Grid Medium
End
NOCV
  ALL
END
eor
mv TAPE41 nocv3.t41

```

Example: NOCV: CH₂ – Cr(CO)₅Download NOCV_CrCO₅-CH₂.run

```

#!/bin/sh

# Example for calculation of ETS-NOCV for spin-restricted fragments. ETS-NOCV:
# energy analysis using the Natural Orbitals for Chemical Valence. The CH2
# molecule and Cr(CO)5 are the fragments, which form Cr(CO)5 CH2 molecule.

# First the two fragments are calculated.

AMS_JOBNAME=CH2 $AMSBIN/ams <<eor
System
  atoms
    C      -0.429104    1.732058    -0.225052
    H       0.407023    2.440417    -0.352323
    H     -1.385325    2.281354    -0.254124
  end
end

Task SinglePoint

Engine ADF
  title CrCO5--[CH2] run from CrCO5 and CH2 closed shell fragments,FULL electron calc.
  ↪!

```

(continues on next page)

(continued from previous page)

```

basis
  core None
  type DZP
end
symmetry NOSYM
xc
  gga becke perdew
end
EndEngine
eor

AMS_JOBNAME=CrCO5 $AMSBIN/ams <<eor
System
atoms
  Cr      -0.248053  -0.169062  0.005810
  C       -0.072963  -2.080685  0.229583
  O        0.030811  -3.223220  0.361925
  C       -0.182894   0.049840  1.909128
  O       -0.142780   0.212309  3.050403
  C       -0.299940  -0.409118 -1.894730
  O       -0.331795  -0.521589 -3.042336
  C       -2.138631  -0.242152  0.075713
  O       -3.295036  -0.249916  0.115045
  C        1.624487   0.092244 -0.083118
  O        2.763411   0.288575 -0.140976
end
end

Task SinglePoint

Engine ADF
  title [CrCO5] run
  basis
    Type DZP
    Core None
    PerAtomType Symbol=Cr Type=TZP
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
EndEngine
eor

# Next these fragments are used in the calculation of the full complex. The keys
# ETSNOCV and 'PRINT etslowdin' are needed in this case to to analyze the
# bonding in the molecule with respect to the fragments. The symmetry must be
# NOSYM.

AMS_JOBNAME=CrCO5_CH2 $AMSBIN/ams <<eor
System
atoms
  C      -0.429104   1.732058  -0.225052  adf.f=f1

```

(continues on next page)

(continued from previous page)

```

    Cr      -0.248053   -0.169062    0.005810  adf.f=f2
    C       -0.072963   -2.080685    0.229583  adf.f=f2
    O        0.030811   -3.223220    0.361925  adf.f=f2
    C       -0.182894    0.049840    1.909128  adf.f=f2
    O       -0.142780    0.212309    3.050403  adf.f=f2
    C       -0.299940   -0.409118   -1.894730  adf.f=f2
    O       -0.331795   -0.521589   -3.042336  adf.f=f2
    C       -2.138631   -0.242152    0.075713  adf.f=f2
    O       -3.295036   -0.249916    0.115045  adf.f=f2
    C        1.624487    0.092244   -0.083118  adf.f=f2
    O        2.763411    0.288575   -0.140976  adf.f=f2
    H        0.407023    2.440417   -0.352323  adf.f=f1
    H       -1.385325    2.281354   -0.254124  adf.f=f1
end
end

Task SinglePoint

Engine ADF
  title CrCO5--[CH2], etsnocv activated by etsnocv and print etslowdin
  etsnocv
  ekmin 1.5
  enocv 0.05
  rhokmin 1.e-3
end
fragments
  f1 CH2.results/adf.rkf
  f2 CrCO5.results/adf.rkf
end
print etslowdin
symmetry NOSYM
xc
  gga becke perdw
end
EndEngine
eor

```

Example: NOCV: CH3 – CH3

Download CH3_CH3_etsnocv.run

```

#!/bin/sh

# Example for calculation of ETS-NOCV for simulated unrestricted fragments. ETS-NOCV:
# energy analysis using the Natural Orbitals for Chemical Valence. The ethane
# molecule is built from two methyl radicals

# First the two methyl fragments are calculated.
# If the FRAGOCCUPATIONS keyword is used in ethane the fragments should be calculated
# spin-restricted.

AMS_JOBNAME=frag1 $AMSBIN/ams <<eor
System

```

(continues on next page)

(continued from previous page)

```

atoms
  C      0.019664   -0.034069   0.009101
  H      0.039672   -0.069395   1.109620
  H      1.063205   -0.065727   -0.341092
  H     -0.474230   -0.953693   -0.341621
end
end

Task SinglePoint

Engine ADF
  title CH3-CH3 built from CH3 radicals,  FULL electron calc.!
  basis
    Type DZP
    Core None
  end
  scf
    converge 1E-6
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  Relativity
    Level None
  End
EndEngine

eor

AMS_JOBNAME=frag2 $AMSBIN/ams <<eor
System
  atoms
    C      -0.703210   1.217999   -0.497874
    H      -0.723753   1.252869   -1.598316
    H      -1.746567   1.250049   -0.147169
    H      -0.208833   2.137544   -0.147653
  end
end

Task SinglePoint

Engine ADF
  title CH3 radical
  basis
    Type DZP
    Core None
  end
  scf
    converge 1E-6
  end
  symmetry NOSYM
  xc
    gga becke perdew
  end
  Relativity

```

(continues on next page)

(continued from previous page)

```

    Level None
  End
EndEngine

eor

# Next these fragments are used in the calculation of the molecule ethane, using
# the key FRAGOCCUPATIONS to use an unrestricted fragment occupation for the
# methyl radicals, such that they are prepared for bonding. In the one fragment
# the singly occupied orbital will be an alpha-orbital, and in the other fragment
# the singly occupied orbital will be a beta-orbital, such that the calculated
# Pauli repulsion between the fragments will be small.

# The block key ETSNOCV used here is in its single line form.
# The symmetry must be NOSYM.

$AMSBIN/ams <<eor
System
  atoms
    C      0.019664  -0.034069   0.009101  adf.f=f1
    H      0.039672  -0.069395   1.109620  adf.f=f1
    H      1.063205  -0.065727  -0.341092  adf.f=f1
    H      -0.474230  -0.953693  -0.341621  adf.f=f1
    C     -0.703210   1.217999  -0.497874  adf.f=f2
    H     -0.723753   1.252869  -1.598316  adf.f=f2
    H     -1.746567   1.250049  -0.147169  adf.f=f2
    H     -0.208833   2.137544  -0.147653  adf.f=f2
  end
end

Task SinglePoint

Engine ADF
  title final [CH3]-[CH3], etsnocv activated by etsnocv
  etsnocv
    ekmin 1.5
    enocv 0.05
    rhokmin 1.e-3
    tvanalysis
  end
  fragments
    f1 frag1.results/adf.rkf
    f2 frag2.results/adf.rkf
  end
  fragoccupations
    f1
    A 5 // 4
    subend
    f2
    A 4 // 5
    subend
  end
  scf
    converge 1E-6
  end
  symmetry NOSYM
xc

```

(continues on next page)

(continued from previous page)

```

    gga becke perdew
end
Relativity
    Level None
End
EndEngine
eor

# Next densf calculations, to view the natural orbitals in this method, see
# also the the documentation for the densf analysis program and the ADF-GUI.
# Input is the adf.rkf of the molecular calculation.

$AMSBIN/densf <<eor
    adffile ams.results/adf.rkf
    Grid Medium
End
NOCV
    Alpha
        1
        2
        59
        60
    Beta
        1
        2
        59
        60
    END
eor
mv TAPE41 nocv1.t41

$AMSBIN/densf <<eor
    adffile ams.results/adf.rkf
    Grid Medium
End
NOCV
    THRESH 0.01
    RESTSUM
    END
eor
mv TAPE41 nocv2.t41

$AMSBIN/densf <<eor
    adffile ams.results/adf.rkf
    Grid Medium
End
NOCV
    ALPHA
        SUM 1
    BETA
        SUM 1
    RESTSUM
    END
eor
mv TAPE41 nocv3.t41

$AMSBIN/densf <<eor

```

(continues on next page)

(continued from previous page)

```

adffile ams.results/adf.rkf
Grid Medium
End
NOCV
    SUMBELOW 0.5
END
eor
mv TAPE41 nocv4.t41

```

15.6.4 QTAIM

Example: QTAIM Analysis

Download Bader.run

```

#!/bin/sh

# The Bader atomic charges are calculated using a grid based method. Another
# possibility for Bader's analysis is to use the adf2aim utility such that a
# third party program Xaim can be used.

# With the QTAIM input block the ADF program will calculate Bader charges (AIM
# charges) using a grid based method.

AMS_JOBNAME=water $AMSBIN/ams <<eor
Task SinglePoint

System
  Atoms
    O      0.000000    0.000000   -0.001658
    H     -0.769048    0.000000    0.595209
    H      0.769048    0.000000    0.595209
  End
End

Engine ADF
  Title Calculate Bader analysis for water
  basis
    Type TZP
    Core none
  End
  QTAIM
    AnalysisLevel Extended
    Spacing 0.1
  End
EndEngine
eor

# Next a similar calculation for ferrocene is given

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=ferrocene $AMSBIN/ams <<eor
Task SinglePoint

System
  Symmetrize Yes
  Atoms
    Fe      0.000000    0.000000    0.000000
    C      1.215650    0.000000    1.600813
    C      0.375656   -1.156152    1.600813
    C     -0.983481   -0.714541    1.600813
    C     -0.983481    0.714541    1.600813
    C      0.375656    1.156152    1.600813
    C      1.215650    0.000000   -1.600813
    C      0.375656    1.156152   -1.600813
    C     -0.983481    0.714541   -1.600813
    C     -0.983481   -0.714541   -1.600813
    C      0.375656   -1.156152   -1.600813
    H      2.310827    0.000000    1.629796
    H      0.714085   -2.197727    1.629796
    H     -1.869498   -1.358270    1.629796
    H     -1.869498    1.358270    1.629796
    H      0.714085    2.197727    1.629796
    H      2.310827    0.000000   -1.629796
    H      0.714085    2.197727   -1.629796
    H     -1.869498    1.358270   -1.629796
    H     -1.869498   -1.358270   -1.629796
    H      0.714085   -2.197727   -1.629796
  End
End

Engine ADF
  Title Calculate Bader analysis for ferrocene
  basis
    Type TZP
    Core none
  End
  QTAIM
    AnalysisLevel Extended
  End
  NumericalQuality Good
EndEngine
eor

```

Example: QTAIM Reactivity

Download Bader_Reactivity.run

```

#!/bin/sh

# With the CONCEPTUALDFT input block the ADF program will calculate
# certain conceptual DFT descriptors,
# such as atomic Fukui functions f+ and f-, the Koopmans dual descriptor, the
# Jenkin's metallicity and the atomic electronegativity by integrating
# corresponding properties over the atomic basin. Besides, MO populations per

```

(continues on next page)

(continued from previous page)

```

# basin, the localization and delocalization indices (LI/DI), and the matrix of
# the condensed linear response function are computed.
# ConceptualDFT requires the symmetry to be NOSYM.

$AMSBIN/ams <<eor
Task SinglePoint

System
  Atoms
    C      1.06434610      -0.70982731      -0.00004522
    C      -0.17846421      -1.32042953      -0.00163715
    C      -0.19884953      -2.73466243      -0.00296149
    C      1.00825259      -3.45497625      -0.00262955
    C      2.24377213      -2.78457605      -0.00098836
    C      2.28117568      -1.37069091       0.00034973
    H      -1.10692850      -0.74587638      -0.00187350
    H      -1.15592647      -3.26173790      -0.00423999
    H      0.98594687      -4.54659148      -0.00365721
    H      3.17851894      -3.35030989      -0.00073866
    H      3.23233560      -0.83454684       0.00163171
  End
End

Engine ADF
  Title Calculate Bader analysis for benzene-radical
  basis
    Type TZ2P
    Core none
  End
  Unrestricted
  SpinPolarization 1
  BeckeGrid
    Quality good
  End
  ConceptualDFT
    AnalysisLevel Full
    Electronegativity true
  End
  Relativity
    Level None # QTAIM energies are incompatible with the Scalar-ZORA relativistic_
↪model
  End
  Symmetry NOSYM
  XC
    GGA PBE
  END
EndEngine
eor

```

Example: IQA/QTAIM analysis

Download IQA.run

```

#!/bin/sh

# An IQA/QTAIM analysis is performed to analyze selected interactions
# in formic acid dimer

AMS_JOBNAME=IQA $AMSBIN/ams <<eor
System
  atoms
    C      -4.777280616716      -2.237679070420      0.027134922119
    O      -4.316098016052      -1.091055032354     -0.045982864295
    O      -4.095233471752      -3.376211708158     -0.036303239453
    H      -5.858352595246      -2.416180987684      0.158163319700
    H      -3.096816965327      -3.182195213950     -0.161436385033
    C      -1.043719708731      -1.744256936204     -0.434121365892
    O      -1.505389993838      -2.890945383925     -0.365122472158
    O      -1.725417179069      -0.605694491898     -0.367592891810
    H      -2.724119170709      -0.799847829461     -0.245243925045
    H       0.037480148811      -1.565749121998     -0.563863149179
  end
end

Task SinglePoint

Engine ADF
  title IQA Analysis for (HCOOH)2
  IQA
    Enabled True
    atomstodo 2 5 7 9
    print Normal
  end
  basis
    type TZP
    core None
  end
  symmetry NOSYM
  xc
    dispersion Grimme3
    gga BLYP
  end
EndEngine

eor

# Another IQA analysis for a halogen bonded complex: F-Cl...NH3
# All interactions are calculated - Details printed (verbose mode)
# Switch off ZORA because the intra-atomic kinetic energy term is gauge-dependent

AMS_JOBNAME=IQA2 $AMSBIN/ams <<eor
System
  atoms
    F      0.000001582319      0.000000000000     -3.410515944395
    Cl     0.000001582319      0.000000000000     -1.623156530960
    N      0.000001582319      0.000000000000      0.662184762067
  end
end

```

(continues on next page)

(continued from previous page)

```

      H      -0.482577891417      0.835852167201      0.991662308171
      H      -0.482577891417     -0.835852167201      0.991662308171
      H       0.965160529792      0.000000000000      0.991662308171
    end
  end
end

```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title IQA Analysis for F-Cl...NH3
```

```
  IQA
```

```
    Enabled True
```

```
    print Verbose
```

```
  end
```

```
  basis
```

```
    type TZ2P
```

```
    core None
```

```
  end
```

```
  symmetry NOSYM
```

```
  xc
```

```
    dispersion Grimme3
```

```
    gga BLYP
```

```
  end
```

```
  Relativity
```

```
    Level None
```

```
  End
```

```
EndEngine
```

```
eor
```

```
# IQA analysis for PF5
```

```
AMS_JOBNAME=IQA3 "$AMSBIN/ams" << eor
```

```
Task SinglePoint
```

```
System
```

```
  Atoms
```

```
    P  0.0      0.0      0.0
```

```
    F  0.0      0.0     -1.59029681775
```

```
    F  1.56093864075  0.0      0.0
```

```
    F -0.78046932037  1.35181251664  0.0
```

```
    F  0.0      0.0     1.59029681775
```

```
    F -0.78046932037 -1.35181251664  0.0
```

```
  End
```

```
End
```

```
Engine ADF
```

```
  Title IQA Analysis PF5
```

```
  Basis
```

```
    Type DZP
```

```
    Core None
```

```
  End
```

```
  Symmetry NOSYM
```

```
  IQA
```

```
    Enabled Yes
```

```
    Print Verbose
```

(continues on next page)

(continued from previous page)

```

    AtomsToDo 1 3
  End
EndEngine
eor

```

Example: QTAIM Aromaticity indices

Download Aromaticity.run

```

#!/bin/sh

# The aromaticity indices Iring and MCI can be calculated with ADF. Calculation
# of these aromaticity indices invokes the QTAIM analysis automatically and uses
# its results so all accuracy considerations for the QTAIM key are also valid
# here. The rings should be specified using the AROMATICITY input block, one
# line per ring. The atoms must be listed in the order they are connected in the
# ring. Note that although a partial QTAIM analysis is performed, its results
# are not printed to the output file.
# Relativistic hamiltonian cannot be used when computing AROMATICITY.

$AMSBIN/ams <<eor
System
  atoms
    C      -0.000000000000    -1.402840000000    -1.219800000000
    C      0.000000000000    -0.698820000000    -2.427560000000
    C      0.000000000000    0.698820000000    -2.427560000000
    C      0.000000000000    1.402840000000    -1.219800000000
    C      0.000000000000    0.708650000000    -0.000000000000
    C     -0.000000000000    -0.708650000000     0.000000000000
    C     -0.000000000000    -1.402840000000     1.219800000000
    C     -0.000000000000    -0.698820000000     2.427560000000
    C     -0.000000000000     0.698820000000     2.427560000000
    C      0.000000000000     1.402840000000     1.219800000000
    H     -0.000000000000    -2.486200000000    -1.238920000000
    H     -0.000000000000    -1.237890000000    -3.366130000000
    H      0.000000000000     1.237890000000    -3.366130000000
    H      0.000000000000     2.486200000000    -1.238920000000
    H     -0.000000000000    -2.486200000000     1.238920000000
    H     -0.000000000000    -1.237890000000     3.366130000000
    H      0.000000000000     1.237890000000     3.366130000000
    H      0.000000000000     2.486200000000     1.238920000000
  end
end

Task SinglePoint

Engine ADF
  aromaticity
    ringatoms 1 2 3 4 5 6
    ringatoms 5 6 7 8 9 10
  end
  basis
    core None

```

(continues on next page)

(continued from previous page)

```

    type TZP
  end
  xc
    gga PBE
  end
  Relativity Level=None
EndEngine
eor

```

15.6.5 DOS: Density of states

Example: Density of States: Cu₄CO

Download DOS_Cu4CO.run

```

#!/bin/sh

# This sample illustrates the DOS property program to compute density-of-states
# data, for energy-dependent analysis.

# First, the Cu4 CO molecule is calculated (ADF), using single-atom fragments.

$AMSBIN/ams <<eor
System
  atoms [Bohr]
    Cu      2.784      0.0      0.0
    Cu     -1.392     2.411014724135877  0.0
    Cu     -1.392    -2.411014724135877  0.0
    Cu      0.0      0.0     -3.9371705576466964
    C       0.0      0.0      2.65
    O       0.0      0.0      4.91
  end
end

Task SinglePoint

Engine ADF
  title Cu4CO (3,1) from atoms
  basis
    core small
    type TZP
  end
  print SFO
  xc
    gga PostSCF      Becke Perdew
  end
EndEngine
eor

# The PostSCF feature in the specification of the XC functional is used: the

```

(continues on next page)

(continued from previous page)

```

# 'Becke-Perdew' GGA corrections are not included self-consistently but applied
# to the energy evaluation after the self-consistent LDA solution has been
# obtained.

# The utility program dos requires as input file a file named TAPE21 in the current_
↪directory,
# or if one uses the key ADFFILE a (relative) path to an adf.rkf file.

$AMSBIN/dos <<eor
adffile ams.results/adf.rkf
file dostxt

energyrange npoint=36 e-start=-25 e-end=10

tdos

! Cu 3d partial DOS
gpdos
  a1    14:22 32:34
  a2     5:10
  e1:1  18:32 37:42
  e1:2  18:32 37:42
end

! The same but using BAS
gpdos
  BAS 17:34 57:74 97:114 137:154
end

! The same as above, but using much less complicated input
gpdos
  ATYPE Cu d
end

! Overlap PDOS Cu 3d and CO 2p
opdos
  ATYPE Cu 3d
SUBEND
  ATOM 5 2p
  ATOM 6 2p
end

eor

echo "DOS result file"
echo "======"
cat dostxt
echo "END of DOS result file"

# Here, the total density of states, as well as various partial densities of
# states, are computed. You may feed the results found in the dostxt file into a
# plotting program such as gnuplot. The result is not displayed here. See the
# ADF manual for more detailed info about the dos program.

```

15.6.6 Third party analysis software

Example: adf2aim: convert an ADF adf.rkf to WFN format (for Bader analysis)

Download AIM_HF.run

```
#!/bin/sh

# One can calculate Bader atomic charges and other Atoms in Molecule properties
# directly in ADF using a grid based method, see also an example that uses the
# grid based method. Another possibility for Bader's analysis, an example is
# described here, is to use the adf2aim utility such that a third party program
# Xaim can be used.

# The ADF utility adf2aim (original name rdt21, now part of the ADF package)
# developed by Xavi Lopez, Engelber Sans and Carles Bo converts an ADF adf.rkf to
# WFN format (for Bader analysis).

# The WFN file is an input file for the third party program Xaim (see
# http://www.quimica.urv.es/XAIM for details), which is a graphical user
# interface to programs that can perform the Bader analysis.

# Usage of adf2aim:

AMS_JOBNAME=HF $AMSBIN/ams <<eor
System
  atoms
    H  0.000  0.000  0.000
    F  0.000  0.000  0.917
  end
end

Task SinglePoint

Engine ADF
EndEngine
eor

$AMSBIN/adf2aim HF.results/adf.rkf
echo ""
echo 'Contents of rdt21.res:'
cat rdt21.res | grep -v RunTime
echo 'Contents of WFN:'
cat WFN | grep -v RunTime

rm rdt21.res WFN

# In an unrestricted calculation adf2aim will ask if the MOs should be split in
# two files. In this example the answer is yes (y).

AMS_JOBNAME=HF_unrestricted $AMSBIN/ams <<eor
System
  atoms
```

(continues on next page)

(continued from previous page)

```

      H  0.000  0.000  0.000
      F  0.000  0.000  0.917
    end
  end

Task SinglePoint

Engine ADF
  spinpolarization 0
  unrestricted Yes
EndEngine
eor

$AMSBIN/adf2aim HF_unrestricted.results/adf.rkf <<eor
y
eor

echo ""
echo 'Contents of rdt21.res:'
cat rdt21.res| grep -v RunTime
echo 'Contents of WFN-alpha:'
cat WFN-alpha| grep -v RunTime
echo 'Contents of WFN-beta:'
cat WFN-beta| grep -v RunTime

```

Example: NBO analysis: adfnbo, gennbo

Download H2O_ADFNBO.run

```

#!/bin/sh

# Dr. Autschbach, SCM, and Prof. Weinhold have collaborated to prepare a simple
# in put file generator, called adfnbo, for the GENNBO program of Prof.
# Weinholds Natural Bond Orbital (NBO) 6.0 package: http://nbo6.chem.wisc.edu
# The GENNBO executable is included in the ADF distribution and can be enabled
# via the license file ( info@scm.com).

$AMSBIN/ams <<eor
System
  atoms
    O      0.000000    0.000000    0.000000
    H      0.900000    0.000000    0.000000
    H     -0.156283    0.886327    0.000000
  end
end

Task SinglePoint

Engine ADF
  aomat2file
  fullfock
  basis
  core NONE

```

(continues on next page)

(continued from previous page)

```

    type DZ
end
save TAPE15
symmetry NOSYM
title simple NBO example for water
EndEngine
eor

# Note added: recommended is to use the key 'spherical' in the adfnbo input.
# Note added: recommended is not to include the argument 'NRT' for the
# key NBOkeylist in the adfnbo input for larger calculations.
# The calculation of NRT (natural resonance theory) can be very expensive
# for larger systems (or may fail to converge)

# A File named FILE47 is generated by adfnbo which is an input file for the
# general NBO program gennbo. ADF needs to write some data to file, which is
# done by including these keywords in the adf input file:

# == GENNBO ==

# Next a brief summary of the capabilities of GENNBO is given (by Prof.
# Weinhold). GENNBO implements most capabilities of the full NBO 6.0 program
# suite as described on the NBO website: http://nbo6.chem.wisc.edu These include
# determination of natural atomic orbitals (NAOs), bond orbitals (NBOs), and
# localized MOs (NLMOs), as well as the associated NPA (atomic charges and
# orbital populations) and NRT (resonance structures, weightings, bond orders)
# valence descriptors, for a wide variety of uncorrelated and correlated
# (variational, perturbative, or density functional) theoretical levels. GENNBO-
# supported options include all keywords except those explicitly requiring
# interactive communication with the host electronic structure system (viz.,
# $DEL deletions, NEDA, NCS, NJC). The GENNBO program typically sits
# conveniently on the PC desktop, ready to analyze (or re-analyze at will, with
# altered options) the final results of a complex ADF calculation performed on a
# remote cluster.

# GENNBO 'communicates' with the original ADF calculation through an archive
# file (JOB.47 file, preserving all necessary details of the final density) that
# is initially generated by ADF and subsequently becomes the input file for
# GENNBO. The .47 file contains a standard $NBO ... $END keylist that can be
# edited with a standard word processor or text editor to include chosen NBO
# keyword options, just as though they might have appeared in the original input
# stream of an interactive ADFNBO run. The stand-alone GENNBO program therefore
# allows many alternative NBO analysis options to be explored at leisure,
# without costly re-calculation of the wave function.

# Using the GENNBO executable is possible only if NBO6 is enabled in your
# license file by SCM (info@scm.com). In that case you will get access to an
# NBO 6.0 manual in electronic form that explains in detail how GENNBO can be
# used and how the output should be interpreted.

$AMSBIN/adfnbo <<eor
ADFFile ams.results/adf.rkf
TAPE15file ams.results/TAPE15
write
fock

```

(continues on next page)

(continued from previous page)

```

spherical
NBOkeylist BNDIDX NBONLMO=W AONBO=W AONLMO=W NLMOMO=W NAOMO=PVAL NRT STERIC CMO_
↪3CBOND DIST
eor

echo " "
echo " "
echo "Contents of FILE47 ="
echo " "
echo " "
cat FILE47

$AMSBIN/gennbo6 FILE47

echo " "
echo " "
echo "Contents of adfnbo.37 ="
echo " "
echo " "
cat adfnbo.37

echo " "
echo " "
echo "Contents of adfnbo.39 ="
echo " "
echo " "
cat adfnbo.39

echo " "
echo " "
echo "Contents of adfnbo.49 ="
echo " "
echo " "
cat adfnbo.49

```

Example: NBO analysis: EFG

Download AlCl3_efgnbo.run

```

#!/bin/sh

# Example shows an NBO analysis of an EFG calculation for AlCl3 .

# In the ADF input one then needs to include the QTENS (EFG calculation) and
# include the subkey EFG of the key AORESPONSE. The BeckeGrid quality is good,
# which may be needed to accurately calculate core properties. Other keywords
# are necessary because of the NBO analysis afterwards. Note that ADF, ADFNBO,
# and GENNBO have to run several times.

# Note added: recommended is not to include the key 'TESTJOB' in the adfnbo input
# for larger calculations. The key TESTJOB will include the NRT key in FILE47.
# The calculation of NRT (natural resonance theory) can be very expensive
# for larger systems (or may fail to converge)

```

(continues on next page)

(continued from previous page)

```

AMS_JOBNAME=first $AMSBIN/ams <<eor
System
  atoms
    Al      0.000000      0.000000      -0.237368
    Cl      1.808813      0.000000      0.807083
    Cl      0.000000      0.000000      -2.326083
    Cl     -1.808813      0.000000      0.807083
  end
end

Task SinglePoint

Engine ADF
  aomat2file
  aoresponse
    efg atom=1 nbo=true
  end
  beckegrid
    quality good
  end
  fullfock
  basis
    core none
    type TZP
  end
  qtens
  save TAPE15
  symmetry NOSYM
  xc
    gga revPBE
    lda vwn
  end
  Relativity
    Level None
  End
EndEngine
eor

# end ADF, run gennbo
# =====

$AMSBIN/adfnbo <<eor
adffile first.results/adf.rkf
TAPE15file first.results/TAPE15
write
spherical
fock
TESTJOB
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48

$AMSBIN/gennbo6 FILE47

$AMSBIN/adfnbo <<eor

```

(continues on next page)

(continued from previous page)

```

adffile first.results/adf.rkf
TAPE15file first.results/TAPE15
copy
spherical
fock
TESTJOB
eor

$AMSBIN/adfnbo <<eor
adffile first.results/adf.rkf
TAPE15file first.results/TAPE15
read
spherical
fock
TESTJOB
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48

# end gennbo, rerun ADF with NBO property analysis
# =====

AMS_JOBNAME=second $AMSBIN/ams <<eor
System
  atoms
    Al      0.000000      0.000000      -0.237368
    Cl      1.808813      0.000000      0.807083
    Cl      0.000000      0.000000      -2.326083
    Cl     -1.808813      0.000000      0.807083
  end
end

Task SinglePoint

Engine ADF
  aoresponse
    efg
      atom 1
      nbo true
    end
  end
  beckegrid
    quality good
  end
  basis
    core none
    type TZP
  end
  qtens
  symmetry NOSYM
  xc
    gga revPBE
    lda vwn
  end
  Relativity
    Level None
End

```

(continues on next page)

(continued from previous page)

```
EndEngine
eor
```

Example: NBO analysis: NMR chemical shift

Download CH4_nmrnbo.run

```
#!/bin/sh

# Example shows an NBO analysis of an NMR shielding calculation for CH4.

# Some keywords are necessary because of the NBO analysis afterwards. A 'Good'
# integration grid is used. First the scalar relativistic calculation is
# performed and the scalar relativistic localized orbitals are made. Next the
# spin-orbit coupled ADF calculation is done, and a calculation of NMR shielding
# constants is performed with an analysis in scalar relativistic localized
# orbitals.

AMS_JOBNAME=Scalar $AMSBIN/ams <<eor
System
  atoms
    C  0.0000  0.0000  0.0000
    H  0.6316  0.6316  0.6316
    H  0.6316 -0.6316 -0.6316
    H -0.6316  0.6316 -0.6316
    H -0.6316 -0.6316  0.6316
  end
end

Task SinglePoint

Engine ADF
  aomat2file
  beckegrid
  quality good
end
  fullfock
  basis
    core None
    type DZP
  end
  save TAPE15
EndEngine
eor

##### end scalar, run gennbo #####

$AMSBIN/adfnbo <<eor
  ADFfile Scalar.results/adf.rkf
  TAPE15file Scalar.results/TAPE15
  write
  spherical
  :: read
```

(continues on next page)

(continued from previous page)

```

    fock
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48
$AMSBIN/gennbo6 FILE47

# run adfnbo in COPY mode

$AMSBIN/adfnbo <<eor
  ADFfile Scalar.results/adf.rkf
  TAPE15file Scalar.results/TAPE15
  spherical
  fock
  copy
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48

##### end gennbo

AMS_JOBNAME=NOSYM $AMSBIN/ams <<eor
System
  atoms
    C  0.0000  0.0000  0.0000
    H  0.6316  0.6316  0.6316
    H  0.6316 -0.6316 -0.6316
    H -0.6316  0.6316 -0.6316
    H -0.6316 -0.6316  0.6316
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type DZP
  end
  noprint sfo
  save TAPE10
  symmetry nosym
EndEngine
eor

$AMSBIN/nmr <<eor
  adffile NOSYM.results/adf.rkf
  tape10file NOSYM.results/TAPE10
  fakeso
  nmr
    atoms 2 1
    ulk best
    out iso tens
  end
  analysis

```

(continues on next page)

(continued from previous page)

```
    print 0.01
    canonical
    nbo
    components
end
eor

### scalar done, redo computation with spin-orbit coupling

AMS_JOBNAME=Spinorbit $AMSBIN/ams <<eor
System
  atoms
    C  0.0000  0.0000  0.0000
    H  0.6316  0.6316  0.6316
    H  0.6316 -0.6316 -0.6316
    H -0.6316  0.6316 -0.6316
    H -0.6316 -0.6316  0.6316
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type DZP
  end
  noprint sfo
  relativity
    level spin-orbit
  end
  save TAPE10
  symmetry nosym
EndEngine
eor

$AMSBIN/nmr <<eor
  adffile Spinorbit.results/adf.rkf
  tape10file Spinorbit.results/TAPE10
  nmr
    atoms 2 1
    ulk best
    out iso tens
  end
  analysis
    print 0.01
    canonical
    nbo
    components
  end
eor
```

Example: NBO analysis: NMR spin-spin coupling

Download CPL_CH3OH_NBO.run

```
#!/bin/sh

# Example shows an NBO analysis of an NMR spin-spin coupling constants
# calculation for CH3 OH.

# Some keywords are necessary because of the NBO analysis afterwards. A good
# quality integration is used. First the scalar relativistic calculation is
# performed and the scalar relativistic localized orbitals are made, and a
# calculation of NMR spin-spin coupling constants is performed with an analysis
# in scalar relativistic localized orbitals. Next the spin-orbit coupled ADF
# calculation is done, and a calculation of NMR spin-spin coupling constants is
# performed with an analysis in scalar relativistic localized orbitals.

AMS_JOBNAME=scalar $AMSBIN/ams <<eor
System
  atoms
    O      0.151078120000    -0.158942890000    -0.184382010000
    H      0.762854510000     0.480823600000     0.187867830000
    C      0.654254930000    -1.481762230000     0.026343630000
    H      1.616760580000    -1.581906770000    -0.455670800000
    H      -0.035909520000    -2.200223490000    -0.393433960000
    H      0.761359880000    -1.661537720000     1.087000640000
  end
end

Task SinglePoint

Engine ADF
  aomat2file
  beckegrid
  quality good
end
fullfock
basis
  core None
  type DZP
end
relativity
  level scalar
  formalism ZORA
end
save TAPE15
symmetry nosym
xc
  lda SCF VWN
end
EndEngine
eor

##### end scalar, run gennbo #####
```

(continues on next page)

(continued from previous page)

```

rm -f adfnbo.kf

$AMSBIN/adfnbo <<eor
  ADFFile scalar.results/adf.rkf
  TAPE15file scalar.results/TAPE15
  write
  spherical
  :: read
  fock
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48
$AMSBIN/gennbo6 FILE47

# run adfnbo in COPY mode

$AMSBIN/adfnbo <<eor
  ADFFile scalar.results/adf.rkf
  TAPE15file scalar.results/TAPE15
  spherical
  fock
  copy
eor

# run adfnbo in READ mode: prepare locorb on TAPE21

$AMSBIN/adfnbo <<eor
  ADFFile scalar.results/adf.rkf
  TAPE15file scalar.results/TAPE15
  spherical
  fock
  read
eor

rm -f adfnbo.37 adfnbo.39 adfnbo.49 adfnbo.48

##### end gennbo

## end scalar and gennbo run, now do the coupling constant

$AMSBIN/cpl <<eor
  adffile scalar.results/adf.rkf
  nmrcoupling
  xalpha
  dso
  pso
  sd
  scf converge=1e-5 iterations=10
  contributions 1e19 nbo
  nuclei 3 5 6
end
eor

# redo the coupling constant without the SD term

rm -f TAPE10 TAPE15 TAPE13

```

(continues on next page)

(continued from previous page)

```

$AMSBIN/cpl <<eor
  adffile scalar.results/adf.rkf
  nmrcoupling
    xalpha
    dso
    pso
    scf converge=1e-5 iterations=10
    contributions 1e19 nbo
    nuclei 3 5 6
  end
eor

### scalar CPL done, redo computation with spin-orbit coupling
for f in TAPE*; do rm -f $f ; done

AMS_JOBNAME=spinorbit $AMSBIN/ams <<eor
System
  atoms
    O      0.151078120000    -0.158942890000    -0.184382010000
    H      0.762854510000     0.480823600000     0.187867830000
    C      0.654254930000    -1.481762230000     0.026343630000
    H      1.616760580000    -1.581906770000    -0.455670800000
    H     -0.035909520000    -2.200223490000    -0.393433960000
    H      0.761359880000    -1.661537720000     1.087000640000
  end
end

Task SinglePoint

Engine ADF
  beckegrid
    quality good
  end
  basis
    core None
    type DZP
  end
  noprint sfo
  relativity
    level spin-orbit
    formalism ZORA
  end
  symmetry nosym
  xc
    lda SCF VWN
  end
EndEngine
eor

## end spinorbit run, now do the coupling constant

$AMSBIN/cpl <<eor
  adffile spinorbit.results/adf.rkf
  nmrcoupling

```

(continues on next page)

(continued from previous page)

```

xalpha
dso
pso
sd
scf converge=1e-5 iterations=10
contributions 1e19 nbo
nuclei 3 5 6
end
eor

```

Example: Multiple excited state gradients: H2O

Download EGO_H2O_multi.run

```

#!/bin/sh

# Basic example of TDDFT calculation with different number of singlets and triplets.
# ↳ (LOWEST 10 8)
# and multiple gradient calculation (SING_GRADS, TRIP_GRADS)
# Could be useful for external programs like SHARC.

$AMSBIN/ams <<eor
System
  atoms
    O      0.0000000    0.0000000   -0.0668805
    H     -0.7658756    0.0000000    0.5307937
    H      0.7658756    0.0000000    0.5307937
  end
end

Task SinglePoint
Properties
  Gradients True
End

Engine ADF
  title H2O TDDFT Multiple Gradients
  excitations
    lowest 10 8
  end
  excitedgo
    sing_grads
      A1 1 2
      A2 1
      B1 1
    end
    trip_grads
      A1 1 2 3
      A2 1
      B1 3
      B2 1
    end
  end
end
basis

```

(continues on next page)

(continued from previous page)

```

    type SZ
    core None
    CreateOutput Yes
end
numericalquality Good
print SOMATRIX
relativity
  level scalar
  formalism ZORA
end
sopert
  gscorr True
end
symmetry C(2v)
tda
xc
  gga BP86
end
EndEngine
eor

```

Example: Calculation of overlap of primitive basis functions

Download CalcOverlapOnly.run

```

#!/bin/sh

# Example for calculating overlaps of primitive basis functions for almost
# coinciding nuclear coordinates, using the key CALCOVERLAPONLY. ADF will stop
# after the calculation of these overlaps. The overlap is printed in the output,
# but is also present on TAPE15 in binary format in Matrices%Smat.
# Could be useful for external programs like SHARC.

$AMSBIN/ams <<eor
System
  atoms
    C      0.1662008  -0.0114225   0.0220295  region=one
    S      1.7387976   0.003246  -0.0021948  region=one
    H     -0.3207087   0.9655128  -0.0963368  region=one
    H     -0.479404   -0.9324828  -0.0963367  region=one
    C      0.167746   -0.0109425   0.0203042  region=two
    S      1.7382268   0.002927  -0.0020154  region=two
    H     -0.329981   0.9728265  -0.0893183  region=two
    H     -0.4704213  -0.9353924  -0.088502   region=two
  end
  # Prevents AMS from stopping in case of almost-coinciding nuclei
  AllowCloseAtoms True
end

Task SinglePoint

Engine ADF
  Title CH2S overlap of near identical geometries
  CalcOverlapOnly

```

(continues on next page)

(continued from previous page)

```
Basis
  Type DZP
  Core None
End
Print SMAT
Save TAPE15
EndEngine

eor
```

15.7 Accuracy and Efficiency

15.7.1 BSSE, SCF convergence, Frequencies

Example: Basis Set Superposition Error (BSSE): Cr(CO)₅ + CO

Download BSSE_CrCO6.run

```
#!/bin/sh

# A study of the Basis Set Superposition Error (BSSE) in the formation of
# Cr(CO)_6. from CO and Cr(CO)_5.
# This example uses scalar relativistic ZORA calculations.

# For the BSSE calculation special chemical elements must be created to describe
# the 'ghost' atoms, which have zero nuclear charge and mass. They do have basis
# functions (and fit functions), however, and they are used to calculate the
# lowering of the energy of the system to which the ghost atoms are added, due
# to the enlargement of the basis by the ghost basis. The ghost atom has the
# same basis and fit set as the normal element but no nuclear charge and no
# frozen core. The BASIS key recognizes elements denoted with Gh.atom in the
# ATOMS key as being ghost atoms. If the basis file specifies a frozen core ADF
# will treat it as if no frozen core is present.

# The following calculations are carried out:

# 1. CO from C and O. This yields the bond energy of CO with respect to
#    the (restricted) basic atoms.
# 2. CO from the fragments CO (as calculated in 1) and the ghost atom Cr
#    and 5 Carbon and 5 Oxygen ghost atoms. The ghost atomic fragments
#    provide basis and fit functions but do not contribute charge or
#    potential to the molecule. The bond energy of this calculation is
#    the energy lowering of CO due to the additional basis functions.
#    This is the BSSE for CO.
# 3. Cr(CO)5 from Cr and 5 CO's. This yields the ('normal') bond energy
#    with respect to the given fragments.
# 4. Cr(CO)5 from Cr(CO)5 as fragment (as calculated in 3) but with the
#    CO basis functions added on the position of the 6th CO ('ghost' CO).
#    The bond energy is the BSSE for Cr(CO)5 .
# 5. Cr(CO)6 with Cr(CO)5 and CO as fragments. The bond energy is the one
#    without BSSE. This bond energy can now be corrected by the sum of
#    superposition contributions of calculations 2 and 4.
```

(continues on next page)

(continued from previous page)

```

# This series of calculations is carried out with basis set DZ.

# Finally, the whole thing might be redone with basis set TZP, to show that the
# BSSE decreases with larger basis.

# The calculations for the type DZ basis are contained in the sample script
# (with input- and output files). Those for type TZP bases can be set up easily
# and may be done as an exercise.

# For the first series of calculations, with basis type DZ, the input files are
# discussed below and the relevant parts are echoed from the output files where
# the energy decomposition and the total bond energy are printed.

# For the other series, using type TZP basis sets, only a summary of the results
# is given.

# =====
# Computational details
# =====

# The calculations in this example all use:

# Small core DZ basis set Frozen core level for the Chromium atom: 2p, for
# Carbon and Oxygen: 1s Numerical integration precision 4.0 (in Create runs
# 10.0, the default) Default settings for model parameters such as density
# functional (key XC) and for the remaining computational settings For the BSSE
# calculations we first do the 'normal' calculations of CO and Cr(CO)5 ,
# yielding the fragment files t21.CO and t21.CrCO5. The input files for these
# calculations are not shown here.

# =====
# BSSE for CO
# =====

# For the CO BSSE calculation the standard CO must have been computed first. In
# the BSSE run a Cr(CO)5 ghost fragment basis set is then added to the 'normal'
# CO input. Important is the use of the BASIS key. In this case the BASIS key is
# used for the generation of the ghost atoms, it should have the same definition
# for the atoms as will be used later for the Cr(CO)5 fragment. The FRAGMENTS
# key is used for the fragment CO. The energy change (the printed 'bond energy'
# in the output) is the BSSE.

AMS_JOBNAME=CO $AMSBIN/ams <<eor
Task SinglePoint
System
  atoms
    C    0    0    1.86
    O    0    0    3.03
  end
end
Engine ADF
  title CO (normal run)

```

(continues on next page)

(continued from previous page)

```

    basis
      Type DZ
      Core Small
    End
    symmetry C(lin)
  EndEngine
eor

# The input file for the CO-BSSE run is:

AMS_JOBNAME=CO_with_fake_CrC5O5 $AMSBIN/ams <<eor
Task SinglePoint
System
  atoms
    Gh.Cr    0      0      0
    Gh.C    -1.86   0      0
    Gh.C     1.86   0      0
    Gh.C     0     1.86   0
    Gh.C     0    -1.86   0
    Gh.C     0     0    -1.86
    Gh.O     3.03   0      0
    Gh.O    -3.03   0      0
    Gh.O     0     3.03   0
    Gh.O     0    -3.03   0
    Gh.O     0     0    -3.03
    C        0     0     1.86    adf.f=CO
    O        0     0     3.03    adf.f=CO
  end
end
Engine ADF
  title BSSE for CO due to Cr(CO)5 ghost
  noprint sfo,frag,functions
  basis
    Type DZ
    Core Small
  end
  fragments
    CO CO.results/adf.rkf
  end
  symmetry C(4V)
EndEngine
eor

# In the output we find in the Bond Energy section: The BSSE for CO is computed
# as 2.40 kcal/mol

# =====
# BSSE for Cr(CO)5
# =====

# In similar fashion the BSSE is computed for Cr(CO)_5 . In the BSSE run a ghost
# atoms C and O at the positions they will have in the Cr(CO)_6 molecule are
# added to the normal Cr(CO)_5 input:

AMS_JOBNAME=CrCO5 $AMSBIN/ams <<eor

```

(continues on next page)

(continued from previous page)

```

Task SinglePoint
System
  atoms
    Cr    0      0      0
    C     1.86    0      0      adf.f=CO|1
    C    -1.86    0      0      adf.f=CO|2
    C     0      1.86    0      adf.f=CO|3
    C     0     -1.86    0      adf.f=CO|4
    C     0      0     -1.86    adf.f=CO|5
    O     3.03    0      0      adf.f=CO|1
    O    -3.03    0      0      adf.f=CO|2
    O     0      3.03    0      adf.f=CO|3
    O     0     -3.03    0      adf.f=CO|4
    O     0      0     -3.03    adf.f=CO|5
  end
end
Engine ADF
  title Cr(CO)5 (normal run)
  noprint sfo,frag,functions
  SCF
    mixing 0.1
  END
  basis
    Type DZ
    Core Small
  end
  fragments
    CO CO.results/adf.rkf
  end
  symmetry C(4v)
EndEngine
eor

```

```
AMS_JOBNAME=final $AMSBIN/ams <<eor
```

```

Task SinglePoint
System
  atoms
    Cr    0      0      0      adf.f=CrCO5
    C     1.86    0      0      adf.f=CrCO5
    C    -1.86    0      0      adf.f=CrCO5
    C     0      1.86    0      adf.f=CrCO5
    C     0     -1.86    0      adf.f=CrCO5
    C     0      0     -1.86    adf.f=CrCO5
    O     3.03    0      0      adf.f=CrCO5
    O    -3.03    0      0      adf.f=CrCO5
    O     0      3.03    0      adf.f=CrCO5
    O     0     -3.03    0      adf.f=CrCO5
    O     0      0     -3.03    adf.f=CrCO5
    Gh.C   0      0      1.86
    Gh.O   0      0      3.03
  end
end
Engine ADF
  title BSSE for Cr(CO)5 due to CO ghost
  noprint sfo,frag,functions
  basis

```

(continues on next page)

(continued from previous page)

```

        Type DZ
        Core Small
    end
    fragments
        CrCO5    CrCO5.results/adf.rkf
    end
    symmetry C(4v)
EndEngine
eor

# The Bond Energy result yields 1.97 kcal/mol for the BSSE.

# =====
# Bond Energy calculation with BSSE correction
# =====

# The bonding of CO to Cr(CO)5 is computed in the normal way: from fragments CO
# and Cr(CO)5 . The obtained value for the bond energy can then simply corrected
# for the two BSSE terms, (2.40+1.97=) 4.37 kcal/mol together.

# =====
# Relevance of Core Functions
# =====

# The two BSSE runs can also be repeated, but now with the core
# orthogonalization functions omitted from the ghost bases. To to this one can
# not use the BASIS key, but one needs to explicitly 'create' the ghost atoms.
# This will not be done here, but only the results will be discussed. One may
# argue about whether these functions should be included in the ghost basis
# sets, but since they are very contracted around the ghost nuclei they are not
# expected to contribute significantly anyway and may then just as well be
# omitted. This has been explicitly verified by test examples. The Core
# Functions (the functions in the valence basis set that serve only for core-
# orthogonalization, for instance the 1S 5.40 in the Carbon basis set (see the
# $AMSHOME/atomicdata/ADF/ZORA/DZ/C.1s basis set file) are removed from the Create_
→data
# files used for the creation of the ghost atoms. This yields as BSSE values for
# CO and Cr(CO)5 respectively 2.32 and 1.97 kcal/mol (compare 2.40 and 1.97
# kcal/mol for the case with Core Functions included). The net total effect of
# including/removing the Core Functions is therefore
# (2.40-2.32)+(1.97-1.97)=0.08 kcal/mol. This is an order of magnitude smaller
# than the BSSE effect itself.

# =====
# BSSE and the size of the basis set
# =====

# BSSE effects should diminish with larger bases and disappear in the limit of a
# perfect basis. This can be studied by comparing the BSSE for basis DZ, see
# above, with the BSSE for basis TZP. The procedure is completely similar to the
# one above and yields: For the BSSE terms: 0.7 kcal/mol for CO (compare: 2.4
# kcal/mol for basis DZ), and 0.5 kcal/mol for Cr(CO)5 (1.9 for basis DZ) The
# total BSSE drops from 4.4 kcal/mol in basis DZ to 1.2 in basis TZP.

```

(continues on next page)

(continued from previous page)

```

# =====
# Reference
# =====

# A systematic study with adf of the BSSE in metal-carbonyl complexes can be
# found in Rosa, A., et al., Basis Set Effects in Density Functional
# Calculations on the Metal-Ligand and Metal-Metal Bonds of Cr(CO)5-CO and
# (CO)5. Journal of Physical Chemistry, 1996, 100: p. 5690-5696.

$AMSBIN/ams <<eor
Task SinglePoint
System
  atoms
    Cr    0      0      0      adf.f=CrCO5
    C     1.86    0      0      adf.f=CrCO5
    C    -1.86    0      0      adf.f=CrCO5
    C     0      1.86    0      adf.f=CrCO5
    C     0     -1.86    0      adf.f=CrCO5
    C     0      0     -1.86    adf.f=CrCO5
    O     3.03    0      0      adf.f=CrCO5
    O    -3.03    0      0      adf.f=CrCO5
    O     0      3.03    0      adf.f=CrCO5
    O     0     -3.03    0      adf.f=CrCO5
    O     0      0     -3.03    adf.f=CrCO5
    C     0      0      1.86    adf.f=CO
    O     0      0      3.03    adf.f=CO
  end
end
Engine ADF
  symmetry C(4V)
  title Bond energy without BSSE for Cr(CO)6 made of Cr(CO)5 and CO
  noprint sfo,frag,functions
  basis
    Type DZ
    Core Small
  end
  fragments
    CrCO5  CrCO5.results/adf.rkf
    CO     CO.results/adf.rkf
  end
EndEngine
eor

```

Example: Troubleshooting SCF convergence: Ti2O4

Download SCF_Ti2O4.run

```

#!/bin/sh

# One can run into SCF convergence problems when calculating certain types of
# systems. Some of the notorious examples are transition metal oxides and
# lanthanide compounds. Below, several approaches to solving the SCF convergence

```

(continues on next page)

(continued from previous page)

```

# problem are demonstrated.

AMS_JOBNAME=Default $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000
    O  -3.850   0.000   0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (default case)
  basis
    core Small
    type DZ
  end
  scf
    converge 1.0e-6 1.0e-6
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

AMS_JOBNAME=MESA $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000
    O  -3.850   0.000   0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test MESA
  basis
    core Small
    type DZ
  end
  scf
    accelerationmethod MESA
    converge 1.0e-6 1.0e-6
  end

```

(continues on next page)

(continued from previous page)

```

xc
  gga Becke Perdew
end
EndEngine
eor

AMS_JOBNAME=LISTb $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730  0.000  0.000
    Ti -1.730  0.000  0.000
    O   0.000  1.224  0.000
    O   0.000 -1.224  0.000
    O   3.850  0.000  0.000
    O  -3.850  0.000  0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (LISTb by Alex Wang)
  basis
    core Small
    type DZ
  end
  scf
    accelerationmethod LISTb
    converge 1.0e-6 1.0e-6
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

```

```

AMS_JOBNAME=LISTf $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730  0.000  0.000
    Ti -1.730  0.000  0.000
    O   0.000  1.224  0.000
    O   0.000 -1.224  0.000
    O   3.850  0.000  0.000
    O  -3.850  0.000  0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (LISTf by Alex Wang)
  basis
    core Small
    type DZ

```

(continues on next page)

(continued from previous page)

```

end
scf
  accelerationmethod LISTf
  converge 1.0e-6 1.0e-6
end
xc
  gga Becke Perdew
end
EndEngine
eor

AMS_JOBNAME=fDIIS $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000
    O  -3.850   0.000   0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (fDIIS by Alex Wang)
  basis
    core Small
    type DZ
  end
  scf
    accelerationmethod fDIIS
    converge 1.0e-6 1.0e-6
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

# A-DIIS method. The A-DIIS method combines the strength of the ARH and DIIS
# methods. It does not require energy evaluation so it is much cheaper than the
# ARH and Energy-DIIS methods.

AMS_JOBNAME=ADIIS $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000

```

(continues on next page)

(continued from previous page)

```

    O  -3.850   0.000   0.000
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title Ti2O4 SCF aid test (A-DIIS by Hu and Yang)
  basis
    core Small
    type DZ
  end
  occupations KeepOrbitals=100
  scf
    accelerationmethod ADIIS
    converge 1.0e-6 1.0e-6
    iterations 300
    mixing 0.05
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

```

```

# This example uses the LISTi method. LISTi is very
# similar to the usual DIIS but typically it performs much better. It is also
# computationally less expensive and scales better in parallel even though DIIS
# is rarely a scaling bottleneck.

```

```
AMS_JOBNAME=LISTi $AMSBIN/ams <<eor
```

```

System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000
    O  -3.850   0.000   0.000
  end
end

```

```
Task SinglePoint
```

```

Engine ADF
  title Ti2O4 SCF aid test (LISTi)
  basis
    core Small
    type DZ
  end
  scf
    accelerationmethod LISTi
    iterations 300
  end

```

(continues on next page)

(continued from previous page)

```

xc
  gga Becke Perdew
end
EndEngine
eor

# This example uses the Augmented Roothaan-Hall (ARH) method.
# The basic idea of this method is that the density matrix is
# optimized directly to minimize the total energy. Important: the ARH method can
# be used with SYMMETRY NOSYM only.

AMS_JOBNAME=ARH $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730   0.000   0.000
    Ti -1.730   0.000   0.000
    O   0.000   1.224   0.000
    O   0.000  -1.224   0.000
    O   3.850   0.000   0.000
    O  -3.850   0.000   0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (Augmented Roothaan-Hall)
  basis
    core Small
    type DZ
  end
  scf
    arh
  end
  iterations 300
  mixing 0.05
end
symmetry NOSYM
xc
  gga Becke Perdew
end
EndEngine
eor

# This is an extension to the so-called 'electron smearing' method.
# In this method, the electrons are distributed among orbitals around Fermi-
# level using a pseudo-thermal distribution function. Although the result with
# fractional occupation number has no physical sense, the method can be used to
# achieve integer occupation numbers by reducing the smearing parameter step-
# wise.
# A few notes:

```

(continues on next page)

(continued from previous page)

```
# You can specify up to ten comma-delimited values after Smear= (no spaces are
# allowed). ADF will start from the first value and try to converge SCF using
# it. If it succeeds, the next value will be picked and so on.
```

```
# Because the whole process may require many cycles to converge it is important
# to set the number of SCF cycles to a large value to avoid a premature
# termination.
```

```
AMS_JOBNAME=Smear $AMSBIN/ams <<eor
```

```
System
```

```
atoms
```

```
  Ti  1.730   0.000   0.000
  Ti -1.730   0.000   0.000
   O   0.000   1.224   0.000
   O   0.000  -1.224   0.000
   O   3.850   0.000   0.000
   O  -3.850   0.000   0.000
```

```
end
```

```
end
```

```
Task SinglePoint
```

```
Engine ADF
```

```
  title Ti2O4 SCF aid test (Smear)
```

```
  debug DIIS SDIIS
```

```
  basis
```

```
    core Small
```

```
    type DZ
```

```
end
```

```
occupations Smear=0.2,0.1,0.07,0.05,0.03,0.02,0.01,0.007,0.005,0.001
```

```
scf
```

```
  iterations 300
```

```
  oldscf
```

```
end
```

```
xc
```

```
  gga Becke Perdew
```

```
end
```

```
EndEngine
```

```
eor
```

```
# This example demonstrates the use of the Occupations Steep= option (see
# the User's Guide for details).
```

```
# One difference is, obviously, in the Occupations keyword. The other difference
# is more subtle. For stable convergence, it is often essential to switch off
# DIIS and set the mixing parameter to a low value. Of course, it will make
# convergence quite (sometimes very) slow. Ultimately you should get either an
# aufbau configuration or a configuration with exactly degenerate HOMO. In this
# example, the result is an aufbau solution.
```

```
# Both methods should, in principle, give the same result, which is the case in
# this example.
```

```
AMS_JOBNAME=Steep $AMSBIN/ams <<eor
```

(continues on next page)

(continued from previous page)

```

System
  atoms
    Ti  1.730  0.000  0.000
    Ti -1.730  0.000  0.000
    O   0.000  1.224  0.000
    O   0.000 -1.224  0.000
    O   3.850  0.000  0.000
    O  -3.850  0.000  0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (Steep)
  basis
    core Small
    type DZ
  end
  occupations Steep=0.5,0.3
  scf
    diis
      n 0
    end
    iterations 300
    mixing 0.05
  end
  xc
    gga Becke Perdew
  end
EndEngine
eor

# This example uses the so called Energy-DIIS method. Please note that similar
# to ARH and unlike the standard SCF procedure in ADF this method requires
# energy evaluation at each SCF cycle, which makes it significantly slower
# compared to energy-free SCF.

AMS_JOBNAME=EDIIS $AMSBIN/ams <<eor
System
  atoms
    Ti  1.730  0.000  0.000
    Ti -1.730  0.000  0.000
    O   0.000  1.224  0.000
    O   0.000 -1.224  0.000
    O   3.850  0.000  0.000
    O  -3.850  0.000  0.000
  end
end

Task SinglePoint

Engine ADF
  title Ti2O4 SCF aid test (Energy-DIIS)
  basis

```

(continues on next page)

(continued from previous page)

```

    core Small
    type DZ
end
scf
    converge 1.0e-6 1.0e-6
    ediis
    iterations 300
    mixing 0.05
end
xc
    gga Becke Perdew
end
EndEngine
eor

```

Example: Rescan frequencies: NH3

Download Freq_NH3_Scan.run

```

#!/bin/sh

# Sometimes spurious imaginary frequencies are calculated where one would expect
# a very low (nearly zero) frequency. Most frequently this happens when there is
# a barrier-free rotation of, for example, methyl groups. The VibrationalAnalysis
# task (using ModeRefinement) allows one to rescan calculated frequencies in order
# to find out if they were calculated accurately.

# In this example analytical frequencies are calculated. Next recalculation of
# certain NH3 frequencies are performed by scanning along normal modes from a
# restart file. In this calculation the frequencies are calculated numerically
# with finite displacements using symmetry.

AMS_JOBNAME=NH3 $AMSBIN/ams <<eor
System
  Symmetrize Yes
  atoms
    N      0.0000    0.0000    0.0000
    H      0.4729    0.8190    0.3821
    H     -0.9457    0.0000    0.3821
    H      0.4729   -0.8190    0.3821
  end
end

Task SinglePoint

Properties
  NormalModes Yes
End

Engine ADF
  title NH3 analytic frequencies
  beckegrid quality=Good
  basis
    type TZP
    core Small

```

(continues on next page)

(continued from previous page)

```
end
EndEngine
eor

AMS_JOBNAME=ScanFreq $AMSBIN/ams <<eor
LoadSystem
  File NH3.results/adf.rkf
End
LoadEngine NH3.results/adf.rkf

Task VibrationalAnalysis

VibrationalAnalysis
  Type ModeRefinement
  NormalModes
    ModeFile NH3.results/adf.rkf
    ModeSelect
      FreqRange 0 4000
    End
  End
End
eor
```

15.7.2 Speed

Example: Multiresolution

Download Multiresolution_H2O.run

```
#!/bin/sh

# This example demonstrates how to use different levels of numerical precision
# for different regions, with the aim of increasing computational efficiency.

# Let us assume that we are interested in having an accurate description only
# for a subregion of a large chemical system (in this simple example, the
# central water molecule). The system can be divided into sub-regions and
# different levels of numerical accuracy can be used for each of these sub-
# regions.

# In this example we will tweak:
# - the basis set (Basis)
# - the numerical integration (BeckeGrid)
# - the density fitting for Coulomb potential (ZlmFit)
# - the fit-set used in the Hartree-Fock Resolution of identity (RIHartreeFock)

# Note: For the regions for which no quality has been explicitly defined
# through a QualityPerRegion keyword, the quality defined in NumericalQuality
# will be used (Normal, in this example).

$AMSBIN/ams <<eor
Task SinglePoint
```

(continues on next page)

(continued from previous page)

```

System
  Atoms
    O    0.00000000    0.00000000    0.00000000    region=Accurate
    H    0.40399229   -0.65578342    0.63241539    region=Accurate
    H    0.81410032    0.55624569   -0.23129097    region=Accurate
    O   -3.02535626   -0.08473104   -0.47678489
    H   -2.56531481    0.62644005    0.07759386
    H   -2.25289644   -0.61700366   -0.80790649
    O    2.95394790   -0.54939973   -0.38206034
    H    3.91427727   -0.21304908   -0.44738291
    H    2.87780992   -1.13241278   -1.20853726
    O   -5.95425742   -0.56764616   -0.02016682    region=Far
    H   -5.26308282   -0.46969096    0.69255963    region=Far
    H   -5.42117992   -0.54361203   -0.86443121    region=Far
    O    6.25171470   -0.62004899   -0.03702467    region=Far
    H    6.16508647   -1.38696453    0.58541903    region=Far
    H    7.09161199   -0.16700550    0.23679419    region=Far

```

```
End
```

```
End
```

```
Engine ADF
```

```
XC
```

```
  LibXC B3LYP
```

```
End
```

```

! =====
! Set different basis sets for atoms in different regions:
! =====

```

```
Basis
```

```
  Type DZ
```

```
  Core None
```

```
  PerRegion Region=Accurate Type=TZP
```

```
  PerRegion Region=Far      Type=SZ
```

```
End
```

```

! =====
! Set the NumericalQuality to be used for the atoms that are not
! explicitly defined through a QualityPerRegion keyword
! =====

```

```
NumericalQuality Normal
```

```

# =====
# Numerical integration:
# =====

```

```
BeckeGrid
```

```
  QualityPerRegion Region=Accurate Quality=Good
```

```
  QualityPerRegion Region=Far      Quality=Basic
```

```
End
```

```

# =====
# Density fitting for Coulomb potential:
# =====

```

(continues on next page)

(continued from previous page)

```

ZlmFit
  QualityPerRegion Region=Accurate Quality=Good
  QualityPerRegion Region=Far      Quality=Basic
End

# =====
# Hartree-Fock Resolution of identity (for hybrid functionals)
# =====

RIHartreeFock
  QualityPerRegion Region=Accurate Quality=Good
  QualityPerRegion Region=Far      Quality=Basic
End

EndEngine

eor

```

15.8 Restarts

15.8.1 Example: Restart analytical Hessian calculation

Download `HessianRestart.run`

```

#!/bin/sh

# This example demonstrates how one can complete an analytical Hessian calculation
# in three steps without re-doing CPKS for all atoms and the subsequent steps.
# We will define regions for the first and second steps right away.
# Note that the region for the second step includes atoms of the first one.
# This is necessary because we want the resulting Hessian in the subsequent steps
# to include the atoms done in the previous calculations.
# First, we calculate the Hessian sub-matrix corresponding to the C atoms.

AMS_JOBNAME=step1 "$AMSBIN/ams" << eor

Task SinglePoint
Properties
  NormalModes Yes
  SelectedRegionForHessian step1
End

System
  Atoms
    C -2.711485799381603 -2.593393872048840 -0.00016442137955 region=step2,step1
    C -1.846368848888818 -1.340467404429865  0.00016453093935 region=step2,step1
    H -2.203636997435432 -3.429266061978078 -0.51549899454129 region=step2
    H -3.673159561801013 -2.414816382275922 -0.51564516686341 region=step2
    H -2.938101685663578 -2.921829124623212  1.03094752484358 region=step2
    H -0.884694282363284 -1.519047266416641  0.51564280107136
    H -2.354216233206031 -0.504595127574485  0.51550071600252
    H -1.619753333793463 -1.012031055604717 -1.03094699007257
  End

```

(continues on next page)

(continued from previous page)

```

      BondOrders
        1 2 1.0
        1 3 1.0
        1 4 1.0
        1 5 1.0
        2 6 1.0
        2 7 1.0
        2 8 1.0
      End
    End
  End

Engine ADF
  save TAPE13
EndEngine
eor

# In the second calculation, we add the Hessian sub-matrix corresponding to H atoms
# of the first methyl group. We use as much data as possible from the first one.
# This includes the part of the analytical Hessian computed for atoms of the "step1"
# region in the previous calculation.
# We use the adf.rkf file for restart but if the 1st calculation had crashed or
# stopped uncontrollably, we would have to use the TAPE13 file instead.
#

AMS_JOBNAME=step2 "$AMSBIN/ams" << eor

Task SinglePoint

Properties
  NormalModes Yes
  SelectedRegionForHessian step2
End

LoadSystem
  File step1.results/ams.rkf
End

LoadEngine step1.results/adf.rkf
EngineRestart step1.results/adf.rkf
eor

# In the third calculation, we do not use the SelectedRegionForHessian key, because
# we want the full Hessian. In this calculation we use data from the second step.

AMS_JOBNAME=step3 "$AMSBIN/ams" << eor

Task SinglePoint

Properties
  NormalModes Yes
End

LoadSystem
  File step2.results/ams.rkf
End

LoadEngine step2.results/adf.rkf

```

(continues on next page)

(continued from previous page)

```
EngineRestart step2.results/adf.rkf
eor
```

15.9 Scripting

15.9.1 Prepare an AMS job and generate a report

Example: Single point for multiple xyz files: Bakerset

Download BakersetSP.run

```
#!/bin/sh

# In this example you will find how to use amsprep to run a particular job (a
# single point calculation in this case) for all molecules in the Baker set. The
# molecules are simply xyz files and contain no ADF specific information.
# amsreport is used to collect the resulting bonding energies.

rm -f runset
for f in $AMSHOME/examples/adf/BakersetSP/Bakerset/*.xyz
do
    "$AMSBIN/amsprep" -t SP -i 2.5 -b DZ -c Large -r None -m "$f" -j `basename $f` .
    xyz`>> runset
done

chmod +x runset
./runset

echo Results
ls -t -1 *.results/adf.rkf | while read f
do
    "$AMSBIN/amsreport" "$f" BondingEnergy
done
echo Ready
```

Example: Basis set and integration accuracy convergence test: Methane

Download ConvergenceTestCH4.run

```
#!/bin/sh

# In this example you will find how to use amsprep to test convergence of the
# bonding energy with respect to basis set and integration accuracy. amsreport
# is used to collect the resulting bonding energies.

rm -f runset
for b in SZ DZ DZP TZP TZ2P QZ4P
do
```

(continues on next page)

(continued from previous page)

```

    "$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b $b
    ↪-j methane.$b>> runset
done

chmod +x runset
./runset

echo Results
echo Basis set convergence of Bonding Energy, SZ DZ DZP TZP TZ2P QZ4P
for b in SZ DZ DZP TZP TZ2P QZ4P
do
    "$AMSBIN/amsreport" "methane.$b.results/adf.rkf" BondingEnergy
done

rm -f runset
for i in 2 3 4 5
do
    "$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b
    ↪DZP -i $i -j methane.$i>> runset
done
"$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b DZP -i
    ↪Basic -j methane.bb>> runset
"$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b DZP -i
    ↪Normal -j methane.bn>> runset
"$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b DZP -i
    ↪Good -j methane.bg>> runset
"$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b DZP -i
    ↪VeryGood -j methane.bv>> runset
"$AMSBIN/amsprep" -t "$AMSHOME/examples/adf/ConvergenceTestCH4/methane.ams" -b DZP -i
    ↪Excellent -j methane.be>> runset

chmod +x runset
./runset

echo Integration convergence of Bonding Energy, 2 3 4 5
for i in 2 3 4 5
do
    "$AMSBIN/amsreport" "methane.$i.results/adf.rkf" BondingEnergy
done

echo Integration Becke convergence of Bonding Energy, Basic, Normal, Good, VeryGood,
    ↪Excellent
"$AMSBIN/amsreport" "methane.bb.results/adf.rkf" BondingEnergy
"$AMSBIN/amsreport" "methane.bn.results/adf.rkf" BondingEnergy
"$AMSBIN/amsreport" "methane.bg.results/adf.rkf" BondingEnergy
"$AMSBIN/amsreport" "methane.bv.results/adf.rkf" BondingEnergy
"$AMSBIN/amsreport" "methane.be.results/adf.rkf" BondingEnergy

echo Ready

```

Example: amsprep: Replace atom with ligand

Download LoopAtomsLigands.run

```
#!/bin/sh

# generate a run file for methane, with 1 H replaced by some ligand (run amsprep
# -liststructures to get full list of available structures) note the -a flag
# makes amsprep produce an .ams file as well, which can be opened by AMSinput to
# check your system

for ligand in CN CO CO3 NC NH2 NH2CH3 NH3 OC OCH3 OH PH3 Pyridine; do
    "$SAMSBIN/amsprep" -t GO -m "$SAMSHOME/examples/adf/LoopAtomsLigands/methane.xyz" -
    ↪structure "2 Ligands/$ligand.ams" -a methane.$ligand.ams
done

# similar, replace the C atom by other atoms

for atom in C Si Ge Sn Pb; do
    "$SAMSBIN/amsprep" -t GO -m "$SAMSHOME/examples/adf/LoopAtomsLigands/methane.xyz" -
    ↪atomtype "1 $atom" -a methane.$atom.ams
done
```

15.10 List of Examples

- *3DRISM-Entropy* (page 525)
- *3DRISM-Glycine* (page 523)
- *Acetamide_SM12* (page 519)
- *Adenine_sTDA* (page 911)
- *Adenine_sTDDFT* (page 913)
- *AgI_SO_Pol* (page 932)
- *AgI_asoexcit* (page 893)
- *AIM_HF* (page 1174)
- *AlCl3_efgnbo* (page 1177)
- *ALPHA_DENSITY* (page 944)
- *Aromaticity* (page 1171)
- *AT_transferintegrals* (page 1032)
- *Au2_Resp* (page 868)
- *Au2_ZORA* (page 502)
- *Au10_POLTDDFT* (page 966)
- *AuH_analyse_exciso* (page 511)
- *Bader* (page 1166)
- *Bader_Reactivity* (page 1167)
- *BakersetSP* (page 1206)
- *Benzene_dimer_tshaped* (page 501)
- *Bimane_wB97X* (page 914)
- *BondOrder* (page 1152)
- *BSSE_CrCO6* (page 1188)
- *C2H3I_SOCD* (page 899)
- *C2H4_TDCDFT* (page 965)
- *CalcOverlapOnly* (page 1187)
- *CAMY-B3LYP_H2O* (page 487)
- *CAMY-B3LYP_TDDFT_H2O* (page 877)
- *Cdplus_ROKS_TDA_SOC* (page 894)
- *CEBE_HI* (page 838)
- *CEBE_NNO* (page 834)
- *CH3_CH3_etsnocv* (page 1162)
- *CH4_SAOP* (page 985)
- *CH4_SecDeriv* (page 850)
- *CH4_nmrnbo* (page 1180)
- *ChargeSeparation_Toluene_TCNE* (page 1051)
- *CM5_chargemodel* (page 1151)
- *CN_SecDeriv* (page 849)
- *CN_unr_excit* (page 869)
- *Co_LFDFT* (page 969)
- *Co_LFDFT_gtensor* (page 973)
- *CO_model* (page 474)
- *ConvergenceTestCH4* (page 1206)
- *CPL_C2H2* (page 994)
- *CPL_CH3OH_NBO* (page 1183)
- *CPL_HF_hybrid* (page 998)
- *Cr3_noncollinear* (page 515)
- *Cu_LFDFT_gtensor* (page 976)
- *CuH+_S-squared* (page 829)
- *DampedVerdet* (page 961)
- *DFTB_modes_ADF_Raman_VROA* (page 865)
- *Diimina_NOCV* (page 1155)
- *DIMQM_CPIM_Excitations* (page 604)
- *DIMQM_DRF2* (page 596)
- *DIMQM_DRF_BE* (page 584)
- *DIMQM_DRF_Hyperpol* (page 585)

- [DIMQM_DRF_plams](#) (page 595)
- [DIMQM_Gradients](#) (page 616)
- [DIMQM_JACOBI](#) (page 606)
- [DIMQM_LOCAL](#) (page 613)
- [DIMQM_PIM_CMM](#) (page 631)
- [DIMQM_PIM_Pol](#) (page 619)
- [DIMQM_Raman](#) (page 625)
- [DIMQM_READLCLFLD](#) (page 614)
- [DIMQM_SEROA](#) (page 628)
- [Disper_HF](#) (page 939)
- [DMO_CD](#) (page 898)
- [DMO_ORD](#) (page 941)
- [DMO_ORD_aoresponse](#) (page 942)
- [DOS_Cu4CO](#) (page 1172)
- [DOS_FCF](#) (page 931)
- [EDA_meta_gga_hybrid](#) (page 1133)
- [EDA_Unr_C2H4_Cu_C2H4](#) (page 1138)
- [EDA_Unr_CH3I](#) (page 1140)
- [Efield.PntQ_N2](#) (page 522)
- [EGO_CH2O_trip_constr](#) (page 919)
- [EGO_CH2_sf](#) (page 920)
- [EGO_H2O_multi](#) (page 1186)
- [EGO_N2](#) (page 917)
- [EGO_N2_EIGENF](#) (page 917)
- [EGO_PH2](#) (page 922)
- [EGO_TD-DFTB](#) (page 924)
- [EGO_TD-DFTB_triplet](#) (page 925)
- [EGO_TD-DFTB_unrestricted](#) (page 926)
- [ElectronTransfer_FDE_H2O](#) (page 1035)
- [Energy_H2O](#) (page 820)
- [Er_LFDFT_MCD](#) (page 977)
- [ESR_HfV](#) (page 1001)
- [ESR_HgF_2der](#) (page 1005)
- [ESR_TiF3](#) (page 1008)
- [Ethanol_SM12_resp](#) (page 520)
- [Ethylene_FOCDFT](#) (page 1046)
- [evGW_H2O](#) (page 1026)
- [ExcitonTransfer_FOCDFT](#) (page 1080)
- [FDE_CPL_NH3-H2O](#) (page 562)
- [FDE_Energy_H2O-Ne_unrestricted](#) (page 553)
- [FDE_Energy_NH3-H2O](#) (page 549)
- [FDE_H2O_128](#) (page 527)
- [FDE_HeCO2_freezeandthaw](#) (page 543)
- [FDE_NMR_relax](#) (page 557)
- [Fe4S4_BrokenSymm](#) (page 832)
- [Field_PtCO](#) (page 521)
- [Formamide_CVnDFT](#) (page 904)
- [FQQM_aoresponse](#) (page 695)
- [FQQM_GO](#) (page 682)
- [FQQM_response](#) (page 721)
- [FQQM_scf](#) (page 656)
- [FQQM_td](#) (page 747)
- [FQQM_FQFMU_aoresponse](#) (page 695)
- [FQQM_FQFMU_response](#) (page 721)
- [FQQM_FQFMU_scf](#) (page 656)
- [FQQM_FQFMU_td](#) (page 747)
- [FQQM_FDE](#) (page 773)
- [wFQ_na_aoresponse](#) (page 789)
- [wFQ_carbon_aoresponse](#) (page 793)
- [wFQFmu_ag_aoresponse](#) (page 798)
- [wFQFmu_RQRmu_au_response](#) (page 802)
- [Fraggs_NiCO4](#) (page 1108)
- [Fraggs_PtCl4H2](#) (page 1110)
- [FranckCondon_NO2](#) (page 927)
- [Freq_NH3](#) (page 843)
- [Freq_NH3_RAMAN](#) (page 854)
- [Freq_NH3_Scan](#) (page 1201)
- [Freq_UF6](#) (page 846)
- [Furan-TDDFT-aas](#) (page 910)
- [G3W2_H2O](#) (page 1029)
- [GO_FDE_H2O-Li](#) (page 555)
- [GO_H2O](#) (page 804)
- [GO_LiF_Efield](#) (page 812)
- [GO_constraints](#) (page 806)
- [GO_restraint](#) (page 804)
- [green_Al](#) (page 1085)
- [green_Au](#) (page 1089)
- [green_BDT](#) (page 1100)
- [green_WBL](#) (page 1095)
- [GW_CH2O_Embed](#) (page 1030)
- [GW_H2O](#) (page 1022)
- [GW_O3](#) (page 1023)
- [GW_Phenol](#) (page 1024)
- [H2O_ADFNBO](#) (page 1175)
- [H2O_HF_freq](#) (page 848)
- [H2O_MCD](#) (page 902)
- [H2O_MCD_ZFS](#) (page 903)
- [H2O_SO_HDA](#) (page 907)
- [H2O_TD_magnet](#) (page 964)
- [H2O_Verdet](#) (page 938)
- [H2O_magnet](#) (page 962)
- [H2PO_B3LYP](#) (page 485)
- [HBr](#) (page 980)
- [HCN](#) (page 814)
- [HessianRestart](#) (page 1204)
- [HF_ResonanceRaman](#) (page 862)
- [Hgl2](#) (page 512)
- [Hg_Mossbauer_X2C](#) (page 1019)
- [HgMeBr_pnr](#) (page 982)
- [HgMeBr_psc](#) (page 982)
- [HgMeBr_zso](#) (page 982)
- [HI_EFG](#) (page 482)
- [HI_PZora_NMR](#) (page 990)
- [HI_Raman](#) (page 857)
- [HI_SecDer_ZORA](#) (page 851)
- [Hplus_CO_etsnocv](#) (page 1158)
- [Hyperpol](#) (page 959)
- [I2_SO_MP2](#) (page 514)

- *InitHess* (page 810)
- *IQA* (page 1169)
- *LCY-BP_H2O* (page 486)
- *LiH_DampedBeta* (page 933)
- *LiH_DampedGamma* (page 935)
- *LoCOSMO_H2O-NH3* (page 579)
- *LoCOSMO_H2O-NH3_TDDFT* (page 582)
- *LocMO_Resp* (page 1147)
- *LoopAtomsLigands* (page 1208)
- *MBH_CH4* (page 853)
- *MBH_Ethanol* (page 852)
- *methane_dimer_dispersion* (page 500)
- *MM_Dispersion* (page 496)
- *ModStPot_N2+* (page 831)
- *Mossbauer* (page 1016)
- *MP2_Li* (page 494)
- *Multiresolution_H2O* (page 1202)
- *N2_TDHF* (page 873)
- *NaCl_ionicbonding* (page 1124)
- *NaCl_pairbonding* (page 1126)
- *Naphthalene_VST* (page 929)
- *Ne_CoreExci* (page 888)
- *Ne_exciso* (page 888)
- *NH_ZFS* (page 1014)
- *NH3_HDA* (page 906)
- *NH3_POLTDDFT* (page 967)
- *NMR_B3LYP* (page 987)
- *NMR_NICS* (page 986)
- *NOCV_CrCO5-CH2* (page 1160)
- *NpF6_ROKS_TDA_SOC* (page 894)
- *O2_ROKS* (page 841)
- *O2_pNMR* (page 992)
- *OH_MetaGGA* (page 475)
- *PCCP_Unr_BondEnergy* (page 1118)
- *PbF_excisou* (page 897)
- *PbH4_finitenuc* (page 999)
- *pdb2adf* (page 584)
- *PdH_ESR_X2C* (page 1012)
- *Phenylnitrene_ZFS* (page 1015)
- *POLTDDFT_CAMYB3LYP* (page 968)
- *Pr_LFDFT* (page 971)
- *PyFrag* (page 1146)
- *Pyridine_CAM-B3LYP* (page 876)
- *QM/MM* (page 584)
- *qsGW_Br2_frozenCore* (page 1028)
- *qsGW_N2* (page 1027)
- *Quild* (page 584)
- *r2SCAN-3c* (page 473)
- *Rose_TDDFT* (page 1148)
- *RPA_H2O* (page 494)
- *RPA-SOSSX_H2O* (page 495)
- *SCF_Ti2O4* (page 1193)
- *SD_CrNH3_6* (page 824)
- *SF_ROKS* (page 842)
- *SiH2_spinflip* (page 872)
- *SO_ZORA_Bi2* (page 503)
- *Solv_HCl* (page 516)
- *SUBEXCI_dimer* (page 566)
- *TCNE-Benzene_wB97* (page 915)
- *TD-DFTB_betacarotene* (page 908)
- *TiCl4_CoreExci* (page 880)
- *TiCl4_XASXES* (page 885)
- *TIH_SO_analysis* (page 1143)
- *Tl_noncollinear* (page 507)
- *Transit_H2O* (page 819)
- *TSRC_SN2* (page 818)
- *TS_C2H6* (page 815)
- *TS_CH4_HgCl2* (page 817)
- *Twist_Ethene_TDDFT* (page 900)
- *UnrFrag_H2* (page 1112)
- *VCD_CHFClBr_DZP* (page 867)
- *VCD_COG_NHDT* (page 867)
- *VO_collinear* (page 1003)
- *VROA* (page 863)
- *VROA_RESO* (page 864)
- *Water_MeOH_B2GPPLYP* (page 489)
- *Water_MeOH_DODSCAN* (page 493)
- *Water_MP2_AO* (page 488)
- *WaterDimer* (page 840)
- *WaterDimer_SOS-MP2_AO* (page 489)
- *XCDFT_FDE_ET_ethylene* (page 1068)
- *XCFUN_FULLKERNEL_TDDFT_H2O* (page 878)
- *XCFUN_TDDFT_H2O* (page 879)

KEYWORDS

16.1 Links to manual entries

- *AIFIT* (page 381)
- *ADDDIFFUSEFIT* (page 383)
- *ALLOW* (page 393)
- *ALLPOINTS* (page 397)
- *ANALYTICALFREQ* (page 170)
- *AORESPONSE* (page 217)
- *ARH* (page 372)
- *AROMATICITY* (page 318)
- *ATOMS* (page 37)
- *BASIS* (page 44)
- *BECKEGRID* (page 373)
- *BONDORDERS* (page 305)
- *CDFT* (page 74)
- *CDSPECTRUM* (page 205)
- *CM5* (page 304)
- *CONCEPTUALDFT* (page 319)
- *COREPOTENTIALS* (page 68)
- *cpl* (page 244)
- *cpl GGA* (page 247)
- *cpl HYPERFINE* (page 250)
- *cpl NMRCOUPLING* (page 244)
- *CREATE* (page 50)
- *CURRENTRESPONSE* (page 177)
- *CVNDFT* (page 198)
- *DEBUG* (page 327)
- *densf* (page 342)
- *DEPENDENCY* (page 391)
- *DIMPAR* (page 130)
- *DIMQM* (page 125)
- *disper* (page 226)
- *dos* (page 360)
- *DRF* (page 125)
- *ELECTRONTRANSFER* (page 272)
- *ELECTROSTATICEMBED-*
- *DING* (page 162)
- *ENERGYFRAG* (page 105)
- *EPRINT* (page 328)
- *ESP-CHELPG* (page 304)
- *ESP-RESP* (page 304)
- *ESR* (page 250)
- *ETSNOCV* (page 309)
- *EXACTDENSITY* (page 381)
- *EXCITATIONS* (page 179)
- *EXCITEDGO* (page 212)
- *EXCITONTRANSFER* (page 281)
- *EXTENDEDPOPAN* (page 307)
- *EXTERNALS* (page 129)
- *FDE* (page 145)
- *FDEFRAGMENTS* (page 145)
- *FOCDFT* (page 79)
- *FORCEALDA* (page 188)
- *QMFQ* (page 136)
- *FRAGMENTS* (page 56)
- *FRAGMETAGGATOTEN* (page 89)
- *FRAGOCCUPATIONS* (page 71)
- *FULLFOCK* (page 397)
- *green* (page 286)
- *GW* (page 263)
- *HARTREEFOCK* (page 105)
- *HFATOMSPERPASS* (page 383)
- *HFMAXMEMORY* (page 383)
- *HYPERPOL* (page 216)
- *INTEGRATION* (page 375)
- *IQA* (page 296)
- *IRREPOCCUPATIONS* (page 66)
- *lfdft* (page 229)
- *lfdft_tdm* (page 231)
- *LINEARSCALING* (page 396)
- *LOCORB* (page 297)
- *MBPT* (page 387)
- *MCD* (page 205)
- *METAGGA* (page 105)
- *MODIFYEXCITATION* (page 190)
- *MODIFYSTARTPOTENTIAL* (page 69)
- *nmr* (page 234)
- *nmr GFACTORS* (page 251)
- *nmr NMR* (page 234)
- *NOBECKEGRID* (page 374)
- *NOPRINT* (page 329)
- *NOSHAREDARRAYS* (page 394)
- *NUCLEARMODEL* (page 52)
- *NUMERICALQUALITY* (page 367)
- *OCCUPATIONS* (page 64)
- *OPTICALROTATION* (page 217)
- *PARTIALZORA* (page 111)
- *POLTDDFT* (page 223)
- *PRINT* (page 324)
- *QTAIM* (page 316)
- *QTENS* (page 254)
- *RADIALCOREGRID* (page 380)
- *RELATIVITY* (page 106)
- *REMOVEALLFRAGVIRTUALS* (page 72)
- *REMOVEFRAGORBITALS* (page 73)
- *RESPONSE* (page 215)
- *RESTART* (page 400)
- *RIHARTREEFOCK* (page 382)
- *RISM* (page 157)
- *ROSE* (page 301)

- *SAVE* (page 397)
- *SCF* (page 368)
- *SELECTEXCITATION* (page 189)
- *SFTDDFT* (page 185)
- *SINGLEORBTRANS* (page 192)
- *SKIP* (page 393)
- *SLATERDETERMINANTS* (page 426)
- *SM12* (page 120)
- *SOLVATION* (page 112)
- *SOMCD* (page 205)
- *SOPERT* (page 194)
- *SPINFLIP* (page 69)
- *SPINPOLARIZATION* (page 60)
- *SPINORBITMAGNETIZATION* (page 62)
- *STCONTRIB* (page 197)
- *STOFIT* (page 381)
- *STOPAFTER* (page 392)
- *SUBEXCI* (page 154)
- *SYMMETRY* (page 39)
- *SYMMETRYTOLERANCE* (page 39)
- *TAILS* (page 395)
- *TDA* (page 181)
- *TOTALENERGY* (page 294)
- *TRANSFERINTEGRALS* (page 270)
- *UNRESTRICTED* (page 59)
- *VANDERWAALS* (page 225)
- *VECTORLENGTH* (page 395)
- *XC* (page 80)
- *XES* (page 193)
- *ZFS* (page 253)
- *ZLMFIT* (page 380)

16.2 Summary of all keywords

16.2.1 Engine ADF

A1Fit

Type

Float

Default value

10.0

Unit

Angstrom

GUI name

Symmetric fit for distance >

Description

STO-Fit keyword: distance between atoms, in Angstrom. The symmetric fit approximation is applied only for atoms farther apart.

AccurateGradients

Type

Bool

Default value

No

Description

Print the nuclear gradients with more digits than usual.

AddDiffuseFit

Type

Bool

Default value

No

GUI name

Add diffuse functions in fit: Yes

Description

STO-Fit keyword: One can get more diffuse fit functions by setting this to True.

AllDipMat**Type**

Bool

Default value

No

Description

Print all dipole matrix elements between occupied and virtual Kohn-Sham orbitals.

Allow**Type**

String

Recurring

True

Description

Controlled aborts can in some cases be overruled. Of course, the checks have been inserted for good reasons and one should realize that ignoring them probably produces incorrect results or may lead to a program-crash.

AllPoints**Type**

Bool

Default value

No

GUI name

Force use of all points

Description

ADF makes use of symmetry in the numerical integrations. Points are generated for the irreducible wedge, a symmetry unique sub region of space. Optionally the symmetry equivalent points are also used. This is achieved by setting this key to True.

AnalyticalFreq**Type**

Block

Description

Define options for analytical frequencies.

B1Size**Type**

Float

Description

Sparse grid max memory size

B1Thresh**Type**

Float

Default value

1e-10

Description

MMGF_DENB1 and MMGF_GRADB1 cutoff values

Check_CPKS_From_Iteration**Type**

Integer

Default value

1

Description

Solution of the CPKS equations is an iterative process, and convergence is achieved if the difference between U1 matrix of successive iterations falls below a certain threshold. This key can be used to determine at which iteration the checking should start taking place.

Debug**Type**

String

Description

For debugging purposes. Options: fit, hessian, b1, densities, numbers, symmetry, all.

Hessian**Type**

Multiple Choice

Default value

reflect

Options

[reflect, average]

Description

Whether the final Hessian is obtained by reflecting or averaging?

Max_CPKS_Iterations**Type**

Integer

Default value

20

Description

Calculating the analytical frequencies requires the solution of the Coupled Perturbed Kohn-Sham (CPKS) equations, which is an iterative process. If convergence is not achieved (a warning will be printed in the output if this is the case) then this subkey can be used to increase the number of iterations, although convergence is not guaranteed. The user required accuracy of the U1 matrix, as well as the ADF integration accuracy, can effect the rates of convergence.

Print**Type**

String

Description

Primarily for debugging purposes. Options: eigs, u1, parts. Choosing EIGS results in the print out of the MO eigenvectors, while U1 results in the print out of the U1 matrices. Except for

small molecules this will result in a lot of data being output, and so they are not recommended. Choosing PARTS results in the print out of various sub-hessians that add up to give the final analytical hessian.

PrintNormalModeAnalysis**Type**

Bool

Default value

No

Description

Request ADF to print analysis of the normal modes independently of AMS.

U1_Accuracy**Type**

Float

Default value

5.0

Description

Solution of the CPKS equations is an iterative process, and convergence is achieved if the difference between U1 matrix of successive iterations falls below a certain threshold. This subkey can be used to set the threshold. The accuracy of the U1 will be $10^{*(-x)}$. So, the higher the number the more accurate the U1 will be. While this parameter effects the accuracy of the frequencies, other factors also effect the accuracy of the frequencies, especially the ADF integration accuracy.

AOMat2File**Type**

Bool

Default value

No

Description

Write PMatrix, Fock matrix, and overlap matrix on AO basis to file for future analysis purposes

AOResponse**Type**

Block

Description

If the block key AORESPONSE is used, by default, the polarizability is calculated. Note that if the molecule has symmetry the key ALLPOINTS should be included

ALDA**Type**

Bool

Default value

No

Description

Use ALDA only

Alpha

Type

Bool

Default value

No

Description

Calculate linear response

Beta**Type**

Bool

Default value

No

DescriptionWill use $2n+1$ rule to calculate beta.**CALCTransformProp****Type**

String

Description

Transformation Properties of Polarizabilities

Components**Type**

String

Description

Limit the tensor components to the specified ones. Using this option may save the computation time. Options: XX, XY, XZ, YX, YY, YZ, ZX, ZY, ZZ

Cubic**Type**

Bool

Default value

No

Description

Calculate cubic response

Damp**Type**

Float

Default value

0.4

Description

Specify damping for non-acceleration iteration

Debug**Type**

Integer

Default value

0

Description

Debug level for AOResponse.

DoNothing**Type**

Bool

Default value

No

Description

Do nothing.

EFG**Type**

Block

Description

Perform a Mulliken type analysis of the EFG principal components, and an analysis in terms of canonical MOs.

Atom**Type**

Integer

Default value

1

Description

The number of the nucleus at which the EFG is to be analyzed (ADF input ordering).

NBO**Type**

Bool

Default value

No

Description

Perform an NBO/NLMO analysis of the EFG. Requires a series of calculations. See documentation.

Nuc**Type**

Integer

Default value

1

Description

The number of the nucleus at which the EFG is to be analyzed (ADF internal atom ordering).

Thresh**Type**

Float

Default value

0.05

Description

The threshold for printing the EFG-NBO contributions. The default is 0.05, which means that only orbitals with absolute value contribution larger than 5% of the total EFG are printed. To increase the number of contributions printed, specify a smaller threshold.

EFIOR**Type**

Bool

Default value

No

Description**EFISHG****Type**

Bool

Default value

No

Description**EFPLOT****Type**

Bool

Default value

No

Description**EL_DIPOLE_EL_DIPOLE****Type**

String

Description**EL_DIPOLE_EL_OCTUPOLE****Type**

String

Description**EL_DIPOLE_EL_QUADRUPOLE****Type**

String

Description**EL_DIPOLE_MAG_DIPOLE****Type**

String

Description**EL_DIPOLE_MAG_QUADRUPOLE**

Type

String

Description**EL_QUADRUPOLE_EL_QUADRUPOLE****Type**

String

Description**EL_QUADRUPOLE_MAG_DIPOLE****Type**

String

Description**EOPE****Type**

Bool

Default value

No

Description**FitAODeriv****Type**

Bool

Default value

No

Description

Use FITAODERIV for Coulomb potential

Frequencies**Type**

Float List

Default value

[0.0]

Unit

eV

Description

List of frequencies of incident light, the perturbing field, at which the time-dependent properties will be calculated.

GIAO**Type**

Bool

Default value

No

Description

Use gauge-included atomic orbitals

Gamma**Type**

Bool

Default value

No

DescriptionWill use $2n+1$ rule to calculate gamma.**HirshPol****Type**

Bool

Default value

No

Description

Hirshfeld Polarizability of fragments

IDRI**Type**

Bool

Default value

No

Description**LifeTime****Type**

Float

Unit

Hartree

Description

Specify the resonance peak width (damping) in Hartree units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule, however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. A value of 0.004 Hartree was used in Ref. [266].

MAG_DIPOLE_MAG_DIPOLE**Type**

String

Description**MagOptRot****Type**

Bool

Default value

No

Description

Calculate magneto-optical rotation

MagneticPert**Type**

Bool

Default value

No

Description

Use magnetic field as a perturbation

NBO**Type**

Bool

Default value

No

Description

Perform NBO analysis

NoCore**Type**

Bool

Default value

No

Description

if NOCORE is set we skip the core potential in diamagnetic term and/or in the unperturbed density of the CPKS solvers

OKE**Type**

Bool

Default value

No

Description**OPTICALR****Type**

Bool

Default value

No

Description**OpticalRotation****Type**

Bool

Default value

No

Description

Calculate optical rotation

QuadBeta

Type

Bool

Default value

No

Description

Quadrupole operators with beta tensor

QuadPert**Type**

Bool

Default value

No

Description

Calculate quadrupole-quadrupole polarizability

Quadratic**Type**

Bool

Default value

No

Description

Calculate quadratic response

Quadrupole**Type**

Bool

Default value

No

Description

Calculate dipole-quadrupole polarizability

Raman**Type**

Bool

Default value

No

Description**SCF****Type**

String

Description

Specify CPKS parameters such as the degree of convergence and the maximum number of iterations: NOCYC - disable self-consistence altogetherNOACCEL - disable convergence accelerationCONV - convergence criterion for CPKS. The default value is 10-6 . The value is relative to the uncoupled result (i.e. to the value without self-consistence).ITER - maximum number of CPKS iterations, 50 by default.Specifying ITER=0 has the same effect as specifying NOCYC.

SHG**Type**

Bool

Default value

No

Description**STATIC****Type**

Bool

Default value

No

Description**THG****Type**

Bool

Default value

No

Description**TPA****Type**

Bool

Default value

No

Description**Traceless****Type**

Bool

Default value

No

Description

Traceless quadrupole tensors

VROA**Type**

Bool

Default value

No

Description

Calculate Vibrational Raman Optical Activity.

VelocityOrd**Type**

Bool

Default value

No

Description

Use VelocityOrd without GIAOs

XAlpha**Type**

Bool

Default value

No

Description

Xalpha potential

Aromaticity**Type**

Block

Description

Calculate aromaticity indicators, i.e. the matrix of localization/delocalization indices (LI-DI), Iring (ring index) and MCI (multi center index) aromaticity indices.

RingAtoms**Type**

Integer List

Recurring

True

Description

List of the atom numbers that form a ring. For each ring a separate line.

AtomicChargesTypeForAMS**Type**

Multiple Choice

Default value

Mulliken

Options

[Mulliken, Hirshfeld, CM5, Voronoi, MDC-M, MDC-D, MDC-Q, QTAIM, ESP-CHELPG, ESP-RESP]

GUI name

Atomic charges for AMS

Description

Type of atomic charges to be used by AMS.

Note that some of these atomic charges are computed and printed by default in ADF.

Hirshfeld charges are available only for default atomic fragments.

Balance**Type**

Bool

Default value

No

Description

Measure the actual speed of the nodes in the parallel machine

Basis**Type**

Block

Description

Definition of the basis set

Core**Type**

Multiple Choice

Default value

Large

Options

[None, Small, Large]

GUI name

Frozen core

Description

Select the size of the frozen core you want to use.

Small and Large will be interpreted within the basis sets available (of the selected quality), and might refer to the same core in some cases.

If you specify 'None' you are guaranteed to have an all-electron basis set.

CreateOutput**Type**

Bool

Default value

No

Description

If true, the output of the atomic create runs will be printed to standard output. If false, it will be saved to the file CreateAtoms.out in the AMS results folder.

FitType**Type**

Multiple Choice

Default value

Auto

Options

[Auto, SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE]

GUI name

STO fit set

Description

Expert option.

Select the auxiliary fit to be used for STOfit or old Hartree-Fock RI scheme.

The fit set for a given atom is taken from the all-electron basis set file for the specified choice, for the same element as the atom.

By default (Auto) the fit set is taken from the original basis set file.

Path**Type**

String

Description

The name of an alternative directory with basis sets to use. ADF looks for appropriate basis sets only within this directory. Default \$AMSRESOURCES/ADF.

PerAtomType**Type**

Block

Recurring

True

Description

Defines the basis set for all atoms of a particular type.

Core**Type**

Multiple Choice

Options

[None, Small, Large]

Description

Size of the frozen core.

File**Type**

String

Description

The path of the basis set file (the path can either absolute or relative to \$AMSRESOURCES/ADF). Note that one should include ZORA in the path for relativistic calculations, for example 'ZORA/QZ4P/Au'. Specifying the path to the basis file explicitly overrides the automatic basis file selection via the Type and Core subkeys.

Symbol**Type**

String

Description

The symbol for which to define the basis set.

Type**Type**

Multiple Choice

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

Description

The basis sets to be used.

PerRegion**Type**

Block

Recurring

True

Description

Defines the basis set for all atoms in a region. If specified, this overwrites the values set with the Basis%Type and Basis%PerAtomType keywords for atoms in that region. Note that if this keyword is used multiple times, the chosen regions may not overlap.

Core**Type**

Multiple Choice

Default value

Large

Options

[None, Small, Large]

Description

Size of the frozen core.

File**Type**

String

Description

The path of the basis set file (the path can either absolute or relative to \$AMSRE-SOURCES/ADF). Note that one should include ZORA in the path for relativistic calculations, for example 'ZORA/QZ4P/Au'. Specifying the path to the basis file explicitly overrides the automatic basis file selection via the Type and Core subkeys.

Region**Type**

String

Description

The identifier of the region for which to define the basis set. Note that this may also be a region expression, e.g. 'myregion+myotherregion' (the union of two regions).

Type**Type**

Multiple Choice

Default value

DZ

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

Description

The basis sets to be used.

Type**Type**

Multiple Choice

Default value

DZ

Options

[SZ, DZ, DZP, TZP, TZ2P, QZ4P, TZ2P-J, QZ4P-J, mTZ2P, AUG/ASZ, AUG/ADZ, AUG/ADZP, AUG/ATZP, AUG/ATZ2P, ET/ET-pVQZ, ET/ET-QZ3P, ET/ET-QZ3P-1DIFFUSE, ET/ET-QZ3P-2DIFFUSE, ET/ET-QZ3P-3DIFFUSE, Corr/TZ3P, Corr/QZ6P, Corr/ATZ3P, Corr/AQZ6P, POLTDDFT/DZ, POLTDDFT/DZP, POLTDDFT/TZP]

GUI name

Basis set

Description

Select the basis set to use.

SZ: Single Z

DZ: Double Z

DZP: Double Z, 1 polarization function

TZP: Triple Z, 1 polarization function

TZ2P: Triple Z, 2 polarization functions

QZ4P: Quad Z, 4 pol functions, all-electron

AUG: Augmented (extra diffuse functions)

ET: Even tempered all electron basis sets

J: Extra tight functions

These descriptions are meant to give an indication of the quality,

but remember that ADF uses Slater type functions.

For standard calculations (energies, geometries, etc.) the relative quality is:

SZ < DZ < DZP < TZP < TZ2P < ET-pVQZ < QZ4P

The basis set chosen will apply to all atom types in your molecule. If no matching basis set is found, ADF will try to use a basis set of better quality.

For TDDFT applications and small negatively charged atoms or molecules, use basis sets with extra diffuse functions.

J: TZ2P-J, QZ4P-J: for use in ESR hyperfine or NMR spin-spin couplings.

Use the Basis panel to select a basis set per atom type, and to see what basis set actually will be used.

BeckeGrid**Type**

Block

Description

Options for the numerical integration grid.

AllowAngularBoost**Type**

Bool

Default value

Yes

Description

Allow automatic augmentation of the Lebedev spherical grid for highly coordinated atoms.

InnerShellsPruning**Type**

Bool

Default value

Yes

Description

Allow automatic pruning of the Lebedev spherical grid for shells close to the nuclei.

PartitionFunPruning**Type**

Bool

Default value

Yes

Description

Allow pruning of integration points based on the value of the partition function.

QPNear**Type**

Float

Unit

Angstrom

Description

Only relevant if you have specified point charges in the input file. ADF generates grids only about those point charges that are close to any real atoms. The criterion, input with the qpnear subkey, is the closest distance between the point charge at hand and any real atom.

Quality**Type**

Multiple Choice

Default value

Auto

Options

[Auto, Basic, Normal, Good, VeryGood, Excellent]

Description

Quality of the integration grid. For a description of the various qualities and the associated numerical accuracy see reference. If 'Auto', the quality defined in the 'NumericalQuality' will be used.

QualityPerRegion**Type**

Block

Recurring

True

Description

Sets the grid quality for all atoms in a region. If specified, this overwrites the globally set quality.

Quality**Type**

Multiple Choice

Options

[Basic, Normal, Good, VeryGood, Excellent]

Description

The region's integration grid quality.

Region**Type**

String

Description

The identifier of the region for which to set the quality.

RadialGridBoost**Type**

Float

Description

The number of radial grid points will be boosted by this factor. Some XC functionals require very accurate radial integration grids, so ADF will automatically boost the radial grid by a factor 3 for the following numerically sensitive functionals: LibXC M05, LibXC M05-2X, LibXC M06-2X, LibXC M06-HF, LibXC M06-L, LibXC M08-HX, LibXC M08-SO, LibXC M11-L, LibXC MS0, LibXC MS1, LibXC MS2, LibXC MS2H, LibXC MVS, LibXC MVSH, LibXC N12, LibXC N12-SX, LibXC SOGGA11, LibXC SOGGA11-X, LibXC TH1, LibXC TH2, LibXC WB97, LibXC WB97X, MetaGGA M06L, MetaHybrid M06-2X, MetaHybrid M06-HF, MetaGGA MVS.

BondOrders**Type**

Block

Description

Options for the calculation of bond orders. Note: the calculation of bond orders should be requested via the Properties%BondOrders input option in the AMS driver input.

Calculate**Type**

Bool

Default value

No

Description

Whether or not the bond orders should be calculated. This is for internal use/debug purposes, except for multi-atomic fragments. In case of atomic fragments one should request the bond orders at the AMS driver level via the `Properties%BondOrders` input option. For multi-atomic fragments, however, one should not request the bond orders at the AMS driver level, but instead use this key.

PrintAll**Type**

Bool

Default value

No

Description

If 'Yes', all five types of bond orders (i.e. Nalewajski-Mrozek-1,2 & 3, Mayer and Gopinathan-Jug) will be printed to the output. Otherwise only the Nalewajski-Mrozek-3 and the type requested in `BondOrders%TypeForAMS` will be printed.

PrintTolerance**Type**

Float

Default value

0.2

Description

Only bond orders larger than this threshold will be printed in the output (this threshold applies only to the printing in the 'BOND-ORDER ANALYSIS' section of the ADF output).

TypeForAMS**Type**

Multiple Choice

Default value

Nalewajski-Mrozek-3

Options

[Nalewajski-Mrozek-1, Nalewajski-Mrozek-2, Nalewajski-Mrozek-3, Mayer, Gopinathan-Jug]

GUI name

Bond order type for AMS

Description

The type of bond order that will be saved, printed and used by AMS.

Nalewajski-Mrozek-1,2: bond orders calculated from two-electron valence indices based on partitioning of $\text{tr}(\Delta_P^2)$ using 3-index set or 4-index set respectively. Nalewajski-Mrozek-3: bond-orders calculated from valence indices based on partitioning of $\text{tr}(P \cdot \Delta_P)$. Inter-atomic bond orders are not defined with non-atomic fragments.

CalcOverlapOnly**Type**

Bool

Default value

No

Description

Calculate overlaps of primitive basis and stops after computing them.

CC**Type**

Block

Description

Technical aspects of CC methods

ConvThreshold**Type**

Float

Default value

1e-09

Description

Minimum threshold of convergence for the CC energy

Extrapolation**Type**

Multiple Choice

Default value

CROP

Options

[LinMix, DIIS, CROP]

Description

Specifies the t-amplitude extrapolation algorithm to be used in a CC calculation

MaxIts**Type**

Integer

Default value

50

Description

The maximum number of iterations to be used in a Coupled Cluster calculation.

TensBuffer**Type**

Integer

Default value

50

Description

The amount of memory, in GB, available for the tensor contraction library.

Type**Type**

Multiple Choice

Default value

SD

Options

[None, SD, D, SDT, SDTQ, SD(T)]

Description

The excitation level of the CC calculation. Spin-restricted calculations go up to CCSD.

CDFT**Type**

Block

Description

CDFT is a tool for carrying out DFT calculations in the presence of a constraint.

AllAtoms**Type**

Bool

Default value

No

Description

If AllAtoms is true, then TheAtoms is overridden and all the atoms in the active fragment are included in the set.

AnalyticalHessian**Type**

Integer

Default value

0

Description

This will calculate the analytical derivative of the energy w.r.t. the Lagrange multiplier up to the specified SCF iteration. This key is not recommended due to the high computational cost that comes with it. The calculation is equivalent to a ground state Hessian, and it is carried out with the full sum-over-states formula.

ChargeAndSpin**Type**

Bool

Default value

No

Description

will constrain both the charge and the spin

Constraints**Type**

Float List

Description

The values of the constraints. If CHARGEANDSPIN, constraints to the alpha and beta electrons need to be specified sequentially. One more electron => CONSTRAINTS -1.0.

One less electron => CONSTRAINTS 1.0. If the CDFT type is EXCITEDCDFT, CONSTRAINTS=1.0 is recommended. Other values are technically possible but have not been tested yet.

DoNotOptimize**Type**

Bool

Default value

No

Description

If true, the multipliers chosen in INITIALMULTIPLIERS will not be optimized and will be constant throughout the entire SCF procedure.

ExcitedCDFT**Type**

Bool

Default value

No

Description

will generate an excited state with CONSTRAINTS number of ALPHA electrons constrained to occupy the virtual space of a ground state reference calculation. This is the essence of the eXcited Constrained DFT (XCDFD) method(P. Ramos, M. Pavanello, Low-lying excited states by constrained DFT, Journal of Chemical Physics 148, 144103 (2018) <https://doi.org/10.1063/1.5018615>) for the calculation of low-lying single excitations. XCDFD is found to correctly reproduce the energy surface topology at conical intersections between the ground state and the first singly excited state and can also accounts for the condensed phase effects in solvated chromophores where typical Delta SCF methods variationally collapse.

InitialMultipliers**Type**

Float List

Description

If available, a guess for the Lagrange multipliers can be entered.

MaxIter**Type**

Integer

Default value

200

Description

Maximum number of CDFT iterations. CDFT carries out a loop nested inside the SCF cycle.

Metric**Type**

Bool

Default value

No

Description

Relevant for XCDFT. In the XCDFT method orthogonality is not imposed between the KS-orbitals of ground and excited states. If METRIC is specified, the degree of mixing of the single excited state with the ground state or high-order excitations is calculated. Three parameters are calculated: p, m and d. The parameters p and m will give information about the amount of mixing with the ground state, while parameter d will determine the mixing with high order excitations. Additional information about the origin of these parameters can be found in the literature (P. Ramos, M. Pavanello, Low-lying excited states by constrained DFT, Journal of Chemical Physics 148, 144103 (2018) <https://doi.org/10.1063/1.5018615>)

NAtomsPerSet**Type**

Integer List

Description

The number of atoms in each moiety (set).

NConstraints**Type**

Integer

Default value

1

Description

This specifies the number of sets of atoms to be considered. For example, if the user wishes to constrain a positive charge on one part of the system, and a negative charge on another part, NCONSTRAINTS should be set to two. There is no limit on the number of constraints. However, SCF convergence becomes an issue with more than 2 constraints. Note: NCONSTRAINTS>1 is untested.

OnlyCharge**Type**

Bool

Default value

Yes

Description

Will constrain only the charge, letting spin relax (and potentially delocalize)

OnlySpin**Type**

Bool

Default value

No

Description

Will constrain only the spin

PopType**Type**

Multiple Choice

Default value

yukawalike

Options

[yukawalike, fuzzyvoronoibecke, fuzzyvoronoifermi]

Description

The population analysis chosen for determining the constraint.

Print**Type**

Multiple Choice

Default value

low

Options

[low, medium, high]

Description

Print level and debugging.

SelfConsistent**Type**

Bool

Default value

No

Description

Self-Consistent CDFT

StepSize**Type**

Float

Default value

0.5

Description

The amount of the Lagrange multipliers step taken in each CDFT iteration

TheAtoms**Type**

Integer List

Description

The atom numbers of the moieties in the input geometry order. If NCONSTRAINTS is larger than 1, the sets of atoms are entered as a single list.

Threshold**Type**

Float

Default value

1e-10

Description

The threshold for convergence of the CDFT constraints. The tighter the SCF convergence criteria, the tighter the THRESHOLD should be.

CM5

Type

Bool

Default value

No

GUI name

: CM5 charges

Description

Calculate the charge model 5 (CM5) analysis.

comment**Type**

Non-standard block

Description

The content of this block will be copied to the output header as a comment to the calculation.

ConceptualDFT**Type**

Block

Description

Conceptual DFT Properties

AnalysisLevel**Type**

Multiple Choice

Default value

Normal

Options

[Normal, Extended, Full]

Description

Set the level of the ConceptualDFT analysis:

Normal - global descriptors only,

Extended - both global and condensed (QTAIM) local descriptors,

Full - all descriptors including non local ones.

AtomsToDo**Type**

Integer List

GUI name

Include atoms

Description

Define a subset of atoms for which properties are calculated. If the [Domains] block is present then this list specifies which atoms are used to define the domains bounding box.

Domains**Type**

Block

Description

Calculate integrated properties for the domains (same sign) of the dual descriptor.

Border**Type**

Float

Default value

7.0

Unit

Bohr

Description

Set the extent of the Cartesian grid. Extent is the distance between a face of the grid's bounding box and the most outlying atom in the corresponding direction. If the [AtomsToDo] key is present, the bounding box is created around the specified atoms.

Display**Type**

Float

Default value

0.005

Description

Domains for which the integrated DD value is smaller (in magnitude) than the specified value are omitted from the printed output.

Enabled**Type**

Bool

Default value

No

GUI name

Properties of reactivity domains

Description

Calculate properties of reactivity domains.

Ensemble**Type**

Multiple Choice

Default value

Canonical

Options

[Canonical, GrandCanonical]

Description

Statistical ensemble for DD domains. Canonical: DD values are calculated using the statistical canonical ensemble. GrandCanonical: DD values are calculated using the statistical grand canonical ensemble. The grand canonical DD corresponds to $(S^2 f(2) - (\gamma/\eta^3) f^0)$, where $f(2)$ is the canonical DD, γ and η - the hyper-hardness and hardness of the chemical system, respectively, and f^0 is the mean Fukui function. This statistical

ensemble is a natural choice when comparing two chemical systems with a different number of electrons.

Radius

Type

Float

Default value

0.0

Description

This option adds a sphere around each nucleus, excluding all points inside it. This can help to separate domains around an atom or to exclude core electrons. Be careful when using this option. In particular, the radius of the sphere should exceed two or three times the [Spacing] value to be effective. By default, no spheres are added.

Spacing

Type

Float

Default value

0.1

Unit

Bohr

Description

Specifies spacing (distance between neighboring points) of the rectangular Cartesian grid used when searching for DD domains. It may be useful to specify a smaller value (or increase the size of the grid, see [Border] key) if a substantial part of the electronic density is accounted for.

Threshold

Type

Float

Default value

0.001

Description

Arbitrary value of dual descriptor used to separate DD domains (values below this threshold are ignored).

Electronegativity

Type

Bool

Default value

No

GUI name

Atomic electronegativities

Description

Calculate atomic electronegativities. Requires an all-electron calculation (no frozen core), triggers the TotalEnergy and increases the [AnalysisLevel] to at least Extended.

Enabled

Type

Bool

Default value

No

GUI name

Conceptual DFT (FMO): Calculate

Description

Calculate Conceptual DFT properties.

ConstructPot**Type**

Block

Description

Reads a density from a TAPE41 file and constructs numerically the corresponding potential to it

CPBasis**Type**

Bool

Default value

Yes

Description**CPGrid****Type**

Bool

Default value

No

Description**Converge****Type**

Float

Default value

1e-06

Description**CutNegativeDens****Type**

Float

Default value

0.0001

Description**Damp****Type**

Float

Default value

1.0

Description**DensConv****Type**

Float

Description**EigenShift****Type**

Float

Default value

0.01

Description**FitBas****Type**

Bool

Default value

Yes

Description**FixedLambda****Type**

Bool

Default value

No

Description**ImportDens****Type**

String

Description

Filename of density...

Lambda**Type**

Float

Default value

0.01

Description**PotBas****Type**

String

Description

Filename...

PotProj**Type**

String

Description**ProjChange****Type**

Float

Default value

-1.0

Description**ProjSmallDens****Type**

Float

Default value

1e-50

Description**QPiterations****Type**

Integer

Default value

1000

Description**SVD****Type**

Bool

Default value

No

Description**SmallEigThresh****Type**

Float

Default value

0.0001

Description**StartPot****Type**

String

Description

Filename of potential...

StepSize

Type

Float

Default value

1.0

Description**TIKH****Type**

Float

Default value

0.0

Description**CorePotentials****Type**

Non-standard block

Description

With the key COREPOTENTIALS you specify the core file and (optionally) which sections pertain to the distinct atom types in the molecule.

Create**Type**

String

Description

Keywords for create run. {Atomtype Datafile}

CurrentResponse**Type**

Block

Description**CDSpec****Type**

Bool

Default value

No

Description**Damping****Type**

Float

Default value

0.0

Description**GTensor****Type**

Bool

Default value

No

Description

Magnet

Type

Bool

Default value

No

Description

NCT

Type

Float

Default value

0.0

Description

NMRShielding

Type

Bool

Default value

No

Description

NoVK

Type

Bool

Default value

No

Description

PARTVK

Type

Float

Default value

1.0

Description

Parabolic

Type

Float

Default value

0.0

Description

QIANVignale

Type

Bool

Default value

No

Description**Static****Type**

Bool

Default value

No

Description**CVNDFT****Type**

Block

Description

The CVNDFT block key regulates the execution of the CV(n)-DFT code, which calculates the singlet or triplet electronic excitations for the closed shell molecules.

CV_DFT**Type**

Block

Description

The simplest case: the TDDFT transition density U-vector is substituted into the infinite order CV(infinity)-DFT excitation energy

InitGuess**Type**

Multiple Choice

Default value

TDDFT

Options

[TDDFT, SOR]

Description

Initial guess

DSCF_CV_DFT**Type**

Block

Description

The simplest case: the TDDFT transition density U-vector is substituted into the infinite order CV(infinity)-DFT excitation energy

DampOrbRelax**Type**

Float

Default value

0.2

Description

The `mix_relax` parameter defines the relative weight of the new relaxation vector that is added to the one from the previous iteration.

DampVariable**Type**

Bool

Default value

No

Description

Damping condition

Damping**Type**

Float

Default value

0.2

Description

Damping

InitGuess**Type**

Multiple Choice

Default value

SOR

Options

[TDDFT, SOR]

Description

Initial guess

Optimize**Type**

Multiple Choice

Default value

SVD

Options

[SVD, SOR, COL]

Description

Gradient optimization method

RelaxAlpha**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of alpha orbitals starts.

RelaxBeta**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of beta orbitals starts.

Iteration**Type**

Integer

Default value

50

Description

The maximum number of iterations

RSCF_CV_DFT**Type**

Block

Description

The simplest case: the TDDFT transition density U-vector is substituted into the infinite order CV(infinity)-DFT excitation energy

DampOrbRelax**Type**

Float

Default value

0.2

Description

The mix_relax parameter defines the relative weight of the new relaxation vector that is added to the one from the previous iteration.

DampVariable**Type**

Bool

Default value

No

Description

Damping condition

Damping**Type**

Float

Default value

0.2

Description

Damping

InitGuess**Type**

Multiple Choice

Default value

TDDFT

Options

[TDDFT, SOR]

Description

Initial guess

RelaxAlpha**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of alpha orbitals starts.

RelaxBeta**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of beta orbitals starts.

R_CV_DFT**Type**

Block

Description

The simplest case: the TDDFT transition density U-vector is substituted into the infinite order CV(infinity)-DFT excitation energy

DampOrbRelax**Type**

Float

Default value

0.2

Description

The mix_relax parameter defines the relative weight of the new relaxation vector that is added to the one from the previous iteration.

DampVariable**Type**

Bool

Default value

No

Description

Damping condition

InitGuess**Type**

Multiple Choice

Default value

TDDFT

Options

[TDDFT, SOR]

Description

Initial guess

RelaxAlpha**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of alpha orbitals starts.

RelaxBeta**Type**

Integer

Default value

1

Description

The SCF cycle number at which the relaxation of beta orbitals starts.

SCF_CV_DFT**Type**

Block

Description

The simplest case: the TDDFT transition density U-vector is substituted into the infinite order CV(infinity)-DFT excitation energy

DampVariable**Type**

Bool

Default value

No

Description

Damping condition

Damping

Type

Float

Default value

0.2

Description

Damping

InitGuess**Type**

Multiple Choice

Default value

TDDFT

Options

[TDDFT, SOR]

Description

Initial guess

Tolerance**Type**

Float

Default value

0.0001

Description

The convergence criterion, i.e. the SCF-CV(infinity)-DFT procedure stops when the given accuracy is achieved.

Debug**Type**

String

Recurring

True

Description

The amount of printed output is regulated with the keys Print, NoPrint, EPrint and Debug.

Dependency**Type**

Block

Description**Enabled****Type**

Bool

Default value

No

GUI name

Fix dependencies

Description

Used to make the basis or fit set linearly independent, up to the threshold specified below.

This is typically important when you have many diffuse functions in your basis or fit set.

bas**Type**

Float

Default value

0.0001

GUI name

Threshold for basis

Description

A criterion applied to the overlap matrix of unoccupied normalized SFOs. Eigenvectors corresponding to smaller eigenvalues are eliminated from the valence space.

Note: if you choose a very coarse value, you will remove too many degrees of freedom in the basis set, while if you choose it too strict, the numerical problems may not be countered adequately.

eig**Type**

Float

Default value

100000000.0

Description

Merely a technical parameter. When the DEPENDENCY key is activated, any rejected basis functions (i.e.: linear combinations that correspond with small eigenvalues in the virtual SFOs overlap matrix) are normally processed until diagonalization of the Fock matrix takes place. At that point, all matrix elements corresponding to rejected functions are set to zero (off-diagonal) and BigEig (diagonal).

In AMSinput you must check the Fix Linear dependency check box for this option to be used.

fit**Type**

Float

Default value

1e-10

GUI name

Threshold for fit

Description

Similar to Dependency%bas.

The criterion is now applied to the overlap matrix of fit functions.

The fit coefficients, which give the approximate expansion of the charge density in terms of the fit functions (for the evaluation of the coulomb potential) are set to zero for fit functions (i.e.: combinations of) corresponding to small-eigenvalue eigenvectors of the fit overlap matrix.

Diffuse

Type

Bool

Default value

No

Description

Adding diffuse integration points in case of the old Voronoi numerical integration grid.

DIMPAR

Type

Non-standard block

Description

In this block, the parameters for the DIM atoms are defined in DIM/QM calculations.

DIMQM

Type

Non-standard block

Description

Input for DIM/QM

DipoleLength

Type

Bool

Default value

No

Description

Use dipole-length elements for perturbing (external) integrals in CURRENT response

DipoleResponse

Type

Bool

Default value

No

Description

DumpBasisOnly

Type

Bool

Default value

No

Description

Dump basis and fit set files use for each atom.

ElectronTransfer

Type

Block

Description

Block key for charge transfer integrals with FDE.

CDFT

	Type
	Bool
	Default value
	No
	Description
Debug	Type
	Bool
	Default value
	No
	Description
Disjoint	Type
	Bool
	Description
FDE	Type
	Bool
	Default value
	No
	Description
InvThr	Type
	Float
	Default value
	0.001
	Description
Joint	Type
	Bool
	Description
KNADD	Type
	Bool
	Default value
	No
	Description
NonCT	Type
	Bool

Default value

No

Description**NumFrag****Type**

Integer

Description**Print****Type**

String

Description**EnergyFrag****Type**

Non-standard block

Description**EPrint****Type**

Block

Description

Print switches that require more specification than just off or on

AtomPop**Type**

String

Description

Mulliken population analysis on a per-atom basis

BASPop**Type**

String

Description

Mulliken population analysis on a per-bas-function basis

Eigval**Type**

String

Description

One-electron orbital energies

Fit**Type**

String

Description

Fit functions and fit coefficients

Frag

Type

String

Description

Building of the molecule from fragments

FragPop**Type**

String

Description

Mulliken population analysis on a per fragment basis

Freq**Type**

String

Description

Intermediate results in the computation of frequencies (see debug: freq).

GeoStep**Type**

String

Description

Geometry updates (Optimization, Transition State, ...)

NumInt**Type**

String

Description

Numerical Integration

OrbPop**Type**

Non-standard block

Description

(Mulliken type) population analysis for individual MOs

OrbPopEr**Type**

String

Description

Energy Range (ER) in hartree units for the OrbPop subkey

Repeat**Type**

String

Description

Repetition of output in Geometry iterations (SCF, optimization, ...)

SCF**Type**

String

Description

Self Consistent Field procedure

SFO**Type**

String

Description

Information related to the Symmetrized Fragment Orbitals and the analysis

TF**Type**

String

Description

Transition Field method

ESP-CHELPG**Type**

Bool

Default value

No

GUI name

: ESP-CHELPG charges

Description

Calculate the ESP-CHELPG atomic charges.

ESP-RESP**Type**

Bool

Default value

No

GUI name

: ESP-RESP charges

Description

Calculate the ESP-RESP atomic charges.

ESR**Type**

Block

Description**Enabled****Type**

Bool

Default value

No

Description

Calculate ESR (g- and/or A tensors)

PARAMMR

Type

Bool

Default value

No

Description

Paramagnetic part NMR shielding.

ETSNOCV**Type**

Block

Description

Perform ETS-NOCV analysis.

EKMin**Type**

Float

Default value

2.0

Unit

kcal/mol

GUI name

Energy threshold

Description

The threshold for orbital interaction energy contributions corresponding to deformation density components originating from each NOCV-pairs

ENOCV**Type**

Float

Default value

0.05

GUI name

NOCVs with ev larger than

Description

The threshold for NOCV-eigenvalues

Enabled**Type**

Bool

Default value

No

Description

Perform ETS-NOCV analysis.

RhoKMin**Type**

Float

Default value

0.01

GUI name

Population threshold

Description

The threshold for population analysis of each deformation density contribution in terms of individual SFOs.

TVanalysis**Type**

Bool

Default value

No

GUI name

T/V analysis

Description

Perform T/V decomposition

ExactDensity**Type**

Bool

Default value

No

Description

Use the exact density (as opposed to the fitted density) for the computation of the exchange-correlation potential

Excitations**Type**

Block

Description

Excitation energies: UV/Vis

AAS**Type**

Bool

Default value

No

Description

Use the molecular orbitals from a DFT ground state calculation as input to an excited state calculation with TDDFT-aas coupling matrices

ALLXASMOMENTS**Type**

Bool

Default value

No

Description

To be used in combination with XAS. This will print out all the individual transition moments used within the calculation of the total oscillator strength

ALLXASQUADRUPOLE**Type**

Bool

Default value

No

Description

To be used in combination with XAS. This will print out the individual oscillator strength components to the total oscillator strength.

Allowed**Type**

Bool

Default value

No

Description

Treat only those irreducible representations for which the oscillator strengths will be nonzero (as opposed to all)

AlsoRestricted**Type**

Bool

Description

Include also excitation energies in which a spin-restricted exchange-correlation kernel is used

Analytical**Type**

Bool

Default value

No

Description

The required integrals for the CD spectrum are calculated analytically, instead of numerically. Only used in case of CD spectrum

AsympCor**Type**

Float

Default value

500.0

Description**BSE****Type**

Bool

Default value

No

Description

Solve the static Bethe-Salpeter equation based on a GW calculation

CDSpectrum**Type**

Bool

Default value

No

Description

Compute the rotatory strengths for the calculated excitations, in order to simulate Circular Dichroism (CD) spectra

DTensor**Type**

String

Description

MCD gtensor

Davidson**Type**

Non-standard block

Description

Use the Davidson procedure

Descriptors**Type**

Bool

Default value

No

Description

Compute charge-transfer descriptors and SFO analysis

Descriptors_CT_AT_Rab**Type**

Float

Default value

2.0

Description

Atomic distance criterion used for the calculation of CT_AT descriptors

ESESTD**Type**

Bool

Default value

No

Description

Compute transition dipole moments between excited states

Exact

Type

Non-standard block

Description

The most straightforward procedure is a direct diagonalization of the matrix from which the excitation energies and oscillator strengths are obtained. Since the matrix may become very large, this option is possible only for very small molecules

FullKernel**Type**

Bool

Default value

No

Description

Use the non-ALDA kernel (with XCFUN)

GTensor**Type**

String

Description

MCD gtensor

HDA**Type**

Bool

Default value

No

GUI name

Hybrid diagonal approximation

Description

Activate the diagonal HF exchange approximation.

This is only relevant if a (meta-)hybrid is used in the SCF.

HDA_CutOff**Type**

Float

Default value

10000000.0

Unit

eV

GUI name

HDA cutoff

Description

This is cutoff based on differences in energy between $\text{eps\_virt} - \text{eps\_occ}$, to reduce number of diagonal HF exchange integrals.

Iterations**Type**

Integer

Default value

200

Description

The maximum number of attempts within which the Davidson algorithm has to converge

KFWrite**Type**

Integer

Default value

3

Description

If kfwrite is 0 then do not write contributions, transition densities, and restart vectors to TAPE21, since this can lead to a huge TAPE21, especially if many excitations are calculated. 3 means that contributions, transition densities, and restart vectors are written to TAPE21.

Lowest**Type**

Integer List

Default value

[10]

GUI name

Number of excitations

Description

Number of lowest excitations to compute

MCD**Type**

String

Description

TODO: Magnetic Circular Dichroism

NTO**Type**

Bool

Default value

No

Description

Compute the Natural Transition Orbitals

N_HDA_integral**Type**

Integer

Default value

1000000000

Description

Maximum number of HDA integrals

N_SFO

Type

Integer

Default value

40

Description

Number of SFO analyzed and printed

OnlySing**Type**

Bool

Description

Compute only singlet-singlet excitations

OnlyTrip**Type**

Bool

Description

Compute only singlet-triplet excitations

Orthonormality**Type**

Float

Default value

1e-06

Description

The Davidson algorithm orthonormalizes its trial vectors. Increasing the default orthonormality criterion increases the CPU time somewhat, but is another useful check on the reliability of the results.

Residu**Type**

Float

Default value

1e-06

Unit

Hartree

Description**RoksTddftType****Type**

Block

Description

Excitation energies from RoksTddft: UV/Vis

Calculate**Type**

Multiple Choice

Default value

SS

Options

[SD, SS, SU, SD-SS, SS-SU, SD-SS-SU]

GUI name

RoksTddft Calculate

Description

Specifies the types of RoksTddft methods to target several target spins: spin-down (SD), same-spin (SS), and/or spin-up (SU).

SDType**Type**

Multiple Choice

Default value

QSD-TDA

Options

[SD-TDA, SD-CIS, QSD-TDA]

GUI name

RoksTddft SD-Type

Description

Specifies the flavor to be used in the case of spin-down (SD) RoksTddft

SSType**Type**

Multiple Choice

Default value

S-TDA

Options

[R-TDA, S-TDA, X-TDA]

GUI name

RoksTddft SS-Type

Description

Specifies the flavor to be used in the case of same-spin (SS) RoksTddft

SUType**Type**

Multiple Choice

Default value

SF-TDA

Options

[SF-TDA]

GUI name

RoksTddft SU-Type

Description

Specifies the flavor to be used in the case of spin-up (SU) RoksTddft

SFOAnalysis

Type

Bool

Default value

No

Description

Do SFO analysis

SOSFreq**Type**

Float

Description**STDA****Type**

Bool

Default value

No

Description

Simplified Tamm-Dancoff approach

STDDFT**Type**

Bool

Default value

No

Description

Simplified time-dependent DFT

ScaleCoul**Type**

Float

Default value

1.0

Description

Scaling of Coulomb kernel with scale parameter

ScaleHF**Type**

Float

Default value

1.0

Description

Scaling of the HF part of the kernel with scale parameter

ScaleXC**Type**

Float

Default value

1.0

Description

Scaling of the XC-kernel (excluding a possible HF-part) with scale parameter

Select**Type**

String

Description

Rather than selecting the first nmcdterm transitions for consideration individual transitions can be selected through the SELECT keyword

SingleOrbTrans**Type**

Bool

Default value

No

Description

keyword to use only orbital energy differences

TD-DFTB**Type**

Bool

Default value

No

Description

Use the molecular orbitals from a DFT ground state calculation as input to an excited state calculation with TD-DFTB coupling matrices

TDA-DFTB**Type**

Bool

Default value

No

Description

Use the molecular orbitals from a DFT ground state calculation as input to an excited state calculation with TDA-DFTB coupling matrices

Tolerance**Type**

Float

Default value

1e-06

Unit

Hartree

Description**Vectors**

Type

Integer

Description

The maximum number of trial vectors in the Davidson algorithm for which space is allocated. If this number is small less memory will be needed, but the trial vector space is smaller and has to be collapsed more often, at the expense of CPU time. The default is usually adequate.

Velocity**Type**

Bool

Default value

No

GUI name

Velocity representation

Description

Calculates the dipole-velocity representation of the oscillator strength. If applicable, the dipole-velocity representation of the rotatory strength is calculated. Default the dipole-length representation of the oscillator strength and rotatory strength is calculated

XAS**Type**

Bool

Default value

No

Description

Calculation of the higher order multipole moment integrals and the calculation of the quadrupole oscillator strengths. This will only print the total oscillator strength and the excitation energy.

ExcitedEDA**Type**

Block

Description

Options for excited energy decomposition (EDA).

Calc**Type**

Multiple Choice

Default value

None

Options

[None, Electrostatic, Pauli, All]

Description

None: No calculation of parts of excited EDA.

Electrostatic: calculate electrostatic part EDA excited state.

Pauli: calculate Pauli repulsion part of excited state.

ElectrostaticFile

Type

String

Default value**Description**

Path to adf.rkf file from which ADF reads electrostatic part excited EDA.

PauliFile**Type**

String

Default value**Description**

Path to adf.rkf file from which ADF reads Pauli repulsion part excited EDA.

ExcitedGO**Type**

Block

Description

Excited state geometry optimization

ALLGRADIENTS**Type**

Bool

Default value

No

Description**CPKS****Type**

Block

Description

Some control parameters for the CPKS(Z-vector) part of the TDDFT gradients calculation

Eps**Type**

Float

Default value

0.0001

Description

Convergence requirement of the CPKS

IterOut**Type**

Integer

Default value

5

Description

Details of the CPKS calculation are printed every iter iterations

NoPreConiter

Type

Integer

Default value

200

Description

maximum number of iterations allowed for the unpreconditioned solver.

PreConiter**Type**

Integer

Default value

30

Description

maximum number of iterations allowed for the preconditioned solver

EigenFollow**Type**

Bool

Default value

No

Description

This key tries to follow the eigenvector in excited state geometry optimizations

Output**Type**

Integer

Default value

0

Description

The amount of output printed. A higher value requests more detailed output

SING_GRADS**Type**

Non-standard block

Description**Singlet****Type**

Bool

Default value

Yes

Description

Singlet-singlet excitation is considered

State**Type**

String

Description

Choose the excitation for which the gradient is to be evaluated: 'State Irreplab nstate'. 'Irreplab' is the label from the TDDFT calculation. NOTE: the TDDFT module uses a different notation for some representation names, for example, A' is used instead of AA. 'nstate': this value indicates that the nstate-th transition of symmetry Irreplab is to be evaluated. Default is the first fully symmetric transition.

TRIP_GRADS**Type**

Non-standard block

Description**Triplet****Type**

Bool

Default value

No

Description

Singlet-triplet excitation is considered

ExcitonTransfer**Type**

Block

Description

Block key for exciton transfer integrals with ROSE or FOCDFT.

CoupleFinalStates**Type**

Bool

Default value

No

Description

Calculate delocalized excited states in the basis of the localized excited states that are calculated, thus couple the localized excited states.

FilteredCouplings**Type**

Block

Description

Details on filter used for electronic couplings in the output

MaxEnergy**Type**

Float

Default value

10.0

Unit

eV

Description

Max. energy (in eV) of diabatic states

MaxEnergyDiff**Type**

Float

Default value

0.5

Unit

eV

Description

Max. energy difference (in eV) between diabatic states

MinCoupling**Type**

Float

Default value

0.1

Description

Min. coupling value (in meV) that is printed

MinEnergy**Type**

Float

Default value

0.0

Unit

eV

Description

Min. energy (in eV) of diabatic states

FullRun**Type**

Bool

Default value

No

Description

Include run without restriction of localization of occupied and/or virtual orbitals.

LocalCouplingsOnly**Type**

Bool

Default value

No

Description

Only account for couplings between local diabatic states

Localize

Type

Multiple Choice

Default value

OccupiedOnly

Options

[OccupiedOnly, OccupiedAndVirtual]

Description

Localize OccupiedAndVirtual means that separately purely localized excitations and purely charge-transfer excitations are calculated. Localize OccupiedOnly means that an excitation may have local and charge-transfer character, but the excitation only has contributions from occupied orbitals on one fragment. Only relevant in case block key FOCDFE is used or ROSE orbitals are used.

Lowest**Type**

Integer List

GUI name

Number of excitations

Description

Number of lowest excitations to compute for each fragment. These are purely local excitations if the Localize OccupiedAndVirtual key is specified.

LowestCT**Type**

Integer List

GUI name

Number of charge-transfer excitations

Description

Number of lowest charge-transfer excitations to compute for each fragment. Only relevant if the Localize OccupiedAndVirtual key is also specified.

Output**Type**

Multiple Choice

Default value

AllCouplings

Options

[AllCouplings, FilteredCouplings, AllAndFilteredCouplings]

Description

Amount of output

SecondOrder**Type**

Bool

Default value

No

Description

Include 2nd-order correction to electronic couplings

ExtendedPopan**Type**

Bool

Default value

No

GUI name

: Extended population analysis

Description

Calculate the Mayer bond orders and Mulliken atom-atom populations per l-value

Externals**Type**

Non-standard block

Description

Legacy support of the older DRF code.

FDE**Type**

Block

Description

Frozen Density Embedding options

AMOLFDE**Type**

Bool

Default value

No

Description

placeholder

CAPDENS CONV**Type**

Float

Default value

0.0001

Description

placeholder

CAPPOTBASIS**Type**

Bool

Default value

No

Description

placeholder

CAPPOTLINESEARCH

Type

Bool

Default value

No

Description

placeholder

CAPRADIUS**Type**

Float

Default value

3.0

Description

placeholder

CJCORR**Type**

Float

Default value

0.1

Description

Option to switch on a long-distance correction

Coulomb**Type**

Bool

Description

Neglecting completely $vt[\rho_A, \rho_B]$ ($vt[\rho_A, \rho_B]$ equals zero) together with the exchange-correlation component of the embedding potential introduced by Wesolowski and Warshel.

Dipole**Type**

Bool

Default value

No

Description

placeholder

E00**Type**

Bool

Description

placeholder

EIGENSHIFT**Type**

Float

Default value

0.01

Description

placeholder

ENERGY

Type

Bool

Default value

No

Description

placeholder

EXTERNALORTHO

Type

Float

Default value

1000000.0

Description

Used to specify the use of external orthogonality (EO) in the FDE block

EXTPRINTENERGY

Type

Bool

Default value

No

Description

placeholder

FULLGRID

Type

Bool

Default value

No

Description

placeholder

FreezeAndThawCycles

Type

Integer

Description

This keyword duplicates RelaxCycles

FreezeAndThawDensType

Type

String

Description

placeholder

FreezeAndThawPostSCF**Type**

Bool

Description

This keyword duplicates RelaxPostSCF

GGA97**Type**

Bool

Description

placeholder

GGAPotCFD**Type**

String

Description

The correlation approximant is used in the construction of the embedding potential. The same correlation approximants as in the XC key are available.

GGAPotXFD**Type**

String

Description

The exchange approximant is used in the construction of the embedding potential. The same exchange approximants as in the XC key are available.

LAMBDATIKH**Type**

Float

Default value

0.1

Description

placeholder

LBDAMP**Type**

Float

Default value

0.25

Description

placeholder

LBMAXSTEP**Type**

Float

Default value

0.05

Description
placeholder

LLP91

Type
Bool

Description
placeholder

LLP91S

Type
Bool

Description
placeholder

NDSD

Type
String

Description
placeholder

NOCAPSEPCONV

Type
Bool

Description
placeholder

NOFDKERN

Type
Bool

Default value
Yes

Description
placeholder

OL91A

Type
Bool

Description
placeholder

OL91B

Type
Bool

Description
placeholder

ONEGRID

Type
Bool

Default value

No

Description

placeholder

P92**Type**

Bool

Description

placeholder

PBE2**Type**

Bool

Description

placeholder

PBE3**Type**

Bool

Description

placeholder

PBE4**Type**

Bool

Description

placeholder

PDFT**Type**

Bool

Default value

No

Description

placeholder

PRINTEACHCYCLE**Type**

Bool

Default value

No

Description

placeholder

PRINTRHO2**Type**

Bool

Default value

No

Description

placeholder

PW86K**Type**

Bool

Description

placeholder

PW91K**Type**

Bool

Description

placeholder

PW91Kscaled**Type**

Bool

Description

placeholder

RHO1FITTED**Type**

Bool

Default value

No

Description

placeholder

RelaxCycles**Type**

Integer

Default value

5

Description

This gives the maximum number of freeze-and-thaw cycles that are performed for this fragment. If the maximum number given in the FDE block is smaller, or if convergence is reached earlier, then fewer cycles are performed.

RelaxDensType**Type**

String

Default value**Description**

placeholder

RelaxPostSCF

Type

Bool

Default value

No

Description

this option is included, several post-SCF properties will be calculated after each freeze-and-thaw cycle. These are otherwise only calculated in the last cycle.

SCFCONVTHRESH**Type**

Float

Default value

0.001

Description

placeholder

SDFTEnergy**Type**

Bool

Default value

No

Description

placeholder

SHORTPRINTENERGY**Type**

Bool

Default value

No

Description

placeholder

SMALLEIGTHRESH**Type**

Float

Default value

0.0001

Description

placeholder

TF9W**Type**

Bool

Description

placeholder

THAKKAR92

Type

Bool

Description

placeholder

THOMASFERMI**Type**

Bool

Description

Local-density-approximation form of $v_t[\rho_A, \rho_B]$ derived from Thomas-Fermi expression for $T_s[\rho]$

TW02**Type**

Bool

Description

placeholder

WEIZ**Type**

Bool

Description

placeholder

XCFun**Type**

Bool

Default value

No

Description

Use XCFUN for nonadditive functionals

XCNAdd**Type**

String

Description**FDEFragments****Type**

Non-standard block

Description

Definitions of the FDE fragment types.

FitExcit**Type**

Bool

Default value

No

Description

FOCDFT**Type**

Block

Description

Localize orbitals on fragments and constrain charge and spin polarization on fragments.

Charge**Type**

Float List

Description

Constrain charge on fragments. Number of charges should be the same as number of fragments, and sum should add up to total charge.

ElectronTransfer**Type**

Block

Description**Charge****Type**

Float List

Description

Constrain charge on fragments for the second calculation. Number of charges should be the same as number of fragments, and sum should add up to total charge.

OffDiagonalHF**Type**

Bool

Default value

No

GUI name

Off diagonal HF

Description

Off diagonal HF matrix elements.

OffDiagonalHFValue**Type**

Float

Default value

1.0

GUI name

Off diagonal HF value

Description

Amount of HF in case off diagonal HF matrix elements.

SpinPolarization**Type**

Float List

Description

Constrain spin polarization on fragments for the second calculation. Number of spin polarization values should be the same as number of fragments, and sum should add up to total spin polarization. Calculation should be spin unrestricted.

SpinPolarization**Type**

Float List

Description

Constrain spin polarization on fragments. Number of spin polarization values should be the same as number of fragments, and sum should add up to total spin polarization. Calculation should be spin unrestricted.

ForceALDA**Type**

Bool

Default value

No

Description

In spin-flip TDDFT, the XC kernel can be calculated directly from the XC potential. To use the LDA potential for the XC kernel, which roughly corresponds to the ALDA in ordinary TDDFT, one must specify the key

Fragments**Type**

Non-standard block

Description

Definitions of the fragment type/files: {FragmentName FragmentFile}. In the block header one can specify the directory where the fragment files are located

FragMetaGGAToten**Type**

Bool

Default value

No

GUI name

XC energy difference (for meta XCs): Use molecular grid

Description

By setting this to true the difference in the metahybrid or metagga exchange-correlation energies between the molecule and its fragments will be calculated using the molecular integration grid, which is more accurate than the default, but is much more time consuming.

FragOccupations**Type**

Non-standard block

Description

Simulation of unrestricted fragments with the key FRAGOCCUPATIONS. Fragments need to be calculated spin-restricted. One can specify occupation numbers as if these fragments are calculated spin-unrestricted. The sum of spin-alpha and spin-beta occupations must, for each fragment

orbital in each irrep separately, be equal to the total spin-restricted occupation of that orbital in the fragment.

FullFock**Type**

Bool

Default value

No

GUI name

Full Fock matrix: Always

Description

Calculate the full Fock matrix each SCF iteration (instead of the difference with the previous cycle).

FullTotEn**Type**

Bool

Default value

No

Description**Fuzzy_BO****Type**

Bool

Default value

No

Description**GPU****Type**

Block

Description

Set GPU options

Enabled**Type**

Bool

Default value

No

GUI name

Use GPU

Description

Use a CUDA-compatible GPU.

UseDevices**Type**

Integer List

GUI name

Only use devices

Description

Use only specified devices for this calculation. Multiple devices will be distributed evenly among MPI ranks.

GW

Type

Block

Description

Perform a GW calculation. G0W0 is the default for GW%SelfConsistency.

AdaptiveMixing**Type**

Float List

Description

Requests to use adaptive mixing instead of DIIS and sets the starting mixing parameter for mixing of Green's function in case of self-consistency.

Adaptive mixing is recommended in case a qsGW calculation does not converge with DIIS.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

AnalyticalIntegration**Type**

Block

Description

Use analytical integration to calculate the self-energy. Very slow, unless the system is very small but useful to check the accuracy of the frequency integration

Enabled**Type**

Bool

Default value

No

GUI name

analytical integration

Description

Enable the calculation of the GW quasi-particle energies via analytical integration.

SpectralFunctionResolution**Type**

Integer

Default value

800

Description

Number of points at which spectral function is evaluated.

TDA**Type**

Bool

Default value

No

Description

Solve the linear response equations in the Tamm-Dancoff approximation.

eta**Type**

Float

Default value

0.001

Description

Artificial (positive) broadening parameter for evaluation of self-energy in analytical integration.

Ideally should be as small as possible but this might lead to convergence issues in partially self-consistent approaches.

In this case, a value of up to 0.1 is possible.

Converge**Type**

Block

Description

Sets convergence criteria for the GW calculation in self-consistent case

Density**Type**

Float List

Default value

[1e-08, 1e-05]

Description

First Criterion for self-consistency procedure to terminate.

Criterion is the trace of the density matrix. Ignored in non-selfconsistent Calculation and in eigenvalue self-consistent GW

It is possible to run a qsGW calculation with an inner SCF loop which updates the static part of the elf-energy only. This can be useful to accelerate the convergence in case linear mixing is used. It is not recommended to use linear mixing, so it is also not recommended to use that inner loop as well. The second number in this list specifies the convergence criterion for the inner SCF loop.

HOMO**Type**

Float

Default value

0.003

Unit

eV

GUI name

HOMO energy convergence

Description

Criterion for self-consistency procedure to terminate.

The self-consistent GW calculation terminates, when the difference between the HOMO QP energies between 2 consecutive iterations is below this number.

The LUMO energy converged faster than the HOMO energy so when the HOMO energy is converged according to this criterion, the LUMO energy will be converged as well.

In non-selfconsistent Calculation, this criterion is ignored.

DIIS**Type**

Integer

Default value

10

Description

Requests to use DIIS. This is the Default. Number of expansion coefficients can be requested as well. Ignored in non-selfconsistent calculation

Enabled**Type**

Bool

Default value

No

GUI name

Calculate GW quasi-particle energies

Description

Enable the calculation of the GW quasi-particle energies.

LinearMixing**Type**

Float List

Description

Requests to use linear mixing instead of DIIS and sets the mixing parameter for linear mixing of Green's function in case of self-consistency.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

LinearizeQPequations**Type**

Bool

Default value

No

Description

Instead of solving the non-linear QP equations in a G0W0 (or evGW calculation) by bisection exactly, linearize them by first-order Taylor expansion.

This is not recommended since it does not save computational time when used together with analytical continuation (as implemented in AMS). It might however be useful for benchmarking or for validating results.

If the results on the linearization differ by a lot (for instance, more than 0.1 eV in frontier QP energies) from the non-linearized results, this might indicate that the GW calculation is not reliable.

Polarizability**Type**

Multiple Choice

Default value

RPA

Options

[RPA, BSE, G4W1, G4V1, TDHF]

Description

Sets the expression for the Polarizability used in the GW calculation.

RPA is the Default and amounts to a standard GW calculation.

BSE denotes screening in the Bethe-Salpeter-equation formalism.

PrintAllSolutions**Type**

Bool

Default value

No

Description

Print out all solutions for all requested states. Detects multiple solutions of the QP equations.

PrintSpectralFunction**Type**

Bool

Default value

No

Description

Plot the self-energy as a function of frequency. Automatically done in case of analytical continuation. However, this is expensive in the analytical integration formalism.

QPHamiltonian**Type**

Multiple Choice

Default value

KSF2

Options

[KSF1, KSF2, SRG, LQSGW]

Description

The quasi-particle Hamiltonian can be constructed in different ways.

KSF1 refers to the original construction by Kotani, Van Schilfgaarde and Faleev (KSF) which is also implemented in TURBOMOLE.

KSF2 refers to an alternative construction by KSF.

KSF1 is not recommended since it is numerically less stable than KSF2 in case analytical continuation is used (the default).

In case the analytical integration algorithm is used, only KSF1 is implemented. Therefore, make sure that KSF1 is specified. The results are typically very similar.

The QP energies at which the matrix elements are evaluated can be tweaked further, see the two subsequent keys: However, KSF2 is recommended since it typically leads to QP energies with the best agreement with experiment.

Ignored when not a quasi-particle self-consistent GW calculation is performed

ScissorShift

Type

Bool

Default value

No

Description

Only calculate the HOMO and LUMO QP energies and shift the remaining QP energies by the same amount.

This is a rather crude approximation and not recommended.

It might again be useful for benchmarking purposes.

SelfConsistency

Type

Multiple Choice

Default value

G0W0

Options

[G0W0, EVGW0, EVGW, QSGW0, QSGW]

Description

Sets the level of self-consistency in a GW calculation.

G0W0 calculates a one-shot, perturbative correction to the KS eigenvalues.

In evGW and evGW0, the quasi-particle energies are updated until self-consistency is reached.

evGW0 requests that the Green's function is evaluated self-consistently but not the screened interaction.

In qsGW, the density is updated as well, however, the self-energy is mapped to a static effective potential and the Dyson equation is solved by diagonalization instead of inversion. The results of a qsGW are independent of the choice of the underlying exchange-correlation functional and are usually the most accurate ones.

The same is done in qsGW0, but the screened interaction is not updated.

SelfEnergy

Type

Multiple Choice

Default value

GW

Options

[HF, GW, G3W2, SOSEX, GWGamma, G3W2dynamic, GWGammaInf, GWGammaInfDyn]

Description

Controls the form of the self-energy.

GW is the default and corresponds to the standard GW calculation.

G3W2 is a GW calculation plus a perturbative second-order statically screened exchange correction (second order expansion in the self-energy). Note, that there the self-energy is always static.

nIterations**Type**

Integer List

Default value

[10]

GUI name

Number of iterations

Description

The maximum number of iterations within the (partially or fully) self-consistent GW calculation has to converge.

Ignored when Formalism is set to G0W0

nLowest**Type**

Integer

Default value

1

GUI name

N Lowest

Description

Number of lowest occupied QP levels to be evaluated, overwrites nStates'

nStates**Type**

Integer

Default value

5

GUI name

N states

Description

Number of Quasiparticle States to be printed to output.

The default is 5 states which in this case means that min(5, Number of particle states) occupied and min(5, Number of hole states) hole states are printed. The whole list of states can be printed by setting this parameter to -1'

GZip**Type**

String

Description

GZip the corresponding tape (possibly working only for TAPE21)

HartreeFock**Type**

Bool

Default value

No

Description

Compute hybrid meta-GGA energy functionals (if METAGGA key is True)

HFAtonsPerPass**Type**

Integer

Description

Memory usage option for old HF scheme

HFMaxMemory**Type**

Integer

Description

Memory usage option for old HF scheme

hydrogenbonds**Type**

Bool

Default value

No

Description

Option for SFO population analysis to print small numbers.

IgnoreOverlap**Type**

Bool

Default value

No

Description

Expert option. Ignore that atoms are close.

ImportEmbPot**Type**

String

Description

File containing an external embedding potential (FDE calculations only)

ImportGrid**Type**

String

Description

FDE option for importing numerical integration grid.

Integration**Type**

Block

Description

Options for the Voronoi numerical integration scheme

ACCINT**Type**

Float List

Description

The main precision parameter. Its value defines the number of significant digits by which an internal set of standard integrals must be evaluated. The number and distribution of integration points is tuned accordingly. For normal applications this should yield a nearly optimal (given the underlying method) generation of points and weights. The default depends on the run type.

ACCOUT**Type**

Float

Description

The region of space further away from the atoms, outside the polyhedrons, has its own precision parameter. By default `accout=accint`.

ACCPYR**Type**

Float

Description

Similarly this subkey sets the test level for the parts of the pyramids outside the atomic sphere. Default: `accpyr=accint`.

ACCPYU**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. `Accpyw` controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal `accpyr`.

ACCPYV**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. `Accpyw` controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal `accpyr`.

ACCPYW**Type**

Float

Description

The truncated pyramids are mathematically transformed into unit cubes. A product Gauss integration formula is applied to the cubes, with three (test precision) parameters for the three dimensions. Accpyw controls the direction that is essentially the radial integration from the surface of the atomic sphere to the base of the pyramid. The other two control the orthogonal directions (angular). By default all three equal accpyr.

ACCSPH**Type**

Float

Description

The polyhedron method of generating integration points partitions space in atomic polyhedrons, partitioned in pyramids with their tops at the atom in the center of the polyhedron. A core like atomic sphere is constructed around the atom; this truncates the tops of the pyramids. accsph specifies the test precision for the generation of points within the spheres. By default accsph=accint.

DISHUL**Type**

Float

Unit

Bohr

Description

Sets the distance between the outermost nuclei of the molecule and the boundary planes that define the boundary between the polyhedrons and the outer region. By default dishul=2.3*R, where R is the radius of the largest atomic sphere in the molecule.

FRANGE**Type**

Float

Unit

Bohr

Description

The outward range of the outer region: integration is not performed to infinity but to a distance frange from the outermost atoms, where all functions can be assumed to be essentially zero. By default frange is derived both from accint, the general precision parameter, and from the present chemical elements: heavier atoms have longer-range functions than hydrogen say. The precise relations can be found in the implementation.

LINROT**Type**

Integer

Description

This parameter is significant only for symmetries with an axis of infinite rotational symmetry: C and D. It is the highest rotational quantum number around this axis that occurs among the integrands. This depends on the employed basis functions and fit functions. By default the program finds this out for itself.

LINTEG**Type**

Integer List

Description

The maximum angular momentum quantum number of integrands centered on an atom of that type (one value for each atom type). This depends on the basis functions and on the fit functions. By default the program checks the function sets and sets the linteg values accordingly. This subkey is applied for the generation of grid points in the atomic spheres.

NOUTER**Type**

Integer

Description

This outer region is treated by a product formula: outwards times parallel. The latter involves two dimensions: the surface of the molecule say. The outward integration is performed with Gauss-Legendre quadrature, in a few separate steps. The lengths of the steps are not equal, they increase by constant factors. The total length is fixed. The number of steps is controlled with this subkey; default: 2.

OUTPAR**Type**

Float

Description

Similarly the integration in the directions parallel to the surface of the atomic system is controlled by a parameter. See the implementation for details.

OUTRAD**Type**

Float

Description

The parameter that defines the number of Gauss-Legendre integration points for each outward step. The precise relation between the actual number of points and this subkey, and the default relation between outrad and accout can be found in the implementation.

QPNEAR**Type**

Float

Unit

Angstrom

Description

If you specify point charges in the input file, there are two considerations implied for the numerical integration grid. First, since the point charges create a Coulomb singularity. The integrands (of for instance the basis function products against the Coulomb potential) can only be evaluated with high precision if the grid around the point charges has spherical symmetry and uses local spherical coordinates, exactly as is done for the atomic nuclei. Second, the point charges do not carry fit or basis functions, hence they play only a role in the more diffuse tails of the actual functions involved in integrals. Therefore, a relative low precision of the integral part close to the point charge may have little effect on the total integration accuracy. Since additional 'spherical centers' with their own surrounding grids increase the total number of points

significantly, typically a few thousands per Coulomb center, this may result in high computational effort. Therefore, the program generates spherical grids only about those point charges that are close to the other atoms. The criterion, input with the `qpnear` subkey, is the closest distance between the point charge at hand and any real atom. Default 4.0 Angstrom.

RSPHER**Type**

Float List

Unit

Bohr

Description

Gives the radii of the atomic spheres, one value for each atom type. By default, the radii are derived from the chemical element (heavier atoms get larger spheres) and from the environment: the sphere must not be too large for the atomic cell (polyhedron).

IQA**Type**

Block

Description

Total energy decomposition based on the interacting quantum atoms (IQA) approach and using QTAIM real-space partition.

AtomsToDo**Type**

Integer List

GUI name

Include atoms

Description

Define a subset of atoms for which the IQA atom-atom interactions are calculated (no intra-atomic terms).

If left empty, all atoms will be included (full IQA).

Enabled**Type**

Bool

Default value

No

GUI name

Calculate: Interacting Quantum Atoms (IQA)

Description

Calculate the total energy decomposition using the interacting quantum atoms (IQA) approach and the QTAIM real-space partitioning.

Print**Type**

Multiple Choice

Default value

normal

Options

[normal, verbose]

Description

Minimal output (default) or verbose mode (detailed energy decomposition)

IrrepOccupations**Type**

Non-standard block

Description

Explicit occupation numbers per irrep

IsotopicShift**Type**

String

Description

Untested

LinearScaling**Type**

Block

Description**Cutoff_Coulomb****Type**

Float

Description

determines the radii for the fit functions in the evaluation of the (short-range part of) the Coulomb potential.

Cutoff_Fit**Type**

Float

Description

determines how many atom pairs are taken into account in the calculation of the fit integrals and the density fit procedure. If the value is too low, charge will not be conserved and the density fitting procedure will become unreliable. This parameter is relevant for the timings of the FITINT and RHOFIH routines of ADF.

Cutoff_Multipoles**Type**

Float

Description

determines the cut-offs in the multipole (long-range) part of the Coulomb potential

HF_Fit**Type**

Float

Description

Parameter for HF exchange

Overlap_Int**Type**

Float

Description

determines the overlap criterion for pairs of AOs in the calculation of the Fock-matrix in a block of points. Indirectly it determines what the cut-off radii for AO's should be. The value of ovint has a strong influence on the timing for the evaluation of the Fock matrix, which is very important for the overall timings

ProgConv**Type**

Float

Description

determines how the overall accuracy changes during the SCF procedure

LocOrb**Type**

Non-standard block

Description

The computation of localized orbitals is controlled with this block-type key

MBPT**Type**

Block

Description

Technical aspects of the MP2 algorithm.

Dependency**Type**

Bool

Default value

Yes

Description

If true, to improve numerical stability, almost linearly-dependent combination of basis functions are removed from the Green's function that are used in the MBPT equations. Disabling this key is strongly discouraged. Its value can however be changed. The key to adjust this value is `RiHartreeFock%DependencyThreshold`

ExcludeCore**Type**

Bool

Description

If active, excludes core states from the calculation of the optimal imaginary time and frequency grids.

The core states are still included in all parts of the calculations.

In case a frozen core calculation is performed, this key is ignored.

For MP2 and double hybrid calculation, it defaults to false. For RPA and GW calculations, it defaults to true.

FitSetQuality**Type**

Multiple Choice

Default value

Auto

Options

[Auto, VeryBasic, Basic, Normal, Good, VeryGood]

Description

Specifies the fit set to be used in the MBPT calculation.

‘Normal’ quality is generally sufficient for basis sets up to and including TZ2P.

For larger basis sets (or for benchmarking purposes) a ‘VeryGood’ fit set is recommended. Note that the FitSetQuality heavily influences the computational cost of the calculation.

If not specified or ‘Auto’, the RIHartreeFock%FitSetQuality is used.

Formalism**Type**

Multiple Choice

Default value

Auto

Options

[Auto, RI, LT, All]

Description

Specifies the formalism for the calculation of the MP2 correlation energy.

‘LT’ means Laplace Transformed MP2 (also referred to as AO-PARI-MP2),

‘RI’ means that a conventional RI-MP2 is carried out.

If ‘Auto’, LT will be used in case of DOD double hybrids and SOS MP2, and RI will be used in all other cases.

‘All’ means that both RI and LT formalisms are used in the calculation.

For a RPA or GW calculation, the formalism is always LT, irrespective of the formalism specified with this key.

FrequencyGridType**Type**

Multiple Choice

Default value

LeastSquare

Options

[LeastSquare, GaussLegendre]

Description

Use Gauss-legendre grid for imaginary frequency integration in RPA and GW calculations instead of the usually used Least-Square optimized ones. Has the advantage that it can be systematically converged and an arbitrary number of grid points can be used. Typically more grid points will be needed to get the same level of accuracy. However, the convergence of the results with the size of the grid can be more systematic. These grids can only be used when Formalism is set to RI.

IntegrationQuality**Type**

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood]

Description

Specifies the integration quality to be used in the MBPT calculation. If not specified, the RI-HartreeFock%IntegrationQuality is used.

SigmaFunctionalParametrization**Type**

Multiple Choice

Default value

S1re

Options

[W1, W2, S1, S2, S1re]

Description

Only relevant if a sigma-functional calculation is performed. Possible choices for the parametrization of the sigma-functional. Not all options are supported for all functionals.

ThresholdQuality**Type**

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Controls the distances between atomic centers for which the product of two basis functions is not fitted any more. Especially for spatially extended, large systems, 'VERYBASIC' and 'BASIC' can lead to large computational savings, but the fit is also more approximate. If not specified, the RIHartreeFock%ThresholdQuality is used.

UseScaledZORA**Type**

Bool

Default value

Yes

Description

If true, use the scaled ZORA orbital energies instead of the ZORA orbital energies in the MBPT equations.

frozenscore**Type**

Bool

Default value

No

Description

Freeze core states in correlation part of MBPT calculation

nCore**Type**

Integer

Default value

0

GUI name

Number of core levels

Description

Number of core states which will be excluded from the correlated calculation.

Will be ignored if frozencore is false.

In case nothing is specified, the number of core levels will be determined automatically.

Needs to be smaller than the number of occupied states.

nFreqIntegration**Type**

Integer

Default value

32

GUI name

N freq points for G3W2 integration

Description

Number of imaginary frequency points for G3W2 integration

nFrequency**Type**

Integer

Default value

12

GUI name

N freq points

Description

Number of imaginary frequency points. This key is only relevant for RPA and GW and will be ignored if used in an AO-PARI-MP2 calculation. 12 Points is the default for a RPA calculation. It is technically possible to use a different number of imaginary frequency points than for imaginary time. The maximum number of points which can be requested for imaginary frequency integration is 42. Important note: The computation time and memory requirements roughly scale linearly with the number of imaginary frequency points. However, memory can be an issue for RPA and GW when the number of imaginary frequency points is high. In case a job crashes, it is advised to increase the number of nodes since the necessary memory distributes over all nodes.

nLambda**Type**

Integer

Default value

1

GUI name

Number of lambda points

Description

Size of coupling constant integration grid for SOSEX variants in RPA. Default is 4 points

nTime**Type**

Integer

GUI name

Number of time points

Description

Number of imaginary time points (only relevant in case the Laplace Transformed (LT) formalism is used).

In the many-body-perturbation theory module in ADF, the polarizability (or Kohn-Sham density response function) is evaluated in imaginary time to exploit sparsity in the AO basis. For MP2, this is often referred to as a Laplace transform. For MP2, 9 points are the default. This is a safe choice, guaranteeing accuracies higher than 1 Kj/mol for most systems (For many simple organic systems, 6 points are sufficient for good accuracy).

Only for systems with a very small HOMO-LUMO gap or low-lying core states (heavy elements starting from the 4th row of the periodic table) more points might be necessary.

In principle, the same considerations apply for RPA and GW as well, however, the accuracy requirements are somewhat higher and 12 point are the default for RPA. In a GW calculation, the number of points is adjusted according to the numerical quality. Using less than 9 points is strongly discouraged except for the simplest molecules.

In ADF2019, it can happen that the algorithm determining the imaginary time grid does not converge. In this case, the usual reason is that the number of points is too small and more points need to be specified. Starting from AMS2020, this does not happen any more. In case the imaginary time grid does not converge, the number of points is automatically adjusted until it does.

The computation time of AO-PARI-MP2, RPA, and GW scales linearly with the number of imaginary time points.

useGreenXgrids**Type**

Bool

Default value

No

Description

Use GreenX library to generate grid points. This is recommended for larger number of grid points (> 20). Up to 34 points can be requested.

MetaGGA**Type**

Bool

Default value

No

Description

ModifyExcitation

Type

Block

Description

DipStrength

Type

Float

Description

GRIMMEAEX

Type

Float

Description

GRIMMEALPHA

Type

Float

Description

GRIMMEBETA

Type

Float

Description

GRIMMEDEMAX

Type

Float

Description

GRIMMEPERTC

Type

Bool

Description

GRIMMETPMIN

Type

Float

Description

HighExcit

Type

Float

Description

NOGRIMMEPERTC

Type

Bool

Description**NOverlap****Type**

Integer

Default value

0

Description**OscStrength****Type**

Float

Description

Use only pairs of an occupied and virtual orbital as guess vectors, for which the oscillator strength of the single-orbital transition is larger than this value

SetLargeEnergy**Type**

Float

Default value

1000000.0

Unit

Hartree

Description

The orbital energies of the uninteresting occupied orbitals are changed to -epsbig Hartree, and the orbital energies of the uninteresting virtual orbitals are changed to epsbig Hartree

SetOccEnergy**Type**

Float

Description

All occupied orbitals that have to be used will change their orbital energy to this value. In practice only useful if one has selected one occupied orbital energy, and one want to change this to another value. Default: the orbital energies of the occupied orbitals that are used are not changed.

UseOccRange**Type**

Float List

Unit

Hartree

Description

Use only occupied orbitals which have orbital energies between the two numbers.

UseOccVirtNumbers**Type**

Integer List

Description

Use only pairs of an occupied and virtual orbital as guess vectors, for which in the sorted list

of the orbital energy differences, the number of the single-orbital transition is between the two numbers.

UseOccVirtRange**Type**

Float List

Unit

Hartree

Description

Use only pairs of an occupied and virtual orbital, for which the orbital energy difference is between the two numbers

UseOccupied**Type**

Non-standard block

Description

Use only the occupied orbitals which are specified

UseScaledZORA**Type**

Bool

Default value

No

Description

Use everywhere the scaled ZORA orbital energies instead of the ZORA orbital energies in the TDDFT equations. This can improve deep core excitation energies. Only valid if ZORA is used.

UseVirtRange**Type**

Float List

Unit

Hartree

Description

Use only virtual orbitals which have orbital energies between the two numbers

UseVirtual**Type**

Non-standard block

Description

Use only the virtual orbitals which are specified

ModifyStartPotential**Type**

Non-standard block

Description

Modify the starting spin-dependent potential for unrestricted calculations.

NoBeckeGrid

Type

Bool

Default value

No

Description

If true ADF will use the Voronoi numerical integration grid.

NoFDEPot**Type**

Bool

Default value

No

Description

Expert FDE option.

NoPrint**Type**

String

Recurring

True

Description

The amount of printed output is regulated with the keys Print, NoPrint, EPrint and Debug.

NoSharedArrays**Type**

Bool

Default value

No

Description

To disable the use of shared memory.

NoSymFit**Type**

Bool

Default value

No

Description

Do not use only an A1 symmetric fit.

NoTotEn**Type**

Bool

Default value

No

Description**NuclearModel**

Type

Multiple Choice

Default value

PointCharge

Options

[PointCharge, Gaussian]

Description

Model for the nuclear charge distribution.

To see effects from your choice you will need to use a basis set with extra steep functions. For example you can find these in the ZORA/TZ2P-J basis directory.

NumericalQuality**Type**

Multiple Choice

Default value

Normal

Options

[Basic, Normal, Good, VeryGood, Excellent]

Description

Set the quality of several important technical aspects of an ADF calculation (with the notable exception of the basis set). It sets the quality of: BeckeGrid (numerical integration) and Zlm-Fit (density fitting). Note: the quality defined in the block of a specific technical aspects supersedes the value defined in NumericalQuality (e.g. if I specify 'NumericalQuality Basic' and 'BeckeGrid%Quality Good', the quality of the BeckeGrid will be 'Good')

Occupations**Type**

String

Description

Occupations options

OPop_Analysis**Type**

String

Description**OrbitalsCoulombInteraction****Type**

Integer List

Recurring

True

Description

Compute the Coulomb interaction energy between the density of two orbitals. After the key, specify the indices of the two orbitals for which you want to compute the Coulomb interaction energy. Can only be used for spin-restricted calculations. Cannot be used in case of Symmetry (use Symmetry NoSym).

OrthFragPrep

Type

Bool

Default value

No

Description

Expert FDE option.

PertLoc**Type**

Block

Description

Perturbed localized molecular orbitals, correct to first order in an applied field, can be calculated in case of AORESPONSE. Can be used if the applied field changes the density in first order.

Alfa**Type**

Bool

Default value

No

Description

Analyze the static or dynamic polarizability

BField**Type**

Bool

Default value

No

Description

The perturbation is a magnetic field. Should be consistent with AORESPONSE

Beta**Type**

Bool

Default value

No

Description

Analyze the optical rotation parameter beta. The relation to G' is $\beta = -G'/\omega$. The optical rotation parameter beta is calculated directly and has a well-defined static limit, i.e. omega can be zero or non-zero

Diag**Type**

Bool

Default value

Yes

Description

Only analyze the diagonal of the response tensor

Dynamic

Type

Bool

Default value

No

Description

Should be used for a frequency dependent perturbation field.

EField**Type**

Bool

Default value

Yes

Description

The perturbation is an electric field

Fulltens**Type**

Bool

Default value

No

Description

The full tensor is analyzed

GPrime**Type**

Bool

Default value

No

DescriptionAnalyze the G' (gyration) tensor, for optical rotation dispersion. Requires a frequency dependent perturbation field, with a frequency (ω) unequal to zero.**Static****Type**

Bool

Default value

Yes

Description

should be used for a static field

POLTDFFT**Type**

Block

Description

POLTDFFT is a fast algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set. The (real and imaginary part of the) diagonal of the polarizability tensor and rotatory strengths will be calculated, which can be used to calculate the photoabsorption and circular dichroism (CD) spectra.

Analysis**Type**

Bool

Default value

No

Description

An analysis of the absorption and CD spectrum in terms of single orbital transitions.

CutOff**Type**

Float

Default value

4.0

Unit

eV

Description

For a given point in the spectrum, only include pairs of an occupied and virtual orbital, for which the orbital energy difference is lower than the energy of the point in the spectrum plus cutoff.

Enabled**Type**

Bool

Default value

No

GUI name

UV/Vis and CD spectrum

Description

Calculate UV/Vis and CD spectrum from the imaginary part of the polarizability tensor at any given photon energy. This avoids the bottleneck of Davidson diagonalization.

FreqRange**Type**

Float List

Default value

[0.0, 5.0]

Unit

eV

Description

Specifies a frequency range of frequencies of incident light, the perturbing field, at which the complex dynamical polarizability will be calculated. 2 numbers: an upper and a lower bound. Use subkey NFreq to specify the number of frequencies.

HDA_fitted**Type**

Bool

Default value

No

GUI name

Fitted HDA

Description

Use fit functions to calculate HDA (Hybrid diagonal approximation), only relevant for hybrids.

Irrep**Type**

Non-standard block

Description

Subblock key for selecting which symmetry irreps of the excitations to calculate (all excitations by default). In the subkey data block list the symmetry irrep labels, like B1, for example

KGrid**Type**

Float

Default value

9.0

Unit

eV

Description

Keyword KGRID is used to discretize the energy scale for calculating the complex dynamical polarizability. Only pairs of an occupied and virtual orbital are included, for which the orbital energy difference is lower than this value. Use key NGRID to set the number of points within the energy grid.

Lambda**Type**

Float

Default value

1.0

Description

Jacob's scaling factor for the study of plasmonic resonances.

This factor, $0 < \lambda < 1$, turns on the coupling matrix K.

Lifetime**Type**

Float

Default value

0.1

Unit

eV

Description

Specify the resonance peak width (damping).

Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule,

however, the values do not vary a lot between similar molecules, so it is not hard to estimate values.

NFreq**Type**

Integer

Default value

100

Description

NFreq is the number of frequencies of incident light, the perturbing field, at which the complex dynamical polarizability will be calculated. Use FreqRange to specify the frequency range.

NGrid**Type**

Integer

Default value

180

Description

Ngrid is the number of points within the energy grid.

N_FitOrb**Type**

Integer

Default value

1000000000

Description

The number of vectors containing the coefficients we use to expand the projection of each fitting function over the electron density (of a particular molecular orbital) as a linear combination of overlap matrices between fitting functions pair

N_HDA_integral**Type**

Integer

Default value

1000000000

Description**N_SubMatricesAk****Type**

Integer

Default value

1000000000

Description**Print_Int_Time****Type**

Integer

Default value

0

Description

Print detailed timing during calculation of integrals of Tape63 and Tape64

RegionsForAnalysis**Type**

String

Description

Names of regions for analysis per region using the fragment projection analysis approach. Will split the absorption and CD spectrum in region_i -> region_j terms.

Velocity**Type**

Bool

Default value

No

GUI name

Velocity representation

Description

If True, ADF calculates the dipole moment in velocity gauge.

If false: dipole-length representation is used

Print**Type**

String

Recurring

True

Description

The amount of printed output is regulated with the keys Print, NoPrint, EPrint and Debug.

QMFO**Type**

Block

Description

Block input key for QM/(w)FQ(FMu).

AtomType**Type**

Block

Recurring

True

Description

Definition of atomic types in MM environment

Alpha**Type**

Float

Description

Polarizability of FQFMU atom

Area**Type**

Float

Description

Effective charge-transfer area time between same-type wFQ atoms

Charge**Type**

Float

Description

MM fixed charge (non-polarizable only)

Chi**Type**

Float

Description

Electronegativity of FQ atom

Dfermi**Type**

Float

Description

wFQ d parameter for Fermi damping

Efermi**Type**

Float

Description

Fermi Energy of wFQ carbon-based structure

Eta**Type**

Float

Description

Chemical Hardness of FQ atom

R0**Type**

Float

Description

wFQ R0 parameter for Fermi damping

Sfermi**Type**

Float

Description

wFQ s parameter for Fermi damping

Sigma0**Type**

Float

Description

Static conductivity time of wFQ atom

Symbol**Type**

String

Description

Symbol associated with atom type

Tau**Type**

Float

Description

Scattering time of wFQ atom

wFQFMuFile**Type**

String

Description

The absolute path to the wFQFMu interband polarizability file

Coords**Type**

Non-standard block

Description

Coordinates and fragment information (FQ only)

FDERESP**Type**

Bool

Default value

No

Description

In response calculations (TD), the polarization contribution of the FDE part is introduced at the FQ level [See F. Egidi et al. J. Chem. Phys. 2021, 154, 164107].

Forcefield**Type**

Multiple Choice

Default value

FQ

Options

[FQ, FQFMU, wFQ, wFQ_RQ, wFQFmu, wFQFmu_RQRMU]

Description

Version of the FQ family of polarizable forcefields

Frozen**Type**

Bool

Default value

No

Description

Expert option. Do not introduce polarization effect in response calculations.

Kernel**Type**

Multiple Choice

Default value

OHNO

Options

[OHNO, COUL, GAUS]

Description

Expert option. KERNEL can be used to choose the functional form of the charge-charge interaction kernel between MM atoms. Recommended is to use the default OHNO. The COUL screening is the standard Coulomb interaction $1/r$. The OHNO choice introduce the Ohno functional (see [K. Ohno, Theoret. Chim. Acta 2, 219 (1964)]), which depends on a parameter n that is set equal to 2. Finally, the GAUS screening models each FQ charge by means of a spherical Gaussian-type distribution, and the interaction kernel is obtained accordingly. For QM/FQFMU only GAUS SCREEN is implemented.

LifeFrequency**Type**

Float

Default value

0.0

Description

Input frequency for calculating TDDFT/wFQ(Fmu) lifetimes

LifeState**Type**

Integer

Default value

0

Description

Target excited state for state-specific TDDFT/wFQ(Fmu) lifetimes

MolCharge**Type**

Float

Default value

0.0

Description

Total charge of each fragment (FQ only)

NonEle**Type**

Multiple Choice

Default value

LJ

Options

[LJ, None]

Description

Whether to include non-electrostatic contributions to the energy. Default is the Lennard-Jones (LJ) model.

QMSCREEN**Type**

Multiple Choice

Default value

GAUS

Options

[ERF, EXP, GAUS, NONE]

Description

Expert option. QMSCREEN can be used to choose the functional form of the charge-charge interaction kernel between MM atoms and the QM density. The screening types available are ERF (error function), EXP (exponential), GAUS (Gaussian), or NONE. The default is GAUS.

QMSCREENFACTOR**Type**

Float

Default value

0.2

Description

Expert option. Sets the QM/MM interaction kernel screening length. Recommended is to use the default value 0.2 with the GAUS QM/MM screening function.

ReadDynamicMatrix**Type**

String

Description

The absolute path to the decomposed wFQ(FMu) matrix file

QTAIM**Type**

Block

Description

This block is used to request a topological analysis of the gradient field of the electron density, also known as the Bader's analysis. If this block is specified without any sub-key, only local properties are calculated.

AnalysisLevel

Type

Multiple Choice

Default value

Normal

Options

[Normal, Extended, Full]

Description

Set the level of the QTAIM analysis:

Normal - topology analysis and properties at the density critical points,

Extended - same as Normal plus condensed atomic descriptors, plus basin information on TAPE10

Full - same as Extended plus non-local descriptors.

AtomsToDo**Type**

Integer List

GUI name

Include atoms

Description

List of atoms for which condensed descriptors are to be calculated. By default all atoms are included.

Enabled**Type**

Bool

Default value

No

GUI name

Perform QTAIM analysis

Description

Calculate QTAIM (also known as Bader) properties.

Energy**Type**

Bool

Default value

No

GUI name

Atomic energies

Description

Calculate atomic energies. Requires an all-electron calculation (no frozen core), triggers the TotalEnergy and increases the [AnalysisLevel] to at least Extended.

Source**Type**

Bool

Default value

No

GUI name

Source Function

Description

Calculate the Source Function at BCPs and RCPs.

Spacing**Type**

Float

Default value

0.5

Unit

Bohr

Description

Specifies spacing of the initial Cartesian grid when searching for critical points. It may be useful to specify a smaller value than the default if some critical points are missed. This will result in a more accurate but slower calculation.

QTens**Type**

Bool

Default value

No

Description

Calculate the the Nuclear Electric Quadrupole Hyperfine interaction (Q-tensor, NQCC, NQI), related to the Electric Field Gradient (EFG).

RadialCoreGrid**Type**

Block

Description

For each atom the charge densities and the coulomb potentials of frozen core and valence electrons are computed in a radial grid. The radial grid consists of a sequence of r-values, defined by a smallest value, a constant multiplication factor to obtain each successive r-value, and the total number of points. Equivalently it can be characterized by the smallest r-value, the largest r-value, and the number of points; from these data the program computes then the constant multiplication factor.

NRad**Type**

Integer

Default value

5000

Description

The number of radial grid points

RMax

Type

Float

Default value

100.0

Unit

Angstrom

Description

The largest distance in the radial grid

RMin**Type**

Float

Default value

1e-06

Unit

Angstrom

Description

The shortest distance used in the radial grid

Relativity**Type**

Block

Description

Options for relativistic effects.

Formalism**Type**

Multiple Choice

Default value

ZORA

Options

[Pauli, ZORA, X2C, RA-X2C]

Description

Note that if Level is None, no relativistic effects are taken into account, irrespective of the chosen formalism.

Pauli stands for the Pauli Hamiltonian.

ZORA means the Zero Order Regular Approximated Hamiltonian, recommended.

X2C and RA-X2C both stand for an exact transformation of the 4-component Dirac equation to 2-components.

X2C is the modified Dirac equation by Dyal.

RA-X2C is the regular approach to the modified Dirac equation.

Level**Type**

Multiple Choice

Default value

Scalar

Options

[None, Scalar, Spin-Orbit]

GUI name

Relativity

Description

None: No relativistic effects.

Scalar: Scalar relativistic.

This option comes at very little cost.

Spin-Orbit: Spin-orbit coupled.

This is the best level of theory, but it is (4-8 times) more expensive than a normal calculation. Spin-orbit effects are generally quite small, unless there are very heavy atoms in your system, especially with p valence electrons (like Pb).

See also the SpinOrbitMagnetization subkey.

Potential**Type**

Multiple Choice

Default value

MAPA

Options

[MAPA, SAPA]

Description

Starting from ADF2017 instead of SAPA (the Sum of neutral Atomic potential Approximation) MAPA is used by default for ZORA. The MAPA (the Minimum of neutral Atomic potential Approximation) at a point is the minimum of the neutral Atomic potentials at that point. Advantage of MAPA over SAPA is that the gauge dependence of ZORA is reduced. The ZORA gauge dependency is small for almost all properties, except for the electron density very close to a heavy nucleus. The electron density very close to a heavy nucleus can be used for the interpretation of isomer shifts in Mossbauer spectroscopy.

SpinOrbitMagnetization**Type**

Multiple Choice

Default value

CollinearZ

Options

[NonCollinear, Collinear, CollinearX, CollinearY, CollinearZ]

Description

Relevant only for spin-orbit coupling and if unrestricted key has been activated.

Most XC functionals have as one ingredient the spin polarization in case of unrestricted calculations. Normally the direction of the spin quantization axis is arbitrary and conveniently chosen to be the z-axis.

However, in a spin-orbit calculation the direction matters, and it is arbitrary to put the z-component of the magnetization vector into the XC functional. There is also the exotic option to choose the quantization axis along the x or y axis.

It is also possible to plug the size of the magnetization vector into the XC functional. This is called the non-collinear approach.

- NonCollinear: the non-collinear method.
- CollinearXYZ: use the x, y, or z component as spin polarization for the XC functional.
- Collinear: the same as CollinearZ.

RemoveAllFragVirtuals

Type

Bool

Default value

No

Description

Remove all virtual fragment orbitals.

RemoveFragOrbitals

Type

Non-standard block

Description

Block key to remove selected virtual fragment orbitals.

RemoveOtherFragVirtuals

Type

Bool

Default value

No

Description

Remove all virtual fragment orbitals, except on first fragment.

Response

Type

Block

Description

The calculation of frequency-dependent (hyper)polarizabilities and related properties (Raman, ORD)

ALLCOMPONENTS

Type

Bool

Description

ALLHYPER

Type

Bool

Description

ALPHAINANG

Type
Bool

Description

ANALYTIC

Type
Bool

Description

AllCycles

Type
Bool

Default value
No

Description
Convergence printout

AllTensor

Type
Bool

Default value
No

Description
Higher dispersion coefficients are also calculated

C8

Type
Bool

Description

CUTTAILS

Type
Bool

Description

DYNAHYP

Type
Bool

Description

Dipole

Type
Bool

Description

DmpDII

Type

Float

Default value

0.8

Description

DmpRsp

Type

Float

Default value

0.9

Description

ERABSX

Type

Float

Default value

1e-06

Description

ERRALF

Type

Float

Default value

1e-05

Description

ERRTMX

Type

Float

Default value

1e-06

Description

EpsRho

Type

Float

Description

Rho threshold

FXCALPHA

Type

Float

Description

Frequencies

Type

Float List

Default value

[0.0]

Unit

eV

Description

List of frequencies of incident light, the perturbing field, at which the time-dependent properties will be calculated.

GXCALPHA**Type**

Float

Description**HyperPol****Type**

Float

Default value

0.0

Unit

Hartree

Description**IFILES****Type**

Integer

Default value

0

Description

Integration run including external files. Used for Van der Waals dispersion coefficients calculations.

IPRESP**Type**

Integer

Default value

1

Description**IReal****Type**

Integer

Default value

1

Description**KSORBRUN****Type**

Bool

Description**MAGNETICPERT****Type**

Bool

Description**MAXWAALS****Type**

Integer

Default value

8

Description**NCycMx****Type**

Integer

Default value

30

Description**NUMERIC****Type**

Bool

Description**OPTICALROTATION****Type**

Bool

Description**Octupole****Type**

Bool

Description**Quadrupole****Type**

Bool

Description**Raman****Type**

Bool

Description**STARTREALGR****Type**

Bool

Description**SYMRUN****Type**

Bool

Description**Temperature****Type**

Float

Default value

300.0

Unit

Kelvin

Description

Wavelength of incoming light is equal to the wavelength at which the calculation is performed and temperature is equal to room temperature (300K) Total Raman band is default, not the Q-branch of diatomic. (Relevant for Raman scattering cross section)

VANDERWAALS**Type**

Integer

Description**VERDET****Type**

Float

Default value

0.01

Description

For numerical differentiation $d\alpha(\omega)/d\omega$, needed for Verdet constant, the default frequencies are $\omega + d\text{verdt}$ and $\omega - d\text{verdt}$

ResponseFormalism**Type**

Multiple Choice

Default value

Auto

Options

[Auto, Response, AOResponse]

Description

Set to RESPONSE or AORESPONSE.

RESPPMATSAVE**Type**

Bool

Default value

No

Description

Needed for SubResponse (EO) calculations. Hacked by JN. Restored by Pengchong Liu

Restart**Type**

Block

Description

Options for restarts

NoOrb**Type**

Bool

Default value

No

GUI name

Ignore orbitals

Description

Do not use orbitals from the restart file

NoSCF**Type**

Bool

Default value

No

GUI name

Ignore SCF fit coefficients

Description

Do not use any fit coefficients from the restart file as a first approximation to the (fitted) SCF density for the new calculation. Instead, the sum-of-fragments density will be used, as in a non-restart run. Note, typically noSCF should be used in combination with noORB.

NoSmear**Type**

Bool

Default value

No

GUI name

Ignore smearing

Description

Do not use any electron smearing data from the restart file.

SpinFlip**Type**

Integer List

GUI name

Spin flip on restart for

Description

Select the atoms for which the spin is to be flipped upon restart.

RESTOCC**Type**

Bool

Default value

No

Description**RIHartreeFock****Type**

Block

Description**DependencyCoreRange****Type**

Float

Description

Basis functions may be given a core character based on the range. For now only active in Band and only if present in the input

DependencyThreshold**Type**

Float

Default value

0.001

Description

To improve numerical stability, almost linearly-dependent combination of basis functions are removed from the Hartree-Fock exchange matrix.

If you obtain unphysically large bond energy in an Hybrid calculation, or an unphysically low correlation energy in an RPA, MP2, or double hybrid calculation, you might try setting the DependencyThreshold to a larger value (e.g. 3.0E-3)

Note, that in GW calculations and GW-BSE calculations the default for this key is 5.0e-3.

ExplicitThresholds**Type**

Block

Description

Override the thresholds as implied by the ThresholdQuality.

Basis**Type**

Float

Description

Threshold for the basis functions.

Fit**Type**

Float

Description

Threshold for the fit functions.

Potential**Type**

Float

Description

Threshold for the potential of the functions.

FitGenerationDetails**Type**

Block

Description

Technical details about how the RI Hartree-Fock fit functions are generated.

BoostL**Type**

Bool

Default value

No

Description

Add extra $\max(l)+1$ diffuse function

When l denotes the highest angular momentum present in the primary basis,

FromBasisProducts will generate auxiliary fit functions with up to $2l$ angular momentum.

When this key is set to true, the maximum angular momentum in the auxiliary fit set becomes $2l+2$.

Typically, this option is not needed and when precision issues arise, it is rather advised to adjust the OneCenterDependencyThreshold key to a smaller value.

LapackWorkAround**Type**

Bool

Default value

No

Description

GetFitFunctionsForAtomType diagonalization done with Lapack instead of Scalapack

Method**Type**

Multiple Choice

Default value

Auto

Options

[Auto, FromBasisProducts]

Description

The way in which fit functions are generated. The main distinction is whether it depends on the basis functions used.

When FromBasisProducts is used, the auxiliary basis is generated directly from the products of primary basis functions.

This has the advantage that the auxiliary fit adapts automatically to the basis set size.

Especially for basis sets of QZ quality or larger, this is often necessary to obtain highly precise correlation energies using RPA or double hybrids

FromBasisProducts option is also useful for GW or BSE calculations with basis sets of QZ quality or larger.

OneCenterDependencyThreshold

Type

Float

Default value

1e-08

Description

This key is only active when FromBasisProducts is chosen as method to generate the auxiliary basis.

This threshold controls the size, and at the same time, the precision of the auxiliary basis set. A smaller number leads to a larger auxiliary fit set.

The default value of 1e-8 is typically sufficient to converge correlation energies and QP energies to a very high precision.

It corresponds to an auxiliary basis which is typically 8-9 times larger than the primary basis.

UseBandRadialGrid

Type

Bool

Default value

Yes

Description

Only applies to band. The band logarithmic grid ranges (by default) from 1e-6 to 100 with 3000 points. Otherwise 300 points will be used.

For 0-periodicity (molecules) it is advisable to set this key to false since lots of memory is needed to evaluate all necessary integrals.

FitSetQuality

Type

Multiple Choice

Default value

Auto

Options

[Auto, VeryBasic, Basic, Normal, Good, VeryGood, Excellent, FromBasisProducts]

Description

The quality of auxiliary fit set employed in the RI scheme.

If 'Auto', the value of the RIHartreeFock Quality option will be used.

Normal quality is generally sufficient for basis sets up to and including TZ2P.

For larger basis sets (or for benchmarking purposes) a VeryGood fit set is recommended.

Note that the FitSetQuality heavily influences the computational cost of the calculation.

IntegrationQuality

Type

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Quality of the numerical integration for evaluating the integrals between basis functions and fit functions. If IntegrationQuality is not defined in input, the value defined in RI-HartreeFock%Quality will be used.

Quality

Type

Multiple Choice

Default value

Auto

Options

[Auto, VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Numerical accuracy of the RI procedure. If 'Auto', the quality specified in the 'NumericalQuality' will be used.

QualityPerRegion

Type

Block

Recurring

True

Description

Sets the fit-set quality for all atoms in a region. If specified, this overwrites the globally set quality.

Quality

Type

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

This region's quality of the auxiliary fit set employed in the RI scheme.

Region

Type

String

Description

The identifier of the region for which to set the quality.

ResponseQuality

Type

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Numerical accuracy of the RI procedure for the Response module.

ThresholdQuality**Type**

Multiple Choice

Options

[VeryBasic, Basic, Normal, Good, VeryGood, Excellent]

Description

Linear scaling thresholds (also used for determining at what range the multiple approximation is used). To disable all linear scaling thresholds set this to Excellent.

UseMe**Type**

Bool

Default value

Yes

Description

Set to False if you want to use the old RI scheme (ADF only)

RISM**Type**

Non-standard block

Description

3D-RISM-related input keys.

ROSE**Type**

Block

Description

Options for orbital localization

Additional_virtuals_cutoff**Type**

Float

Default value

2.0

Unit

Hartree

GUI name

Additional virtuals cutoff

Description

Specifies the energy threshold to determine the number of additional hard virtuals to localize for the supermolecule. If not specified the default value is used.

Exponent

Type

Integer

Description

The value of the exponent (for the default Pipek-Mezey type of localization, the exponent is equal to 2. A higher value of 3 or 4 is sometimes useful.).

Frag_bias**Type**

Float List

Description

Expert key. Specifies the bias applied to each fragment when assigning the localized orbitals to a particular fragment. Use a negative value for default behavior for a given fragment. If not specified, or if the number of items is unequal the number of fragments, a default bias is used.

Frag_threshold**Type**

Float

Default value

10.0

Unit

Hartree

GUI name

Frag threshold

Description

Specifies energy threshold to determine number of reference hard virtuals to use for the fragments (needed to localize the additional hard virtuals). The total number of reference virtuals should be larger than the number of virtual MOs to localize (similar to having more reference valence orbitals than occupied valence orbitals to localize), so it is advisable to use a relatively high value for this parameter. If not specified the default value is used.

Frag_valence**Type**

Integer List

Description

Expert key. Specifies the number of valence orbitals for each fragment. Use a negative value for default behavior for a given fragment. If not specified, or if the number of items is unequal the number of fragments, by default the code generates the valence space for each fragment as the sum of valence orbitals of individual atoms within each fragment.

FragmentFile**Type**

String

Recurring

True

Description

Path (either absolute or relative) of each fragment file. The number of fragments used to project on will be number of occurrences of this key.

Version

Type

Multiple Choice

Options

[Stdndr_2013, Simple_2013, Simple_2014]

Description

Expert key, specifies version of the IAO generation. If not specified a default value is used.

nfragments**Type**

Integer

Default value

2

Description

Expert key, preferably use the FragmentFile key for each fragment instead, and do not use this key. If the FragmentFile key is not used, then with this key one can specify the number of fragments used to project on. If this key is used the fragment file names should be called frag1.rkf, frag2.rkf, etcetera, and should be present at the directory where ams is started.

Save**Type**

String

Recurring

True

Description

A sequence of file names separated by blanks or commas. Possible file names are TAPE10, TAPE13, TAPE14.

scaledkinfunctionals**Type**

Bool

Default value

No

Description

FDE option.

SCF**Type**

Block

Description

Control aspects of the Self Consistent Field procedure

AccelerationMethod**Type**

Multiple Choice

Default value

ADIIS

Options

[ADIIS, fDIIS, LISTb, LISTf, LISTi, MESA, SDIIS]

Description

SCF acceleration method.

The default method is ADIIS, which is actually a mix of A-DIIS and SDIIS: A-DIIS is used at the start of the SCF and SDIIS is used closer to convergence, with a smooth switching function.

The other methods are from the LIST family developed by Alex Wang and co-workers. They may perform better than the default in some situations.

Setting AccelerationMethod to SDIIS effectively disables A-DIIS and is equivalent to the legacy mixing+DIIS method.

Converge**Type**

Float List

Default value

[1e-06, 0.001]

Description

The criterion to stop the SCF updates.

The tested error is the commutator of the Fock matrix and the P-matrix (=density matrix in the representation of the basis functions) from which the F-matrix was obtained. This commutator is zero when absolute self-consistency is reached. Convergence is considered reached when the maximum element falls below SCFcvn and the norm of the matrix below 10*SCFcvn. The default is fairly strict.

A second criterion which plays a role when the SCF procedure has difficulty converging. When in any SCF procedure the currently applicable criterion does not seem to be achievable, the program stops the SCF. When the secondary criterion (sconv2) has been met, only a warning is issued and the program continues normally.

DIIS**Type**

Block

Description

The maximum number of SCF cycles allowed.

BFac**Type**

Float

Default value

0.0

GUI name

Bias DIIS towards latest vector with

Description

By default, the latest vector is not favored in the DIIS algorithm (value 0.0). A sensible value would be 0.2.

CX**Type**

Float

Default value

5.0

GUI name

Reduce DIIS space when coefs >

Description

The DIIS space is reduced when very large DIIS coefficients appear. The value is the threshold.

CXX**Type**

Float

Default value

25.0

GUI name

No DIIS (but damping) when coefs >

Description

When very large DIIS coefficients appear, switch to traditional damping. The value is the threshold.

Cyc**Type**

Integer

Default value

5

GUI name

Start DIIS anyway at cycle

Description

When A-DIIS is disabled, the Pulay DIIS will start at this iteration irrespective of the DIIS OK value.

N**Type**

Integer

Default value

10

GUI name

Size of DIIS space

Description

The number of expansion vectors used for accelerating the SCF. The number of previous cycles taken into the linear combination is then $n-1$ (the new computed potential is also involved in the linear combination)

Ok**Type**

Float

Default value

0.5

GUI name

Start DIIS when $\max [F,P] <$

Description

The Pulay DIIS starting criterion, when A-DIIS is disabled,

Iterations**Type**

Integer

Default value

300

GUI name

Maximum number of SCF cycles

Description

The maximum number of SCF cycles allowed.

LShift**Type**

Float

Default value

0.0

Unit

Hartree

GUI name

Level shift

Description

The level shifting parameter.

The diagonal elements of the Fock matrix, in the representation of the orbitals of the previous iteration, are raised by vshift hartree energy units for the virtual orbitals. This may help to solve convergence problems when during the SCF iterations charge is sloshing back and forth between different orbitals that are close in energy and all located around the Fermi level.

Level shifting is not supported in the case of Spin-Orbit coupling.

At the moment properties that use virtuals, like excitation energies, response properties, NMR calculations, will give incorrect results if level shifting is applied.

LShift_cyc**Type**

Integer

Default value

1

Description

Specifies that level shifting is not turned on before the given SCF cycle number (for the start-up geometry).

LShift_err**Type**

Float

Default value

0.0

Description

Specifies that level shifting will be turned off by the program as soon as the SCF error drops below a threshold.

MESA**Type**

String

Description**Mixing****Type**

Float

Default value

0.2

GUI name

Mixing (% new vector included)

Description

When none of the SCF acceleration methods is active, the next Fock matrix is determined $F = \text{mixing} * F_n + (1 - \text{mixing})F_{(n-1)}$.

Mixing1**Type**

Float

Default value

0.2

GUI name

Mixing 1st SCF cycle

Description

The mixing parameter at the 1st SCF cycle.

OldSCF**Type**

Bool

Default value

No

Description

Disable the default SCF algorithm and use the old SCF algorithm.

The default SCF improves performance for big systems on big machines (when your calculation uses many tasks).

It is also recommended for machines with slow disk I/O as it writes less data to disk.

The default convergence method supported is A-DIIS, but LISTi is also supported.

ROSCF**Type**

Block

Description

Settings for the ROSCF method.

Alpha**Type**

Float List

Default value

[0.5, 0.5, 0.5]

Description

Coefficients to build the alpha-spin orbital contribution to the diagonal closed-, open-, and virtual-shell blocks of the Fock matrix. The beta-spin orbital contributions are 1.0 minus the alpha ones.

SCRf**Type**

Non-standard block

Description

SCRf is no longer supported. Use AMS2023 or earlier.

SelectExcitation**Type**

Block

Description**DipStrength****Type**

Float

Description**GRIMMEAEX****Type**

Float

Description**GRIMMEALPHA****Type**

Float

Description**GRIMMEBETA****Type**

Float

Description**GRIMMEDEMAX****Type**

Float

Description**GRIMMEPERTC****Type**

Bool

Description**GRIMMETPMIN****Type**

Float

Description**HighExcit****Type**

Float

Description**NOGRIMMEPERTC****Type**

Bool

Description**NOverlap****Type**

Integer

Default value

0

Description**OscStrength****Type**

Float

Description

Use only pairs of an occupied and virtual orbital as guess vectors, for which the oscillator strength of the single-orbital transition is larger than this value

SetLargeEnergy**Type**

Float

Default value

1000000.0

Unit

Hartree

Description

The orbital energies of the uninteresting occupied orbitals are changed to -epsbig Hartree, and the orbital energies of the uninteresting virtual orbitals are changed to epsbig Hartree

SetOccEnergy**Type**

Float

Description

All occupied orbitals that have to be used will change their orbital energy to this value. In practice only useful if one has selected one occupied orbital energy, and one want to change

this to another value. Default: the orbital energies of the occupied orbitals that are used are not changed.

UseOccRange**Type**

Float List

Unit

Hartree

Description

Use only occupied orbitals which have orbital energies between the two numbers.

UseOccVirtNumbers**Type**

Integer List

Description

Use only pairs of an occupied and virtual orbital as guess vectors, for which in the sorted list of the orbital energy differences, the number of the single-orbital transition is between the two numbers.

UseOccVirtRange**Type**

Float List

Unit

Hartree

Description

Use only pairs of an occupied and virtual orbital, for which the orbital energy difference is between the two numbers

UseOccupied**Type**

Non-standard block

Description

Use only the occupied orbitals which are specified

UseScaledZORA**Type**

Bool

Default value

No

Description

Use everywhere the scaled ZORA orbital energies instead of the ZORA orbital energies in the TDDFT equations. This can improve deep core excitation energies. Only valid if ZORA is used.

UseVirtRange**Type**

Float List

Unit

Hartree

Description

Use only virtual orbitals which have orbital energies between the two numbers

UseVirtual**Type**

Non-standard block

Description

Use only the virtual orbitals which are specified

SFTDDFT**Type**

Bool

Default value

No

GUI name

Spin-flip excitations

Description

Calculate spin-flip excitation energies (requires TDA and FORCEALDA keys).

SharcoOverlap**Type**

Bool

Default value

No

Description**Skip****Type**

String

Recurring

True

Description

Expert key. To restrict which parts of the program are actually executed.

SlaterDeterminants**Type**

Non-standard block

Description

The calculation of the one-determinant states based on the AOC reference state is controlled with this key.

Solvation**Type**

Block

Description**ARO****Type**

Float

	Description
Acid	
	Type
	Float
	Description
Ass	
	Type
	Bool
	Description
Base	
	Type
	Float
	Description
BornC	
	Type
	Float
	Description
	Coulomb constant for Born
C-Mat	
	Type
	String
	Description
COSKFAtoms	
	Type
	Integer List
	Recurring
	True
	Description
	This subkey COSKFATOMS specifies for which nuclei the segments in the COSMO section of the COSKF file should be used. Default all nuclei should be used, i.e. as for omitting the subkey COSKFATOMS. The numbers refer to the input ordering in the ADF calculation.
Charged	
	Type
	String
	Description
Chga1	
	Type
	Float
	Description
CsmRsp	

	Type
	Bool
	Description
Cust	
	Type
	String
	Description
Debug	
	Type
	String
	Description
Disc	
	Type
	String
	Description
Div	
	Type
	String
	Description
EPS	
	Type
	Float
	Description
ForceCosmo	
	Type
	String
	Description
HALO	
	Type
	Float
	Description
Lpr	
	Type
	Bool
	Description
NoAss	
	Type
	Bool
	Description

NoCsmRsp**Type**

Bool

Description**NoLpr****Type**

Bool

Description**NoPVec****Type**

Bool

Description**PVec****Type**

Bool

Description**PrintSM12****Type**

Bool

Description**RADII****Type**

Non-standard block

Description**RadSolv****Type**

Float

Description**Ref****Type**

Float

Description**SCF****Type**

String

Description**SM12SolvationPotential****Type**

Multiple Choice

Default value

CM5

Options

[CM5, CHELPG, RESP]

Description

Partial Charges to use in SCRF for SM12

SM12espgridorder**Type**

Integer

Default value

19

Description

ESP Lebedev Grid order for SM12 CHELPG and RESP. Accepted values are 19, 23, 29,31, and 41

SM12espgridspacing**Type**

Float

Default value

0.5

Unit

Angstrom

Description

ESP Lebedev Grid spacing for SM12 CHELPG and RESP in Angstrom. Sensible choices are 0.1, 0.2, 0.3 or 0.5 Angstrom.

SM12printSCRF**Type**

Bool

Default value

No

Description

Print Control for SM12 SCRF data

Solv**Type**

String

Description

Solvent details

Surf**Type**

Multiple Choice

Default value

delley

Options

[wsurf, asurf, esurf, klamt, delley, wsurf nokeep, asurf nokeep, esurf nokeep, klamt nokeep, delley nokeep]

Description

Defines the type of cavity to be used.

Tens**Type**

Float

Description**SOMCD****Type**

Bool

Default value

No

Description

MCD option. Required for a calculation of MCD temperature-dependent C terms. The calculation must be an unrestricted and scalar relativistic ZORA.

SOPert**Type**

Block

Description

Key for perturbative inclusion of spin-orbit coupling.

EShift**Type**

Float

Default value

0.2

Description

The actually calculated eigenvalues are calculated up to the maximum singlet-singlet or singlet-triplet scalar relativistic excitation energy plus eshift (in Hartree).

GSCorr**Type**

Bool

Default value

Yes

GUI name

Include GS

Description

The singlet ground state is included, which means that spin-orbit coupling can also have some effect on energy of the ground state. The spin-orbit matrix in this case is on basis of the ground state and the singlet and triplet excited states.

NCalc

Type

Integer

Description

Number of spin-orbit coupled excitation energies to be calculated. Default (and maximum) value: 4 times the number of scalar relativistic singlet-singlet excitations.

sozero**Type**

Bool

Default value

No

Description

Debug option to set spin-orbit matrix to zero.

SpinOrbitMagnetization**Type**

Block

Description

Starting artificial spin-orbit magnetization at first SCF cycle

PerRegion**Type**

Block

Recurring

True

Description

Defines the starting spin-polarization direction for all atoms in a region. Note that if this keyword is used multiple times, the chosen regions may not overlap.

Direction**Type**

Float List

Default value

[0.0, 0.0, 1.0]

Description

The starting spin-polarization direction for a region.

Region**Type**

String

Description

The identifier of the region for which to define the starting spin-polarization direction.

Strength**Type**

Float

Default value

0.2

Unit

Hartree

Description

Strength of artificial spin-polarization in this region

Strength**Type**

Float

Default value

0.2

Unit

Hartree

Description

Strength of artificial spin-polarization at first SCF cycle

SpinPolarization**Type**

Float

Description

The spin polarization of the system, which is the number of spin-alpha electrons in excess of spin-beta electrons. Specification is only meaningful in a spin-unrestricted calculation. However, specification is not meaningful in an unrestricted Spin-Orbit coupled calculation using the (non-)collinear approximation.

STContrib**Type**

Bool

Default value

No

Description

For an analysis of spin-orbit coupled excitations in terms of scalar relativistic singlet and triplet excitations. In order to get this analysis one needs to perform a scalar relativistic TDDFT calculation of excitation energies on the closed shell molecule first, and use the resulting adf.rkf as a fragment in the spin-orbit coupled TDDFT calculation of excitation energies, including this keyword STCONTRIB.

STOFit**Type**

Bool

Default value

No

Description

Computation of the Coulomb potential with the pair fit method.

StopAfter**Type**

String

Description

SubExci**Type**

Block

Description

Subsystem TDDFT (FDE)

CICoupl**Type**

Bool

Default value

No

Description

Within the Tamm-Dancoff Approximation, the couplings between localized excited states on different subsystems correspond directly to so-called exciton couplings. The CICOUPL keyword, in conjunction with TDA, prints these exciton couplings. It is also possible to use CICOUPL with full FDEc-TDDFT. In that case, the excitonic couplings between monomers are reconstructed from an effective 2x2 CIS-like eigenvalue problem.

COULKERNEL**Type**

Bool

Default value

Yes

Description**COUPLBLOCK****Type**

Bool

Default value

No

Description**COUPLSYS****Type**

Integer List

Description**CPLTAPE****Type**

String

Description**CThres****Type**

Float

Default value

30.0

Unit

eV

Description

all excitations of all subsystems (present on the fragment TAPE21 files) with an excitation energy that differs by less than coupling_threshold. From one of the reference states are selected to be included in the coupling. Note that additional excited states of system 1 may be included here.

DIPVEL**Type**

Bool

Default value

No

Description**DiagType****Type**

Multiple Choice

Default value

EXACT

Options

[EXACT]

Description**EIGPRINT****Type**

Integer

Default value

100

Description**ETHRES****Type**

Float

Default value

0.0

Unit

eV

Description

Threshold for effective coupling

EXTERNALORTHO**Type**

Float

Default value

1000000.0

Description

EO factor

FULLGRID**Type**

Bool

Default value

No

Description**InvGuess****Type**

Multiple Choice

Default value

EigVal-OrbDiff

Options

[EigVal-OrbDiff, OrbDiff-OrbDiff, Exact]

Description

Type of states to be coupled

LOCALFXCK**Type**

Bool

Default value

No

Description**Lowest****Type**

Integer

Default value

10

Description

The selection of the excited states to be coupled consists of two steps

NITER**Type**

Integer

Default value

1

Description**NOINTERSOLV****Type**

Bool

Default value

No

Description**NOSOLVCCHECK****Type**

Bool

Default value

No

Description**ONEGRID****Type**

Bool

Default value

No

Description**OptStates****Type**

Integer List

Description

If the keyword OPTSTATES is given, only those excited states of the first subsystem are considered as reference states that are given in this list.

PFRAGOUT**Type**

Bool

Default value

No

Description**PTHRES****Type**

Float

Default value

1.0

Description**SETDIAG****Type**

Float

Description**SFThres****Type**

Float

Default value

1e-05

Description

To reduce the computational effort, it is possible to ignore the effect of orbital pairs with coefficients less than `solutionfactor_threshold` in the solution factors (TDDFT eigenvectors) of the underlying uncoupled calculation in the construction of the exact trial densities during the calculation of the coupling matrix elements. These orbital pair contributions are not ignored in the subsequent calculation of transition moments, oscillator, and rotational strengths.

SMARTGRID**Type**

Bool

Default value

No

Description**Stat2CPL****Type**

Multiple Choice

Default value

OnlyKnown

Options

[OnlyKnown]

Description

Type of states to be coupled

TCOMEGA**Type**

Bool

Default value

No

Description

Transpose construction of Omega matrix

TDA**Type**

Bool

Default value

No

Description

TDA specifies the use of the Tamm-Dancoff-Approximation (Tamm-Dancoff approximation) in the underlying uncoupled FDE-TDDFT calculations. Contrary to the full SUBEXCI-TDDFT variant, SUBEXCI-TDA allows for the usage of hybrid functionals in the underlying uncoupled FDE-TDDFT calculations.

TKINKERNEL**Type**

Bool

Default value

Yes

Description**XCKERNEL****Type**

Bool

Default value

Yes

Description**Symmetry****Type**

Multiple Choice

Default value

AUTO

Options

[AUTO, NOSYM, ATOM, C(LIN), D(LIN), C(I), C(S), C(2), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), O(H), T(D)]

Description

Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. Coordinates must be symmetric within SymmetryTolerance.

SymmetryTolerance**Type**

Float

Default value

1e-07

Description

Tolerance used to detect symmetry in the system. If symmetry Schoenflies symbol is specified, the coordinates must be symmetric within this tolerance.

Tails**Type**

Block

Description

Obsolete option for linear scaling and distance effects. We recommend using the LinearScaling key instead.

Bas**Type**

Float

Description

Parameter related to the threshold for the calculation of basis functions on a block of integration points. A higher value implies higher precision. The default depends on the Integration numerical quality.

Fit

Type

Float

Description

Parameter related to the threshold for the calculation of fit functions on a block of integration points. A higher value implies higher precision. The default depends on the Integration numerical quality.

TDA**Type**

Bool

Default value

No

Description

Use the Tamm-Dancoff approximation (TDA) (requires the EXCITATIONS block key)

TDDFTSO**Type**

Bool

Default value

No

Description**TIDegeneracyThreshold****Type**

Float

Default value

0.1

Unit

eV

Description

If the orbital energy of the fragment MO is within this threshold with fragment HOMO or LUMO energy, then this fragment MO is included in the calculation of the transfer integrals. Relevant in case there is (near) degeneracy.

Title**Type**

String

Default value

*** (NO TITLE) ***

Description

Title of the calculation.

TotalEnergy**Type**

Bool

Default value

No

GUI name

Print: Total Energy

Description

Calculate the total energy.

Normally only the bonding energy with respect to the fragments is calculated.

The total energy will be less accurate than the bonding energy (about two decimal places), and is not compatible with some options.

In most cases the total energy will not be needed.

TransferIntegrals**Type**

Bool

Default value

No

GUI name

: Charge transfer integrals (for transport properties)

Description

Calculate the charge transfer integrals, spatial overlap integrals and site energies.

Charge transfer integrals can be used in models that calculate transport properties.

Unrestricted**Type**

Bool

Default value

No

Description

By default, a spin-restricted calculation is performed where the spin alpha and spin beta orbitals are spatially the same.

UnrestrictedFragments**Type**

Bool

Default value

No

Description

Use fragments calculated a spin-unrestricted calculation: the spin alpha and spin beta orbitals may be spatially different.

The total spin polarization of your fragments must match the spin polarization of your final molecule.

UseSPCode**Type**

Bool

Default value

No

Description

Use Patchkovskii routines for PBE

VectorLength**Type**

Integer

GUI name

Vectorlength (blocksize)

Description

Specify a different batch size for the integration points here (default: 128 on most machines and 2047 on vector machines).

VSCRF**Type**

Non-standard block

Description

VSCRF is no longer supported. Use AMS2023 or earlier.

XC**Type**

Block

Description

Definition of the XC.

Dispersion**Type**

String

Description

Dispersion corrections.

DoubleHybrid**Type**

String

Description

Specifies the double hybrid functional that should be used during the SCF.

EmpiricalScaling**Type**

Multiple Choice

Default value

None

Options

[None, SOS, SCS, SCSMI]

Description

Calculate the (SOS/SCS/SCSMI)-MP2 correlation energy.

GALITSKIIMIGDAL**Type**

Bool

Default value

No

Description

Calculate the Galitskii-Migdal correlation energy after the SCF is completed.

GCPparameters**Type**

String

Description

Applying parameters for the geometrical counter poise correction.

GGA**Type**

String

Description

Specifies the GGA part of the XC Functional

HartreeFock**Type**

Bool

Default value

No

Description

Use the Hartree-Fock exchange should be used during the SCF.

Hybrid**Type**

String

Description

Specifies the hybrid functional that should be used during the SCF.

LDA**Type**

String

Description

Defines the LDA part of the XC functional

LibXC**Type**

String

Description

Use the LibXC library with the specified functional.

MP2**Type**

Bool

Default value

No

Description

Calculate the MP2 correlation energy after the HF SCF is completed.

MetaGGA**Type**

String

Description

Specifies that a meta-GGA should be used during the SCF

MetaHybrid**Type**

String

Description

Specifies the meta-hybrid functional that should be used during the SCF.

Model**Type**

String

Description

Model potential to be used

NoLibXC**Type**

Bool

Default value

No

Description

Prevent the usage of the LibXC library

OEP**Type**

String

Description

Defines the optimized effective potential expanded into a set of the fit functions

RPA**Type**

Multiple Choice

Default value

None

Options

[None, Direct, Sigma, SOSEX, SOSSEX]

Description

Specifies the use of an RPA or post-RPA method. By default, RPA is not enabled.

RangeSep**Type**

String

Description

Range separated hybrids parameters

XCFun**Type**

Bool

Default value

No

Description

Use the XCFun library

gCP**Type**

String

Description

Use the geometrical counter poise correction.

XES**Type**

Block

Description

X-ray emission spectroscopy

AllXESMoments**Type**

Bool

Default value

No

GUI name

Print: All XES Moments

Description

Print out all the individual transition moments used within the calculation of the total oscillator strength

AllXESQuadrupole**Type**

Bool

Default value

No

GUI name

: All XES Quadrupole

Description

Print out the individual oscillator strength components to the total oscillator strength

CoreHole**Type**

String

GUI name

Acceptor orbital

Description

selection of the acceptor orbital for the calculation of the emission oscillator strengths. For example 'CoreHole A1 2' calculates oscillator strengths to the orbital 2 in irrep A1.

In AMSinput you may also use the notation 2A1 (so first the orbital number, next the symmetry)

Enabled**Type**

Bool

Default value

No

GUI name

Calculate XES

Description

Calculate the X-ray emission energies to a core orbital.

By default it calculates the emission to the first orbital in the first symmetry.

ZExact**Type**

Bool

Default value

No

Description

Expert option in TDDFT excitations.

ZFS**Type**

String

Description

Calculate the zero-field splitting (ZFS) of an open shell ground state. An unrestricted calculation is required and a spin larger than 1/2, and no no spatial degeneracy. Scalar relativistic ZORA is required.

ZlmFit**Type**

Block

Description

Options for the density fitting scheme 'ZlmFit'.

AllowBoost**Type**

Bool

Default value

Yes

Description

Allow automatic atom-dependent tuning of maximum l of spherical harmonics expansion.

Whether or not this boost is needed for a given atom is based on an heuristic estimate of how complex the density around that atom is.

DensityThreshold**Type**

Float

Default value

1e-07

Description

Threshold below which the electron density is considered to be negligible.

GridAngOrder**Type**

Integer

Default value

21

Description**GridRadialFactor****Type**

Float

Default value

1.0

Description**PartitionFunThreshold****Type**

Float

Default value

0.0

Description**PotentialThreshold****Type**

Float

Default value

1e-07

Description**Pruning****Type**

Bool

Default value

Yes

Description**Quality**

Type

Multiple Choice

Default value

Auto

Options

[Auto, Basic, Normal, Good, VeryGood, Excellent]

Description

Quality of the density-fitting approximation. For a description of the various qualities and the associated numerical accuracy see reference. If 'Auto', the quality defined in the 'NumericalQuality' will be used.

QualityPerRegion**Type**

Block

Recurring

True

Description

Sets the ZlmFit quality for all atoms in a region. If specified, this overwrites the globally set quality.

Quality**Type**

Multiple Choice

Options

[Basic, Normal, Good, VeryGood, Excellent]

Description

The region's quality of the ZlmFit.

Region**Type**

String

Description

The identifier of the region for which to set the quality.

lExpansion**Type**

Integer

Default value

4

Description**lMargin****Type**

Integer

Default value

4

Description

16.2.2 adfnbo

ADFFile

Type

String

Default value

TAPE21

Description

Path to TAPE21 file from which adfnbo reads data and to which adfnbo possibly writes data

Choose

Type

Non-standard block

Description

Copy

Type

Bool

Default value

No

Description

Debug

Type

Bool

Default value

No

Description

Fock

Type

Bool

Default value

No

Description

NBOKeyList

Type

String

Default value

BNDIDX NBONLMO=W AONBO=W AONLMO=W NLMOMO=W STERIC DIST

Description

\$NBO keylist

Read

Type

Bool

Default value

No

Description

Spherical

Type

Bool

Default value

Yes

Description

TAPE15File

Type

String

Default value

TAPE15

Description

Path to the TAPE15 file from which adfnbo reads data

TestJob

Type

Bool

Default value

No

Description

include extra options in FILE47, such as NRT (natural resonance theory) which is expensive for large molecules

Write

Type

Bool

Default value

No

Description

16.2.3 cpl

ADFFile

Type

String

Default value

TAPE21

Description

Path to TAPE21 file from which cpl reads data and to which cpl writes data

CALCV2007

Type

Bool

Default value

No

Description

compatibility with older versions of CPL that did not use the SAPA approximation but always calculated the potential during the CPL run, which is inconsistent with SAPA settings in ADF

Fractional**Type**

Bool

Default value

No

Description

Allow Fractional occupations

GGA**Type**

Bool

Default value

No

Description

Use first-order GGA potential instead of the first-order VWN potential

Hyperfine**Type**

Block

Description

control the computation of the NSSCCs

ADFGUI**Type**

Bool

Description**Atoms****Type**

Integer List

Recurring

True

Description**Enabled****Type**

Bool

Default value

No

Description

FC**Type**

Bool

Default value

No

Description**NOFC****Type**

Bool

Default value

No

Description**NOPSOSO****Type**

Bool

Default value

No

Description**NOSD****Type**

Bool

Default value

No

Description**Nuclei****Type**

Integer List

Recurring

True

Description**PSOSO****Type**

Bool

Default value

No

Description**SCF****Type**

Block

Description

Converge**Type**

Float

Default value

0.0001

Description

maximum number of iterations

Iterations**Type**

Integer

Default value

25

Description

maximum number of iterations

NOCYC**Type**

Bool

Default value

No

Description**SD****Type**

Bool

Default value

No

Description**NMRCoupling****Type**

Block

Description

control the computation of the NSSCCs

ADFGUI**Type**

Bool

Description**ALDA****Type**

Bool

Default value

No

Description

AtomPert**Type**

Integer List

Recurring

True

Description**AtomResp****Type**

Integer List

Recurring

True

Description**Contributions****Type**

String

Description

Analyze orbital contributions

DSO**Type**

Bool

Default value

No

Description**FC****Type**

Bool

Default value

No

Description**Gamma****Type**

String

Recurring

True

Description**NOFC****Type**

Bool

Default value

No

Description

NOSD**Type**

Bool

Default value

No

Description**Nuclei****Type**

Integer List

Recurring

True

Description**PSO****Type**

Bool

Default value

No

Description**PertAllAtomsOfType****Type**

String

Description

Space separated list of type of perturbing nuclei (like H, C, P) for which the NMR spin-spin coupling should be calculated.

RespAllAtomsOfType**Type**

String

Description

Space separated list of type of responding nuclei (like H, C, P) for which the NMR spin-spin coupling should be calculated.

SCF**Type**

Block

Description**Converge****Type**

Float

Default value

0.0001

Description

maximum number of iterations

Iterations

Type

Integer

Default value

25

Description

maximum number of iterations

NOCYC

Type

Bool

Default value

No

Description

SD

Type

Bool

Default value

No

Description

XAlpha

Type

Bool

Default value

No

Description

Save

Type

String

Recurring

True

Description

TAPE10File

Type

String

Default value

TAPE10

Description

Path to the TAPE10 file from which cpl reads data

16.2.4 densf

ADFFile

Type

String

Default value

TAPE21

Description

Path to the TAPE21 file from which densf reads the input data

AOResponse

Type

String

Description

Convert

Type

Bool

Default value

No

Description

COSMO

Type

Bool

Default value

No

Description

CubInput

Type

String

Description

If the CubInput keyword is present then the grid as specified in the file is used to calculate all requested quantities. Any volume data found in the cube file is also saved in the output file. NOTE: CUBINPUT option cannot be used with a pre-existing TAPE41 file because they both specify the grid, which may lead to a conflict.

CubOutput

Type

String

Description

Presence of the CubOutput keyword tells densf to save all computed quantities as cube files using file as filename prefix. The prefix can also contain a complete path including directories. For example, specifying the following in the densf input

DenGrad

Type

String

Recurring

True

Description**DenHess****Type**

String

Recurring

True

Description**Density****Type**

String

Recurring

True

Description**DualDescriptor****Type**

Bool

Default value

No

Description**Extend****Type**

Float

Description

Extend grid?

FOD**Type**

Bool

Default value

No

Description**GenFit****Type**

Non-standard block

Description**Grid****Type**

Non-standard block

Description

IrrepDensity**Type**

Non-standard block

Description

Select particular symmetry to compute the electron density for.

KinDens**Type**

String

Recurring

True

Description**Laplacian****Type**

String

Recurring

True

Description**Line****Type**

Non-standard block

Description**NCI****Type**

String

Description**NEBImage****Type**

Integer

Description**NOCV****Type**

Non-standard block

Description**Orbitals****Type**

Non-standard block

Recurring

True

Description**OutputFile**

Type

String

Default value

TAPE41

Description

Path to the (possibly existing) TAPE41 file. If the file exists, densf will read grid specifications from it ignoring GRID keyword in the input. Computed quantities are saved in the file overwriting existing data with the same name, if any

POLTDDFT**Type**

Integer

Default value

0

Description

Frequency point for transition density

Potential**Type**

String

Recurring

True

Description**QP****Type**

Bool

Default value

No

Description**Ridge****Type**

Bool

Default value

No

Description**RISM****Type**

Bool

Default value

No

Description**SEDD****Type**

Bool

Default value

No

Description**Spinor****Type**

Non-standard block

Description**StericInteraction****Type**

Non-standard block

Description**TAPE16File****Type**

String

Default value

TAPE16

Description

Path to the TAPE16 file from which densf reads the input data

TransitionDensity**Type**

Non-standard block

Description

Select particular excitations to calculate the transition density for. Format: SS|ST SymLabel Index

Units**Type**

Block

Description

Definitions of the units.

length**Type**

Multiple Choice

Default value

angstrom

Options

[bohr, angstrom]

Description

Units of length

VTKFile**Type**

String

Description

Specifies path to a file in the format readable by VTK directly. This option exists primarily for better integration with AMS-GUI and the user should not specify it.

16.2.5 green

DOS**Type**

String

Description

Enables the calculation of the density of states. The string specifies the TAPE21 file containing the result of an ADF calculation of the extended molecule (performed with SYMMETRY NOSYM)

Eps**Type**

String

Description

mineps maxeps numeps: The energy range for which either the self-energy matrices or the DOS and transmission have to be calculated. The range consists of numeps (≤ 1) points running from mineps to maxeps inclusive.

ETA**Type**

Float

Default value

1e-06

Unit

Hartree

Description

The imaginary energy, or the distance from the real axis, in the calculation of the Green's function. The value needs to be a small positive number to prevent singularities in the calculation.

FermiLevel**Type**

String

Description**Left****Type**

Block

Description

Specify the left self-energies used in a calculation of the DOS and transmission. If a filename is specified in the header, the self-energy matrices are read from that file.

ETA**Type**

Float

Default value

0.001

Unit

Hartree

Description

Magnitude of the coupling

Fragment**Type**

String

Description**NoSave****Type**

String

Description**Right****Type**

Block

Description

Specify the right self-energies used in a calculation of the DOS and transmission. If a filename is specified in the header, the self-energy matrices are read from that file.

ETA**Type**

Float

Default value

0.001

Unit

Hartree

Description

Magnitude of the coupling

Fragment**Type**

String

Description**SO****Type**

Float List

Description**Surface****Type**

Block

Description

Enables the calculation of the self-energy matrices. The filename in the header specifies the TAPE21 file resulting from an ADF calculation of the contacts

Fragments**Type**

String

Description

The two principal layers between which the surface is defined

Trans**Type**

String

Description

16.2.6 lfdft

ADFFile**Type**

String

Default value

TAPE21

Description

Path to TAPE21 file from which lfdft reads data and to which lfdft writes data

BField**Type**

Float List

Default value

[0.0, 0.0, 0.0]

Unit

Tesla

Description

Include a finite magnetic Field. For MCD calculations include a magnetic field in the z-direction. The DegeneracyThreshold should be small to see the splitting of levels due to the magnetic field.

DegeneracyThreshold**Type**

Float

Default value

0.001

Unit

eV

Description

Energy difference threshold to determine degenerate levels

MOIND1

Type

Integer List

Default value

[0, 0, 0, 0, 0, 0, 0]

Description

The indices of the MOs that participate for shell 1.

MOIND2**Type**

Integer List

Default value

[0, 0, 0, 0, 0, 0, 0]

Description

The indices of the MOs that participate for shell 2.

NLVAL1**Type**

Integer List

Default value

[0, 0]

Description

n and l value of shell 1.

NLVAL2**Type**

Integer List

Default value

[0, 0]

Description

n and l value of shell 2.

NSHELL**Type**

Integer

Default value

1

Description

number of shells

SOC**Type**

Float List

Default value

[1.0, 1.0, 1.0, 1.0]

Description

Include Spin-Orbit coupling for the shells, scaling it with the specified factor(s).

SOCType

Type

Block

Description

Choose the type of Spin-Orbit coupling calculation used for the shells.

Shell1**Type**

Multiple Choice

Default value

ZORA

Options

[ZORA, Core]

Description

Type of Spin-Orbit coupling for the first shell

Shell2**Type**

Multiple Choice

Default value

ZORA

Options

[ZORA, Core]

Description

Type of Spin-Orbit coupling for the second shell

16.2.7 lfdft_tdm

STATE1**Type**

String

Default value

NONE

Description

NAME of the state1 file.

STATE2**Type**

String

Default value

NONE

Description

NAME of the state2 file.

16.2.8 nmr

ADFFile

Type

String

Default value

TAPE21

Description

Path to TAPE21 file from which nmr reads data and to which nmr writes data

AllInOne

Type

Bool

Description

Tensor in one step

Analysis

Type

Block

Description

Block for analysis options.

Components

Type

Bool

Default value

No

Description

The components keyword is optional and enables an analysis not only of the isotropic shielding but also of the diagonal Cartesian components of the tensor XX, YY, and ZZ). In order to analyze the principal shielding tensor components with canonical MOs you can calculate the shielding tensor first with the NMR code, rotate the molecule such that the principal axes system aligns with the Cartesian coordinate system, and then repeat the NMR calculation with the analysis features switched on.

FakeSO

Type

Bool

Default value

No

Description

NoPrincipal

Type

Bool

Default value

No

Description

Do not transform to principal axes for analysis

Print**Type**

Float

Default value

0.001

Description

The print keyword selects printout of contributions relative to the total diamagnetic, paramagnetic. For example in case of print 0.01 only contributions greater than 1% are printed. Set to zero to print ALL contributions.

ZSOAO2007**Type**

Bool

Default value

No

Description**canonical****Type**

Bool

Default value

No

Description

It enables an analysis of the shielding in terms of the canonical MOs.

nbo**Type**

Bool

Default value

No

Description**FakeSO****Type**

Bool

Default value

No

Description**Fractional****Type**

Bool

Default value

No

Description

HFAtonsPerPass**Type**

Integer

Description

Memory usage option for old HF scheme

HFMaxMemory**Type**

Integer

Description

Memory usage option for old HF scheme

Logfile**Type**

String

Default value

Flush

Description**NBO****Type**

Bool

Description**NMR****Type**

Block

Description

Main NMR options.

ADFGUI**Type**

Bool

Default value

No

Description**AllAtomsOfType****Type**

String

Description

Space separated list of type of nuclei (like H, C, P) for which the NMR shielding should be calculated. In addition to Nuc or Atoms.

Analysis**Type**

Integer

GUI name

Number of MOs in analysis

Description

This key controls the MO analysis. Its value should be an integer, which then specifies that the first so many MOs are to be analyzed.

Default no Analysis.

The value of this analysis subkey in the block key NMR is somewhat limited. The separate ANALYSIS block key can give more analysis of the NMR chemical shielding.

Atoms**Type**

Integer List

Recurring

True

Description

This subkey ATOMS specifies for which nuclei the NMR shielding is calculated. Default all nuclei are calculated, i.e. as for omitting the subkeys ATOMS and NUC. The numbers refer to the input ordering in the ADF calculation. Use the subkey NUC to specify the nuclei according to the internal NMR numbers of the atoms.

Calc**Type**

String

Default value

All

Description

The sub key Calc controls what is actually calculated. All: Implies all of the other options to this key. Para: The paramagnetic part, Dia: The diamagnetic part, FC: The Fermi-contact part in case of the Pauli Hamiltonian, SO: The Fermi-contact part in case of the ZORA Hamiltonian.

GFactors**Type**

Bool

Default value

No

Description

Calculate g-factors

Ghosts**Type**

Non-standard block

Description

The subkey GHOSTS is a block type subkey. The format is Ghosts | xx1 yy1 zz1 | xx2 yy2 zz2 | ... | SubEnd

Nuc**Type**

Integer List

Description

This subkey NUC specifies for which nuclei the NMR shielding is calculated. Default all nuclei are calculated, i.e. as for omitting the subkeys ATOMS and NUC. Else you may use this options by simply typing Nuc in the NMR block (without any further data); this means: for no nuclei at all. Alternatively you may type the index of the atom(s) you want to see analyzed. Default all nuclei are calculated, i.e. as for omitting this subkey. The numbers refer to the internal numbering of the nuclei as it appears somewhere early in the general ADF output. This internal numbering is also the internal NMR numbering, but it is not necessarily the same as the input ordering. Use the subkey ATOMS to specify the nuclei according to this input ordering in the ADF calculation. Note that the number of nuclei has a significant consequence for the total CPU time.

Out**Type**

String

Default value

ISO TENS

Description

Controls printed output. Options: All: All the other options, ISO: Isotropic shielding constants, Tens: Shielding tensors, Eig: Eigenvectors, U1: The U1 Matrix, F1: The first order change in the Fock matrix, S1: The first order change in the Overlap matrix, AOP: The paramagnetic AO matrix (= the matrix in the representation of elementary atomic basis functions), AOD: The diamagnetic AO matrix, AOF: The Fermi-contact AO matrix, Refs: Literature references, INFO: General information.

SCF**Type**

Float

Default value

1e-06

Description

Convergence threshold for CPKS cycle

U1K**Type**

String

Default value

Best

Description

Determines which terms are included in the calculation of the U1 matrix (first order changes in MO coefficients). Best: The best (recommended) options for each relativistic option are included for this subkey. Implies None for non-relativistic and scalar relativistic ZORA, SO + SOFULL for spin-orbit coupled ZORA, and MV + Dar for the Pauli Hamiltonian. None: Implies none of the other options to this key. All: Implies all the other options to this key. MV: The mass-velocity term. Dar: The Darwin term. ZMAN: The Spin-Zeeman term (can be included only in case of spin-orbit coupled Pauli Hamiltonian). SO: ZORA spin-orbit part. SOFULL: ZORA spin-orbit part.

Use**Type**

String

Description

The subkey Use controls some optional options. FXC: Improves the exchange-correlation kernel used, as was implemented by J. Autschbach [<http://dx.doi.org/10.1080/00268976.2013.796415>]. Important only in case of spin-orbit coupled calculations. This may give some (small) gauge dependent results when using this. Important option that should be seriously considered and has been advocated in Ref [<http://dx.doi.org/10.1080/00268976.2013.796415>]. SCALED: Implies the scaled ZORA method, which gives (slightly) gauge dependent results. Note that in case of the ZORA Hamiltonian default the unscaled ZORA method is used. For chemical shifts, only compare results with the same options. SO1C: Before ADF2008.01 in the the spin-orbit term a 1-center approximation was used, which does not suffer from gauge dependence. This 1-center approximation can be used with USE SO1C.

NoScale**Type**

Bool

Description**PNMRFile****Type**

String

Default value**Description**

Path to file that contains pNMR data

RecalculateTAPE10**Type**

Bool

Default value

No

Description**Save****Type**

String

Recurring

True

Description**Scaled****Type**

Bool

Description**TAPE10File****Type**

String

Default value

TAPE10

Description

Path to the TAPE10 file from which nmr reads data

Temperature**Type**

Float

Default value

298.15

Description

Temperature (Kelvin) for temperature dependent part shielding tensor.

KF OUTPUT FILES

Main binary output files

- *ams.rkf* (page 439)
- *adf.rkf* (page 439)

Special binary output files

- *TAPE10* (page 441)
- *TAPE13* (page 441)
- *TAPE15* (page 442)
- *TAPE41* (page 342)

17.1 Accessing KF files

KF files are Direct Access binary files. KF stands for Keyed File: KF files are keyword oriented, which makes them easy to process by simple procedures. Internally all the data on KF files is organized into sections containing variables, so each datum on the file can be identified by the combination of section and variable.

All KF files can be opened using the [KFbrowser](#) GUI program:

```
$AMSBIN/kfbrowser path/to/ams.rkf
```

By default KFbrowser shows a just a curated summary of the results on the file, but you can make it show the raw section and variable structure by switching it to expert mode. To do this, click on **File → Expert Mode** or press **ctrl/cmd + e**.

KF files can be opened and read with [Command line tools](#).

For working with the data from KF files, it is often useful to be able to read them from Python. Using the [AMS Python Stack](#), this can easily be done with the [AKFReader](#) class:

```
>>> from scm.akfreader import AKFReader
>>> kf = AKFReader("path/to/ams.rkf")
>>> "Molecule%Coords" in kf
True
>>> kf.description("Molecule%Coords")
{
  '_type': 'float_array',
  '_shape': [3, 'nAtoms'],
  '_comment': 'Coordinates of the nuclei (x,y,z)',
  '_unit': 'Bohr'
}
```

(continues on next page)

(continued from previous page)

```
>>> kf.read("Molecule%Coords")
array([[ -11.7770694 ,  -4.19739597,   0.04934546],
       [  -9.37471321,  -2.63234227,  -0.13448698],
       ...,
       [ 10.09508738,  -1.06191208,   1.45286913],
       [ 10.11689333,  -1.5080196 ,  -1.87916127]])
```

Tip: For a full overview of the available methods in AKFReader, see the [AKFReader API](#) documentation.

17.2 Sections and variables on adf.rkf

adf.rkf is the general result file of an ADF calculation. In ADF<=2019 it was known as TAPE21.

17.2.1 ActiveFrag

KF Section: ActiveFrag

Content: Data related to the active fragment.

ActiveFrag%alfbas

Type

float_array

Description

Basis set: alpha values (the exponent in the Slater type-function) of function sets.

Shape

[nbset]

ActiveFrag%alfcor

Type

float_array

Description

Core functions set: alpha values (the exponent in the Slater type-function) of function sets.

Shape

[ncset]

ActiveFrag%alffit

Type

float_array

Description

Fit functions set: alpha values (the exponent in the Slater type-function) of function sets.

Shape

[nfset]

ActiveFrag%AOIndex

Type

int_array

Description

?

ActiveFrag%atomIndices**Type**

int_array

Description

indices of the atoms in the fragments of this type in the 'global' geometry

Shape

[nr of atoms]

ActiveFrag%atomtype**Type**

lchar_string_array

Description

The names of the atom types.

Shape

[nr of atomtypes]

ActiveFrag%atomtype effective charge**Type**

float_array

Description

The effective charge of the atom types (i.e. the nuclear charge minus the number of electrons in the frozen core).

Shape

[nr of atomtypes]

ActiveFrag%atomtype isGhost**Type**

bool_array

Description

Whether this atom type is a ghost type.

Shape

[nr of atomtypes]

ActiveFrag%atomtype total charge**Type**

float_array

Description

The nuclear charge of the atom types.

Shape

[nr of atomtypes]

ActiveFrag%atomtypeIndices**Type**

int_array

Description

indices of the atom types in this fragment type in the 'global' geometry

Shape

[nr of atomtypes]

ActiveFrag%Bas-I***Type**

float_array

Description

?

ActiveFrag%Bas-R***Type**

float_array

Description

?

ActiveFrag%ccor**Type**

float_array

Description

Some core related stuff...?

ActiveFrag%cofcom**Type**

float_array

Description

STO-fit: coefficients in atomic fit a1-comb's

Shape

[na1cof]

ActiveFrag%Coordinates**Type**

float_array

Description

The coordinates of the fragments.

Shape

[3, nr of atoms, numFrag]

ActiveFrag%cum nr of atoms**Type**

int_array

Description

Cumulative number of atoms, up to a certain atomtype.

Shape

[nr of atomtypes+1]

ActiveFrag%electrons

Type

float

Description

Number of valence electrons in the fragment.

ActiveFrag%faith**Type**

float_array

Description

The symmetry operator matrices.

Shape

[3, 3, nogr]

ActiveFrag%frgmap**Type**

float_array

Description

Affine transformation from the master fragments geometry to the actual fragments.

Shape

[3, 4, numFrag]

ActiveFrag%frgtyp**Type**

string

Description

The fragment type (name)

ActiveFrag%grouplabel**Type**

string

Description

Schoenflies symbol of the symmetry group.

ActiveFrag%igr**Type**

int

Description

Point group identification number. 1: atom, 10: c(lin), 20: d(lin), 30: t(d), 60: o(h), 100: c(n), 200: c(nh), 400: c(nv), 450: d(n), 500: d(nh), 600: d(nd), 700: c(i), 800: c(s), 999: nosym

ActiveFrag%initialCoordinates**Type**

float_array

Description

Coordinates of the initial fragment. These are rotated and translated to obtain the 'true' geometry.

Shape

[3, nr of atoms]

ActiveFrag%ioprel**Type**

int

Description

Integer code for relativistic option used. 0: non-relativistic, 1: scalar Pauli + sum of frozen core pot., 3: scalar ZORA + MAPA, 4: scalar ZORA + full pot. (not supported anymore), 5: scalar ZORA + APA (Band), 6: scalar X2C + MAPA, 7: scalar X2C ZORA + MAPA, 11: spin-orbit Pauli + sum of frozen core pot., 13: spin-orbit ZORA + MAPA, 14: spin-orbit ZORA + full pot. (not supported anymore), 15: spin-orbit ZORA + APA (Band), 16: spin-orbit X2C + MAPA, 17: spin-orbit X2C ZORA + MAPA

ActiveFrag%isfrozen**Type**

bool

Description

FDE (frozen density embedding): whether the fragment is frozen.

ActiveFrag%iskf**Type**

int_array

Description

STO-fit: pointer array for atomic parts of fit a1-comb's.

Shape

[4, niskf]

ActiveFrag%jalok**Type**

int_array

Description

An array (1:npeq), with values 0 or 1. 1=the pair density can be fitted using A1 fit functions only. 0=all fit functions (on the involved atoms) are to be used. The value 1 may arise because of symmetry properties, or because the distance between the atoms is so large that the inaccuracy from using only A1 fit functions can be neglected.

Shape

[npeq]

ActiveFrag%jasym**Type**

int_array

Description

An array that runs over the npeq sets of equivalent atom pairs. Its value gives for the indicated the set the number of pairs in that set.

Shape

[npeq]

ActiveFrag%jsym1**Type**

int_array

Description

For each of the nsym representations: if it belongs to a one-dimensional irrep, the value is 1, otherwise: for the first subspecies in the irrep the value is the dimension of the irrep, for the other subspecies in the same irrep the value is 0.

Shape

[nsym]

ActiveFrag%lnosymfit**Type**

bool

Description

STO-fit: whether the symmetry should be used for density fitting or not.

ActiveFrag%lqbas**Type**

int_array

Description

Basis set: l values (angular momentum) of function sets.

Shape

[nbset]

ActiveFrag%lqcor**Type**

int_array

Description

Core functions set: l values (angular momentum) of function sets.

Shape

[ncset]

ActiveFrag%lqfit**Type**

int_array

Description

Fit functions set: l values (angular momentum) of function sets.

Shape

[nfset]

ActiveFrag%lrl**Type**

int

Description

STO-fit: fitint dimensions...?

ActiveFrag%mass**Type**

float_array

Description

Atomic masses of the various atom types.

Shape

[nr of atomtypes]

ActiveFrag%maxsf**Type**

int

Description

STO-fit: fitint dimensions...?

ActiveFrag%na1cof**Type**

int

Description

STO-fit: Number of elements in numcom/cofcom.

ActiveFrag%na1ptr**Type**

int_array

Description

STO-fit: index array (like nfptr, but only for the symmetric fit functions; per nucleus)

Shape

[nnuc+1]

ActiveFrag%naos**Type**

int

Description

Number of cartesian basis functions.

ActiveFrag%naosx**Type**

int

DescriptionNumber of elements in a triangular matrix of size naos*naos, i.e. $(naos*(naos + 1))/2$.**ActiveFrag%nbaspt****Type**

int_array

Description

Basis set: cumulative number of functions per atom type.

Shape

[ntyp+1]

ActiveFrag%nbset**Type**

int

Description

Basis set: total number of function sets (not counting spherical/cartesian components).

ActiveFrag%ncorpt

Type

int_array

Description

Core functions set: cumulative number of functions per atom type.

Shape

[ntyp+1]

ActiveFrag%ncset**Type**

int

Description

Core functions set: total number of function sets (not counting spherical/cartesian components).

ActiveFrag%nfcn**Type**

int_array

Description

Number of primitive functions in the various irreps.

Shape

[nsym]

ActiveFrag%ffitpt**Type**

int_array

Description

Fit functions set: cumulative number of functions per atom type.

Shape

[ntyp+1]

ActiveFrag%nfset**Type**

int

Description

Fit functions set: total number of function sets (not counting spherical/cartesian components).

ActiveFrag%ngr**Type**

int

Description

One of the integer-code components that fix the symmetry group. See routine adf/maisya

ActiveFrag%niskf**Type**

int

Description

STO-fit: counts the number of g functions.

ActiveFrag%nnuc

Type

int

Description

The total number of atoms.

ActiveFrag%noat**Type**

int_array

Description

Map between normal list of atoms and symmetry sets.

Shape

[nr of atoms]

ActiveFrag%nogr**Type**

int

Description

The number of symmetry operators. NB, for the special cases of infinite symmetries, only the operators corresponding to finite elements are counted. Therefore, ATOM has nogr=1 (only the unit operator); C(LIN) has nogr=1, D(LIN) has nogr=2

ActiveFrag%norb**Type**

int_array

Description

Number of orbitals for the various irreps.

Shape

[nsym]

ActiveFrag%notyps**Type**

int_array

Description

For each set of symmetry equivalent atoms, the atom type to which the set belongs.

Shape

[nsetat]

ActiveFrag%npeq**Type**

int

Description

The number of symmetry unique pairs of atoms.

ActiveFrag%nbas**Type**

int_array

Description

Basis set: n values (main quantum number) of function sets.

Shape

[nbset]

ActiveFrag%ncor**Type**

int_array

Description

Core functions set: n values (main quantum number) of function sets.

Shape

[ncset]

ActiveFrag%ncfit**Type**

int_array

Description

Fit functions set: n values (main quantum number) of function sets.

Shape

[nfset]

ActiveFrag%nr of atoms**Type**

int

Description

The total number of atoms.

ActiveFrag%nr of atomtypes**Type**

int

Description

The number of atom types in the fragment.

ActiveFrag%nratst**Type**

int_array

Description

Number of atoms in each set of symmetry equivalent atoms.

Shape

[nsetat]

ActiveFrag%ncorb**Type**

int_array

Description

Number of core orbitals...?

Shape

[4, ntyp]

ActiveFrag%ncset

Type

int_array

Description

Some core information...?

ActiveFrag%nrorb**Type**

int_array

Description

Number number of orbitals per the various relativistic irreps.

Shape

[nrsym]

ActiveFrag%nrsym**Type**

int

Description

Number of double group irreps.

ActiveFrag%nsetat**Type**

int

Description

Number of sets of symmetry equivalent atoms.

ActiveFrag%nsfos**Type**

int

Description

STO-fit: total no. of fully symmetric (a1) fit functions.

ActiveFrag%nspin**Type**

int

Description

nspin used in this fragment.

ActiveFrag%nsym**Type**

int

Description

Number of irreps.

ActiveFrag%ntyp**Type**

int

Description

The number atom types in the fragment

ActiveFrag%numcom

Type
int_array

Description
STO-fit: no's of functions in atomic fit a1-comb's.

Shape
[na1cof]

ActiveFrag%numFrag

Type
int

Description
Number of times this fragment is used.

ActiveFrag%Pmat_AO

Type
float_array

Description
?

ActiveFrag%Pmat_AO_beta

Type
float_array

Description
?

ActiveFrag%Smat_AO

Type
float_array

Description
?

ActiveFrag%symlab

Type
lchar_string_array

Description
Labels of the irreps.

Shape
[nsym]

ActiveFrag%symlabr

Type
lchar_string_array

Description
Labels of the double group irreps.

Shape
[nrsym]

ActiveFrag%usebasis

Type

bool

Description

FDE (frozen density embedding). ?

ActiveFrag%xyz**Type**

float_array

Description

Coordinates of the atoms in the fragment... same as initialCoordinates?

Shape

[3, nr of atoms]

17.2.2 ActiveFrag*

KF Section: ActiveFrag***Content:** ?**ActiveFrag**Bas-I_A *****Type**

float_array

Description

Spin-orbit data.

ActiveFragBas-R_A *****Type**

float_array

Description

Spin-orbit data.

ActiveFragEigen-Bas_A****Type**

float_array

Description

MO expansion coefficients in the BAS representation for all nmo_A orbitals (in unrestricted case for spin A). The coefficients run over all BAS functions indicated by npart.

Shape

[nbas, nmo_A]

ActiveFragEigen-Bas_B****Type**

float_array

Description

Unrestricted case: same as 'Eigen-Bas_A', but for spin B.

Shape

[nbas, nmo_A]

ActiveFrageps_A**

Type

float_array

Description

The orbital energies for the nmo_A orbitals (in unrestricted case for spin A). When they result from a ZORA calculations, the non-scaled values are stored on file, see qscal how to scale.

Shape

[nmo_A]

ActiveFrag*%eps_B**Type**

float_array

Description

Unrestricted case: same as 'eps_A', but for spin B.

ActiveFrag*%escale_A ***Type**

float_array

Description

Spin-orbit data.

ActiveFrag*%froc**Type**

float_array

Description

The occupation numbers of the MOs in the irrep.

Shape

[nmo_A]

ActiveFrag*%froc_A**Type**

float_array

Description

The occupation numbers of the MOs in the irrep (in unrestricted case for spin A).

Shape

[nmo_A]

ActiveFrag*%froc_B**Type**

float_array

Description

Unrestricted case: the occupation numbers of the MOs in the irrep, for spin B

Shape

[nmo_A]

ActiveFrag*%frocr_A ***Type**

float_array

Description

Spin-orbit data.

ActiveFrag*%nbas

Type

int

Description

Number of primitive STOs in this symmetry group.

ActiveFrag*%nmo_A

Type

int

Description

Number of alpha molecular orbitals in this symmetry group (in unrestricted case for spin A).

ActiveFrag*%nmo_B

Type

int

Description

Unrestricted case: number of beta molecular orbitals in this symmetry group. Should be equal to nmo_A.

ActiveFrag*%npart

Type

int_array

Description

A list of indices of the BAS functions that are used in this irrep.

Shape

[nbas]

ActiveFrag*%qscal_A

Type

float_array

Description

Used only for ZORA. Scaled eps is $(\text{eps}/(1+\text{qscal}))$.

Shape

[nmo_A]

ActiveFrag*%qscal_B

Type

float_array

Description

Unrestricted case: same as 'qscal_A', but for spin B.

Shape

[nmo_A]

ActiveFrag*%qscalr_A *

Type

float_array

Description

Spin-orbit data.

17.2.3 All excitations**KF Section: All excitations****Content:** Section related to all excitations.**All excitations%All Sing-Sing excitations****Type**

float_array

Description

Singlet-Singlet excitation energies.

Unit

hartree

Shape

[nr Sing-Sing excitations]

All excitations%All Sing-Trip excitations**Type**

float_array

Description

Singlet-Triplet excitation energies.

Unit

hartree

Shape

[nr Sing-Trip excitations]

All excitations%All Spin-Polar excitations**Type**

float_array

Description

Spin-orbit coupled spin-polarized excitation energies

Unit

hartree

Shape

[nr excitations]

All excitations%All Spin-Restr excitations**Type**

float_array

Description

Spin-orbit coupled spin-restricted excitation energies

Unit

hartree

Shape

[nr excitations]

All excitations%ES DIP**Type**

float_array

Description

Unrelaxed approximate singlet excited state dipole moments.

Unit

bohr

Shape

[3, nr Sing-Sing including deg]

All excitations%ESES OSC**Type**

float_array

Description

Unrelaxed approximate oscillator strengths between singlet excited states.

Unit**Shape**

[nr Sing-Sing including deg, nr Sing-Sing including deg]

All excitations%ESES TDM**Type**

float_array

Description

Unrelaxed approximate transition dipole moments between singlet excited states.

Unit

bohr

Shape

[3, nr Sing-Sing including deg, nr Sing-Sing including deg]

All excitations%ET DIP**Type**

float_array

Description

Unrelaxed approximate triplet excited state dipole moments.

Unit

bohr

Shape

[3, nr Sing-Trip including deg]

All excitations%ETET OSC**Type**

float_array

Description

Unrelaxed approximate oscillator strengths between triplet excited states.

Unit**Shape**

[nr Sing-Trip including deg, nr Sing-Trip including deg]

All excitations%ETET TDM**Type**

float_array

Description

Unrelaxed approximate transition dipole moments between triplet excited states.

Unit

bohr

Shape

[3, nr Sing-Trip including deg, nr Sing-Trip including deg]

All excitations%GSES TDM**Type**

float_array

Description

Transition dipole moments between singlet ground state and singlet excited state.

Unit

bohr

Shape

[3, nr Sing-Sing including deg]

All excitations%nr excitations**Type**

int

Description

Number of excitations.

All excitations%nr excitations including deg**Type**

int

Description

Number of excitations including subspecies in case of multidimensional irreps.

All excitations%nr Sing-Sing excitations**Type**

int

Description

Number of Singlet-Singlet excitations.

All excitations%nr Sing-Sing including deg**Type**

int

Description

Number of Singlet-Singlet excitations including subspecies in case of multidimensional irreps.

All excitations%nr Sing-Trip excitations**Type**

int

Description

Number of Singlet-Triplet excitations.

All excitations%nr Sing-Trip including deg

Type

int

Description

Number of Singlet-Triplet excitations including subspecies in case of multidimensional irreps.

All excitations%Spin-Polar ES DIP

Type

float_array

Description

Unrelaxed approximate excited state dipole moments. Spin-orbit coupled spin-polarized calculation.

Unit

bohr

Shape

[3, nr excitations including deg]

All excitations%Spin-Polar ESES OSC

Type

float_array

Description

Unrelaxed approximate oscillator strengths between excited states. Spin-orbit coupled spin-polarized calculation.

Unit**Shape**

[nr excitations including deg, nr excitations including deg]

All excitations%Spin-Polar ESES TDM

Type

float_array

Description

Unrelaxed approximate transition dipole moments between excited states. Real and imaginary part. Spin-orbit coupled spin-polarized calculation.

Unit

bohr

Shape

[3, 2, nr excitations including deg, nr excitations including deg]

All excitations%Spin-Restr ES DIP

Type

float_array

Description

Unrelaxed approximate excited state dipole moments. Spin-orbit coupled spin-restricted calculation.

Unit

bohr

Shape

[3, nr excitations including deg]

All excitations%Spin-Restr ESES OSC**Type**

float_array

Description

Unrelaxed approximate oscillator strengths between excited states. Spin-orbit coupled spin-restricted calculation.

Unit**Shape**

[nr excitations including deg, nr excitations including deg]

All excitations%Spin-Restr ESES TDM**Type**

float_array

Description

Unrelaxed approximate transition dipole moments between excited states. Real and imaginary part. Spin-orbit coupled spin-restricted calculation.

Unit

bohr

Shape

[3, 2, nr excitations including deg, nr excitations including deg]

All excitations%SS energy order index**Type**

int_array

Description

Energy order index array Singlet-Singlet excitations.

Shape

[nr Sing-Sing excitations]

All excitations%ST energy order index**Type**

int_array

Description

Energy order index array Singlet-Triplet excitations.

Shape

[nr Sing-Trip excitations]

17.2.4 All excitations *

KF Section: All excitations *

Content: Section related to all excitations for a given localization.

All excitations *%All Sing-Sing excitations

Type

float_array

Description

Singlet-Singlet excitation energies.

Unit

hartree

Shape

[nr Sing-Sing excitations]

All excitations *%All Sing-Trip excitations

Type

float_array

Description

Singlet-Triplet excitation energies.

Unit

hartree

Shape

[nr Sing-Trip excitations]

All excitations *%All Spin-Polar excitations

Type

float_array

Description

Spin-orbit coupled spin-polarized excitation energies

Unit

hartree

Shape

[nr excitations]

All excitations *%All Spin-Restr excitations

Type

float_array

Description

Spin-orbit coupled spin-restricted excitation energies

Unit

hartree

Shape

[nr excitations]

All excitations *%ES DIP

Type

float_array

Description

Unrelaxed approximate singlet excited state dipole moments.

Unit

bohr

Shape

[3, nr Sing-Sing including deg]

All excitations *%ESES OSC

Type

float_array

Description

Unrelaxed approximate oscillator strengths between singlet excited states.

Unit**Shape**

[nr Sing-Sing including deg, nr Sing-Sing including deg]

All excitations *%ESES TDM

Type

float_array

Description

Unrelaxed approximate transition dipole moments between singlet excited states.

Unit

bohr

Shape

[3, nr Sing-Sing including deg, nr Sing-Sing including deg]

All excitations *%ET DIP

Type

float_array

Description

Unrelaxed approximate triplet excited state dipole moments.

Unit

bohr

Shape

[3, nr Sing-Trip including deg]

All excitations *%ETET OSC

Type

float_array

Description

Unrelaxed approximate oscillator strengths between triplet excited states.

Unit**Shape**

[nr Sing-Trip including deg, nr Sing-Trip including deg]

All excitations *%ETET TDM

Type

float_array

Description

Unrelaxed approximate transition dipole moments between triplet excited states.

Unit

bohr

Shape

[3, nr Sing-Trip including deg, nr Sing-Trip including deg]

All excitations *%GSES TDM

Type

float_array

Description

Transition dipole moments between singlet ground state and singlet excited state.

Unit

bohr

Shape

[3, nr Sing-Sing including deg]

All excitations *%nr excitations

Type

int

Description

Number of excitations.

All excitations *%nr excitations including deg

Type

int

Description

Number of excitations including subspecies in case of multidimensional irreps.

All excitations *%nr Sing-Sing excitations

Type

int

Description

Number of Singlet-Singlet excitations.

All excitations *%nr Sing-Sing including deg

Type

int

Description

Number of Singlet-Singlet excitations including subspecies in case of multidimensional irreps.

All excitations *%nr Sing-Trip excitations

Type

int

Description

Number of Singlet-Triplet excitations.

All excitations *%nr Sing-Trip including deg

Type
int

Description
Number of Singlet-Triplet excitations including subspecies in case of multidimensional irreps.

All excitations *%Spin-Polar ES DIP

Type
float_array

Description
Unrelaxed approximate excited state dipole moments. Spin-orbit coupled spin-polarized calculation.

Unit
bohr

Shape
[3, nr excitations including deg]

All excitations *%Spin-Polar ESES OSC

Type
float_array

Description
Unrelaxed approximate oscillator strengths between excited states. Spin-orbit coupled spin-polarized calculation.

Unit

Shape
[nr excitations including deg, nr excitations including deg]

All excitations *%Spin-Polar ESES TDM

Type
float_array

Description
Unrelaxed approximate transition dipole moments between excited states. Real and imaginary part. Spin-orbit coupled spin-polarized calculation.

Unit
bohr

Shape
[3, 2, nr excitations including deg, nr excitations including deg]

All excitations *%Spin-Restr ES DIP

Type
float_array

Description
Unrelaxed approximate excited state dipole moments. Spin-orbit coupled spin-restricted calculation.

Unit
bohr

Shape
[3, nr excitations including deg]

All excitations *%Spin-Restr ESES OSC**Type**

float_array

Description

Unrelaxed approximate oscillator strengths between excited states. Spin-orbit coupled spin-restricted calculation.

Unit**Shape**

[nr excitations including deg, nr excitations including deg]

All excitations *%Spin-Restr ESES TDM**Type**

float_array

Description

Unrelaxed approximate transition dipole moments between excited states. Real and imaginary part. Spin-orbit coupled spin-restricted calculation.

Unit

bohr

Shape

[3, 2, nr excitations including deg, nr excitations including deg]

All excitations *%SS energy order index**Type**

int_array

Description

Energy order index array Singlet-Singlet excitations.

Shape

[nr Sing-Sing excitations]

All excitations *%ST energy order index**Type**

int_array

Description

Energy order index array Singlet-Triplet excitations.

Shape

[nr Sing-Trip excitations]

17.2.5 AMSResults

KF Section: AMSResults

Content: Generic results of the ADF evaluation.

AMSResults%AAT_Transpose**Type**

float_array

Description

VCD atomic axial tensors (AATs).

Shape

[3, 3, Molecule%nAtoms]

AMSRResults%Bonds**Type**

subsection

Description

Bond info

AMSRResults%Bonds.Atoms**Type**

archived_int_array

Description

?

AMSRResults%Bonds.CellShifts**Type**

archived_int_array

Description

?

AMSRResults%Bonds.description**Type**

string

Description

A string containing a description of how the bond orders were calculated / where they come from

AMSRResults%Bonds.hasCellShifts**Type**

bool

Description

Whether there are cell shifts (relevant only in case of periodic boundary conditions)

AMSRResults%Bonds.Index**Type**

archived_int_array

Description

index(i) points to the first element of Atoms, Orders, and CellShifts belonging to bonds from atom 'i'. Index(1) is always 1, Index(nAtoms+1) is always nBonds + 1

AMSRResults%Bonds.nLattVec**Type**

int

Description

Number of lattice vectors (0:molecule, 1:chain, 2:slab, 3:bulk). This determines how the lattice displacements for bonds are interpreted.

AMSRResults%Bonds.Orders

Type

archived_float_array

Description

The bond orders.

AMSResults%BulkModulus**Type**

float

DescriptionThe Bulk modulus (conversion factor from hartree/bohr³ to GPa: 29421.026)**Unit**hartree/bohr³**AMSResults%Charges****Type**

float_array

Description

Net atomic charges as computed by the engine (for example, the Charges for a water molecule might be [-0.6, 0.3, 0.3]). The method used to compute these atomic charges depends on the engine.

Unit

e

Shape

[Molecule%nAtoms]

AMSResults%DipoleGradients**Type**

float_array

Description

Derivative of the dipole moment with respect to nuclear displacements.

Shape

[3, 3, Molecule%nAtoms]

AMSResults%DipoleMoment**Type**

float_array

Description

Dipole moment vector (x,y,z)

Unit

e*bohr

Shape

[3]

AMSResults%DipQuadPolarizability**Type**

float_array

Description

Electric dipole-quadrupole polarizability. Element order [X,Y,Z]
[XX,XY,XZ,YX,YY,YZ,ZX,ZY,ZZ].

Unit

a.u.

Shape

[3, 9]

AMSRResults%DipQuadPolarizabilityDerivs**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative electric dipole-quadrupole polarizability. Element order [X,Y,Z] [XX,XY,XZ,YX,YY,YZ,ZX,ZY,ZZ].

Unit

a.u.

Shape

[3, 9, :]

AMSRResults%DipQuadPolarizabilityDerivsImag**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative imaginary part electric dipole-quadrupole polarizability. Element order [X,Y,Z] [XX,XY,XZ,YX,YY,YZ,ZX,ZY,ZZ].

Unit

a.u.

Shape

[3, 9, :]

AMSRResults%DipQuadPolarizabilityImag**Type**

float_array

Description

Imaginary part electric dipole-quadrupole polarizability. Element order [X,Y,Z]
[XX,XY,XZ,YX,YY,YZ,ZX,ZY,ZZ].

Unit

a.u.

Shape

[3, 9]

AMSRResults%ElasticTensor**Type**

float_array

Description

The elastic tensor in Voigt notation (6x6 matrix for 3D periodic systems, 3x3 matrix for 2D periodic systems, 1x1 matrix for 1D periodic systems).

Unit

hartree/bohr^nLatticeVectors

Shape

[:, :]

AMSRResults%Energy**Type**

float

Description

The energy computed by the engine.

Unit

hartree

AMSRResults%fractionalOccupation**Type**

bool

Description

Whether or not we have fractionally occupied orbitals (i.e. not all occupations are integer numbers).

AMSRResults%Gradients**Type**

float_array

Description

The nuclear gradients.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

AMSRResults%GSESDerivs**Type**

float_array

Description

Thermally averaged ground-to-excited state electronic transition properties?

Shape

[:, 3*Molecule%nAtoms]

AMSRResults%GSESEnergies**Type**

float_array

Description

Thermally averaged ground-to-excited state electronic transition properties?

Shape

[:]

AMSRResults%GSESProperties

Type

float_array

Description

Thermally averaged ground-to-excited state electronic transition properties?

Shape

[:]

AMSResults%Hessian**Type**

float_array

Description

The Hessian matrix

Unithartree/bohr²**Shape**

[3*Molecule%nAtoms, 3*Molecule%nAtoms]

AMSResults%HOMOEnergy**Type**

float_array

Description

Molecular Orbital Info: energy of the HOMO.

Unit

hartree

Shape

[nSpin]

AMSResults%HOMOIndex**Type**

int_array

Description

Molecular Orbital Info: index in the arrays orbitalEnergies and orbitalOccupations corresponding to the HOMO.

Shape

[nSpin]

AMSResults%HOMOLUMOGap**Type**

float_array

Description

Molecular Orbital Info: HOMO-LUMO gap per spin.

Unit

hartree

Shape

[nSpin]

AMSResults%LUMOEnergy

Type

float_array

Description

Molecular Orbital Info: energy of the LUMO.

Unit

hartree

Shape

[nSpin]

AMSResults%LUMOIndex**Type**

int_array

Description

Molecular Orbital Info: index in the arrays orbitalEnergies and orbitalOccupations corresponding to the LUMO.

Shape

[nSpin]

AMSResults%Molecules**Type**

subsection

Description

Molecules

AMSResults%Molecules.AtCount**Type**

archived_int_array

Description

shape=(nMolType), Summary: number of atoms per formula.

AMSResults%Molecules.Atoms**Type**

archived_int_array

Description

shape=(nAtoms), atoms(index(i):index(i+1)-1) = atom indices of molecule i

AMSResults%Molecules.Count**Type**

archived_int_array

Description

Mol count per formula.

AMSResults%Molecules.Formulas**Type**

string

Description

Summary: unique molecule formulas

AMSResults%Molecules.Index

Type

archived_int_array

Description

shape=(nMol+1), index(i) = index of the first atom of molecule i in array atoms(:)

AMSResults%Molecules.Type**Type**

archived_int_array

Description

shape=(nMol), type of the molecule, reference to the summary arrays below

AMSResults%nOrbitals**Type**

int

Description

Molecular Orbital Info: number of orbitals.

AMSResults%nSpin**Type**

int

Description

Molecular Orbital Info: number spins (1: spin-restricted or spin-orbit coupling, 2: spin unrestricted).

AMSResults%OpticalRotation**Type**

float_array

Description

Optical rotation.

Unit

a.u.

Shape

[9]

AMSResults%OpticalRotationDerivs**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative optical rotation.

Unit

a.u.

Shape

[9, :]

AMSResults%OpticalRotationDerivsImag**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative imaginary part optical rotation.

Unit

a.u.

Shape

[9, :]

AMSResults%OpticalRotationImag**Type**

float_array

Description

Imaginary part optical rotation.

Unit

a.u.

Shape

[9]

AMSResults%orbitalEnergies**Type**

float_array

Description

Molecular Orbital Info: the orbital energies.

Unit

hartree

Shape

[nOrbitals, nSpin]

AMSResults%orbitalOccupations**Type**

float_array

Description

Molecular Orbital Info: the orbital occupation numbers. For spin restricted calculations, the value will be between 0 and 2. For spin unrestricted or spin-orbit coupling the values will be between 0 and 1.

Shape

[nOrbitals, nSpin]

AMSResults%PESPointCharacter**Type**

string

Description

The character of a PES point.

Possible values

['local minimum', 'transition state', 'stationary point with >1 negative frequencies', 'non-stationary point']

AMSResults%PoissonRatio

Type

float

Description

The Poisson ratio

AMSRResults%Polarizability**Type**

float_array

Description

(electric dipole-dipole) Polarizability. Elements order: [XX,XY,YY,XZ,YZ,ZZ].

Unit

a.u.

Shape

[6]

AMSRResults%PolarizabilityDerivs**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative (electric dipole-dipole) polarizability. Elements order: [XX,XY,YY,XZ,YZ,ZZ].

Unit

a.u.

Shape

[6, :]

AMSRResults%PolarizabilityDerivsImag**Type**

float_array

Description

(Cartesian or symmetry-adapted) Nuclear derivative imaginary part (electric dipole-dipole) polarizability. Elements order: [XX,XY,YY,XZ,YZ,ZZ].

Unit

a.u.

Shape

[6, :]

AMSRResults%PolarizabilityImag**Type**

float_array

Description

Imaginary part (electric dipole-dipole) polarizability. Elements order: [XX,XY,YY,XZ,YZ,ZZ].

Unit

a.u.

Shape

[6]

AMSResults%ShearModulus**Type**

float

DescriptionThe Shear modulus (conversion factor from hartree/bohr³ to GPa: 29421.026)**Unit**hartree/bohr³**AMSResults%SmallestHOMOLUMOGap****Type**

float

Description

Molecular Orbital Info: the smallest HOMO-LUMO gap irrespective of spin (i.e. min(LUMO) - max(HOMO)).

Unit

hartree

AMSResults%StressTensor**Type**

float_array

Description

The clamped-ion stress tensor in Cartesian notation.

Unithartree/bohrⁿLatticeVectors**Shape**

[:, :]

AMSResults%YoungModulus**Type**

float

DescriptionThe Young modulus (conversion factor from hartree/bohr³ to GPa: 29421.026)**Unit**hartree/bohr³

17.2.6 AngularBoost

KF Section: AngularBoost**Content:** Both the Becke grid and the Zlm fit grid may boost the angular grid for certain areas.**AngularBoost%boost****Type**

bool_array

Description

Whether to use a booster grid per atom.

17.2.7 AOMatrices

KF Section: AOMatrices

Content: Some matrices on AO

17.2.8 AORESPONSE

KF Section: AORESPONSE

Content: Results of AOResponse calculation

17.2.9 aoresponse_data

KF Section: aoresponse_data

Content: Technical AOresponse data

17.2.10 atens

KF Section: atens

Content: Data for spin-orbit unrestricted calculation of ESR A-tensor

17.2.11 Atyp*

KF Section: Atyp*

Content: The core (and possibly also valence) radial density and potential of one particular atom type. The radial densities and potentials may be represented as simple tables - a sequence of values for r , the distance to the nucleus, and the corresponding density or potential - or as a piecewise expansion in Chebyshev polynomials over a sequence of intervals ($r1, r2$). The core density and potential have been constructed from the Frozen Core orbitals, which are defined in the section Core.

Atyp*%ccheb core

Type

float_array

Description

Coefficients of the Chebyshev expansion for the core. All coefficients, for all intervals, are stored contiguously in one linear array. The parts pertaining to a particular interval are determined by using the arrays ncheb.

Atyp*%ccheb val

Type

float_array

Description

Coefficients of the Chebyshev expansion for the valence. All coefficients, for all intervals, are stored contiguously in one linear array. The parts pertaining to a particular interval are determined by using the arrays ncheb.

Atyp*%core den

Type

float_array

Description

The core density on the radial grid

Shape

[nrاد]

Atyp*%core den ext

Type

float_array

Description

The core density on the radial grid calculated with Dirac interpolated on standard grid

Shape

[nrاد]

Atyp*%core pot

Type

float_array

Description

The core Coulomb potential on the radial grid (including a nuclear term $-Q_{\text{core}}/r$).

Shape

[nrاد]

Atyp*%core pot ext

Type

float_array

Description

The core Coulomb potential on the radial grid (including a nuclear term $-Q_{\text{core}}/r$) calculated with Dirac interpolated on standard grid

Shape

[nrاد]

Atyp*%core totpot ext

Type

float_array

Description

Total KS potential calculated with Dirac interpolated on standard grid.

Shape

[nrاد]

Atyp*%ncheb core

Type

int_array

Description

Number of expansion coefficients for each interval (core).

Shape

[nrاد core]

Atyp*%ncheb val

Type
int_array

Description
Number of Chebyshev expansion coefficients for each interval.

Shape
[nrint val]

Atyp*%nrad

Type
int

Description
Number of points used in the direct tabular representation of the atomic densities and potentials.

Atyp*%nrad12

Type
int

Description
equals nrad

Atyp*%nrint core

Type
int

Description
Number of intervals for piecewise expansion of the core density in Chebyshev polynomials.

Atyp*%nrint val

Type
int

Description
Number of intervals for piecewise expansion of the valence density in Chebyshev polynomials.

Atyp*%qcore

Type
float

Description
The number of electrons contained in the core density.

Atyp*%qval

Type
float

Description
The number of electrons contained in the valence density.

Atyp*%rfac

Type
float

Description
The multiplication factor of the radial grid.

Atyp*%rmin

Type

float

Description

The first r-value of the table: the radial grid is defined by a first value (rmin), a constant multiplication factor defining rk+1 w.r.t. rk (rfac, see next), and the total nr of points (nrad).

Atyp*%rup core**Type**

float_array

Description

Upper bounds of the intervals (core). The lower bound of the first interval is zero.

Shape

[nrint core]

Atyp*%rup val**Type**

float_array

Description

Upper bounds of the intervals. The lower bound of the first interval is zero.

Shape

[nrint val]

Atyp*%rx core**Type**

float

Description

Maximum r-value for which the core density is non-negligible.

Atyp*%rx val**Type**

float

Description

Maximum r-value for which the valence density is non-negligible.

Atyp*%valence den**Type**

float_array

Description

The valence density on the radial grid.

Shape

[nrad]

Atyp*%valence pot**Type**

float_array

Description

The valence Coulomb potential on the radial grid (including a nuclear term -Qval/r).

Shape
[nrad]

17.2.12 Basis

KF Section: Basis

Content: Description of the (valence) basis set.

Basis%alf

Type
float_array

Description
Exponential decay factors of the nbos Cartesian STO basis functions.

Shape
[nbos]

Basis%alfbas

Type
float_array

Description
The exponential decay parameters of the STO functions in the basis set.

Shape
[nbset]

Basis%basnrm

Type
float_array

Description
Normalization coefficients for the basis sets.

Shape
[nbset]

Basis%bnorm

Type
float_array

Description
Normalization factors for the nbos Cartesian STO basis functions.

Shape
[nbos]

Basis%kr

Type
int_array

Description
Powers of r of the nbos Cartesian STO basis functions.

Shape
[nbos]

Basis%kx**Type**

int_array

Description

Powers of x of the nbos Cartesian STO basis functions.

Shape

[nbos]

Basis%ky**Type**

int_array

Description

Powers of y of the nbos Cartesian STO basis functions.

Shape

[nbos]

Basis%kz**Type**

int_array

Description

Powers of z of the nbos Cartesian STO basis functions.

Shape

[nbos]

Basis%lorde**Type**

int_array

Description

Maximum of the angular momentum quantum number (l) for all STO basis and fit functions corresponding to that atom type.

Shape

[Geometry%nr of atomtypes]

Basis%lqbas**Type**

int_array

Description

Angular momentum quantum number of each basis set. The current implementation of ADF supports only s, p, d, and f basis functions, so the allowed lqbas values are 0, 1, 2, and 3.

Shape

[nbset]

Basis%naos**Type**

int

Description

The total number of basis functions, counting all Cartesian polynomials and all copies of the functions on the atoms of the pertaining atom type.

Basis%nbaspt**Type**

int_array

Description

Cumulative number of basis sets (see nbset variable, for 'set'), on a per atom type basis.

Basis%nbos**Type**

int

Description

The total number of Cartesian basis functions, not counting the copies of the functions on the different atoms of the atom type: the functions are defined per atom type and are (for nbos) counted only once. Essentially, this means counting all functions with distinct characteristics (apart from their geometrical center).

Basis%nbptr**Type**

int_array

Description

Index array of the nbos functions, where the entries are the cumulative numbers of functions.

Basis%nbset**Type**

int

Description

The total number of basis 'sets', where a 'set' here means a Cartesian function set (3 for a p-type function, 6 for a d-type function, and so on),

Basis%norde**Type**

int_array

Description

Maximum of the main quantum number for all STO basis and fit functions corresponding to that atom type.

Shape

[Geometry%nr of atomtypes]

Basis%nppta**Type**

int_array

Description

nppta(i) contains number of Cartesian basis function i in an ordering in which all Cartesian core orthogonalization functions precede all Cartesian valence functions.

Shape

[naos]

Basis%nqbas**Type**

int_array

Description

Main quantum number of each basis set. A 4p function has main quantum number 4.

Shape

[nbset]

17.2.13 BeckeGridConfig

KF Section: BeckeGridConfig

Content: Configuration used to create the Becke grid.

BeckeGridConfig%angLOrder**Type**

int_array

Description

?

Shape

[:]

BeckeGridConfig%beckeMapParams**Type**

float_array

Description

Mapping parameter per atom.

Shape

[nAtoms]

BeckeGridConfig%includeRadialWeights**Type**

bool

Description

Whether or not to include the radial weights. Normally you want this.

BeckeGridConfig%isSymmetryUnique**Type**

bool_array

Description

Is an atom symmetry unique?

Shape

[nAtoms]

BeckeGridConfig%minimumRadius**Type**

float

Description

To solve the exact singularity a small hard sphere around the nuclei can be used. The partition function starts beyond this radius.

BeckeGridConfig%mpvPartitionCheckSpheres

Type

bool

Description

Whether or not to check the spheres for the MPV partitioning.

BeckeGridConfig%nAtoms**Type**

int

Description

Number of atoms.

BeckeGridConfig%nRadPoints**Type**

int_array

Description

Number of radial points per atom.

Shape

[nAtoms]

BeckeGridConfig%oper**Type**

float_array

Description

Point group part of the symmetry operators.

Shape

[3, 3, :]

BeckeGridConfig%partitionFunThresh**Type**

float

Description

Threshold for the partition function.

BeckeGridConfig%qAtoms**Type**

float_array

Description

Atomic number per atom.

Shape

[nAtoms]

BeckeGridConfig%quality**Type**

string_fixed_length

Description

Quality used.

BeckeGridConfig%transl

Type

float_array

Description

Translational part of the symmetry operators.

Shape

[3, :]

BeckeGridConfig%vectors**Type**

float_array

Description

Lattice vectors

Unit

bohr

BeckeGridConfig%xyzAtoms**Type**

float_array

Description

Atom coordinates.

Unit

bohr

Shape

[3, nAtoms]

17.2.14 ConstrainedDFT

KF Section: ConstrainedDFT**Content:** Constrained DFT data.

17.2.15 ConstructPotential

KF Section: ConstructPotential**Content:** Data related to FDE potential reconstruction.

17.2.16 ConstructPotential_FunctionSet

KF Section: ConstructPotential_FunctionSet**Content:** Data related to FDE potential reconstruction.

17.2.17 Core

KF Section: Core

Content: Description of the auxiliary core functions and core orthogonalization functions.

Core%alfcor

Type

float_array

Description

Alpha values (the exponent in the Slater type-function) for the auxiliary core functions set.

Shape

[ncset]

Core%ccor

Type

float_array

Description

All core coefficients, which expresses the core orbitals in the auxiliary core functions.

Core%cmat

Type

float_array

Description

Overlap matrix between Cartesian core orbitals and Cartesian basis functions. In the list of Cartesian basis functions all Cartesian core orthogonalization functions precede all Cartesian valence basis functions (see array Basis%nprta).

Shape

[ncos, Basis%naos]

Core%cornrm

Type

float_array

Description

Normalization factors for the auxiliary core functions.

Shape

[ncset]

Core%idfcor

Type

int

Description

Integer that indicates whether there are d- and/or f-orbitals in the core. 1=yes, 0=no.

Core%kcos

Type

int

Description

Total number of spherical harmonics core orthogonalization functions, counting 1 d-orbital as 5 functions, and 1 f-orbital as 7 functions.

Core%kinetic_energy

Type
float

Description
Kinetic energy of the core orbitals.

Core%lqcor

Type
int_array

Description
Angular momentum quantum numbers (l-value) for the auxiliary core functions set.

Shape
[ncset]

Core%nccpt

Type
int_array

Description
Index array. 1 + cumulative number of Cartesian core orthogonalization functions.

Shape
[Geometry%ntyp+1]

Core%ncorpt

Type
int_array

Description
Index array. 1 + cumulative number of auxiliary core functions set.

Shape
[Geometry%ntyp+1]

Core%ncos

Type
int

Description
Total number of Cartesian core orthogonalization functions.

Core%ncpt r

Type
int_array

Description
Index array. 1 + cumulative number of Cartesian auxiliary core functions.

Shape
[Geometry%ntyp+1]

Core%ncset

Type
int

Description

The total number of auxiliary core functions set.

Core%nd

Type

int

Description

Total number of d-type auxiliary core functions set.

Core%ndd

Type

int

Description

Equals nd

Core%ndfun

Type

int_array

Description

Array of indices of d-orbital Cartesian core orthogonalization functions (the last of the Cartesian subset of size 6) in an ordering in which all Cartesian core orthogonalization functions precede all Cartesian valence functions (see array Basis%nprta). Equals Size ndd+1. Last element is 0.

Core%ndorb

Type

int_array

Description

Array of indices of d-orbital Cartesian core orthogonalization functions (the first of the Cartesian subset of size 6) in an ordering in which all Cartesian core orthogonalization functions precede all Cartesian valence functions (see array Basis%nprta). Size nd+1. Last element is 0.

Core%nf

Type

int

Description

Total number of f-type auxiliary core functions set.

Core%nff

Type

int

Description

Equals nf

Core%nffun

Type

int_array

Description

Array of indices of f-orbital Cartesian core orthogonalization functions (the last of the Cartesian subset of size 10) in an ordering in which all Cartesian core orthogonalization functions precede all Cartesian valence functions (see array Basis%nprta). Size nff+1. Last element is 0.

Core%*nf*orb**Type**

int_array

Description

Array of indices of f-orbital Cartesian core orthogonalization functions (the first of the Cartesian subset of size 10) in an ordering in which all Cartesian core orthogonalization functions precede all Cartesian valence functions (see array Basis%*np*rta). Size *nf*+1. Last element is 0.

Core%*np*os**Type**

int_array

Description

Index for each atom where core data can be found on TAPE12 file created with Dirac.

Shape[Geometry%*nn*nuc]**Core%*nq*cor****Type**

int_array

Description

Main quantum numbers (*n*-value) for the auxiliary core functions set.

Shape[*nc*set]**Core%*nr*corb****Type**

int_array

Description

The number of frozen core orbitals per *l*-value and atom type.

Shape[4, Geometry%*nt*yp]**Core%*nr*cset****Type**

int_array

Description

The number of auxiliary core functions set per *l*-value and atom type.

Shape[4, Geometry%*nt*yp]**Core%*s*****Type**

float_array

Description

Overlap matrix between spherical harmonics core orbitals and spherical harmonics core orthogonalization functions.

Shape[*k*cos, *k*cos]

17.2.18 COSMO

KF Section: COSMO

Content: COSMO solvation model related data.

COSMO%Area

Type

float

Description

COSMO cavity surface area.

Unit

bohr²

COSMO%Atom Coordinates

Type

float_array

Description

Atom coordinates.

Unit

angstrom

Shape

[3, Number of Atoms]

COSMO%Atom COSMO Radii

Type

float_array

Description

Atom COSMO radii.

Unit

bohr

Shape

[Number of Atoms]

COSMO%Atom Type

Type

lchar_string_array

Description

Atom type names.

Shape

[Number of Atoms]

COSMO%Bond Energy

Type

float

Description

Bond energy (including COSMO).

Unit

hartree

COSMO%Gas Phase Bond Energy**Type**

float

Description

Gas phase bond energy

Unit

hartree

COSMO%HBC angles**Type**

float_array

Description

Angles between the position vector and the eigenvector.

Shape

[Number of HBCs]

COSMO%HBC Atom**Type**

int_array

Description

Atom associated with hydrogen bond center.

Shape

[Number of HBCs]

COSMO%HBC Coordinates**Type**

float_array

Description

hydrogen bond center coordinates.

Shape

[Number of HBCs, 3]

COSMO%HBC Rcut**Type**

float_array

Description

Cut off distance of the hydrogen bonding center.

Shape

[Number of HBCs]

COSMO%Number of Atoms**Type**

int

Description

Number of atoms.

COSMO%Number of HBCs

Type
int

Description
Number of hydrogen bond centers.

COSMO%Number of Segments

Type
int

Description
Number of segments (number of COSMO surface points).

COSMO%Segment Area

Type
float_array

Description
COSMO surface point area.

Unit
angstrom^2

Shape
[Number of Segments]

COSMO%Segment Atom

Type
int_array

Description
Atom associated with COSMO surface point.

Shape
[Number of Segments]

COSMO%Segment Charge

Type
float_array

Description
COSMO surface point charge.

Unit
e

Shape
[Number of Segments]

COSMO%Segment Charge Density

Type
float_array

Description
COSMO surface point charge density.

Unit
e/angstrom^2

Shape

[Number of Segments]

COSMO%Segment Coordinates**Type**

float_array

Description

COSMO surface point coordinates.

Unit

bohr

Shape

[Number of Segments, 3]

COSMO%Segment Potential**Type**

float_array

Description

COSMO surface point solute potential (angstrom length scale).

Shape

[Number of Segments]

COSMO%Volume**Type**

float

Description

COSMO cavity volume.

Unitbohr³

17.2.19 Critical Points

KF Section: Critical Points**Content:** Data related to AIM critical points.

17.2.20 CriticalPoints

KF Section: CriticalPoints**Content:** Data related to the Critical Points of the AIM Local Analysis.**CriticalPoints%Atom association****Type**

int_array

Description

Atom associated with each CP.

CriticalPoints%Atoms Bonded at CP**Type**

int_array

Description

Atoms bonded at the CP.

CriticalPoints%Atoms Bonded with CP**Type**

int_array

Description

Atoms bonded WITH CP.

CriticalPoints%Atoms in Cage**Type**

int_array

Description

Size of the cage, cp associated, atoms in the ring.

CriticalPoints%Atoms in Rings**Type**

int_array

Description

Size of the ring, cp associated, atoms in the ring.

CriticalPoints%Bond length**Type**

float_array

Description

?

CriticalPoints%Energy components**Type**

float_array

Description

Gb, Vb, Hb (Abramov), Ex, Ec (ueg), Delta (ex, ec, et), Pxc, Qxc

CriticalPoints%GLDDQME**Type**

float_array

Description

Gradient, Laplacian, Diamond, QDialapl, Metallicity, Ellipticity

CriticalPoints%Grid change**Type**

bool

Description

Does the grid change for the AIM analysis?

CriticalPoints%Info warning vector**Type**

int_array

Description

Info status of every Critical Point.

CriticalPoints%Inhomogeneity**Type**

float_array

Description

Delta u, Delta s, Delta t, Inhom s, Inhom ex

CriticalPoints%New grid spacing**Type**

float

Description

Grid spacing used for the AIM analysis.

CriticalPoints%Number of Bond CP**Type**

int

Description

Bond Attractors.

CriticalPoints%Number of Cage CP**Type**

int

Description

Cage Attractors.

CriticalPoints%Number of Non-Nuclear CP**Type**

int

Description

Non-Nuclear Attractors.

CriticalPoints%Number of Nuclear CP**Type**

int

Description

Nuclear Attractors.

CriticalPoints%Number of Ring CP**Type**

int

Description

Ring Attractors.

CriticalPoints%Poincare-Hopf relationship**Type**

bool

Description

Poincare-Hopf relationship

CriticalPoints%Type of CP

Type
int_array

Description
Type of every CP.

17.2.21 CSMRSP

KF Section: CSMRSP
Content: COSMO response data.

17.2.22 CurrentMatrix

KF Section: CurrentMatrix
Content: Current response data.

17.2.23 DIMQM

KF Section: DIMQM
Content: Data related to the DIM/QM procedure.

17.2.24 Dipole velocity matrix

KF Section: Dipole velocity matrix
Content: Dipole velocity matrix.

17.2.25 EgoData

KF Section: EgoData
Content: Data for the EGO (excited states gradients) procedure.

17.2.26 Elec multipole ints OCCOCC

KF Section: Elec multipole ints OCCOCC
Content: Data for XES.

17.2.27 Elec multipole ints OCCVIR

KF Section: Elec multipole ints OCCVIR
Content: Data for XAS.

17.2.28 ElstatEmbed

KF Section: ElstatEmbed

Content: The electrostatic embedding (i.e. point charges, electric field, ...) used in the ADF calculation.

ElstatEmbed%eeAttachTo

Type

int_array

Description

UNUSED IN AMS $\geq$ 2026. A multipole may be attached to an atom. This influences the energy gradient.

ElstatEmbed%eeChargeWidth

Type

float

Description

If charge broadening was used for external charges, this represents the width of the charge distribution.

ElstatEmbed%eeEField

Type

float_array

Description

The external homogeneous electric field.

Unit

hartree/(e*bohr)

Shape

[3]

ElstatEmbed%eeLatticeVectors

Type

float_array

Description

UNUSED IN AMS $\geq$ 2026. The lattice vectors used for the external point- or multipole-charges.

Unit

bohr

Shape

[3, eeNLatticeVectors]

ElstatEmbed%eeMulti

Type

float_array

Description

The values of the external point- or multipole- charges.

Unit

a.u.

Shape

[eeNZlm, eeNMulti]

ElstatEmbed%eeNLatticeVectors**Type**

int

Description

UNUSED IN AMS>=2026. The number of lattice vectors for the external point- or multipole- charges.

ElstatEmbed%eeNMulti**Type**

int

Description

The number of external point- or multipole- charges.

ElstatEmbed%eeNZlm**Type**

int

Description

When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

ElstatEmbed%eeUseChargeBroadening**Type**

bool

Description

Whether or not the external charges are point-like or broadened.

ElstatEmbed%eeXYZ**Type**

float_array

Description

The position of the external point- or multipole- charges.

Unit

bohr

Shape

[3, eeNMulti]

17.2.29 Energy

KF Section: Energy

Content: Energy terms related to energy decomposition analysis.

Energy%Bond Energy

Type

float

Description

Total bonding energy, same as the 'SCF Bond Energy' variable.

Unit

hartree

Energy%CCSD energy

Type

float

Description

CCSD energy.

Unit

hartree

Energy%Corr. due to Orthogonalization

Type

float

Description

For analysis purposes, the concept of 'orthogonalized fragments' has been introduced and the bonding energy is split in a part that describes the difference between the sum-of-fragments situation and the orthogonalized-fragments density at the one hand, and the SCF relaxation (from the orthogonalized fragments density) at the other. Both terms contain a first order fit correction term. The result of adding the two parts is not identical to computing the total bonding energy directly and applying the first order correction to that approach. The difference is given by this term, which therefore corrects for the additional second order fit errors caused by using the orthogonalized fragments split-up.

Unit

hartree

Energy%Dispersion Energy

Type

float

Description

Dispersion energy.

Unit

hartree

Energy%Ebond due to Efield

Type

float

Description

Bond energy term due to any homogeneous electric field.

Unit

hartree

Energy%Electrostatic Energy**Type**

float

Description

Electrostatic Energy.

Unit

hartree

Energy%Electrostatic Interaction**Type**

float

Description

The electrostatic interaction energy including any first order fit correction (if computed from the fit density).

Unit

hartree

Energy%Elstat FitCorrection**Type**

float

Description

The first-order correction to the electrostatic interaction term (putting the fragments together, without any relaxation of Pauli orthogonalization), for the error in the Coulomb energy due to the fit incompleteness.

Unit

hartree

Energy%Elstat Interaction**Type**

float

Description

Elstat interaction.

Unit

hartree

Energy%Energy wrt atomic create runs**Type**

float

Description

(excited state) Bond Energy with respect to atomic create runs.

Unit

hartree

Energy%ET1_Bond Energy**Type**

float

Description

Total bonding energy for state 1 in FO-CDFT electron transfer.

Unit

hartree

Energy%Excited State Bond Energy**Type**

float

Description

Excited State Bond Energy.

Unit

hartree

Energy%HF Exen Ort**Type**

float

Description

HF exchange energy using orthonormalized orbitals.

Unit

hartree

Energy%HF Exen SCF**Type**

float

Description

HF exchange energy using SCF orbitals.

Unit

hartree

Energy%HF SO Exen SCF**Type**

float

Description

HF exchange energy using SCF orbitals related to spin-orbit coupling.

Unit

hartree

Energy%HF SOU Exen SCF**Type**

float

Description

HF exchange energy using SCF orbitals related to open shell spin-orbit coupling.

Unit

hartree

Energy%Hybrid Exen Ort**Type**

float

Description

HF exchange part hybrid exchange energy using orthonormalized orbitals.

Unit

hartree

Energy%Hybrid Exen SCF**Type**

float

Description

HF exchange part hybrid exchange energy using SCF orbitals.

Unit

hartree

Energy%Hybrid SO Exen SCF**Type**

float

Description

HF exchange part hybrid exchange energy using SCF orbitals related to spin-orbit coupling.

Unit

hartree

Energy%Hybrid SOU Exen SCF**Type**

float

Description

HF exchange part hybrid exchange energy using SCF orbitals related to open shell spin-orbit coupling.

Unit

hartree

Energy%Kinetic Energy**Type**

float

Description

Kinetic energy part of bonding energy.

Unit

hartree

Energy%MP2 energy**Type**

float

Description

MP2 energy.

Unit

hartree

Energy%Orb.Int. *

Type

float

Description

- stands for one of the irreps of the point group symmetry. The value gives the orbital interaction (SCF relaxation) term for that symmetry representation.

Unit

hartree

Energy%Orb.Int. Efield**Type**

float

Description

The contribution to the SCF relaxation energy (orbital interactions) due to any electric field.

Unit

hartree

Energy%Orb.Int. FitCorrection**Type**

float

Description

The first-order correction to the electrostatic interaction term in the SCF relaxation energy (Orbital Interactions), for the error in the Coulomb energy due to the fit incompleteness. This term is not printed (anymore) separately, but incorporated in the symmetry-specific interaction terms.

Unit

hartree

Energy%Orb.Int. Total**Type**

float

Description

The total orbital interaction energy.

Unit

hartree

Energy%Orb.Int. TSCorrection (LDA)**Type**

float

Description

The difference between the representation-specific orbital interaction terms added, and a straightforward computation of the SCF relaxation energy is the result of the neglect of higher order terms in the Taylor expansion that underlies the 'Transition State' method. This difference, therefore, corrects exactly this neglect. It is not printed separately anymore in the output, but incorporated in (distributed over) the representation-specific orbital interaction terms. LDA part.

Unit

hartree

Energy%Orb.Int. TSCorrection (NL)

Type

float

Description

Similar as Orb.Int. TSCorrection (LDA), but then for GGA part.

Unit

hartree

Energy%Pauli Coulomb**Type**

float

Description

Coulomb energy term in the Pauli exchange interaction energy.

Unit

hartree

Energy%Pauli Efield**Type**

float

Description

The contribution to the Pauli interaction energy due to any electric field.

Unit

hartree

Energy%Pauli FitCorrection**Type**

float

Description

The first-order correction to the Pauli exchange interaction term, for the error in the Coulomb energy due to the fit incompleteness. This correction term is not printed in the output file but included in the Pauli interaction term.

Unit

hartree

Energy%Pauli Kinetic**Type**

float

Description

Kinetic energy term in the Pauli exchange interaction energy.

Unit

hartree

Energy%Pauli Kinetic+Coulomb**Type**

float

Description

Sum of the kinetic and Coulomb terms in the Pauli exchange interaction energy.

Unit

hartree

Energy%Pauli Total**Type**

float

Description

The Pauli exchange (orbital orthogonalization) interaction energy.

Unit

hartree

Energy%Pauli TS Correction (LDA)**Type**

float

Description

Correction to the 'Transition State' method to compute terms in the bonding energy, in this case the Pauli exchange energy term. The Pauli TS Correction is not separately printed in the standard output file, but included in the Pauli interaction term.

Unit

hartree

Energy%post-SCF Orb.Int. Correlation**Type**

float

Description

post-SCF orbital interaction Correlation energy.

Unit

hartree

Energy%post-SCF Orb.Int. Exchange**Type**

float

Description

post-SCF orbital interaction Exchange energy.

Unit

hartree

Energy%post-SCF Pauli Correlation**Type**

float

Description

post-SCF Pauli Correlation energy.

Unit

hartree

Energy%post-SCF Pauli Exchange**Type**

float

Description

post-SCF Pauli Exchange energy.

Unit

hartree

Energy%RPA energy**Type**

float

Description

RPA energy.

Unit

hartree

Energy%SCF Bond Energy**Type**

float

Description

Total bonding energy.

Unit

hartree

Energy%Solvation Energy (cd)**Type**

float

Description

COSMO Solvation Energy (cd).

Unit

hartree

Energy%Solvation Energy (el)**Type**

float

Description

COSMO Solvation Energy (el).

Unit

hartree

Energy%Solvation Energy (Gcds)**Type**

float

Description

SM12 Solvation Energy (Gcds).

Unit

hartree

Energy%Solvation Energy (Gp)**Type**

float

Description

SM12 Solvation Energy (Gp).

Unit

hartree

Energy%Steric Total**Type**

float

Description

The total steric interaction energy, consisting of the electrostatic and the Pauli interactions.

Unit

hartree

Energy%SumFragmentsSCF FitCorrection**Type**

float

Description

The 'true' first order fit correction for the complete bonding energy, resulting from a direct calculation that takes the sum-of-fragments as starting point and the SCF as final situation, without the intermediate step of orthogonalized fragments.

Unit

hartree

Energy%Total BE without XC**Type**

float

Description

Total bonding energy without XC energy.

Unit

hartree

Energy%Total BE without XC and Disp**Type**

float

Description

Total bonding energy without XC energy and without Dispersion energy.

Unit

hartree

Energy%XC energies**Type**

float_array

Description

exchange-correlation energies of various charge densities: first index: 1=exchange term, 2=correlation term second index: 1=lda term, 2=gga term third index: 1=energy of fragments (summed over fragments), 2=energy of sum-of-fragments density, 3=energy of orthogonalized fragments, 4=SCF.

Unit

hartree

Shape

[2, 2, 4]

Energy%XC Energy**Type**

float

Description

XC energy

Unit

hartree

Energy%XC SOU spin-polarization energy**Type**

float_array

Description

part of XC energy contributions in case of open shell spin-orbit coupling.

Unit

hartree

Shape

[2, 2]

17.2.30 ETS

KF Section: ETS

Content: Data used for the energy decomposition scheme (EDA), mostly related to core orbitals. ETS is the Extended Transition State method.

17.2.31 Excitations SD *

KF Section: Excitations SD *

Content: Spinflip-Down excitations for a given irrep.

Excitations SD **B Vectors ***Type**

float_array

Description

Similar as F Vectors, but the basis can be different.

Shape

[nr of densities]

Excitations SD **coef_Trans #{ExcitationNumber}**Type**

float_array

Description

Transition density fit coefficients in case of STOFIT.

Excitations SD **contr #{ExcitationNumber}

Type

float_array

Description

Large contributions excited state vector expressed in single-orbital transitions.

Shape

[nr of contributions #{ExcitationNumber}]

Excitations SD *%contr index #{ExcitationNumber}**Type**

int_array

Description

Indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SD *%contr irep index #{ExcitationNumber}**Type**

int_array

Description

Symmetry indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SD *%contr spin #{ExcitationNumber}**Type**

int_array

Description

Integer related to spin symmetry of contribution.

Shape

[nr of contributions #{ExcitationNumber}, 2]

Excitations SD *%contr transdip #{ExcitationNumber}**Type**

float_array

Description

Contribution to transition dipole moment.

Shape

[3, nr of contributions #{ExcitationNumber}]

Excitations SD *%coupling transformation**Type**

float_array

Description

Eigenvectors of the electronic coupling matrix.

Shape

[nr of excenergies, nr of excenergies]

Excitations SD *%%ct_at_pl* **#**{ExcitationNumber}

Type

float

Description

Charge transfer descriptor CT_AT: an atomic distance criterion is used, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SD *%%ct_pl* **#**{ExcitationNumber}

Type

float

Description

Charge transfer descriptor CT: fragment based, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SD *%%CV2DFT excenergies*

Type

float_array

Description

CV(2)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SD *%%Degeneracy*

Type

int_array

Description

MCD related data related to degeneracy of excited states.

Shape

[nr of excenergies]

Excitations SD *%%eigenvector* **#**{ExcitationNumber}

Type

float_array

Description

Excited state eigenvector expressed in single-orbital transitions.

Excitations SD *%%electronic couplings*

Type

float_array

Description

Electronic couplings calculated localized excitation energies.

Shape

[nr of excenergies, nr of excenergies]

Excitations SD *%%excenergies*

Type

float_array

Description

Excitation energies.

Unit

hartree

Shape

[nr of excenergies]

Excitations SD *%Exctyp *

Type

int_array

Description

Excited state type vector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations SD *%F Vectors *

Type

float_array

Description

Excited state eigenvector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations SD *%gradient #{ExcitationNumber}

Type

float_array

Description

Excited state gradients (input order).

Shape

[3, Molecule%nAtoms]

Excitations SD *%Gradients_CART #{ExcitationNumber}

Type

float_array

Description

Excited state gradients (internal order).

Shape

[3, Molecule%nAtoms]

Excitations SD *%index in all localized

Type

int_array

Description

Index array for one type of localized excitations in list of all localized excitations with the same irrep.

Shape

[nr of excenergies]

Excitations SD *%lambda_pt #{ExcitationNumber}

Type
float

Description

Charge-transfer diagnostic overlap quantity LAMBDA, based on Peach, Tozer, et al. A smaller value means more charge transfer character.

Excitations SD *%left eigenvector #{ExcitationNumber}

Type
float_array

Description

Excited state eigenvector (X-Y) expressed in single-orbital transitions.

Excitations SD *%magnetic trans dip

Type
float_array

Description

Magnetic transition dipole moment.

Shape
[3, nr of excenergies]

Excitations SD *%nr of contributions #{ExcitationNumber}

Type
int

Description

Number of large contributions excited state vector expressed in single-orbital transitions.

Excitations SD *%nr of densities

Type
int

Description

Number of single-orbital transitions.

Excitations SD *%nr of excenergies

Type
int

Description

Number of calculated excitation energies.

Excitations SD *%nr of NTOs #{ExcitationNumber}

Type
int

Description

Number of large contributions excited state vector expressed in NTO transitions.

Excitations SD *%NTO #{NTOindex} occ #{ExcitationNumber}

Type
float_array

Description

Occupied natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape

[Basis%naos, :]

Excitations SD *%NTO #{NTOindex} virt #{ExcitationNumber}

Type

float_array

Description

Virtual natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape

[Basis%naos, :]

Excitations SD *%NTO contr #{ExcitationNumber}

Type

float_array

Description

Large contributions excited state vector expressed in NTO transitions.

Shape

[nr of NTOs #{ExcitationNumber}]

Excitations SD *%oscillator strengths

Type

float_array

Description

Oscillator strengths for absorption on ground state to excited state.

Unit**Shape**

[nr of excenergies]

Excitations SD *%R-CVnDFT excenergies

Type

float_array

Description

R-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SD *%rhe_pl #{ExcitationNumber}

Type

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Plasser, Lischka, et al.

Excitations SD *%rhe_pt #{ExcitationNumber}

Type

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Guido, Adamo, et al.

Excitations SD *%rotatory strengths**Type**

float_array

Description

Rotatory strengths.

Shape

[nr of excenergies]

Excitations SD *%SCF-CVnDFT excenergies**Type**

float_array

Description

SCF-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SD *%transition dipole moments**Type**

float_array

Description

Transition dipole moment between ground state and excited state.

Unit

bohr

Shape

[3, nr of excenergies]

Excitations SD *%transition dipoles dip-vel**Type**

float_array

Description

Velocity formula used for calculated transition dipole moment between ground state and excited state.

Shape

[3, nr of excenergies]

Excitations SD *%type of excitations**Type**

string

Description

Type of excitations specifying the spin multiplicity of the excitations.

Excitations SD *%unrelaxed dipole moments**Type**

float_array

Description

Unrelaxed dipole moments of the excited state.

Shape

[3, nr of excenergies]

17.2.32 Excitations SO *

KF Section: Excitations SO *

Content: Spin-orbit excitations for a given irrep

Excitations SO *%%coef_Trans* **#**{ExcitationNumber}

Type

float_array

Description

Transition density fit coefficients in case of STOFIT.

Excitations SO *%%contr* **#**{ExcitationNumber}

Type

float_array

Description

Large contributions excited state vector expressed in single-orbital transitions.

Shape

[nr of contributions #{ExcitationNumber}]

Excitations SO *%%contr index* **#**{ExcitationNumber}

Type

int_array

Description

Indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SO *%%contr irep index* **#**{ExcitationNumber}

Type

int_array

Description

Symmetry indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SO *%%contr slab* **#**

Type

lchar_string_array

Description

Spin symmetry label for each contribution. Size [nr of contributions #].

Excitations SO *%%coupling transformation*

Type

float_array

Description

Eigenvectors of the electronic coupling matrix.

Shape

[nr of excenergies, nr of excenergies]

Excitations SO *%ct_at_pl #{ExcitationNumber}**Type**

float

Description

Charge transfer descriptor CT_AT: an atomic distance criterion is used, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SO *%ct_pl #{ExcitationNumber}**Type**

float

Description

Charge transfer descriptor CT: fragment based, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SO *%CV2DFT excenergies**Type**

float_array

Description

CV(2)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SO *%Degeneracy**Type**

int_array

Description

MCD related data related to degeneracy of excited states.

Shape

[nr of excenergies]

Excitations SO *%eigenvectors Im**Type**

float_array

Description

Imag part of eigenvectors of Omega SO from a ROKS-TDA-SOC state interaction

Excitations SO *%eigenvectors Re**Type**

float_array

Description

Real part of eigenvectors of Omega SO from a ROKS-TDA-SOC state interaction

Excitations SO *%electronic couplings**Type**

float_array

Description

Electronic couplings calculated localized excitation energies.

Shape

[nr of excenergies, nr of excenergies]

Excitations SO *%electronic couplings Im**Type**

float_array

Description

Imag part of electronic couplings between localized ROKS-TDA-SOC states

Excitations SO *%electronic couplings Re**Type**

float_array

Description

Real part of electronic couplings between localized ROKS-TDA-SOC states

Excitations SO *%excenergies**Type**

float_array

Description

Excitation energies.

Unit

hartree

Shape

[nr of excenergies]

Excitations SO *%gradient #{ExcitationNumber}**Type**

float_array

Description

Excited state gradients (input order).

Shape

[3, Molecule%nAtoms]

Excitations SO *%Gradients_CART #{ExcitationNumber}**Type**

float_array

Description

Excited state gradients (internal order).

Shape

[3, Molecule%nAtoms]

Excitations SO *%index in all localized

Type

int_array

Description

Index array for one type of localized excitations in list of all localized excitations with the same irrep.

Shape

[nr of excenergies]

Excitations SO *%index in all localized SO**Type**

int_array

Description

Index array for one type of localized excitations in list of all localized excitations with the same irrep.

Excitations SO *%lambda_pt #{ExcitationNumber}**Type**

float

Description

Charge-transfer diagnostic overlap quantity LAMBDA, based on Peach, Tozer, et al. A smaller value means more charge transfer character.

Excitations SO *%magnetic trans dip**Type**

float_array

Description

Magnetic transition dipole moment.

Shape

[3, nr of excenergies]

Excitations SO *%nr of contributions #{ExcitationNumber}**Type**

int

Description

Number of large contributions excited state vector expressed in single-orbital transitions.

Excitations SO *%nr of densities**Type**

int

Description

Number of single-orbital transitions.

Excitations SO *%nr of excenergies**Type**

int

Description

Number of calculated excitation energies.

Excitations SO *%nr of NTOs #{ExcitationNumber}

Type
int

Description

Number of large contributions excited state vector expressed in NTO transitions.

Excitations SO *%nr of scexcenergies

Type
int

Description

Number of calculated spin-conserved excitation energies that take part in a ROKS-TDA-SOC state interaction.

Excitations SO *%nr of sfexcenergies

Type
int

Description

Number of calculated spin-flip excitation energies that take part in a ROKS-TDA-SOC state interaction.

Excitations SO *%NTO #{NTOindex} occ #{ExcitationNumber}

Type
float_array

Description

Occupied natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape
[Basis%naos, :]

Excitations SO *%NTO #{NTOindex} virt #{ExcitationNumber}

Type
float_array

Description

Virtual natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape
[Basis%naos, :]

Excitations SO *%NTO contr #{ExcitationNumber}

Type
float_array

Description

Large contributions excited state vector expressed in NTO transitions.

Shape
[nr of NTOs #{ExcitationNumber}]

Excitations SO *%oscillator strengths

Type
float_array

Description

Oscillator strengths for absorption on ground state to excited state.

Unit**Shape**

[nr of excenergies]

Excitations SO *%overlap localized states Im

Type

float_array

Description

Imag part of overlap between localized ROKS-TDA-SOC states

Excitations SO *%overlap localized states Re

Type

float_array

Description

Real part of overlap between localized ROKS-TDA-SOC states

Excitations SO *%R-CVnDFT excenergies

Type

float_array

Description

R-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SO *%rhe_pl #{ExcitationNumber}

Type

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Plasser, Lischka, et al.

Excitations SO *%rhe_pt #{ExcitationNumber}

Type

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Guido, Adamo, et al.

Excitations SO *%rotatory strengths

Type

float_array

Description

Rotatory strengths.

Shape

[nr of excenergies]

Excitations SO *%SCF-CVnDFT excenergies

Type

float_array

Description

SCF-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SO *%SOMat-I

Type

float_array

Description

Imaginary part spin-orbit matrix in case of perturbative inclusion of spin-orbit coupling. Packed matrix.

Unit

hartree

Excitations SO *%SOMat-R

Type

float_array

Description

Real part spin-orbit matrix in case of perturbative inclusion of spin-orbit coupling in the basis of solutions without spin-orbit coupling. On the diagonal the excitation energy without spin-orbit coupling is added. Packed matrix.

Unit

hartree

Excitations SO *%symmetry label

Type

string

Description

Double group symmetry label.

Excitations SO *%transition dipole moments

Type

float_array

Description

Transition dipole moment between ground state and excited state.

Unit

bohr

Shape

[3, nr of excenergies]

Excitations SO *%transition dipoles dip-vel

Type

float_array

Description

Velocity formula used for calculated transition dipole moment between ground state and excited state.

Shape

[3, nr of excenergies]

Excitations SO *%%type of excitations*

Type

string

Description

Type of excitations specifying the spin multiplicity of the excitations.

17.2.33 Excitations SS *

KF Section: Excitations SS *

Content: Singlet-Singlet excitations for a given irrep.

Excitations SS *%%B Vectors **

Type

float_array

Description

Similar as F Vectors, but the basis can be different.

Shape

[nr of densities]

Excitations SS *%%coef_Trans #{ExcitationNumber}*

Type

float_array

Description

Transition density fit coefficients in case of STOFIT.

Excitations SS *%%contr #{ExcitationNumber}*

Type

float_array

Description

Large contributions excited state vector expressed in single-orbital transitions.

Shape

[nr of contributions #{ExcitationNumber}]

Excitations SS *%%contr index #{ExcitationNumber}*

Type

int_array

Description

Indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SS *%%contr irep index #{ExcitationNumber}*

Type

int_array

Description

Symmetry indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations SS *%%contr spin* **#{ExcitationNumber}****Type**

int_array

Description

Integer related to spin symmetry of contribution.

Shape

[nr of contributions #{ExcitationNumber}, 2]

Excitations SS *%%contr transdip* **#{ExcitationNumber}****Type**

float_array

Description

Contribution to transition dipole moment.

Shape

[3, nr of contributions #{ExcitationNumber}]

Excitations SS *%%coupling transformation***Type**

float_array

Description

Eigenvectors of the electronic coupling matrix.

Shape

[nr of excenergies, nr of excenergies]

Excitations SS *%%ct_at_pl* **#{ExcitationNumber}****Type**

float

Description

Charge transfer descriptor CT_AT: an atomic distance criterion is used, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SS *%%ct_pl* **#{ExcitationNumber}****Type**

float

Description

Charge transfer descriptor CT: fragment based, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations SS *%%CV2DFT excenergies***Type**

float_array

Description

CV(2)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SS *%Degeneracy**Type**

int_array

Description

MCD related data related to degeneracy of excited states.

Shape

[nr of excenergies]

Excitations SS *%eigenvector #{ExcitationNumber}**Type**

float_array

Description

Excited state eigenvector expressed in single-orbital transitions.

Excitations SS *%electronic couplings**Type**

float_array

Description

Electronic couplings calculated localized excitation energies.

Shape

[nr of excenergies, nr of excenergies]

Excitations SS *%excenergies**Type**

float_array

Description

Excitation energies.

Unit

hartree

Shape

[nr of excenergies]

Excitations SS *%Exctyp ***Type**

int_array

Description

Excited state type vector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations SS *%F Vectors ***Type**

float_array

Description

Excited state eigenvector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations SS *%gradient #{ExcitationNumber}

Type

float_array

Description

Excited state gradients (input order).

Shape

[3, Molecule%nAtoms]

Excitations SS *%Gradients_CART #{ExcitationNumber}

Type

float_array

Description

Excited state gradients (internal order).

Shape

[3, Molecule%nAtoms]

Excitations SS *%index in all localized

Type

int_array

Description

Index array for one type of localized excitations in list of all localized excitations with the same irrep.

Shape

[nr of excenergies]

Excitations SS *%lambda_pt #{ExcitationNumber}

Type

float

Description

Charge-transfer diagnostic overlap quantity LAMBDA, based on Peach, Tozer, et al. A smaller value means more charge transfer character.

Excitations SS *%left eigenvector #{ExcitationNumber}

Type

float_array

Description

Excited state eigenvector (X-Y) expressed in single-orbital transitions.

Excitations SS *%magnetic trans dip

Type

float_array

Description

Magnetic transition dipole moment.

Shape

[3, nr of excenergies]

Excitations SS *%nr of contributions #{ExcitationNumber}

Type
int

Description
Number of large contributions excited state vector expressed in single-orbital transitions.

Excitations SS *%nr of densities

Type
int

Description
Number of single-orbital transitions.

Excitations SS *%nr of excenergies

Type
int

Description
Number of calculated excitation energies.

Excitations SS *%nr of NTOs #{ExcitationNumber}

Type
int

Description
Number of large contributions excited state vector expressed in NTO transitions.

Excitations SS *%NTO #{NTOindex} occ #{ExcitationNumber}

Type
float_array

Description
Occupied natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape
[Basis%naos, :]

Excitations SS *%NTO #{NTOindex} virt #{ExcitationNumber}

Type
float_array

Description
Virtual natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha,Re beta,Im alpha,Im beta].

Shape
[Basis%naos, :]

Excitations SS *%NTO contr #{ExcitationNumber}

Type
float_array

Description
Large contributions excited state vector expressed in NTO transitions.

Shape
[nr of NTOs #{ExcitationNumber}]

Excitations SS *%oscillator strengths**Type**

float_array

Description

Oscillator strengths for absorption on ground state to excited state.

Unit**Shape**

[nr of excenergies]

Excitations SS *%R-CVnDFT excenergies**Type**

float_array

Description

R-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SS *%rhe_pl #{ExcitationNumber}**Type**

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Plasser, Lischka, et al.

Excitations SS *%rhe_pt #{ExcitationNumber}**Type**

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Guido, Adamo, et al.

Excitations SS *%rotatory strengths**Type**

float_array

Description

Rotatory strengths.

Shape

[nr of excenergies]

Excitations SS *%SCF-CVnDFT excenergies**Type**

float_array

Description

SCF-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations SS *%transition dipole moments**Type**

float_array

Description

Transition dipole moment between ground state and excited state.

Unit

bohr

Shape

[3, nr of excenergies]

Excitations SS *%transition dipoles dip-vel

Type

float_array

Description

Velocity formula used for calculated transition dipole moment between ground state and excited state.

Shape

[3, nr of excenergies]

Excitations SS *%type of excitations

Type

string

Description

Type of excitations specifying the spin multiplicity of the excitations.

Excitations SS *%unrelaxed dipole moments

Type

float_array

Description

Unrelaxed dipole moments of the excited state.

Shape

[3, nr of excenergies]

17.2.34 Excitations ST *

KF Section: Excitations ST *

Content: Singlet-Triplet excitations for a given irrep.

Excitations ST *%B Vectors *

Type

float_array

Description

Similar as F Vectors, but the basis can be different.

Shape

[nr of densities]

Excitations ST *%coef_Trans #{ExcitationNumber}

Type

float_array

Description

Transition density fit coefficients in case of STOFIT.

Excitations ST *%contr #{ExcitationNumber}

Type

float_array

Description

Large contributions excited state vector expressed in single-orbital transitions.

Shape

[nr of contributions #{ExcitationNumber}]

Excitations ST *%contr index #{ExcitationNumber}

Type

int_array

Description

Indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations ST *%contr irep index #{ExcitationNumber}

Type

int_array

Description

Symmetry indices of the occupied and virtual orbital (spinor) of the single-orbital transition for which the excited state vector has large contributions.

Shape

[nr of contributions #{ExcitationNumber}, :]

Excitations ST *%contr spin #{ExcitationNumber}

Type

int_array

Description

Integer related to spin symmetry of contribution.

Shape

[nr of contributions #{ExcitationNumber}, 2]

Excitations ST *%contr transdip #{ExcitationNumber}

Type

float_array

Description

Contribution to transition dipole moment.

Shape

[3, nr of contributions #{ExcitationNumber}]

Excitations ST *%coupling transformation

Type

float_array

Description

Eigenvectors of the electronic coupling matrix.

Shape

[nr of excenergies, nr of excenergies]

Excitations ST **%%ct_at_pl** **#{ExcitationNumber}****Type**

float

Description

Charge transfer descriptor CT_AT: an atomic distance criterion is used, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations ST **%%ct_pl** **#{ExcitationNumber}****Type**

float

Description

Charge transfer descriptor CT: fragment based, based on Plasser, Lischka, et al. A larger value means more charge transfer character.

Excitations ST **%%CV2DFT excenergies****Type**

float_array

Description

CV(2)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations ST **%%Degeneracy****Type**

int_array

Description

MCD related data related to degeneracy of excited states.

Shape

[nr of excenergies]

Excitations ST **%%eigenvector** **#{ExcitationNumber}****Type**

float_array

Description

Excited state eigenvector expressed in single-orbital transitions.

Excitations ST **%%electronic couplings****Type**

float_array

Description

Electronic couplings calculated localized excitation energies.

Shape

[nr of excenergies, nr of excenergies]

Excitations ST **%%excenergies**

Type

float_array

Description

Excitation energies.

Unit

hartree

Shape

[nr of excenergies]

Excitations ST *%Exctyp ***Type**

int_array

Description

Excited state type vector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations ST *%F Vectors ***Type**

float_array

Description

Excited state eigenvector expressed in symmetry adapted single-orbital transitions.

Shape

[nr of densities]

Excitations ST *%gradient #{ExcitationNumber}**Type**

float_array

Description

Excited state gradients (input order).

Shape

[3, Molecule%nAtoms]

Excitations ST *%Gradients_CART #{ExcitationNumber}**Type**

float_array

Description

Excited state gradients (internal order).

Shape

[3, Molecule%nAtoms]

Excitations ST *%index in all localized**Type**

int_array

Description

Index array for one type of localized excitations in list of all localized excitations with the same irrep.

Shape

[nr of excenergies]

Excitations ST *%lambda_pt #{ExcitationNumber}**Type**

float

Description

Charge-transfer diagnostic overlap quantity LAMBDA, based on Peach, Tozer, et al. A smaller value means more charge transfer character.

Excitations ST *%left eigenvector #{ExcitationNumber}**Type**

float_array

Description

Excited state eigenvector (X-Y) expressed in single-orbital transitions.

Excitations ST *%magnetic trans dip**Type**

float_array

Description

Magnetic transition dipole moment.

Shape

[3, nr of excenergies]

Excitations ST *%nr of contributions #{ExcitationNumber}**Type**

int

Description

Number of large contributions excited state vector expressed in single-orbital transitions.

Excitations ST *%nr of densities**Type**

int

Description

Number of single-orbital transitions.

Excitations ST *%nr of excenergies**Type**

int

Description

Number of calculated excitation energies.

Excitations ST *%nr of NTOs #{ExcitationNumber}**Type**

int

Description

Number of large contributions excited state vector expressed in NTO transitions.

Excitations ST *%NTO #{NTOindex} occ #{ExcitationNumber}

Type

float_array

Description

Occupied natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha, Re beta, Im alpha, Im beta].

Shape

[Basis%naos, :]

Excitations ST *%NTO #{NTOindex} virt #{ExcitationNumber}**Type**

float_array

Description

Virtual natural transition orbital (NTO) expressed in Cartesian basis functions (BAS). In case of spinor [Re alpha, Re beta, Im alpha, Im beta].

Shape

[Basis%naos, :]

Excitations ST *%NTO contr #{ExcitationNumber}**Type**

float_array

Description

Large contributions excited state vector expressed in NTO transitions.

Shape

[nr of NTOs #{ExcitationNumber}]

Excitations ST *%oscillator strengths**Type**

float_array

Description

Oscillator strengths for absorption on ground state to excited state.

Unit**Shape**

[nr of excenergies]

Excitations ST *%R-CVnDFT excenergies**Type**

float_array

Description

R-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations ST *%rhe_pl #{ExcitationNumber}**Type**

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Plasser, Lischka, et al.

Excitations ST *%rhe_pt #{ExcitationNumber}

Type

float

Description

Charge-transfer descriptor R_HE: hole-electron distance based on Guido, Adamo, et al.

Excitations ST *%rotatory strengths**Type**

float_array

Description

Rotatory strengths.

Shape

[nr of excenergies]

Excitations ST *%SCF-CVnDFT excenergies**Type**

float_array

Description

SCF-CV(n)-DFT excitation energies.

Shape

[nr of excenergies]

Excitations ST *%transition dipole moments**Type**

float_array

Description

Transition dipole moment between ground state and excited state.

Unit

bohr

Shape

[3, nr of excenergies]

Excitations ST *%transition dipoles dip-vel**Type**

float_array

Description

Velocity formula used for calculated transition dipole moment between ground state and excited state.

Shape

[3, nr of excenergies]

Excitations ST *%type of excitations**Type**

string

Description

Type of excitations specifying the spin multiplicity of the excitations.

Excitations ST *%unrelaxed dipole moments

Type

float_array

Description

Unrelaxed dipole moments of the excited state.

Shape

[3, nr of excenergies]

17.2.35 FDE Energy

KF Section: FDE Energy**Content:** FDE Related data.

17.2.36 FDEIntegrals

KF Section: FDEIntegrals**Content:** FDE Related data.

17.2.37 Fit

KF Section: Fit**Content:** Fit functions data for the STO fit procedure.

17.2.38 FitCoefficients

KF Section: FitCoefficients**Content:** Fit coefficients for STO fit procedure

17.2.39 FitFit

KF Section: FitFit**Content:** Data for polTDDFT.

17.2.40 FQQM

KF Section: FQQM**Content:** Data related to QM/FQ**FQQM%chemical hardnesses****Type**

float_array

Description

?

FQQM%electronegativities**Type**

float_array

Description

?

FQOM%external xyz**Type**

float_array

Description

?

FQOM%fqind**Type**

float_array

Description

?

FQOM%fqind_r**Type**

float_array

Description

?

FQOM%group names**Type**

string

Description

?

FQOM%group num**Type**

int_array

Description

?

FQOM%n atoms per mol**Type**

int_array

Description

?

FQOM%n mol index**Type**

int_array

Description

?

FQOM%name**Type**

string

Description

?

FQOM%total charges

Type

float_array

Description

?

FQOM%type index

Type

int_array

Description

?

FQOM%type name

Type

string

Description

?

17.2.41 Fragdepend

KF Section: Fragdepend

Content: Information regarding almost linear dependent orbitals which are removed from fragments.

17.2.42 Fragments

KF Section: Fragments

Content: May contain variable Pmat_SumFrag written as packed reals.

17.2.43 Freq

KF Section: Freq

Content: Internal ADF data concerning frequencies. Use AMSResults data.

Freq%DipoleDerivatives_RAW

Type

float_array

Description

Internal ADF data concerning dipole derivatives. Use AMSResults data.

17.2.44 Freq Symmetry

KF Section: Freq Symmetry

Content: Symmetry information for frequencies...?

17.2.45 Ftyp*

KF Section: Ftyp*

Content: Fragment type data.

17.2.46 General

KF Section: General

Content: General information about the ADF calculation.

General%account

Type

string

Description

Name of the account from the license

General%doublehybrid

Type

string

Description

Double hybrid XC functional used in the calculation

General%electrons

Type

float

Description

Number of (valence) electrons in the calculation. Note that this is not necessarily the same as what may consider, chemically, as the valence space. Rather, it equals the total number of electrons in the calculation minus the electrons in the frozen core orbitals

General%engine input

Type

string

Description

The text input of the engine.

General%engine messages

Type

string

Description

Message from the engine. In case the engine fails to solves, this may contains extra information on why.

General%file-ident

Type

string

Description

The file type identifier, e.g. RKF, RUNKF, TAPE21...

General%ggaen**Type**

string

Description

GGA density functional part for ENERGY

General%ggapot**Type**

string

Description

GGA potential used.

General%ggapotfd**Type**

string

Description

FDE GGA potential used in kinetic energy approximant

General%hybrid**Type**

string

Description

Hybrid XC functional used.

General%iopcor**Type**

int

Description

Deprecated.

General%iopnuc**Type**

int

Description

Nuclear model used. 1: point charge nucleus, 2: Uniform Sphere nucleus, 3: Gaussian nucleus model.

General%ioprel**Type**

int

Description

Integer code for relativistic option used. 0: non-relativistic, 1: scalar Pauli + sum of frozen core pot., 3: scalar ZORA + MAPA, 4: scalar ZORA + full pot. (not supported anymore), 5: scalar ZORA + APA (Band), 6: scalar X2C + MAPA, 7: scalar X2C ZORA + MAPA, 11: spin-orbit Pauli + sum of frozen core pot., 13: spin-orbit ZORA + MAPA, 14: spin-orbit ZORA + full

pot. (not supported anymore), 15: spin-orbit ZORA + APA (Band), 16: spin-orbit X2C + MAPA, 17: spin-orbit X2C ZORA + MAPA

General%isounr**Type**

int

Description

Integer code for how to treat the spin in the xc functional with spin-orbit coupling.

General%itnad**Type**

int

Description

FDE integer used in kinetic energy approximant

General%jobid**Type**

int

Description

Unique identifier for the job.

General%lcjcorr**Type**

bool

Description

FDE use long-distance correction in kinetic energy approximant

General%ldaen**Type**

int

Description

Integer code for type of local XC energy.

General%ldapot**Type**

int

Description

Integer code for type of local XC potential.

General%ldapot_fde**Type**

int

Description

FDE Integer code for type of local XC functional used in kinetic energy approximant

General%ldoublehybrid**Type**

bool

Description

Whether a double hybrid XC functional was used in the calculation.

General%lfrozend**Type**

bool

Description

Whether Frozen Density Embedding (FDE) is used.

General%lhybrid**Type**

bool

Description

Whether a hybrid functional was used in the calculation.

General%lunrfrag**Type**

bool

Description

Whether real unrestricted fragments were used.

General%Molecular_Weight**Type**

float

Description

The molecular weight of the molecule.

Unit

dalton

General%nspin**Type**

int

Description

Number of 'spins' in the calculation. 1: spin-restricted calculation, 2: spin-unrestricted calculation.

Possible values

[1, 2]

General%nspinf**Type**

int

Description

Same as nspin but for a fragment. In case of FRAGOCCUPATIONS nspinf = 2.

General%program**Type**

string

Description

The name of the program/engine that generated this kf file.

General%release

Type

string

Description

The version of the program that generated this kf file (including svn revision number and date).

General%runtype**Type**

string

Description

Run type for ADF calculation. 'CREATE' in the create run of an atom, otherwise 'SINGLE POINT'.

General%scfmod**Type**

string

Description

String indicating whether SCF converged (moderately) or not.

General%termination status**Type**

string

Description

The termination status. Possible values: 'NORMAL TERMINATION', 'NORMAL TERMINATION with warnings', 'NORMAL TERMINATION with errors', 'ERROR', 'IN PROGRESS'.

General%title**Type**

string

Description

Title of the calculation.

General%uid**Type**

string

Description

SCM User ID

General%unit of angle**Type**

float

Description

Deprecated: conversion factor for unit of angle

General%unit of length**Type**

float

Description

Deprecated: conversion factor for unit of length

General%use_libxc

Type
bool

Description
Whether the LIBXC library was used.

General%use_xcfun

Type
bool

Description
Whether XCFUN automatic differentiation to generate functional and derivatives is used.

General%use_xcfun_fde_nadxc

Type
bool

Description
FDE XCFun is used in kinetic energy approximant

General%user input

Type
string

Description
User input ADF part.

General%version

Type
int

Description
Version number?

General%xcpare

Type
float

Description
Parameter for X-alpha (only relevant for X-alpha) energy evaluation

General%xcparv

Type
float

Description
Parameter for X-alpha (only relevant for X-alpha) potential

General%xcparv_fde

Type
float

Description
FDE parameter for X-alpha used in kinetic energy approximant

17.2.47 GenptData

KF Section: GenptData

Content: Data related to grid generation for the auxiliary programs. Technical.

17.2.48 Geometry

KF Section: Geometry

Content: The geometry of the system. Note: ADF internally sorts the atoms in what is referred to as ‘internal order’ (as opposed to ‘input order’, which is the order in which atoms were specified in the input). Atomic arrays in this section are (unless otherwise specified) stored in ‘internal order’. The variable ‘atom order index’ contains the mapping from ‘input order’ to ‘internal order’ (and viceversa).

Geometry%atom order index

Type

int_array

Description

Mapping from input order to internal order. atom order index(:,1): input atom order → internal atom order; atom order index(:,2) is the inverse.

Shape

[nr of atoms, 2]

Geometry%Atomic Distances

Type

float_array

Description

Inter-atomic distances between the atoms, shape: [0:nr of atoms, 0:nr of atoms]. The elements (iAtom,jAtom) are the interatomic distances between the two atoms (the index of the first atom being 1). The elements (0,k), (k,0): nearest neighbor for atom k. The element (0,0) is the overall smallest interatomic distance.

Shape

[nr of atoms+1, nr of atoms+1]

Geometry%atomtype

Type

lchar_string_array

Description

Atom type names.

Shape

[nr of atomtypes]

Geometry%atomtype effective charge

Type

float_array

Description

Effective charge of the atom types, i.e. nuclear charge minus the number of electrons in the frozen core.

Unit

e

Shape

[nr of atomtypes]

Geometry%atomtype total charge**Type**

float_array

Description

Nuclear charge of the atom types.

Unit

e

Shape

[nr of atomtypes]

Geometry%charge**Type**

float_array

Description

Atomic charges for the atom types. The first row is the nuclear charge of the atom type. The second row is the effective nuclear charge (i.e. nuclear charge minus the number of electrons in the frozen core). The third: ?.

Unit

e

Shape

[nr of atomtypes, 3]

Geometry%cum nr of atoms**Type**

int_array

Description

Cumulative number of atoms, up to a certain atomtype. The first element of this array is always zero. The last element is always the total number of atoms.

Shape

[nr of atomtypes+1]

Geometry%cum nr of fragments**Type**

int_array

Description

Cumulative number of fragments of a certain type.

Shape

[nr of fragmenttypes+1]

Geometry%fframe**Type**

lchar_string_array

Description

Signals whether or not special local coordinate frames are used for the atoms. Usually this is

not so, in which case the variable has the value DEFAULT. See the 'z=' option (Orientation of Local Atomic Coordinates)

Shape

[nr of atoms]

Geometry%fragment and atomtype index

Type

int_array

Description

Array containing, for each atom, the index of its fragment type and atom type ((iAtom,1) -> fragment index, (iAtom,2) -> atom type index).

Shape

[nr of atoms, 2]

Geometry%fragmenttype

Type

lchar_string_array

Description

The fragment types (i.e. the fragment names).

Shape

[nr of fragmenttypes]

Geometry%Geometric Symmetry

Type

string

Description

Auto-determined ('true') symmetry (considering the nuclear frame and any external fields, but not taking into account any user-defined MO occupation numbers and hence the electronic charge distribution.)

Geometry%geometry id

Type

string

Description

String id that identifies the structure

Geometry%grouplabel

Type

string

Description

Symmetry used in the electronic structure calculation (this is a subgroup of 'Geometric Symmetry').

Geometry%lrotat

Type

bool

Description

Whether or not a rotation has been applied between the input frame and the internally used frame.

Geometry%mass**Type**

float_array

Description

Atomic masses for the atom types.

Unit

dalton

Shape

[nr of atomtypes]

Geometry%nfragm**Type**

int

Description

Number of fragments (same as 'nr of fragments?'). Sometimes it is not, e.g. in Test/FDE_EO_FHF... why?

Geometry%nnuc**Type**

int

Description

Number of nuclei.

Geometry%nofrag_1**Type**

int_array

Description

Array specifying for each non-dummy atom the fragment it belongs to.

Shape

[nr of atoms]

Geometry%nofrag_2**Type**

int_array

Description

Array specifying for each non-dummy atom the fragment type it belongs to.

Shape

[nr of atoms]

Geometry%npqtr**Type**

int_array

Description

Index of the first atom of particular atom type.

Shape

[nr of atomtypes+1]

Geometry%nr of atoms

Type
int

Description
Number of atoms.

Geometry%nr of atomtypes

Type
int

Description
Number of atom types.

Geometry%nr of dummy fragments

Type
int

Description
Number of dummy fragments.

Geometry%nr of dummy fragmenttypes

Type
int

Description
Number of dummy fragment types.

Geometry%nr of fragments

Type
int

Description
Number of fragments.

Geometry%nr of fragmenttypes

Type
int

Description
Number of fragment types.

Geometry%ntyp

Type
int

Description
Number of atom types (same as 'nr of atomtypes').

Geometry%nuclab

Type
lchar_string_array

Description
Nuclear labels (how is this different from atomtype? is it just the atomic symbol?).

Shape
[nr of atomtypes]

Geometry%NumberofPointCharges

Type

int

Description

Number of point charges.

Geometry%oinver**Type**

float_array

Description

Inverse of 'orient'.

Shape

[3, 4]

Geometry%orient**Type**

float_array

Description

Transform matrix from input to standard orientation.

Shape

[3, 4]

Geometry%PointCharges**Type**

float_array

Description

Positions and values of the point charges. For each point charge, the first 3 values are the coordinates (units: Bhor) and the 4th value is the value of the point charge (units: e).

Shape

[4, NumberofPointCharges]

Geometry%qeff**Type**

float_array

Description

Effective nuclear charge for the various atom types (i.e. nuclear charge minus the number of electrons in the frozen core).

Shape

[nr of atomtypes]

Geometry%qtch**Type**

float_array

Description

Nuclear charge for the various atom types.

Shape

[nr of atomtypes]

Geometry%symmetry tolerance

Type

float

Description

ADF threshold for allowed deviation of input atomic coordinates from symmetry to be detected or verified.

Geometry%xaxis**Type**

float_array

Description

Point in plane of local x-axis for each atom.

Shape

[3, nr of atoms]

Geometry%xyz**Type**

float_array

Description

Atom coordinates in internal order.

Unit

bohr

Shape

[3, nr of atoms]

Geometry%xyz InputOrder**Type**

float_array

Description

Atom coordinates in input order.

Unit

bohr

Shape

[3, nr of atoms]

Geometry%zaxis**Type**

float_array

Description

Orientation of local z-axis for each atom.

Shape

[3, nr of atoms]

17.2.49 GeoOpt

KF Section: GeoOpt

Content: This seems to contain some data for excited state GOs?

17.2.50 Gradient

KF Section: Gradient

Content: The various contributions to the nuclear gradients. The atom-order of the arrays in this section is 'internal order'. This is stored only if the input option 'Debug Gradients' is specified.

Gradient%3D-RISM

Type

float_array

Description

Nuclear gradients contribution from the 3D-RISM model. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%B-matrix

Type

float_array

Description

B-matrix contribution to the nuclear gradients?. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%COSMO

Type

float_array

Description

Nuclear gradients contribution from the COSMO solvation model. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Darwin

Type

float_array

Description

Nuclear gradients contribution from Darwin (pauli?). Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%DIMQM**Type**

float_array

Description

Nuclear gradients contribution from the DIMQM model. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Dispersion**Type**

float_array

Description

xxx contribution to the nuclear gradients. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Electric Field**Type**

float_array

Description

Contribution to the nuclear gradients from the interaction from external electrostatic fields (homogeneous, point charges, ...). Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Electrostatic Energy**Type**

float_array

Description

Electrostatic (pair?) contribution to the nuclear gradients. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Elstat Interaction

Type

float_array

Description

Electrostatic interaction (non pair?) contribution to the nuclear gradients. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%FQOM**Type**

float_array

Description

Nuclear gradients contribution from the presence of the FQ(Fmu) environment

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%HF Energy**Type**

float_array

Description

Nuclear gradients contribution from the Hartree-Fock exchange energy. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Kinetic Energy**Type**

float_array

Description

Kinetic energy contribution to the nuclear gradients. Order: internal atom order.

Unit

hartree/bohr

Shape

[3, Molecule%nAtoms]

Gradient%Mass-Velocity**Type**

float_array

Description

Nuclear gradients contribution from the Mass-Velocity (pauli?). Order: internal atom order.

Unit
hartree/bohr

Shape
[3, Molecule%nAtoms]

Gradient%P-matrix [W-energy]

Type
float_array

Description
P-matrix [W-energy] contribution to the nuclear gradients? . Order: internal atom order.

Unit
hartree/bohr

Shape
[3, Molecule%nAtoms]

Gradient%SM12

Type
float_array

Description
Nuclear gradients contribution from the SM12 solvation method. Order: internal atom order.

Unit
hartree/bohr

Shape
[3, Molecule%nAtoms]

Gradient%Total Gradient

Type
float_array

Description
Total nuclear gradients. Order: internal atom order.

Unit
hartree/bohr

Shape
[3, Molecule%nAtoms]

Gradient%XC Energy

Type
float_array

Description
Nuclear gradients contribution from the exchange correlation energy. Order: internal atom order.

Unit
hartree/bohr

Shape
[3, Molecule%nAtoms]

17.2.51 gtens

KF Section: gtens

Content: Data for spin-orbit unrestricted calculation of ESR g-tensor

17.2.52 GW

KF Section: GW

Content: ?

GW%freqGrid

Type

float_array

Description

?

GW%G0W0_QP_hole_ener

Type

float_array

Description

?

GW%G0W0_QP_hole_ener_dif

Type

float_array

Description

?

GW%G0W0_QP_hole_ener_sp_A

Type

float_array

Description

?

GW%G0W0_QP_hole_ener_sp_A_dif

Type

float_array

Description

?

GW%G0W0_QP_hole_ener_sp_B

Type

float_array

Description

?

GW%G0W0_QP_hole_ener_sp_B_dif

Type

float_array

Description

?

GW%G0W0_QP_hole_energies**Type**

float

Description

?

GW%G0W0_QP_hole_energies_diff**Type**

float

Description

?

GW%G0W0_QP_part_ener**Type**

float_array

Description

?

GW%G0W0_QP_part_ener_dif**Type**

float_array

Description

?

GW%G0W0_QP_part_ener_sp_A**Type**

float_array

Description

?

GW%G0W0_QP_part_ener_sp_A_dif**Type**

float_array

Description

?

GW%G0W0_QP_part_ener_sp_B**Type**

float_array

Description

?

GW%G0W0_QP_part_ener_sp_B_dif**Type**

float_array

Description

?

GW%G0W0_QP_particle_energies

Type
float

Description
?

GW%G0W0_QP_particle_energies_diff

Type
float

Description
?

GW%G3W2

Type
float_array

Description
?

GW%G3Wp2

Type
float_array

Description
?

GW%G3Wp2 - GWGamma

Type
float_array

Description
?

GW%GLRatio

Type
float_array

Description
?

GW%nBas

Type
int_array

Description
?

GW%nFit

Type
int

Description
?

GW%nFreq

Type
int

Description
?

GW%nFreqTotal

Type
int

Description
?

GW%nInnerLoopIterations

Type
int

Description
?

GW%nInnerLoopIterationsTotal

Type
int

Description
?

GW%nIterations

Type
int

Description
?

GW%normV

Type
float

Description
?

GW%normW0

Type
float

Description
?

GW%nremov

Type
int

Description
?

GW%nStates

Type
int

Description

?

GW%nTime**Type**

int

Description

?

GW%nTimeTotal**Type**

int

Description

?

GW%QPocc**Type**

float_array

Description

?

GW%QPocc_A**Type**

float_array

Description

?

GW%QPocc_B**Type**

float_array

Description

?

GW%QPun**Type**

float_array

Description

?

GW%QPun_A**Type**

float_array

Description

?

GW%QPun_B**Type**

float_array

Description

?

GW%SCGW_QP_hole_ener

Type

float_array

Description

?

GW%SCGW_QP_hole_ener_dif

Type

float_array

Description

?

GW%SCGW_QP_hole_energies

Type

float_array

Description

?

GW%SCGW_QP_hole_energies_dif

Type

float_array

Description

?

GW%SCGW_QP_part_ener

Type

float_array

Description

?

GW%SCGW_QP_part_ener_dif

Type

float_array

Description

?

GW%SCGW_QP_particle_energies

Type

float_array

Description

?

GW%SCGW_QP_particle_energies_dif

Type

float_array

Description

?

GW%SOSEX

Type
float_array

Description
?

GW%SOSEX2

Type
float_array

Description
?

GW%SOSEXINF

Type
float_array

Description
?

GW%spectral_*

Type
float_array

Description
?

GW%SSOXcorrection

Type
float_array

Description
?

GW%SSOXgreater

Type
float_array

Description
?

GW%SSOXlesser

Type
float_array

Description
?

GW%tMat_A

Type
float_array

Description
?

GW%tMat_B

Type
float_array

Description

?

17.2.53 Hessian**KF Section: Hessian**

Content: Data related to the analytical calculation of the hessian / frequencies.

Hessian%Analytical Dipole Derivative**Type**

float_array

Description

Dipole derivatives computed analytically by ADF. Atom ordering: internal order.

Shape

[3, 3, Molecule%nAtoms]

Hessian%Analytical Hessian**Type**

float_array

Description

Hessian computed analytically by ADF. Atom ordering: internal order.

Unithartree/bohr²**Shape**

[3*Molecule%nAtoms, 3*Molecule%nAtoms]

Hessian%Any User Selected Atoms?**Type**

bool

Description

Whether second derivatives are only computed for a user-defined sub-set of atoms.

Hessian%Number of User Selected Atoms**Type**

int

Description

Number of user selected atoms for second derivatives.

Hessian%User Selected Atoms**Type**

int_array

Description

Indices (in internal order) of the atoms for which second derivatives are computed.

Shape

[Number of User Selected Atoms]

17.2.54 HFConfigADF

KF Section: HFConfigADF

Content: Configuration for the RI procedure used for computing the Hartree-Fock exchange matrix.

17.2.55 HFdependency

KF Section: HFdependency

Content: Data related to the linear-dependency within the 'old' RI Hartree-Fock scheme.

17.2.56 Irred dip vel matrix elem

KF Section: Irred dip vel matrix elem

Content: Dipole velocity matrix, irreducible matrix elements.

17.2.57 Irred magnetic matrix elem

KF Section: Irred magnetic matrix elem

Content: Magnetic moment matrix, irreducible matrix elements.

17.2.58 Irred matrix elements

KF Section: Irred matrix elements

Content: Section with irreducible matrix elements.

17.2.59 Irreducible CurrentMatrix

KF Section: Irreducible CurrentMatrix

Content: Current response data.

17.2.60 Irreducible CurrentMatrix Factor

KF Section: Irreducible CurrentMatrix Factor

Content: Current response data.

17.2.61 KFDefinitions

KF Section: KFDefinitions

Content: The definitions of the data on this file

KFDefinitions%json

Type

string

Description

The definitions of the data on this file in json.

17.2.62 LF_diag

KF Section: LF_diag

Content: All LFDFT energies (including degeneracies) and eigenvectors.

LF_diag%eigenvec_imag

Type

float_array

Description

Imaginary part LF eigenvector.

Shape

[nr_of_energies, nr_of_energies]

LF_diag%eigenvec_real

Type

float_array

Description

Real part LF eigenvector.

Shape

[nr_of_energies, nr_of_energies]

LF_diag%energies

Type

float_array

Description

All LF energies (including degeneracies) wrt to AOC energy.

Unit

hartree

Shape

[nr_of_energies]

LF_diag%nr_of_energies

Type

int

Description

Total number of energies (including degeneracies).

LF_diag%reference_energy

Type

float

Description

Average of Configuration (AOC) energy, should be equal to Energy%Bond Energy.

Unit

hartree

17.2.63 LF_energies

KF Section: LF_energies

Content: LFDFT energies and properties.

LF_energies%degeneracies**Type**

int_array

Description

Degeneracy of LF levels.

LF_energies%energies**Type**

float_array

Description

Unique LF energies wrt to GS energy.

Unit

hartree

Shape

[nr_of_energies]

LF_energies%J2**Type**

float_array

Description

Expectation value <J2>. If a level is degenerate <J2> is calculated as the maximum value for one of these levels.

Shape

[nr_of_energies]

LF_energies%L2**Type**

float_array

Description

Expectation value <L2>. If a level is degenerate <L2> is calculated as the maximum value for one of these levels.

Shape

[nr_of_energies]

LF_energies%nr_of_energies**Type**

int

Description

Number of unique LF energies. Degenerate levels count as 1.

LF_energies%oscillator strengths**Type**

float_array

Description

Oscillator strengths for absorption of light on GS to an excited state with the same (atomic) electron configuration. This is zero in the electric dipole approximation.

Shape

[nr_of_energies]

LF_energies%reference_energy**Type**

float

Description

Ground state (GS) energy. Should be equal to LF_diag%reference_energy + LF_diag%energies(1).

Unit

hartree

LF_energies%S2**Type**

float_array

Description

Expectation value <S2>. If a level is degenerate <S2> is calculated as the maximum value for one of these levels.

Shape

[nr_of_energies]

LF_energies%transition dipole moments**Type**

float_array

Description

Transition dipole moment between GS and an excited state with the same (atomic) electron configuration. This is zero in the electric dipole approximation.

Shape

[3, nr_of_energies]

17.2.64 LF_excitations

KF Section: LF_excitations

Content: LFDFT excitation energies and oscillator strengths between two atomic multiplet states which come from different electron configurations of the same molecule.

LF_excitations%circular left**Type**

float_array

Description

Oscillator strengths (arbitrary units) circular left for absorption on GS 1 to excited state 2.

LF_excitations%circular right**Type**

float_array

Description

Oscillator strengths (arbitrary units) circular right for absorption on GS 1 to excited state 2.

LF_excitations%degeneracies**Type**

int_array

Description

Degeneracy of levels in the excited state 2.

LF_excitations%degeneracy gs**Type**

int

Description

Degeneracy GS.

LF_excitations%energies**Type**

float_array

Description

LF energies of the excited state wrt ground state 1.

Unit

hartree

Shape

[nr_of_energies]

LF_excitations%excited state**Type**

string

Description

Excited state 2 electron configuration.

LF_excitations%ground state**Type**

string

Description

Ground state (GS) 1 electron configuration.

LF_excitations%J2 gs**Type**

float

Description

Expectation value $\langle J^2 \rangle$ GS 1. If the GS 1 is degenerate $\langle J^2 \rangle$ is calculated as the maximum value for one of these levels.

LF_excitations%L2 gs**Type**

float

Description

Expectation value $\langle L2 \rangle$ GS 1. If the GS 1 is degenerate $\langle L2 \rangle$ is calculated as the maximum value for one of these levels.

LF_excitations%nr_of_energies**Type**

int

Description

Number of unique energies in the excited state 2. Degenerate levels count as 1.

LF_excitations%oscillator strengths**Type**

float_array

Description

Oscillator strengths (arbitrary units) for absorption on GS 1 to excited state 2.

Shape

[nr_of_energies]

LF_excitations%S2 gs**Type**

float

Description

Expectation value $\langle S2 \rangle$ GS 1. If the GS 1 is degenerate $\langle S2 \rangle$ is calculated as the maximum value for one of these levels.

LF_excitations%transition dipole moments**Type**

float_array

Description

Transition dipole moment [1:3,:] (arbitrary units) between GS 1 and excited state 2. [4:5,:] used for circular right $(x+iy)/\sqrt{2}$ and circular left $(x-iy)/\sqrt{2}$ polarized light.

Shape

[5, nr_of_energies]

17.2.65 LF_input

KF Section: LF_input

Content: ?

LF_input%active_electrons**Type**

int

Description

Total number of electrons.

LF_input%electron_configuration**Type**

string

Description

Electron configuration.

LF_input%electrons_per_shell

Type

int_array

Description

Number of electrons for each shell.

Shape

[number_of_shells]

LF_input%l_values

Type

int_array

Description

Angular momentum quantum numbers (l-value) for each shell.

Shape

[number_of_shells]

LF_input%n_values

Type

int_array

Description

The main quantum number n for each shell. For frozen core calculations the number n is reduced with the number of core levels with angular momentum l that are in the frozen core.

Shape

[number_of_shells]

LF_input%number_of_shells

Type

int

Description

Number of shells

17.2.66 LibXCConfig

KF Section: LibXCConfig

Content: ?

LibXCConfig%densityThreshold

Type

float

Description

If the density at a numerical integration point is below this threshold, this numerical integration point is skipped.

LibXCConfig%flag

Type

bool_array

Description

Boolean array [0:20,nfunc] that describes what kind of XC functional.

Shape

[42]

LibXCConfig%fractionHF**Type**

float

Description

Fraction of HF exchange.

LibXCConfig%func**Type**

int_array

Description

LibXC nfunc integer values which XC functional.

Shape

[2]

LibXCConfig%lRangeSep**Type**

bool

Description

Whether or not a range separated functional.

LibXCConfig%nfunc**Type**

int

Description

Number of parts of the DFT part of an XC functionals, maximum 2, for example an exchange and a correlation part.

LibXCConfig%RangeSepLine**Type**

string_fixed_length

Description

Line with an input description in case of a range-separated functional.

LibXCConfig%useTurnoverRule**Type**

bool

Description

Use turn-over rule for (meta-)GGA part XC functional. Needs to be true for meta-GGAs and meta-hybrids, otherwise optional.

LibXCConfig%xc_family**Type**

int_array

Description

LibXC nfunc integer values that describes the family of the functional.

Shape

[2]

17.2.67 LinearScaling

KF Section: LinearScaling

Content: Technical parameters concerning the linear scaling.

17.2.68 LMO_P1

KF Section: LMO_P1

Content: Data for localized orbitals.

17.2.69 LocOrb

KF Section: LocOrb

Content: Data for localized orbitals.

17.2.70 locpert_data

KF Section: locpert_data

Content: Data for localized orbitals.

17.2.71 Low Frequency Correction

KF Section: Low Frequency Correction

Content: Configuration for the Head-Gordon Dampener-powered Free Rotor Interpolation.

Low Frequency Correction%Alpha**Type**

float

Description

Exponent term for the Head-Gordon dampener.

Low Frequency Correction%Frequency**Type**

float

Description

Frequency around which interpolation happens, in 1/cm.

Low Frequency Correction%Moment of Inertia**Type**

float

Description

Used to make sure frequencies of less than ca. 1 1/cm don't overestimate entropy, in kg m².

17.2.72 LqbasxLqfitx_xyznuc

KF Section: LqbasxLqfitx_xyznuc

Content: Contains data for the grid generation for the auxiliary programs. Technical.

17.2.73 Magn multipole ints OCCOCC

KF Section: Magn multipole ints OCCOCC

Content: Data for XES.

17.2.74 Magn multipole ints OCCVIR

KF Section: Magn multipole ints OCCVIR

Content: Data for XAS.

17.2.75 Magnetic moment matrix

KF Section: Magnetic moment matrix

Content: Magnetic moment matrix.

17.2.76 MCD Elements

KF Section: MCD Elements

Content: Data related to MCD calculation.

MCD Elements%B Fields

Type

float_array

Description

?

MCD Elements%B Term

Type

float_array

Description

?

MCD Elements%B Term SOS

Type

float_array

Description

?

MCD Elements%C Term

Type

float_array

Description

?

MCD Elements%C Term SOS**Type**

float_array

Description

?

MCD Elements%C Term SOS AnisoMCD***Type**

float_array

Description

?

MCD Elements%C Term temperature coefficients**Type**

float_array

Description

?

MCD Elements%dipAJ**Type**

float_array

Description

?

MCD Elements%dipAJgr**Type**

float_array

Description

?

MCD Elements%dipAJgrSO**Type**

float_array

Description

?

MCD Elements%Magnetic Field***Type**

float

Description

?

MCD Elements%nMCDTerm**Type**

int

Description

?

MCD Elements%Temperature*

Type

float

Description

?

MCD Elements%Temperatures

Type

float_array

Description

?

17.2.77 METAGGA bonding energies

KF Section: METAGGA bonding energies

Content: Post-SCF bonding energies computed for a set of META-GGA XC functionals.

17.2.78 MetaGGAConfig

KF Section: MetaGGAConfig

Content: Configuration for MetaGGA XC functionals.

17.2.79 Mobile Block Hessian

KF Section: Mobile Block Hessian

Content: Mobile Block Hessian.

Mobile Block Hessian%Coordinates Internal

Type

float_array

Description

?

Mobile Block Hessian%Free Atom Indexes Input

Type

int_array

Description

?

Mobile Block Hessian%Frequencies in atomic units

Type

float_array

Description

?

Mobile Block Hessian%Frequencies in wavenumbers

Type

float_array

Description

?

Mobile Block Hessian%Input Cartesian Normal Modes**Type**

float_array

Description

?

Mobile Block Hessian%Input Indexes of Block #**Type**

int_array

Description

?

Mobile Block Hessian%Intensities in km/mol**Type**

float_array

Description

?

Mobile Block Hessian%MBH Curvatures**Type**

float_array

Description

?

Mobile Block Hessian%Number of Blocks**Type**

int

Description

Number of blocks.

Mobile Block Hessian%Sizes of Blocks**Type**

int_array

Description

Sizes of the blocks.

Shape

[Number of Blocks]

17.2.80 Molecule

KF Section: Molecule

Content: The input molecule of the calculation.

Molecule%AtomicNumbers

Type

int_array

Description

Atomic number 'Z' of the atoms in the system

Shape

[nAtoms]

Molecule%AtomMasses

Type

float_array

Description

Masses of the atoms

Unit

a.u.

Values range

[0, 'infinity']

Shape

[nAtoms]

Molecule%AtomSymbols

Type

string

Description

The atom's symbols (e.g. 'C' for carbon)

Shape

[nAtoms]

Molecule%bondOrders

Type

float_array

Description

The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

Molecule%Charge

Type

float

Description

Net charge of the system

Unit

e

Molecule%Coords**Type**

float_array

Description

Coordinates of the nuclei (x,y,z)

Unit

bohr

Shape

[3, nAtoms]

Molecule%eeAttachTo**Type**

int_array

DescriptionUNUSED IN AMS $\geq$ 2026. A multipole may be attached to an atom. This influences the energy gradient.**Molecule%eeChargeWidth****Type**

float

Description

If charge broadening was used for external charges, this represents the width of the charge distribution.

Molecule%eeEField**Type**

float_array

Description

The external homogeneous electric field.

Unit

hartree/(e*bohr)

Shape

[3]

Molecule%eeLatticeVectors**Type**

float_array

DescriptionUNUSED IN AMS $\geq$ 2026. The lattice vectors used for the external point- or multipole-charges.**Unit**

bohr

Shape

[3, eeNLatticeVectors]

Molecule%eeMulti

Type

float_array

Description

The values of the external point- or multipole- charges.

Unit

a.u.

Shape

[eeNZlm, eeNMulti]

Molecule%eeNLatticeVectors**Type**

int

Description

UNUSED IN AMS>=2026. The number of lattice vectors for the external point- or multipole- charges.

Molecule%eeNMulti**Type**

int

Description

The number of external point- or multipole- charges.

Molecule%eeNZlm**Type**

int

Description

When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

Molecule%eeUseChargeBroadening**Type**

bool

Description

Whether or not the external charges are point-like or broadened.

Molecule%eeXYZ**Type**

float_array

Description

The position of the external point- or multipole- charges.

Unit

bohr

Shape

[3, eeNMulti]

Molecule%EngineAtomicInfo**Type**

string_fixed_length

Description

Atom-wise info possibly used by the engine.

Molecule%fromAtoms**Type**

int_array

Description

Index of the first atom in a bond. See the bondOrders array

Molecule%latticeDisplacements**Type**

int_array

Description

The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

Molecule%LatticeVectors**Type**

float_array

Description

Lattice vectors

Unit

bohr

Shape

[3, nLatticeVectors]

Molecule%nAtoms**Type**

int

Description

The number of atoms in the system

Molecule%nAtomsTypes**Type**

int

Description

The number different of atoms types

Molecule%nLatticeVectors**Type**

int

Description

Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values

[0, 1, 2, 3]

Molecule%toAtoms**Type**

int_array

Description

Index of the second atom in a bond. See the bondOrders array

17.2.81 MP2 energies**KF Section: MP2 energies**

Content: ?

MP2 energies%Contribution to DH energy

Type

float

Description

?

MP2 energies%LT-MP2 energy

Type

float

Description

?

MP2 energies%os LT-MP2 energy

Type

float

Description

?

MP2 energies%os RI-MP2 energy

Type

float

Description

?

MP2 energies%RI-MP2 energy

Type

float

Description

?

MP2 energies%ss LT-MP2 energy

Type

float

Description

?

MP2 energies%ss RI-MP2 energy

Type

float

Description

?

17.2.82 MP2configADF

KF Section: MP2configADF

Content: ?

MP2configADF%Dependency

Type

bool

Description

?

MP2configADF%EmpiricalScaling

Type

string

Description

?

MP2configADF%LT

Type

bool

Description

?

MP2configADF%Memory

Type

bool

Description

?

MP2configADF%nTime

Type

int

Description

?

MP2configADF%RI

Type

bool

Description

?

MP2configADF%UseScaledZORA

Type

bool

Description

?

17.2.83 Multipole matrix elements

KF Section: Multipole matrix elements

Content: Section with multipole matrix elements.

17.2.84 NBOs

KF Section: NBOs

Content: ?

NBOs%Label_{LocalizedOrbitalNumber}

Type

string

Description

Label localized orbital.

NBOs%Label_A_{LocalizedOrbitalNumber}

Type

string

Description

Label localized orbital.

NBOs%Label_B_{LocalizedOrbitalNumber}

Type

string

Description

Label localized orbital, for spin B.

NBOs%nocc_A

Type

int

Description

Number of occupied orbitals.

NBOs%nocc_B

Type

int

Description

Number of occupied orbitals, for spin B.

NBOs%Orbitals_A_{LocalizedOrbitalNumber}

Type

float_array

Description

Localized orbital expressed in Cartesian basis functions (BAS).

Shape

[Basis%naos]

NBOs%Orbitals_B_{LocalizedOrbitalNumber}

Type

float_array

Description

Localized orbital expressed in Cartesian basis functions (BAS), for spin B.

Shape

[Basis%naos]

17.2.85 NLMOs

KF Section: NLMOs**Content:** ?**NLMOs%Label_{LocalizedOrbitalNumber}****Type**

string

Description

Label localized orbital.

NLMOs%Label_A_{LocalizedOrbitalNumber}**Type**

string

Description

Label localized orbital.

NLMOs%Label_B_{LocalizedOrbitalNumber}**Type**

string

Description

Label localized orbital, for spin B.

NLMOs%nocc_A**Type**

int

Description

Number of occupied orbitals.

NLMOs%nocc_B**Type**

int

Description

Number of occupied orbitals, for spin B.

NLMOs%Orbitals_A_{LocalizedOrbitalNumber}**Type**

float_array

Description

Localized orbital expressed in Cartesian basis functions (BAS).

Shape

[Basis%naos]

NLMOs%Orbitals_B_{LocalizedOrbitalNumber}**Type**

float_array

Description

Localized orbital expressed in Cartesian basis functions (BAS), for spin B.

Shape

[Basis%naos]

17.2.86 NOCV

KF Section: NOCV**Content:** Results from the NOCV (Natural Orbitals for Chemical Valence) procedure.**NOCV%Label_A_#****Type**

string_fixed_length

Description

Label of the NOCV (spin-alpha in case of spin-restricted calculation, or the spin-restricted in case of spin-restricted calculation).

NOCV%Label_B_#**Type**

string_fixed_length

Description

Label of the spin-beta NOCV.

NOCV%NOCV_eigenvalues_alpha**Type**

float_array

Description

NOCV eigenvalues for alpha spin (for spin-unrestricted calculations).

Unit

hartree

NOCV%NOCV_eigenvalues_beta**Type**

float_array

Description

NOCV eigenvalues for beta spin (for spin-unrestricted calculations).

Unit

hartree

NOCV%NOCV_eigenvalues_restricted**Type**

float_array

Description

NOCV eigenvalues (in case of spin-restricted calculation).

Unit

hartree

NOCV%NOCV_oi_alpha**Type**

float_array

Description

Orbital interaction contributions from each NOCV for alpha spin (for spin-unrestricted calculations).

Unit

hartree

NOCV%NOCV_oi_beta**Type**

float_array

Description

Orbital interaction contributions from each NOCV for beta spin (for spin-unrestricted calculations).

Unit

hartree

NOCV%NOCV_oi_restricted**Type**

float_array

Description

Orbital interaction contributions from each NOCV (in case of spin-restricted calculation).

Unit

hartree

NOCV%NOCV_T_ALPHA**Type**

float_array

Description

?

NOCV%NOCV_T_BETA**Type**

float_array

Description

?

NOCV%NOCV_V_ALPHA**Type**

float_array

Description

?

NOCV%NOCV_V_BETA**Type**

float_array

Description

?

NOCV%Orbitals_A_#**Type**

float_array

Description

Orbital coefficients the NOCV (spin-alpha in case of spin-restricted calculation, or the spin-restricted in case of spin-restricted calculation).

Shape

[Basis%naos]

NOCV%Orbitals_B_#**Type**

float_array

Description

Orbital coefficients the spin-beta NOCV.

Shape

[Basis%naos]

17.2.87 Num Int Params

KF Section: Num Int Params**Content:** Technical parameters concerning the numerical integration procedure of ADF.

17.2.88 OrbitalInfo

KF Section: OrbitalInfo**Content:** Section containing the orbital information related to a specific symmetry group**OrbitalInfo%AOBas-I_A****Type**

float_array

Description

Imaginary alpha and beta part spinor expressed in Cartesian basis functions (BAS).

Shape

[Basis%naos, 2, nmo_A, nrdim]

OrbitalInfo%AOBas-R_A**Type**

float_array

Description

Real alpha and beta part spinor expressed in Cartesian basis functions (BAS).

Shape

[Basis%naos, 2, nmo_A, nrdim]

OrbitalInfo%Bas-I_A ***Type**

float_array

Description

Spin-orbit data.

OrbitalInfo%Bas-R_A ***Type**

float_array

Description

Spin-orbit data.

OrbitalInfo%BasPhi-***Type**

float_array

Description

Spin-orbit data related to large component spinor.

OrbitalInfo%BasXPhi-***Type**

float_array

Description

Spin-orbit data related to pseudo-large component spinor.

OrbitalInfo%cmatab_A**Type**

float_array

Description

Data relevant for unrestricted fragments.

Shape

[nmo_A, nmo_A]

OrbitalInfo%cmatab_B**Type**

float_array

Description

Data relevant for unrestricted fragments.

Shape

[nmo_A, nmo_A]

OrbitalInfo%Eig-CoreSFO_A**Type**

float_array

Description

MOs expressed in core orthogonalization functions and SFOs, for spin-A MOs.

Shape

[nt, nmo_A]

OrbitalInfo%Eig-CoreSFO_B**Type**

float_array

Description

Same as 'Eig-CoreSFO_A', but for spin B.

Shape

[nt, nmo_A]

OrbitalInfo%Eigen-Bas_A**Type**

float_array

Description

MO expansion coefficients in the BAS representation for all nmo_A orbitals (in unrestricted case for spin A). The coefficients run over all BAS functions indicated by npart.

Shape

[nbas, nmo_A]

OrbitalInfo%Eigen-Bas_B**Type**

float_array

Description

Unrestricted case: same as 'Eigen-Bas_A', but for spin B.

Shape

[nbas, nmo_A]

OrbitalInfo%Eigen-BasPhi_A**Type**

float_array

Description

Large component expressed in Cartesian basis functions (BAS).

Shape

[nbas, nmo_A]

OrbitalInfo%Eigen-BasPhi_B**Type**

float_array

Description

Large component expressed in Cartesian basis functions (BAS) for spin B.

Shape

[nbas, nmo_A]

OrbitalInfo%Eigen-BasXPhi_A**Type**

float_array

Description

Pseudo-large component expressed in Cartesian basis functions (BAS).

Shape

[nbas, nmo_A]

OrbitalInfo%Eigen-BasXPhi_B**Type**

float_array

Description

Pseudo-large component expressed in Cartesian basis functions (BAS) for spin B.

Shape

[nbas, nmo_A]

OrbitalInfo%eps_A**Type**

float_array

Description

The orbital energies for the nmo_A orbitals (in unrestricted case for spin A). When they result from a ZORA calculations, the non-scaled values are stored on file, see qscal how to scale.

Shape

[nmo_A]

OrbitalInfo%eps_B**Type**

float_array

Description

Unrestricted case: same as 'eps_A', but for spin B.

OrbitalInfo%escale_A**Type**

float_array

Description

ZORA only. Scaled orbital eigenvalues.

Shape

[nmo_A]

OrbitalInfo%escale_A ***Type**

float_array

Description

Spin-orbit data.

OrbitalInfo%escale_B**Type**

float_array

Description

ZORA only. Scaled orbital eigenvalues for spin B

Shape

[nmo_A]

OrbitalInfo%FragBas-I_A**Type**

float_array

Description

Imaginary part spinor expressed in SFOs. Note, only used in case fragment is the full molecule.

Shape

[SFOs%number, 2, nmo_A, nrdim]

OrbitalInfo%FragBas-R_A**Type**

float_array

Description

Real part of spinor expressed in SFOs. Note, only used in case fragment is the full molecule.

Shape

[SFOs%number, 2, nmo_A, nrdim]

OrbitalInfo%froc**Type**

float_array

Description

The occupation numbers of the MOs in the irrep.

Shape

[nmo_A]

OrbitalInfo%froc_A**Type**

float_array

Description

The occupation numbers of the MOs in the irrep (in unrestricted case for spin A).

Shape

[nmo_A]

OrbitalInfo%froc_B**Type**

float_array

Description

Unrestricted case: the occupation numbers of the MOs in the irrep, for spin B

Shape

[nmo_A]

OrbitalInfo%froc_f**Type**

float_array

Description

The occupation numbers of the Lowdins and SFOs in this irrep.

Shape

[nmo_A]

OrbitalInfo%frocf_A**Type**

float_array

Description

The occupation numbers of the Lowdins and SFOs in this irrep for spin A.

Shape

[nmo_A]

OrbitalInfo%frocf_B**Type**

float_array

Description

The occupation numbers of the Lowdins and SFOs in this irrep for spin B.

Shape

[nmo_A]

OrbitalInfo%frocor**Type**

float_array

Description

Non-empty Lowdin and SFO occupation numbers.

OrbitalInfo%frocor_A**Type**

float_array

Description

Non-empty Lowdin and SFO occupation numbers for spin A.

OrbitalInfo%frocor_B**Type**

float_array

Description

Non-empty Lowdin and SFO occupation numbers for spin B.

OrbitalInfo%frocr_A ***Type**

float_array

Description

Spin-orbit data.

OrbitalInfo%large QP-Eigen-MO_A**Type**

float_array

Description

Large coefficients quasi particles expressed in MOs.

OrbitalInfo%Low-Bas

Type

float_array

Description

The Lowdin orbitals expressed in the BAS representation: the matrix to transform the MOs from Lowdin representation (Lowdin = orthonormalized SFOs) to the BAS representation.

Shape

[nmo_A, nbas]

OrbitalInfo%Low-Bas_B**Type**

float_array

Description

Same as Low-Bas, but for spn B.

Shape

[nmo_A, nbas]

OrbitalInfo%mo_index large QP-Eigen-MO_A**Type**

int_array

Description

Large coefficients index array quasi particles expressed in which MO.

OrbitalInfo%nbas**Type**

int

Description

Number of primitive STOs in this symmetry group.

OrbitalInfo%ncbas**Type**

int

Description

Number of core orthogonalization functions in this symmetry group.

OrbitalInfo%nmo_A**Type**

int

Description

Number of alpha molecular orbitals in this symmetry group (in unrestricted case for spin A).

OrbitalInfo%nmo_B**Type**

int

Description

Unrestricted case: number of beta molecular orbitals in this symmetry group. Should be equal to nmo_A.

OrbitalInfo%NOCV-Eigen-MO_A

Type

float_array

Description

NOCV orbitals expressed in MOs.

Shape

[nmo_A, nmo_A]

OrbitalInfo%NOCV-Eigen-MO_B**Type**

float_array

Description

Same as NOCV-Eigen-MO_A, but for spin B.

Shape

[nmo_A, nmo_A]

OrbitalInfo%npart**Type**

int_array

Description

A list of indices of the BAS functions that are used in this irrep.

Shape

[nbas]

OrbitalInfo%nrDIM**Type**

int

Description

Dimension (number of subspecies) of this double-group irrep.

OrbitalInfo%nt**Type**

int

Description

Number of core orthogonalization functions plus number of SFOs in this symmetry group.

OrbitalInfo%number large QP-Eigen-MO_A**Type**

int_array

Description

Number of large coefficients quasi particles expressed in MOs.

OrbitalInfo%Orth-Bas**Type**

float_array

Description

The (non-empty) orthogonalized fragment orbitals expressed in the BAS representation.

Shape

[nbas, :]

OrbitalInfo%Orth-Bas_A**Type**

float_array

Description

The (non-empty) orthogonalized fragment orbitals expressed in the BAS representation for spin A.

Shape

[nbas, :]

OrbitalInfo%Orth-Bas_B**Type**

float_array

Description

The (non-empty) orthogonalized fragment orbitals expressed in the BAS representation for spin B.

Shape

[nbas, :]

OrbitalInfo%QP-Eigen-Bas_A**Type**

float_array

Description

Quasi particles expressed in Cartesian basis functions (BAS).

Shape

[nbas, nmo_A]

OrbitalInfo%QP-Eigen-MO_A**Type**

float_array

Description

Quasi particles expressed in MOs.

Shape

[nmo_A, nmo_A]

OrbitalInfo%QP-eps_A**Type**

float_array

Description

Quasi particles orbital energies.

Shape

[nmo_A]

OrbitalInfo%QP-eps_B**Type**

float_array

Description

Same as QP-eps_A, but for spin B.

Shape

[nmo_A]

OrbitalInfo%qscal_A**Type**

float_array

Description

Used only for ZORA. Scaled eps is (eps/(1+qscal)).

Shape

[nmo_A]

OrbitalInfo%qscal_B**Type**

float_array

Description

Unrestricted case: same as 'qscal_A', but for spin B.

Shape

[nmo_A]

OrbitalInfo%qscalr_A ***Type**

float_array

Description

Spin-orbit data.

OrbitalInfo%S-CoreSFO**Type**

float_array

Description

Overlap matrix of both core orthogonalization functions and SFOs. Size [nt*(nt+1)/2].

OrbitalInfo%S-CoreSFO_B**Type**

float_array

Description

Same as 'S-CoreSFO_A', but for spin B.

OrbitalInfo%SFO**Type**

float_array

Description

Coeffs for the symmetrized fragment orbital expressed in Cartesian basis functions (BAS) in this symmetry group. Note these are core orthogonalized SFOs (CSFOs).

Shape

[nmo_A, nbas]

OrbitalInfo%SFO_B**Type**

float_array

Description

Same as SFO, but for spin B.

Shape

[nmo_A, nbas]

OrbitalInfo%smx**Type**

float_array

Description

Overlap matrix of both core orthogonalization functions and core orthogonalized SFOs (CS-FOs). Size [nt*(nt+1)/2].

OrbitalInfo%smx_B**Type**

float_array

Description

Same as smx, but for spin B.

17.2.89 OrbitalsCoulombInteraction

KF Section: OrbitalsCoulombInteraction

Content: ?

OrbitalsCoulombInteraction%IntEnergy_#**Type**

float

Description

?

OrbitalsCoulombInteraction%nPairs**Type**

int

Description

?

OrbitalsCoulombInteraction%OrbitalIndices_#**Type**

int_array

Description

?

17.2.90 Ort C energies

KF Section: Ort C energies

Content: Correlation energies from orthonormalized density.

17.2.91 Ort X energies

KF Section: Ort X energies

Content: Exchange energies from orthonormalized density.

17.2.92 Ort XC energies

KF Section: Ort XC energies

Content: XC energies from orthonormalized density.

17.2.93 PartialZora

KF Section: PartialZora

Content: Data related to the use of the PartialZora functionality.

PartialZora%active

Type

bool

Description

True when original PZora is active

PartialZora%lshell

Type

int

Description

shell type (s,p,d,f) for which PZora is active

PartialZora%nfrag

Type

int

Description

number of fragments for which PZora is active

PartialZora%nonrelso

Type

bool

Description

True when PZora should produce nonrel. result

PartialZora%shellmode

Type

bool

Description

True when PZora shell mode is active

PartialZora%supfrag**Type**

int_array

Description

list of fragments for which PZora is active

Shape

[nfrag]

PartialZora%tpot**Type**

string

Description

potential section name on TAPE10 (for PZora)

PartialZora%tpotfull**Type**

string

Description

potential section name on TAPE10 (rel)

17.2.94 Point_Charges

KF Section: Point_Charges

Content: Data related to point charges.

17.2.95 POLTDDFT

KF Section: POLTDDFT

Content: Data related to the PolTD-DFT procedure.

17.2.96 Properties

KF Section: Properties

Content: A collection of properties computed by ADF.

Properties%alpha_p**Type**

float_array

Description

?

Properties%Aromaticity Ring #**Type**

float_array

Description

The first value in the array is the ring index (Iring). The second value is the multi center index (MCI). (Aromaticity indices with QTAIM results)

Shape

[2]

Properties%AtomCharge CM5**Type**

float_array

Description

Net atomic charges from the Charge Model 5 (CM5) method. (e.g., the charges for a water molecule might be [-0.6, 0.3, 0.3]). Atom order: internal order.

Unit

e

Shape

[Molecule%nAtoms]

Properties%AtomCharge Mulliken**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%AtomCharge_initial Voronoi**Type**

float_array

Description

Voronoi atomic charges for the Initial (sum-of-fragments) density.

Shape

[Molecule%nAtoms]

Properties%AtomCharge_SCF Voronoi**Type**

float_array

Description

Voronoi atomic charges for the SCF density.

Shape

[Molecule%nAtoms]

Properties%AtomIndex Ring #**Type**

int_array

Description

Indices of atoms in a ring for which the aromaticity indices are computed. The aromaticity indices are saved in the variable 'Aromaticity Ring #' (Aromaticity indices with QTAIM results)

Properties%AtomSpinDen Mulliken

Type
float_array

Description
?

Shape
[Molecule%nAtoms]

Properties%Bader atomic charges

Type
float_array

Description
Atomic charges computed using the QTAIM approach, atoms in the internal ADF order.

Properties%Bader atomic dipole moment

Type
float_array

Description
Atomic dipole moments computed using the QTAIM approach, atoms in the internal ADF order.

Properties%Bader atomic ele dipole moment

Type
float_array

Description
Atomic electronic dipole moments computed using the QTAIM approach, atoms in the internal ADF order.

Properties%Bader atomic entropies

Type
float_array

Description
?

Properties%Bader atomic nuc dipole moment

Type
float_array

Description
Atomic nuclear dipole moments computed using the QTAIM approach, atoms in the internal ADF order.

Properties%Bader atomic quadrupole moment

Type
float_array

Description
?

Properties%Bader atomic spin densities

Type
float_array

Description

?

Properties%Bader atomic volumes**Type**

float_array

Description

?

Properties%Bader block n**Type**

int

Description

?

Properties%Bader density**Type**

float

Description

?

Properties%Bader density mat bfunctions**Type**

float_array

Description

?

Properties%Bader ELF**Type**

float_array

Description

?

Properties%Bader Esc**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%Bader Es1c**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%Bader EVF

Type
float_array

Description
?

Shape
[Molecule%nAtoms]

Properties%Bader Laplacian

Type
float_array

Description
?

Properties%Bader MO contrib

Type
float_array

Description
?

Properties%Bader size nblock

Type
int

Description
?

Properties%Bader Tc

Type
float_array

Description
?

Properties%Bader Ts

Type
float_array

Description
?

Properties%Bader Tsl

Type
float_array

Description
?

Properties%BP atoms

Type
int_array

Description
?

Shape

[BP number of, 3]

Properties%BP number of**Type**

int

Description

Number of bond paths (QTAIM).

Properties%BP shift**Type**

float_array

Description

(lattice) shifts for start and end atoms

Shape

[3, BP number of, 2]

Properties%BP step number**Type**

int_array

Description

Number of steps in the path (QTAIM).

Shape

[BP number of]

Properties%BPs and their properties**Type**

float_array

Description

?

Shape

[BP number of, :, 13]

Properties%Cond Linear Response**Type**

float_array

Description

?

Properties%CP code (Rank, Signature)**Type**

float_array

Description

Characterization of the critical points. 1: (3,-3) atom critical point. 2: (3,+3) cage critical point. 3: (3,-1) bond critical point. 4: (3,+1) ring critical point.

Shape

[CP number of]

Properties%CP coordinates

Type

float_array

Description

Coordinates of the critical points (QTAIM).

Shape

[CP number of, 3]

Properties%CP density at**Type**

float_array

Description

Density at the critical points (QTAIM).

Shape

[CP number of]

Properties%CP density gradient at**Type**

float_array

Description

Gradient of the density at the critical points (QTAIM).

Shape

[CP number of, 3]

Properties%CP density Hessian at**Type**

float_array

Description

Hessian of the density at the critical points (QTAIM). Compressed symmetric storage.

Shape

[CP number of, 6]

Properties%CP eigenvalues of Hessian**Type**

float_array

Description

Eigenvalues of the Hessian of the density at the critical points (QTAIM).

Shape

[CP number of, 3]

Properties%CP eigenvectors of Hessian**Type**

float_array

Description

Eigenvectors of the Hessian of the density at the critical points (QTAIM).

Shape

[CP number of, 9]

Properties%CP number of

Type
int

Description
Number of critical points for the density (QTAIM).

Properties%Dipole

Type
float_array

Description
Dipole moment.

Shape
[3]

Properties%EFG asym. par. eta InputOrder

Type
float_array

Description
EFG asymmetry parameter eta, which is the difference between the lowest 2 principal values of the EFG divided by the largest principal value of the EFG, atoms in input order.

Shape
[Molecule%nAtoms]

Properties%EFG NQCC (MHz) InputOrder

Type
float_array

Description
Nuclear Quadrupole Coupling Constant (NQCC) (in MHz) is the largest value of the principal values of the EFG (in a.u.) times 234.9647 times the nuclear quadrupole moment (in barn units), atoms in input order.

Shape
[Molecule%nAtoms]

Properties%EFG tensor (au) InputOrder

Type
float_array

Description
Electric field gradient (EFG) at nuclei (a.u.), atoms in input order.

Shape
[3, 3, Molecule%nAtoms]

Properties%EFG tensor (MHz) InputOrder

Type
float_array

Description
Electric field gradient (EFG) at nuclei (MHz), includes factor $Q/(2I(2I-1))$, atoms in input order.

Shape
[3, 3, Molecule%nAtoms]

Properties%EFG Vzz (au) InputOrder

Type

float_array

Description

The largest value of the principal values of the EFG (in a.u.), atoms in input order.

Shape

[Molecule%nAtoms]

Properties%Electron Density at Nuclei**Type**

float_array

Description

Average electron density at a small sphere around the center of a nucleus.

Shape

[Molecule%nAtoms]

Properties%Electronegativity**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%Electronegativity (omega)**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%Electrostatic Pot.at Nuclei**Type**

float_array

Description

Electrostatic Potential at Nuclei. The contribution from the nucleus itself is excluded.

Shape

[Molecule%nAtoms]

Properties%ESP-CHELPG charges**Type**

float_array

Description

Net atomic charges atomic charges from the ESP Chelpg. Atom order: internal order.

Unit

e

Shape

[Molecule%nAtoms]

Properties%ESP-RESP charges**Type**

float_array

Description

Net atomic charges atomic charges from the ESP RESP. Atom order: internal order.

Unit

e

Shape

[Molecule%nAtoms]

Properties%ESR A-iso (au) InputOrder**Type**

float_array

DescriptionIsotropic value A-tensor (a.u.), not multiplied by g_n/S , atoms in input order.**Shape**

[Molecule%nAtoms]

Properties%ESR A-iso (MHz) InputOrder**Type**

float_array

DescriptionIsotropic value A-tensor (MHz), includes factor g_n/S , atoms in input order.**Shape**

[Molecule%nAtoms]

Properties%ESR A-tens (au) InputOrder**Type**

float_array

DescriptionESR A-tensor (a.u.), not multiplied by g_n/S , atoms in input order.**Shape**

[3, 3, Molecule%nAtoms]

Properties%ESR A-tens (MHz) InputOrder**Type**

float_array

DescriptionESR A-tensor (MHz), includes factor g_n/S , atoms in input order.**Shape**

[3, 3, Molecule%nAtoms]

Properties%ESR g-iso**Type**

float

Description

Isotropic value ESR g-tensor.

Properties%ESR g-tensor**Type**

float_array

Description

ESR g-tensor.

Shape

[3, 3]

Properties%Excited State Dipole**Type**

float_array

Description

Excited state dipole moment.

Shape

[3]

Properties%FermiLevel**Type**

float_array

Description

Fermi energy per spin, typically exactly halfway between HOMO and LUMO energy per spin.

Shape

[General%nspin]

Properties%Fragment Voronoi chrg per irrep**Type**

bool

Description

Whether Voronoi (and other) atomic charges per irreducible representation are written to file.

Properties%FragmentCharge Hirshfeld**Type**

float_array

Description

Hirshfeld fragment charges.

Shape

[Geometry%nfragm]

Properties%FragmentSpin Hirshfeld**Type**

float_array

Description

Hirshfeld fragment spin densities.

Shape

[Geometry%nfragm]

Properties%Fukui Fminus**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%Fukui Fplus**Type**

float_array

Description

?

Shape

[Molecule%nAtoms]

Properties%GophinatanJug BO between frag**Type**

float_array

Description

Matrix containing the Gopinathan-Jug bond order between fragments. Diagonal elements of the BO matrix=?. Atoms order: internal order.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%Hirshfeld Atomic Charge**Type**

float_array

Description

?

Properties%Hirshfeld Effective Volume**Type**

float_array

Description

?

Properties%Hirshfeld Free Volume**Type**

float_array

Description

?

Properties%Hirshfeld Fuzzy Bond Orders**Type**

float_array

Description

Matrix containing the Hirshfeld Fuzzy Bond Orders.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%Hirshfeld Fuzzy Valences**Type**

float_array

Description

Hirshfeld Fuzzy Valences (internal order).

Shape

[Geometry%nr of fragments]

Properties%HOMO**Type**

float

Description

Highest occupied molecular orbital (HOMO) energy.

Properties%index Bader MO contrib**Type**

int_array

Description

indices to read the Bader MO contrib

Properties%IQA atom-atom total**Type**

float_array

Description

Total interaction energy of atoms I and J

Shape

[:]

Properties%IQA Coulomb total**Type**

float_array

Description

?

Properties%IQA e-e Coulomb**Type**

float_array

Description

Coulomb interaction energy of electron densities on atoms I and J

Shape

[:]

Properties%IQA e-e exchange**Type**

float_array

Description

Exchange interaction energy of electron densities on atoms I and J

Shape

[:]

Properties%IQA e-e total**Type**

float_array

Description

Total interaction energy of electron densities on atoms I and J

Shape

[:]

Properties%IQA electron-nucleus**Type**

float_array

Description

Interaction energy of the electron density of atom I with the nucleus of atom J

Shape

[Molecule%nAtoms, Molecule%nAtoms]

Properties%IQA kinetic energy**Type**

float_array

Description

Kinetic energy of all electrons of the atom

Shape

[Molecule%nAtoms]

Properties%IQA pairs disp**Type**

float_array

Description

?

Properties%Koopmans DD**Type**

float_array

Description

Fukui Fplus - Fukui Fminus?

Shape

[Molecule%nAtoms]

Properties%LI-DI indices**Type**

float_array

Description

The matrix of localization/delocalization indices (Aromaticity indices with QTAIM results).
Note: atom order might be 'internal'?

Shape

[Molecule%nAtoms, Molecule%nAtoms]

Properties%LI-DI packed**Type**

float_array

Description

Localization and delocalization indices (matrix elements). Order?

Properties%LUMO**Type**

float

Description

Lowest unoccupied molecular orbital (LUMO) energy.

Properties%Mayer BO between frag**Type**

float_array

Description

Matrix containing the Mayer bond order between fragments. Diagonal elements of the BO matrix=?. Atoms order: internal order.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%MayerBondOrders_A**Type**

float_array

Description

Mayer bond orders matrix. In case of spin-restricted calculation, this contains the full bond orders. In case of spin-unrestricted, this contains the bond orders for the alpha spins. Possibly in internal order? check.

Shape

[Molecule%nAtoms, Molecule%nAtoms]

Properties%MayerBondOrders_B**Type**

float_array

Description

Spin-beta Mayer bond orders matrix (only for spin-unrestricted calculations). Possibly in internal order? check.

Shape

[Molecule%nAtoms, Molecule%nAtoms]

Properties%MDC-d charges**Type**

float_array

Description

MDC-d charges reconstruct monopoles and dipoles.

Shape

[Molecule%nAtoms]

Properties%MDC-d charges_A**Type**

float_array

Description

Spin alpha MDC-d charges.

Shape

[Molecule%nAtoms]

Properties%MDC-d charges_B**Type**

float_array

Description

Spin beta MDC-d charges.

Shape

[Molecule%nAtoms]

Properties%MDC-m charges**Type**

float_array

Description

Multipole derived atomic charges (MDC) reconstruct monopoles.

Shape

[Molecule%nAtoms]

Properties%MDC-m charges_A**Type**

float_array

Description

Spin alpha MDC-m charges.

Shape

[Molecule%nAtoms]

Properties%MDC-m charges_B**Type**

float_array

Description

Spin beta MDC-m charges.

Shape

[Molecule%nAtoms]

Properties%MDC-q charges**Type**

float_array

Description

MDC-d charges reconstruct monopoles, dipoles and quadrupoles.

Shape

[Molecule%nAtoms]

Properties%MDC-q charges_A**Type**

float_array

Description

Spin alpha MDC-q charges.

Shape

[Molecule%nAtoms]

Properties%MDC-q charges_B**Type**

float_array

Description

Spin beta MDC-q charges.

Shape

[Molecule%nAtoms]

Properties%Nalewajski1 BO between frag**Type**

float_array

Description

Matrix containing the Nalewajski-Mrozek-1 bond order between fragments. Diagonal elements of the BO matrix=?. Atoms order: internal order.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%Nalewajski2 BO between frag**Type**

float_array

Description

Matrix containing the Nalewajski-Mrozek-1 bond order between fragments. Diagonal elements of the BO matrix=?. Atoms order: internal order.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%Nalewajski3 BO between frag**Type**

float_array

Description

Matrix containing the Nalewajski-Mrozek-3 bond order between fragments. Diagonal elements of the BO matrix=?. Atoms order: internal order.

Shape

[Geometry%nr of fragments, Geometry%nr of fragments]

Properties%NBO natural charges

Type

float_array

Description

NBO natural charges.

Properties%*n*Entries**Type**

int

Description

Number of properties.

Properties%NFOD**Type**

float

Description

NFOD descriptor: Integrated fractional orbital density.

Properties%NMR Coupling J const InputOrder**Type**

float_array

Description

NMR Nuclear Spin-spin Coupling Constants, atoms in input order.

Shape[Molecule%*n*Atoms, Molecule%*n*Atoms]**Properties%NMR Coupling J tens InputOrder****Type**

float_array

Description

NMR Nuclear Spin-spin Coupling tensors, atoms in input order.

Shape[3, 3, Molecule%*n*Atoms, Molecule%*n*Atoms]**Properties%NMR Coupling K const InputOrder****Type**

float_array

Description

NMR reduced Nuclear Spin-spin Coupling Constants, atoms in input order.

Shape[Molecule%*n*Atoms, Molecule%*n*Atoms]**Properties%NMR Coupling K tens InputOrder****Type**

float_array

Description

NMR reduced Nuclear Spin-spin Coupling tensors, atoms in input order.

Shape[3, 3, Molecule%*n*Atoms, Molecule%*n*Atoms]

Properties%NMR Shielding Tensor InputOrder**Type**

float_array

Description

NMR chemical shielding tensors, atoms in input order.

Shape

[3, 3, Molecule%nAtoms]

Properties%NMR Shieldings InputOrder**Type**

float_array

Description

NMR chemical shieldings, atoms in input order.

Shape

[Molecule%nAtoms]

Properties%OverlapPop**Type**

float_array

Description

?

Shape

[Geometry%nr of fragments, Geometry%nr of fragments, 2]

Properties%pNMR Shielding Tensor InputOrder**Type**

float_array

Description

pNMR chemical shielding tensors, paramagnetic molecules, atoms in input order.

Shape

[3, 3, Molecule%nAtoms]

Properties%pNMR Shieldings InputOrder**Type**

float_array

Description

pNMR chemical shieldings, paramagnetic molecules, atoms in input order.

Shape

[Molecule%nAtoms]

Properties%pNMR sigma_p InputOrder**Type**

float_array

Description

Temperature dependent part pNMR chemical shieldings, paramagnetic molecules, atoms in input order.

Shape

[Molecule%nAtoms]

Properties%pNMR sigma_p Tensor InputOrder**Type**

float_array

Description

Temperature dependent part pNMR chemical shielding tensors, paramagnetic molecules, atoms in input order.

Shape

[3, 3, Molecule%nAtoms]

Properties%pNMR Temperature**Type**

float

Description

Temperature used in the calculation of the temperature dependent part pNMR chemical shieldings, paramagnetic molecules.

Properties%Polarizability**Type**

float_array

Description

Polarizability at first frequency PolarizabilityAtFrequency

Unit

a.u.

Shape

[3, 3]

Properties%Polarizability #**Type**

float_array

Description

Polarizability at frequency PolarizabilityAtFrequency #.

Unit

a.u.

Shape

[3, 3]

Properties%PolarizabilityAtFrequency**Type**

float

Description

First frequency at which Polarizability is calculated.

Unit

a.u.

Properties%PolarizabilityAtFrequency #

Type

float

Description

Frequency at which Polarizability # is calculated.

Unit

a.u.

Properties%PolarizabilityImag**Type**

float_array

Description

Imaginary part polarizability at first frequency PolarizabilityAtFrequency.

Unit

a.u.

Shape

[3, 3]

Properties%Quadrupole**Type**

float_array

Description

Quadrupole moment (Buckingham convention).

Shape

[6]

Properties%RhoDipole**Type**

float_array

Description

Dipole moment from electron density only.

Shape

[3]

Properties%RISM box**Type**

float_array

Description

?

Properties%RISM buv**Type**

float_array

Description

?

Properties%RISM cuv**Type**

float_array

Description

?

Properties%RISM epsu**Type**

float_array

Description

?

Properties%RISM ExChemPotential**Type**

float

Description

?

Properties%RISM grid dims**Type**

int_array

Description

?

Properties%RISM guv**Type**

float_array

Description

?

Properties%RISM guv integral #**Type**

float_array

Description

?

Properties%RISM guv rdf #**Type**

float_array

Description

?

Properties%RISM huv**Type**

float_array

Description

?

Properties%RISM Ndata**Type**

int_array

Description

?

Properties%RISM nga

Type
int

Description
?

Properties%RISM ngk

Type
int

Description
?

Properties%RISM num plane waves

Type
int

Description
?

Properties%RISM num solute sites

Type
int

Description
?

Properties%RISM num solvent sites

Type
int

Description
?

Properties%RISM PartMolVol [A^3]

Type
float

Description
?

Properties%RISM qu

Type
float_array

Description
?

Properties%RISM radial grid #

Type
float_array

Description
?

Properties%RISM ratu

Type

float_array

Description

?

Properties%RISM sigu**Type**

float_array

Description

?

Properties%RISM SiteDegeneracy**Type**

int_array

Description

?

Properties%RISM SiteExChemPotential**Type**

float_array

Description

?

Properties%RISM uuv**Type**

float_array

Description

?

Properties%S2calc**Type**

float

DescriptionElectron spin S^2 expectation value.**Properties%S2pure****Type**

float

DescriptionExact electron spin S^2 expectation value $s(s+1)$, where s is a half-integer value.**Properties%Source Function (cp,nuc)****Type**

float_array

Description

?

Properties%SpinDensity_SCF Voronoi**Type**

float_array

Description

Voronoi spin densities for the SCF density.

Shape

[Molecule%nAtoms]

Properties%Statistics NPoints**Type**

int

Description

?

Properties%Statistics NPoints Failed**Type**

int

Description

?

Properties%Statistics NPoints Screened**Type**

int

Description

?

Properties%Subtype (#)**Type**

string_fixed_length

Description

Extra detail about the property. For a charge property this could be Mulliken.

Properties%Type (#)**Type**

string

Description

Type of the property, like energy, gradients, charges, etc.

Properties%Value (#)**Type**

float_array

Description

The value(s) of the property.

Properties%VDBBondInd**Type**

int_array

Description

Indices of atoms for VVD bond (internal atom order).

Shape

[VDBBonds, 2]

Properties%VDBBonds

Type

int

Description

Number of VDD bonds?

Properties%VDDBondVal**Type**

float_array

Description

Values of the VDD bonds.

Shape

[VDDBonds]

Properties%Voronoi chrg per irrep**Type**

float_array

Description

Voronoi (and other) atomic charges per irreducible representation.

Shape

[Molecule%nAtoms, Symmetry%nsym, 8]

17.2.97 QMFQ

KF Section: QMFQ**Content:** Why is this in the ams.rkf file and not in the adf.rkf file?**QMFQ%atoms to index****Type**

int_array

Description

?

QMFQ%atoms to mol label**Type**

int_array

Description

?

QMFQ%charge constraints**Type**

float_array

Description

?

QMFQ%external xyz**Type**

float_array

Description

?

QMFQ%fde atoms to index**Type**

int_array

Description

?

QMFQ%fde atoms to mol label**Type**

int_array

Description

?

QMFQ%fde charge constraints**Type**

float_array

Description

?

QMFQ%fde external xyz**Type**

float_array

Description

?

QMFQ%fde index to mol label**Type**

int_array

Description

?

QMFQ%fde type index**Type**

int_array

Description

?

QMFQ%index to mol label**Type**

int_array

Description

?

QMFQ%type alpha**Type**

float_array

Description

?

QMFQ%type chi

Type

float_array

Description

?

QMFQ%type eta

Type

float_array

Description

?

QMFQ%type index

Type

int_array

Description

?

QMFQ%type name

Type

string

Description

?

QMFQ%type rmu

Type

float_array

Description

?

QMFQ%type rq

Type

float_array

Description

?

17.2.98 Reference Eigenvector

KF Section: Reference Eigenvector

Content: Reference eigenvector to Excited State Geometry Optimization.

Reference Eigenvector%Eigenvector

Type

float_array

Description

?

Reference Eigenvector%Energy

Type
float

Description
?

Reference Eigenvector%nstate

Type
int

Description
?

17.2.99 Response Data

KF Section: Response Data

Content: ?

Response Data%npnts

Type
int

Description
?

Response Data%polarizabilities

Type
float_array

Description
?

17.2.100 ResponsePmats

KF Section: ResponsePmats

Content: response density matrices

ResponsePmats%pmatei_X

Type
float_array

Description
?

Shape
[vecdimension]

ResponsePmats%pmatei_Y

Type
float_array

Description
?

Shape
[vecdimension]

ResponsePmats%pmatei_Z

Type

float_array

Description

?

Shape

[vecdimension]

ResponsePmats%vecdimension

Type

int

Description

size response density matrix

17.2.101 Rose Data

KF Section: Rose Data

Content: ROSE localized orbitals

Rose Data%Eigen-Bas_A

Type

float_array

Description

MO coefficients for the localized orbitals in the supermolecular AO basis.

Rose Data%eps_A

Type

float_array

Description

Semicanonical orbital energies (obtained by diagonalizing the fragment Fock matrix)

Unit

hartree

Rose Data%Fock_RIBO_A

Type

float_array

Description

Semicanonical Fock matrix (fragment blocks are diagonal)

Rose Data%froc_A

Type

float_array

Description

occupation numbers of the localized orbitals.

Rose Data%nfrag

Type

int

Description

Number of ROSE fragments (can be different from the number of ADF input fragments !).

Rose Data%nmo_A

Type

int

Description

Number of localized orbitals.

Rose Data%ribo_occ_per_frag_A

Type

int_array

Description

Number of occupied orbitals for each fragment.

Rose Data%ribo_vir_per_frag_A

Type

int_array

Description

Number of virtual orbitals for each fragment.

17.2.102 RPA energies

KF Section: RPA energies

Content: ?

RPA energies%Direct RPA correlation

Type

float

Description

?

RPA energies%GM Delta P correlation

Type

float_array

Description

?

RPA energies%RPA correlation

Type

float

Description

?

RPA energies%RPA exchange

Type

float

Description

?

RPA energies%RPA xc

Type

float_array

Description

?

RPA energies%SOS-MP2 correlation

Type

float

Description

?

RPA energies%SOX

Type

float

Description

?

17.2.103 SCF

KF Section: SCF

Content: SCF related data

17.2.104 sDFT Energy

KF Section: sDFT Energy

Content: FDE related data

sDFT Energy%Electron electron repulsion

Type

float_array

Description

Electron electron repulsion.

sDFT Energy%Non-additive kinetic energy

Type

float

Description

Non-additive kinetic energy.

sDFT Energy%Non-additive xc energy

Type

float

Description

Non-additive xc energy.

sDFT Energy%Nuclear electron attraction

Type

float_array

Description

Nuclear-electron attractions.

sDFT Energy%Nuclear repulsion**Type**

float_array

Description

Nuclear-nuclear repulsions.

sDFT Energy%Subsystem total energies**Type**

float_array

Description

Subsystem total energies.

sDFT Energy%Total el-el repulsion**Type**

float

Description

Total electron-electron repulsion.

sDFT Energy%Total elstat interaction**Type**

float

Description

Total elstat interaction.

sDFT Energy%Total interaction energy**Type**

float

Description

Total interaction energy.

sDFT Energy%Total nucel attraction**Type**

float

Description

Total nuclear-electron attraction.

sDFT Energy%Total nuclear repulsion**Type**

float

Description

Total nuclear-nuclear repulsion.

sDFT Energy%Total sDFT energy**Type**

float

Description

Total sDFT energy.

17.2.105 SFO popul

KF Section: SFO popul

Content: SFO population analysis.

SFO popul%number of contributions

Type

int_array

Description

Number of large SFO contributions per MO. Typically size [SFOs%number], in spin-orbit coupled calculation size [2*SFOs%number].

SFO popul%sfo_grosspop

Type

float_array

Description

Gross populations of both core orthogonalization functions and SFOs per symmetry.

SFO popul%sfo_index

Type

int_array

Description

SFO index for each large SFO contribution.

SFO popul%sfo_pop

Type

float_array

Description

Large SFO contributions in MOs.

17.2.106 SFO_Fock

KF Section: SFO_Fock

Content: Fock matrix on SFO basis.

17.2.107 SFO_Overlap

KF Section: SFO_Overlap

Content: SFO overlap matrix.

17.2.108 SFOs

KF Section: SFOs

Content: SFO related data.

SFOs%energy

Type

float_array

Description

Fragment orbital energies.

Shape

[number]

SFOs%energy_B

Type

float_array

Description

Fragment orbital energies, for spin B.

Shape

[number]

SFOs%escale

Type

float_array

Description

ZORA only: scaled ZORA fragment orbital energies.

Shape

[number]

SFOs%escale_B

Type

float_array

Description

ZORA only: scaled ZORA fragment orbital energies for spin B.

Shape

[number]

SFOs%fragment

Type

int_array

Description

Fragment number. Only the number of the first fragment is given in case of symmetry-related fragments.

Shape

[number]

SFOs%fragorb

Type

int_array

Description

Fragment orbital number in fragment. Only the number on the first fragment is given in case of symmetry-related fragments.

Shape

[number]

SFOs%fragtype**Type**

lchar_string_array

Description

Fragment type for each SFO.

Shape

[number]

SFOs%ifo**Type**

int_array

Description

SFO numbers in symmetry irrep of the total system.

Shape

[number]

SFOs%isfo**Type**

int_array

Description

Fragment orbital numbers in symmetry irrep of the fragment.

Shape

[number]

SFOs%number**Type**

int

Description

Total number of (symmetrized) fragment orbitals (SFOs).

SFOs%occupation**Type**

float_array

Description

Fragment orbital occupation numbers.

Shape

[number]

SFOs%occupation_B**Type**

float_array

Description

Fragment orbital occupation numbers, for spin B.

Shape

[number]

SFOs%site_energy**Type**

float_array

Description

Site energy.

Shape

[number]

SFOs%site_energy_B**Type**

float_array

Description

Site energies, for spin B.

Shape

[number]

SFOs%site_lowdin_energy**Type**

float_array

Description

Site Lowdin energies

Shape

[number]

SFOs%site_lowdin_energy_B**Type**

float_array

Description

Site Lowdin energies, for spin B

Shape

[number]

SFOs%subspecies**Type**

lchar_string_array

Description

Fragment orbital symmetry label including subspecies for each SFO.

Shape

[number]

17.2.109 Spin operator matrix

KF Section: Spin operator matrix

Content: Spin operator matrix.

17.2.110 Spin_orbit

KF Section: Spin_orbit

Content: Section for spin-orbit coupling.

Spin_orbit%Bcoef

Type

float_array

Description

Arrays with B-coefficients as given in PhD thesis J.G. Snijders (1979) p102.

Spin_orbit%Hirshfeld_MVEC_#

Type

float_array

Description

Hirshfeld fragment spin magnetization in direction # (1=X,2=Y,3=Z). If fragments are atoms, atoms are in internal order.

Shape

[Molecule%nAtoms]

Spin_orbit%Mulliken_MVEC_#

Type

float_array

Description

Mulliken atomic spin magnetization in direction # (1=X,2=Y,3=Z) per l-value (S,P,D,F), atoms in input order.

Shape

[4, Molecule%nAtoms]

Spin_orbit%Voronoi_RestCell_MVEC_#

Type

float_array

Description

Voronoi atomic spin magnetization outside atomic sphere in rest of Voronoi cell in direction # (1=X,2=Y,3=Z)

Shape

[Molecule%nAtoms]

Spin_orbit%Voronoi_Sphere_MVEC_#

Type

float_array

Description

Voronoi atomic spin magnetization inside atomic sphere in direction # (1=X,2=Y,3=Z)

Shape
[Molecule%nAtoms]

17.2.111 SUB1!*

KF Section: SUB1!*

Content: Data for SUBEXCI.

17.2.112 SUB2!*

KF Section: SUB2!*

Content: Data for SUBEXCI.

17.2.113 SUBEXCI

KF Section: SUBEXCI

Content: Data for SUBEXCI.

17.2.114 SUBRESP

KF Section: SUBRESP

Content: SUBRESP

SUBRESP%SUB1_respp

Type
float_array

Description
?

SUBRESP%SUB2_respp

Type
float_array

Description
?

17.2.115 SumFrag C energies

KF Section: SumFrag C energies

Content: Sum of fragment correlation energies.

17.2.116 SumFrag X energies

KF Section: SumFrag X energies

Content: Sum of fragment exchange energies.

17.2.117 SumFrag XC energies

KF Section: SumFrag XC energies

Content: Sum of fragment XC energies.

17.2.118 SymFit

KF Section: SymFit

Content: Data for the STO fit procedure.

17.2.119 Symmetry

KF Section: Symmetry

Content: Data related to the symmetry of the molecule.

Symmetry%faith**Type**

float_array

Description

The symmetry operator matrices.

Shape

[3, 3, nogr]

Symmetry%grouplabel**Type**

string

Description

Schoenflies symbol of the symmetry group.

Symmetry%idcg**Type**

int_array

Description

Array with for each combination of a rel. symmetry and a non-relativistic one a 1 if this non-relat. symmetry is in the rel. symmetry else a 0.

Shape

[nrsym, nsym]

Symmetry%igr**Type**

int

Description

Point group identification number. 1: atom, 10: c(lin), 20: d(lin), 30: t(d), 60: o(h), 100: c(n), 200: c(nh), 400: c(nv), 450: d(n), 500: d(nh), 600: d(nd), 700: c(i), 800: c(s), 999: nosym

Symmetry%isingtrip excitations**Type**

int

Description

Integer indicating what kind of TD-DFT excitations are calculated.

Symmetry%jalok**Type**

int_array

Description

An array (1:npeq), with values 0 or 1. 1=the pair density can be fitted using A1 fit functions only. 0=all fit functions (on the involved atoms) are to be used. The value 1 may arise because of symmetry properties, or because the distance between the atoms is so large that the inaccuracy from using only A1 fit functions can be neglected.

Shape

[npeq]

Symmetry%jasym**Type**

int_array

Description

An array that runs over the npeq sets of equivalent atom pairs. Its value gives for the indicated the set the number of pairs in that set.

Shape

[npeq]

Symmetry%jjsym**Type**

int_array

Description

An array that runs over the npeq sets of symmetry equivalent atom pairs. Its value gives for the indicated set the index of a (c.f. the first) atom pair in that set.

Symmetry%jsym1**Type**

int_array

Description

For each of the nsym representations: if it belongs to a one-dimensional irrep, the value is 1, otherwise: for the first subspecies in the irrep the value is the dimension of the irrep, for the other subspecies in the same irrep the value is 0.

Shape

[nsym]

Symmetry%lnoci**Type**

bool

Description

If symmetry is NOSYM or C(I) Inoci = true, otherwise false.

Symmetry%lrep2do excitations**Type**

bool_array

Description

Which irrep subspecies [irrep,subspecies] calculated in TD-DFT excitations.

Shape

[20, 5]

Symmetry%lrep2do excitations ST**Type**

bool_array

Description

Which irrep subspecies [irrep,subspecies] calculated in TD-DFT singlet-triplet excitations.

Shape

[20, 5]

Symmetry%napp**Type**

int_array

Description

An array that stores for each atom the number of the symmetry set it belongs to.

Shape

[Geometry%nuc]

Symmetry%ncbs**Type**

int_array

Description

The number of core orthogonalization functions in the corresponding irrep.

Shape

[nsym]

Symmetry%ndim excitations**Type**

int_array

Description

Dimension (number of subspecies) of the irreps used in TD-DFT excitations.

Shape

[nsym excitations]

Symmetry%nfcn**Type**

int_array

Description

Number of primitive functions in the corresponding irrep.

Shape

[nsym]

Symmetry%ngr**Type**

int

Description

One of the integer-code components that fix the symmetry group. See routine adf/maisya

Symmetry%noat**Type**

int_array

Description

Map between normal list of atoms and symmetry sets.

Shape

[Geometry%nnuc]

Symmetry%nogr**Type**

int

Description

The number of symmetry operators. NB, for the special cases of infinite symmetries, only the operators corresponding to finite elements are counted. Therefore, ATOM has nogr=1 (only the unit operator); C(LIN) has nogr=1, D(LIN) has nogr=2

Symmetry%norb**Type**

int_array

Description

For each of the nsym representations the number of basis function combinations (SFOs) that belong to it.

Shape

[nsym]

Symmetry%norboc**Type**

int_array

Description

An array (-2:2,nsym). The column runs over the symmetry representations. The positive row indices (1,2) specify for spin-A and spin-B (the latter only if the calculation is spin-unrestricted), the highest non-empty orbital. The negative indices (-1,-2) specify for spin-A and spin-B (if the unrestricted fragment option is used) the total number of non-empty SFOs. The zero row index specifies the number of non-empty SFOs, before applying any fragment occupation changes.

Symmetry%notyps**Type**

int_array

Description

For each set of symmetry equivalent atoms, the atom type to which the set belongs.

Shape

[nsetat]

Symmetry%npeq**Type**

int

Description

The number of symmetry unique pairs of atoms.

Symmetry%nratst**Type**

int_array

Description

Number of atoms in each set of symmetry equivalent atoms.

Shape

[nsetat]

Symmetry%nrorb**Type**

int_array

Description

For each of the nrsym double group representations the number of spinors that belong to it.

Shape

[nrsym]

Symmetry%nrorc**Type**

int_array

Description

The indices (1,irsym) specifies for each double group irrep irsym the highest non-empty spinor.
Indices (2,irsym) unused.

Shape

[2, nrsym]

Symmetry%nrsym**Type**

int

Description

Number of double group irreps.

Symmetry%nsetat**Type**

int

Description

Number of sets of symmetry equivalent atoms.

Symmetry%nsym**Type**

int

Description

Number of irreps.

Symmetry%nsym excitations**Type**

int

Description

Number of irreps used in TD-DFT excitations.

Symmetry%nsymdav excitations**Type**

int_array

Description

Calculated nr of TD-DFT excitations for each irrep subspecies [irrep,subspecies].

Shape

[20, 5]

Symmetry%nsymdav excitations ST**Type**

int_array

Description

Calculated nr of TD-DFT singlet-triplet excitations for each irrep subspecies [irrep,subspecies].

Shape

[20, 5]

Symmetry%nsymden excitations**Type**

int_array

Description

Maximum nr of TD-DFT excitations for each irrep subspecies [irrep,subspecies].

Shape

[20, 5]

Symmetry%ntr**Type**

int_array

Description

For each atom A and each symmetry operator R, the atom onto with A is mapped by R. The row index runs over all symmetry operators, the column index over the atoms.

Shape

[nogr, Geometry%nnuc]

Symmetry%ntr_setat**Type**

int_array

Description

A condensed variety of array ntr: the columns are not the atoms, but the nsetat sets of symmetry equivalent atoms. The value is the index of the atom, onto which a representative (c.f. the first) atom of the indicated symmetry set is mapped by the given symmetry operator.

Symmetry%rep-D**Type**

int

Description

max. length of array for repr. matrices.

Symmetry%rep-I**Type**

float_array

Description

Imaginary part array with double group repr. matrices.

Shape

[rep-D+1]

Symmetry%rep-R**Type**

float_array

Description

Real part array with double group repr. matrices.

Shape

[rep-D+1]

Symmetry%rep-S**Type**

float_array

Description

Representation matrices for single group.

Shape

[nogr, nogr]

Symmetry%repr**Type**

float_array

Description

Representation matrices.

Symmetry%reprdim**Type**

int_array

Description

Dimension (number of subspecies) of the double-group irreducible representation.

Shape

[nrsym]

Symmetry%symlab**Type**

lchar_string_array

Description

Labels of the irreps.

Shape

[nsym]

Symmetry%symlab excitations**Type**

lchar_string_array

Description

Labels of the irreps used in TD-DFT excitations.

Shape

[nsym excitations]

Symmetry%symlabr**Type**

lchar_string_array

Description

Labels of the double group irreps.

Shape

[nrsym]

Symmetry%vecdimension excitations**Type**

int

Description

Maximum number of the dimension of an eigenvector in TD-DFT excitations.

17.2.120 Thermodynamics

KF Section: Thermodynamics

Content: Thermodynamic properties computed from normal modes.

Thermodynamics%Enthalpy**Type**

float_array

Description

Enthalpy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Entropy rotational**Type**

float_array

Description

Rotational contribution to the entropy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Entropy total**Type**

float_array

Description

Total entropy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Entropy translational**Type**

float_array

Description

Translational contribution to the entropy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Entropy vibrational**Type**

float_array

Description

Vibrational contribution to the entropy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Gibbs free Energy**Type**

float_array

Description

Gibbs free energy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Heat Capacity rotational

Type

float_array

Description

Rotational contribution to the heat capacity.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Heat Capacity total**Type**

float_array

Description

Total heat capacity.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Heat Capacity translational**Type**

float_array

Description

Translational contribution to the heat capacity.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Heat Capacity vibrational**Type**

float_array

Description

Vibrational contribution to the heat capacity.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Inertia direction vectors**Type**

float_array

Description

Inertia direction vectors.

Shape

[3, 3]

Thermodynamics%Internal Energy rotational**Type**

float_array

Description

Rotational contribution to the internal energy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Internal Energy total**Type**

float_array

Description

Total internal energy.

Unit

a.u.

Thermodynamics%Internal Energy translational**Type**

float_array

Description

Translational contribution to the internal energy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Internal Energy vibrational**Type**

float_array

Description

Vibrational contribution to the internal energy.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%lowFreqEntropy**Type**

float_array

Description

Entropy contributions from low frequencies (see 'lowFrequencies').

Unit

a.u.

Shape

[nLowFrequencies]

Thermodynamics%lowFreqHeatCapacity**Type**

float_array

Description

Heat capacity contributions from low frequencies (see 'lowFrequencies').

Unit

a.u.

Shape

[nLowFrequencies]

Thermodynamics%lowFreqInternalEnergy**Type**

float_array

Description

Internal energy contributions from low frequencies (see 'lowFrequencies').

Unit

a.u.

Shape

[nLowFrequencies]

Thermodynamics%lowFrequencies**Type**

float_array

Description

Frequencies below 20 cm⁻¹ (contributions from frequencies below 20 cm⁻¹ are not included in vibrational sums, and are saved separately to 'lowFreqEntropy', 'lowFreqInternalEnergy' and 'lowFreqInternalEnergy'). Note: this does not apply to RRHO-corrected quantities.

Unitcm⁻¹**Shape**

[nLowFrequencies]

Thermodynamics%Moments of inertia**Type**

float_array

Description

Moments of inertia.

Unit

a.u.

Shape

[3]

Thermodynamics%nLowFrequencies**Type**

int

Description

Number of elements in the array lowFrequencies.

Thermodynamics%nTemperatures**Type**

int

Description

Number of temperatures.

Thermodynamics%Pressure**Type**

float

Description

Pressure used.

Unit

atm

Thermodynamics%RRHOCorrectedHeatCapacity**Type**

float_array

Description

Heat capacity $T \cdot S$ corrected using the 'low vibrational frequency free rotor interpolation corrections'.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%RRHOCorrectedInternalEnergy**Type**

float_array

Description

Internal energy $T \cdot S$ corrected using the 'low vibrational frequency free rotor interpolation corrections'.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%RRHOCorrectedTS**Type**

float_array

Description

$T \cdot S$ corrected using the 'low vibrational frequency free rotor interpolation corrections'.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%Temperature**Type**

float_array

Description

List of temperatures at which properties are calculated.

Unit

a.u.

Shape

[nTemperatures]

Thermodynamics%TS**Type**

float_array

Description

T*S, i.e. temperature times entropy.

Unit

a.u.

Shape

[nTemperatures]

17.2.121 Total C energies**KF Section: Total C energies****Content:** Total correlation energies.**17.2.122 Total Energy****KF Section: Total Energy****Content:** Data related to a total energy calculation.**17.2.123 Total X energies****KF Section: Total X energies****Content:** Total exchange energies.**17.2.124 Total XC energies****KF Section: Total XC energies****Content:** Total XC energies.

17.2.125 TransferIntegrals

KF Section: TransferIntegrals

Content: Charge transfer integrals relevant for hole or electron mobility calculations. Electronic coupling V (also known as effective (generalized) transfer integrals J_{eff}) $V = (J - S(e_1 + e_2)/2)/(1 - S^2)$. For electron mobility calculations the fragment LUMOs are considered. For hole mobility calculations the fragment HOMOs are considered.

TransferIntegrals%Determinant

Type

float

Description

Determinant related to overlap integrals used in ADF FOCDFT%electrontransfer.

TransferIntegrals%e1 (electron)

Type

float

Description

Site energy LUMO fragment 1.

Unit

hartree

TransferIntegrals%e1 (hole)

Type

float

Description

Site energy HOMO fragment 1.

Unit

hartree

TransferIntegrals%e2 (electron)

Type

float

Description

Site energy LUMO fragment 2.

Unit

hartree

TransferIntegrals%e2 (hole)

Type

float

Description

Site energy HOMO fragment 2.

Unit

hartree

TransferIntegrals%Electronic coupling

Type

float

Description

Electronic coupling calculated by ADF FOCDFT%electrontransfer.

TransferIntegrals%J(charge recombination 12)

Type

float

Description

Charge transfer integral HOMO fragment 1 - LUMO fragment 2 for charge recombination 1-2.

Unit

hartree

TransferIntegrals%J(charge recombination 21)

Type

float

Description

Charge transfer integral LUMO fragment 1 - HOMO fragment 2 for charge recombination 2-1.

Unit

hartree

TransferIntegrals%J(electron)

Type

float

Description

Charge transfer integral LUMO fragment 1 - LUMO fragment 2 for electron transfer.

Unit

hartree

TransferIntegrals%J(hole)

Type

float

Description

Charge transfer integral HOMO fragment 1 - HOMO fragment 2 for hole transfer.

Unit

hartree

TransferIntegrals%S(charge recombination 12)

Type

float

Description

Overlap integral HOMO fragment 1 - LUMO fragment 2 for charge recombination 1-2.

TransferIntegrals%S(charge recombination 21)

Type

float

Description

Overlap integral LUMO fragment 1 - HOMO fragment 2 for charge recombination 2-1.

TransferIntegrals%S(electron)

Type

float

Description

Overlap integral LUMO fragment 1 - LUMO fragment 2.

TransferIntegrals%S(hole)**Type**

float

Description

Overlap integral HOMO fragment 1 - HOMO fragment 2.

TransferIntegrals%V(charge recombination 12)**Type**

float

Description

Effective charge transfer integral HOMO fragment 1 - LUMO fragment 2 for charge recombination 1-2.

Unit

hartree

TransferIntegrals%V(charge recombination 21)**Type**

float

Description

Effective charge transfer integral LUMO fragment 1 - HOMO fragment 2 for charge recombination 2-1.

Unit

hartree

TransferIntegrals%V(electron)**Type**

float

Description

Effective transfer integral LUMO fragment 1 - LUMO fragment 2 for electron transfer.

Unit

hartree

TransferIntegrals%V(hole)**Type**

float

Description

Effective transfer integral HOMO fragment 1 - HOMO fragment 2 for hole transfer.

Unit

hartree

TransferIntegrals%Vtot(charge recombination 12)**Type**

float

Description

Total electronic coupling for charge recombination 1-2.

Unit

hartree

TransferIntegrals%Vtot (charge recombination 21)

Type

float

Description

Total electronic coupling for charge recombination 2-1.

Unit

hartree

TransferIntegrals%Vtot (electron)

Type

float

Description

Total electronic coupling for electron transfer.

Unit

hartree

TransferIntegrals%Vtot (hole)

Type

float

Description

Total electronic coupling for hole transfer.

Unit

hartree

17.2.126 VCDTools

KF Section: VCDTools

Content: VCDTools data: VCD analysis.

17.2.127 Vibrations

KF Section: Vibrations

Content: Information related to molecular vibrations.

Vibrations%ExcitedStateLifetime

Type

float

Description

Raman excited state lifetime.

Unit

hartree

Vibrations%ForceConstants

Type

float_array

Description

The force constants of the vibrations.

Unithartree/bohr²**Shape**

[nNormalModes]

Vibrations%Frequencies [cm⁻¹]**Type**

float_array

Description

The vibrational frequencies of the normal modes.

Unitcm⁻¹**Shape**

[nNormalModes]

Vibrations%Intensities [km/mol]**Type**

float_array

Description

The intensity of the normal modes.

Unit

km/mol

Shape

[nNormalModes]

Vibrations%IrReps**Type**

lchar_string_array

Description

Symmetry symbol of the normal mode.

Shape

[nNormalModes]

Vibrations%ModesNorm2**Type**

float_array

Description

Norms of the rigid motions.

Shape

[nNormalModes+nRigidModes]

Vibrations%ModesNorm2*

Type

float_array

Description

Norms of the rigid motions (for a given irrep...?).

Shape

[nNormalModes+nRigidModes]

Vibrations%nNormalModes**Type**

int

Description

Number of normal modes.

Vibrations%NoWeightNormalMode (#)**Type**

float_array

Description

?.

Shape

[3, Molecule%nAtoms]

Vibrations%NoWeightRigidMode (#)**Type**

float_array

Description

?

Shape

[3, Molecule%nAtoms]

Vibrations%nRigidModes**Type**

int

Description

Number of rigid modes.

Vibrations%nSemiRigidModes**Type**

int

Description

Number of semi-rigid modes.

Vibrations%PVDOS**Type**

float_array

Description

Partial vibrational density of states.

Values range

[0.0, 1.0]

Shape

[nNormalModes, Molecule%nAtoms]

Vibrations%RamanDepolRatioLin**Type**

float_array

Description

Raman depol ratio (lin).

Shape

[nNormalModes]

Vibrations%RamanDepolRatioNat**Type**

float_array

Description

Raman depol ratio (nat).

Shape

[nNormalModes]

Vibrations%RamanIncidentFreq**Type**

float

Description

Raman incident light frequency.

Unit

hartree

Vibrations%RamanIntens [A^4/amu]**Type**

float_array

Description

Raman intensities

Unit

A^4/amu

Shape

[nNormalModes]

Vibrations%ReducedMasses**Type**

float_array

Description

The reduced masses of the normal modes.

Unit

a.u.

Values range

[0, 'infinity']

Shape

[nNormalModes]

Vibrations%RotationalStrength**Type**

float_array

Description

The rotational strength of the normal modes.

Shape

[nNormalModes]

Vibrations%TransformationMatrix**Type**

float_array

Description

?

Shape

[3, Molecule%nAtoms, nNormalModes]

Vibrations%VROACIDBackward**Type**

float_array

Description

VROA Circular Intensity Differential: Backward scattering.

Unit 10^{-3} **Shape**

[nNormalModes]

Vibrations%VROACIDDePolarized**Type**

float_array

Description

VROA Circular Intensity Differential: Depolarized scattering.

Unit 10^{-3} **Shape**

[nNormalModes]

Vibrations%VROACIDForward**Type**

float_array

Description

VROA Circular Intensity Differential: Forward scattering.

Unit 10^{-3}

Shape

[nNormalModes]

Vibrations%VROACIDPolarized**Type**

float_array

Description

VROA Circular Intensity Differential: Polarized scattering.

Unit 10^{-3} **Shape**

[nNormalModes]

Vibrations%VROADeltaBackward**Type**

float_array

Description

VROA Intensity: Backward scattering.

Unit $10^{-3} \text{ A}^4/\text{amu}$ **Shape**

[nNormalModes]

Vibrations%VROADeltaDePolarized**Type**

float_array

Description

VROA Intensity: Depolarized scattering.

Unit $10^{-3} \text{ A}^4/\text{amu}$ **Shape**

[nNormalModes]

Vibrations%VROADeltaForward**Type**

float_array

Description

VROA Intensity: Forward scattering.

Unit $10^{-3} \text{ A}^4/\text{amu}$ **Shape**

[nNormalModes]

Vibrations%VROADeltaPolarized**Type**

float_array

Description

VROA Intensity: Polarized scattering.

Unit $10^{-3} \text{ A}^4/\text{amu}$ **Shape**

[nNormalModes]

Vibrations%ZeroPointEnergy**Type**

float

Description

Vibrational zero-point energy.

Unit

hartree

17.2.128 XAS DATA**KF Section:** XAS DATA**Content:** XAS data.**17.2.129 XCRangeSeparated****KF Section:** XCRangeSeparated**Content:** ?**XCRangeSeparated%CAMTypeCalculation****Type**

bool

Description

?

XCRangeSeparated%currentRegion**Type**

int

Description

?

XCRangeSeparated%DFTLongRange**Type**

bool

Description

?

XCRangeSeparated%DFTOnly**Type**

bool

Description

?

XCRangeSeparated%ExactLongRange

Type
bool

Description
?

XCRangeSeparated%ExcludeHF

Type
bool

Description
?

XCRangeSeparated%HFOnly

Type
bool

Description
?

XCRangeSeparated%RangeSeparated

Type
bool

Description
?

XCRangeSeparated%RangeSepLine

Type
string

Description
?

XCRangeSeparated%Region_coefficient

Type
float_array

Description
?

Shape
[10]

XCRangeSeparated%Region_gamma

Type
float_array

Description
?

Shape
[10]

XCRangeSeparated%Region_IsDFT

Type
bool_array

Description

?

Shape

[10]

XCRangeSeparated%Region_IsExactExchange

Type

bool_array

Description

?

Shape

[10]

17.2.130 XES DATA

KF Section: XES DATA

Content: XES data.

17.2.131 ZFS

KF Section: ZFS

Content: ?

ZFS%Dtensor

Type

float_array

Description

?

ZFS%DtensorDiag

Type

float_array

Description

?

ZFS%ZFSPrincipleAxis

Type

float_array

Description

?

17.2.132 ZlmFit_*

KF Section: ZlmFit_*

Content: Data related to the density fitting procedure (ZlmFit).

17.2.133 ZlmFitConfig

KF Section: ZlmFitConfig

Content: Configuration options for the Zlm density fit.

ZlmFitConfig%densityThresh

Type

float_array

Description

Threshold for the density.

Shape

[nAtoms]

ZlmFitConfig%gridAngOrder

Type

int_array

Description

Angular order (Lebedev grid) per atom.

Shape

[nAtoms]

ZlmFitConfig%lMaxExpansion

Type

int_array

Description

Maximum l-value for the fit functions per atom.

Shape

[nAtoms]

ZlmFitConfig%nAtoms

Type

int

Description

Number of atoms.

ZlmFitConfig%nRadialPoints

Type

int_array

Description

Number of radial points per atom.

Shape

[nAtoms]

ZlmFitConfig%partitionFunThresh

Type

float_array

Description

Threshold for the partition function.

Shape

[nAtoms]

ZlmFitConfig%partitionSizeAdjustment**Type**

bool

Description

Atom dependent partition size?

ZlmFitConfig%potentialThresh**Type**

float_array

Description

Threshold for the potential.

Unit

a.u.

Shape

[nAtoms]

ZlmFitConfig%pruning**Type**

bool

Description

Whether or not to prune.

ZlmFitConfig%pruningGridAngOrder**Type**

int

Description

?.

ZlmFitConfig%pruningL**Type**

int

Description

?.

ZlmFitConfig%pruningThreshDist**Type**

float

Description

Distance threshold for pruning.

Unit

bohr

18.1 My ADF input does not work in AMS2020?

In our AMS2020 release, *ADF has been fully integrated into the AMS driver* (page 11), simplifying the input. If you run through the GUI this will not affect you. If you use your own command line input with scripts, your old inputs are not compatible with AMS2020 or beyond. Old ADF inputs can be *converted with a simple tool* (page 14). Let us know at support@scm.com with your old input if that does not work.

18.2 Can I use Gaussian type basis (6-31G*, TZVP, etc.) functions in ADF?

No, Gaussian-type orbitals cannot be used in ADF, since ADF uses Slater Type Orbitals (STOs).

Slater orbitals are better from a theoretical point of view since they have the correct behavior near the nucleus (cusp) and the correct asymptotic long-range behavior. Consequently, typically fewer STOs than GTOs are needed to reach a certain level of accuracy, as discussed in this news item [Slaters beat Gaussians](https://www.scm.com/highlights/slaters-beat-gaussians-fe-complexes/) (<https://www.scm.com/highlights/slaters-beat-gaussians-fe-complexes/>) and a [paper benchmarking DFT methods for a catalytic reaction](https://dx.doi.org/10.1002/jcc.23212) (<https://dx.doi.org/10.1002/jcc.23212>).

18.3 Which basis set should I use?

There is no silver bullet. Some general recommendations follow below, which are by no means definite. Please check the literature carefully and check the robustness of the results by using a large basis set eventually, if possible. See also [a more extended discussion on what basis set to use](#) (page 405).

The nomenclature of the STO basis sets in ADF: D, T, and Q stand for double, triple, and quadruple, and (n)P stands for n polarization functions. For example, the DZP basis has double zeta + 1 polarization function. Inner electrons of (atomic) fragments can be frozen during the molecular calculation, this is denoted with 'small', 'medium' or 'large', or by specifically specifying up to which shell the electrons are frozen. In general, we recommend the use of frozen core basis sets for LDA and GGA functionals if available. All electron basis sets are required in case of SAOP, meta-GGA and meta-hybrid functionals, functionals that use LibXC, post-KS calculations like GW, RPA, MP2 or double hybrids. For hybrid functionals, the use of frozen cores usually is fine for geometries and non-core spectroscopic properties.

There are also specialized basis sets, e.g. containing diffuse functions ("AUG", for describing anions and diffuse excitations of small molecules), even-tempered basis sets ("ET", less bias for particular electronic state), and optimized for ESR A-tensor and NMR spin-spin coupling calculations (ZORA/TZ2P-J and ZORA/QZ4P-J). [See also the documentation](#) (page 40) for more technical details and the basis set database in ADF.

The DZP basis set could be a good starting point, especially for geometry optimization. See also this [paper looking at catalytic reactions](https://dx.doi.org/10.1002/jcc.23212) (<https://dx.doi.org/10.1002/jcc.23212>). In general, this basis it is expected to be slightly better than the often used 6-31G* basis set in codes which use Gaussian basis sets. The DZP basis defaults to TZP for transition metals. The frozen core approximation generally does not affect geometries much, but a too large frozen core can lead to inaccuracies.

For accurate predictions of spectroscopic properties, the TZ2P basis (and numerical quality good) is recommended, especially for larger systems. For the most accurate predictions of spectroscopic properties one could use the much more expensive QZ4P basis set (and numerical quality very good), although often the TZ2P basis is already close to the basis set limit. Also, usually an all-electron basis set is necessary to properly describe properties related to inner electrons (NMR, EPR, X-ray absorption), or needed because of the chosen XC functional.

18.4 How do I calculate UV/VIS spectra with ADF?

The tutorial on [calculating UV/VIS spectra with ADF](#) will get you started with the basics. For getting more accurate results, however, you need to consider the technical details used in TDDFT, such as basis set, exchange correlation functional, and other settings.

There are also faster approximate TDDFT methods available, such as TDDFTB (see [tutorial](#)), sTDDFT, TDDFT+TB ([webinar](https://www.scm.com/news/ams2023-webinar-recordings/) (<https://www.scm.com/news/ams2023-webinar-recordings/>)), and POLTDDFT ([tutorial](#)).

We also have an [advanced tutorial / case study on TDDFT methods](#).

One can also go beyond TDDFT using quasiparticle self-consistent GW with the Bethe-Salpeter Equation (qsGW-BSE: [high-lights](#) (<https://www.scm.com/highlights/large-scale-self-consistent-gw-bethe-salpeter-equation-calculations-in-ADF/>), [tutorial](#)), which could be the most accurate approach.

You are advised to check the literature on which approaches are suitable for similar compounds. Here are some general recommendations on what could work well in ADF:

- 1) optimize your molecule. Scalar relativistic, TZP, small core (although a large frozen core could also work), and numerical quality 'Normal' would typically be quite accurate. As to the functional, a GGA perhaps with dispersion corrections could give very good results (e.g. PBE-D3(BJ)). GGAs are much faster in ADF and can yield better geometries than hybrids. Note that the dispersion interactions affect the geometry, and thereby indirectly the electronic structure, including excitations.
- 2) TDDFT calculation for UV/VIS. Scalar relativistic up to 4d-elements is usually sufficient. For heavier elements you may want to check the effect of spin-orbit coupling on the spectrum (see also a highlight on [conversion efficiency of solar cell dyes](https://www.scm.com/highlights/spin-orbit-coupling-increases-dye-sensitized-solar-cells-efficiency/) (<https://www.scm.com/highlights/spin-orbit-coupling-increases-dye-sensitized-solar-cells-efficiency/>)). You may want a larger basis set (e.g. TZ2P) and perhaps all-electron. Also a higher accuracy may be desirable (good, or very good). As to the number of excitations, this depends a bit on the electronic ground state and which excitations you are interested in. You could start with 30 or so to see how much of the blue/UV will be covered. Finally the functional could play an important role. The asymptotically correct SAOP model potential is often used, since this is an accurate Kohn-Sham potential well suited to describe virtual orbitals (see [publication by Baerends et al.](https://dx.doi.org/10.1021/ct500727c) (<https://dx.doi.org/10.1021/ct500727c>)). You could also try hybrids (e.g. B3LYP) or meta-hybrids (M06-2X). Range-separated hybrids (CAMY-B3LYP) are sometimes advised for excitations with long-range charge transfer character (you can also [tune range-separated hybrids](https://www.scm.com/news/tuning-range-separation-lc-wpbe-organic-electronics/) (<https://www.scm.com/news/tuning-range-separation-lc-wpbe-organic-electronics/>)). SAOP calculations will be much faster in ADF than hybrids.

Further comments:

- for symmetric systems, ALLOWEDONLY can reduce the computation time by excluding the excitations which are symmetry-forbidden
- for very large systems you may consider trying out TD-DFTB in combination with filtering out the single orbital transitions with very low oscillator strength

- vibronic fine structure may be included by calculating Franck-Condon Factors. Since this involves calculating excited state frequencies (numerically), the calculations can be very demanding for large systems

18.5 What settings are recommended for NMR calculations?

See also the [tutorial on relativistic NMR calculations](#). Perhaps the unique capabilities of ADF to [analyze orbital contributions to NMR](#) are of interest, too. We also have a tutorial on [how to visualize spin-spin coupling](#).

An all-electron basis set of TZP or higher. TZ2P is usually a good choice. For heavy metals you may consider the QZ4P basis set. For NMR spin-spin couplings you may consider the ZORA/TZ2P-J or ZORA/QZ4P-J basis.

PBE0 is often a good functional for NMR. If you can't afford hybrids you could try PBE or SAOP.

For the relativistic approach we recommend at least scalar ZORA. Spin-orbit (SO) ZORA should be used if you are looking at the shift of a heavy atom, or a light atom near a heavy atom. If SO effects are large, a QZ4P or QZ4P-J basis will improve the description of the induced spin density on the probe nucleus. You may also want to try out the *'fxc'* [kernel option](#) (page 234) – note that this has a small gauge dependency.

The numerical accuracy should be better than default. You could try NUMERICALQUALITY good or verygood to set the grid and density fitting accuracy.

Disclaimer: These general recommendations are based on the work of [Jochen Autschbach's group](#) (<https://ja01.chem.buffalo.edu/>). You should always carefully try out a few different options to test the sensitivity of the DFT methods on the NMR predictions for your own system. Some suggested references:

- <https://dx.doi.org/10.1002/chem.201502346>
- <https://dx.doi.org/10.1021/ja3040762>
- <https://dx.doi.org/10.1002/anie.201005431>

18.6 Do you have tips on how to find a Transition State with ADF?

Finding a Transition State (TS) can be difficult. Two things will help the TS search:

- Get a geometry close to the TS
 - Get a reasonable Hessian (energy curvature)
1. to get a reasonable starting geometry you could e.g. start with a [linear transit](#), [nudged elastic band](#) or from a previous TS geometry of a similar reaction.
 2. defining the reaction coordinate ([TSRC](#)) may be the easiest option to get a reasonable Hessian. You could also calculate the full Hessian (frequency calculation), a partial Hessian or a [Mobile Block Hessian](#), which should be better-conditioned.

For all initial Hessian calculations you could consider using a lower-accuracy method (e.g. lower integration accuracy, smaller basis sets, or even using DFTB). You should however always check the Hessian, e.g. by visualizing the frequencies, to check if it has one single negative eigenvalue and whether that eigenmode corresponds to your reaction. For the TS search itself you should switch to higher accuracy – especially think about the numerical integration and density fitting.

See also the [Tutorial Tips and Tricks for Transition State Searches for Click Reactions](#). See also some older Tips, tricks, examples and exercises for finding Transition States for an older version of ADF (before the AMSification, which changed the input a lot) ([pdf](https://www.scm.com/wp-content/uploads/TransitionStateSearch_ADF_tips_tricks_exercises_examples.pdf) (https://www.scm.com/wp-content/uploads/TransitionStateSearch_ADF_tips_tricks_exercises_examples.pdf), [input files](https://www.scm.com/wp-content/uploads/TransitionStateSearch_Inputs.zip) (https://www.scm.com/wp-content/uploads/TransitionStateSearch_Inputs.zip))

18.7 What's the difference between COSMO and COSMO-RS? Do I need COSMO-RS to include solvent effects?

You can do COSMO calculations with ADF. The COntinuum SOLvation MOdel treats the solvent as a polarizable continuum. You can also use other solvation models (SM12, 3D-RISM) or subsystem DFT (Frozen Density Embedding) to include environment effects.

COSMO-RS (<https://www.scm.com/product/cosmo-rs/>) (Realistic Solvents) is for calculating thermodynamic properties of (mixed) fluids. It uses post-ADF results (sigma profiles) for determining interactions between species in the liquid phase. You will typically not need COSMO-RS if you want to include solvent effects in your DFT calculation, but some properties such as solvation free energies may be more accurately treated with COSMO-RS than with COSMO.

18.8 What does a small, medium, or large frozen core mean?

To speed up a molecular or periodic DFT calculation, inner electrons of atoms can be frozen. Note that this is not a pseudopotential: all electrons are still present, the cores are just frozen at their optimized atomic configuration. The effect on the equilibrium geometry and properties of valence electrons is usually small. For spectroscopic properties of core electrons, or electrons close to the nucleus, typically an all electron (AE) approach is necessary.

In the atomic database (you can browse \$AMSHOME/atomicdata to see which basis sets are available) the AE basis sets are denoted as the element names, while the name is extended with the highest shell that is kept frozen for the frozen core basis sets.

small core: the smallest core available in the basis set database, for example:

- Rh.3d: all 28 electrons up to 3d are frozen: [Ar]3d10. The valence orbitals are: 4s, 4p, 5s, 4d, 5p.
- Au.4d: all 46 electrons up to 4d are frozen: [Kr]4d10. The valence orbitals are: 5s, 5p, 6s, 4f, 5d, 6p.

large core: the largest core available in the basis set database, for example:

- Rh.4p: all 36 electrons up to 4p are frozen: [Kr]. The valence orbitals are: 5s, 4d, 5p.
- Au.4f: all 60 electrons up to 4f are frozen, [Kr]4d104f14. The valence orbitals are: 5s, 5p, 5d, 6s, 6p.

Note that for some elements and basis sets there is just 1 core available (e.g. 1s for C), in which case all core options default to that specific frozen core.

When there are two options available (e.g. Rh.3d and Rh.4p), the **medium** core option typically defaults to the large core option. The use of **medium** core is therefore not recommended. We suggest choosing your specific basis set, either from the GUI in the basis set details panel, or by browsing the available basis sets and specifically defining the appropriate core.

18.9 How did the keywords in ADF change from 2017 to 2018?

In 2018 a few keywords changed their format and *input parsing was made more strict* (page 33). See the *input parsing in the ADF documentation* (page 27).

18.10 How to do an EDA or ETS-NOCV calculation with open-shell fragments?

Fragment files in ADF no longer need to be spin-restricted. So as of ADF2019, you can use unrestricted fragments.

18.11 Can ADF do restricted open shell Kohn-Sham (ROKS)?

In ADF2023 *ROKS for high-spin open shell molecules* (page 61) has been implemented. Starting from ADF2025 this can be used for the calculation of excited states for open shell molecules with well defined spin.

When you do a spin-restricted calculation in ADF with an odd number of electrons, you do not get the energy expression that is used in ROKS. In ROKS, the spin-unrestricted energy is optimized with alpha orbitals restricted to have the same spatial form as the beta orbitals. In ADF using a restricted calculations with an odd number of electrons will just result in fractional occupations of the frontier orbital. The energy of this electronic configuration is not the same as in a ROKS calculation.

Unrestricted calculations (UKS) in ADF should lead to proper integer occupations of the alpha and beta electrons, which are treated independently and can have spatially different forms.

18.12 Can I use GPU acceleration in ADF?

We do not offer a GPU-accelerated version of ADF at this time. See the [Installation manual](#) for more details.

18.13 Where can I find the total energy in the output?

ADF does not calculate total energies. It calculates difference energies with respect to fragment energies. By default, these are the spherical spin-restricted atoms. For this reason total energies from other programs cannot be compared to ADF directly. Only energy difference comparisons are meaningful. These are the only energies that play a role in chemistry of course.

If you do need the total energy, there is a workaround: calculate total energies of the atomic fragments and add them to the bonding energy.

Because the total energy of an atom is, by definition, the energy difference between the atom and the (nucleus+free electrons) system one can calculate it by calculating a single atom with the charge equal to the number of electrons. The 'bonding energy' of such an 'atom' will then be equal to negative of the total energy of the atomic fragment. Care should be taken to apply this trick to frozen-core fragments. In this case, it only makes sense to remove the valence electrons and leave the frozen core.

18.14 How do I calculate atomization energies with ADF?

You need to subtract the bonding energies of the individual atoms from the bonding energy of the molecule. Care must be taken to get the correct atomic reference state. Usually you will need to break the symmetry (otherwise spherical symmetry is used) and note that ADF cannot perform restricted open-shell Kohn-Sham (ROKS) calculations. An example input for the triplet oxygen atom:

```
System
  Atoms
    O 0.0 0.0 0.0
  End
End
Task SinglePoint
Engine adf
  Relativity
    Level None
  End
  SpinPolarization 2
  Unrestricted Yes
  Basis
    Type QZ4P
    Core None
  End
  IrrepOccupations
    A 5 // 3
  End
  numericalquality good
  symmetry nosym
  xc
    hybrid B3LYP
  End
EndEngine
```

18.15 I have problems with SCF convergence (“more iterations needed. not converged”). What to do?

There are a few options to aid SCF convergence:

- modern SCF algorithms: A-DIIS is usually a good option, and is default since ADF2016. Alternative options are LISTi (with good scaling) and ARH (slower per SCF cycle). E-DIIS is similar to A-DIIS but slower
- use the OCCUPATIONS key to specify occupation numbers
- use electron SMEARING for systems with low HOMO-LUMO gap
- use KEEPORBITALS to keep the same orbitals occupied after a certain number of steps

See the *SCF troubleshooting section* (page 412) of the ADF manual and send us (support@scm.com) relevant input and output if you keep having problems.

18.16 The geometry of my molecule is converged but when I do a frequency calculation, ADF finds one or more imaginary frequencies. Why?

There may be a few reasons why imaginary frequencies are found after geometry optimization:

- Visually inspect the negative normal mode in AMS Spectra by selecting it. Pause at some frame to get the distorted structure, and use Play -> Update geometry in input to use that as a new starting point for geometry optimization. If it's a frustrated rotation, you can also in the GUI manually distort it by changing the dihedral.
- The optimization threshold is not strict enough for the molecule's potential energy surface (PES). For example, if there are almost no-barrier rotational modes (e.g. methyl groups in some situations) or cyclopentane-like fragments, then the PES in such cases may be almost flat. In this case, much more strict convergence criteria (and higher integration accuracy) may be necessary to get to the energy minimum.
- Even with tight convergence criteria, one may get a small imaginary frequency due to numerical noise, which is always present in every calculation. In this case, it may be useful to scan the normal mode corresponding to the imaginary frequency and recheck if the frequency is indeed imaginary by finite differences. The latter is done using the SCANFREQ keyword, which is enabled by default in the AMSinput GUI module.
- If the scan shows an imaginary frequency, then it means that the preceding geometry optimization converged to a saddle point. This may happen when optimization was started close to the saddle point without a good Hessian estimate. In such a case, ADF did not make enough steps to get a good Hessian approximation and figure out that it has negative eigenvalue(s).

18.17 Are TDDFT calculations compatible with COSMO?

Yes, it is possible to combine COSMO and TDDFT. This will modify the zeroth-order KS orbitals and their energies, which is usually the most important solvation effect. COSMO could also modify the first-order change in the KS potential. This effect has been implemented and will certainly be important in case of a high value for the dielectric constant. The response of the COSMO surface charges due to the TDDFT-induced modified charges may be switched off (NOCSMRSP), which is probably a better representation of the solvent response for instantaneous (de)excitation.

In the response part of the calculations, one can also use a different dielectric constant. The reason for using two different dielectric constants is that the electronic transition can be so fast that only the electronic component of the solvent dielectric can respond, i.e., one should use the optical part of the dielectric constant. This is typically referred to as non-equilibrium solvation. If one optimizes an excited state, the solvent dielectric has time to fully respond and the same dielectric constant should be used.

18.18 Can I optimize excited states with TDDFT in ADF?

Yes. See the [tutorial](#) and [documentation](#) (page 210) on excited state geometry optimizations.

18.19 Can I determine Raman intensities for open-shell systems?

Yes, this can be done numerically by distorting the structure along the normal modes. First calculate the normal modes “q” with ADF. Then calculate the polarizability tensor by applying finite electric fields at the geometries $q_o + dq$ and $q_o - dq$. From this one can obtain, by double finite difference, the derivative of the polarizability w.r.t. a particular normal mode of interest. This should be less time-consuming than a regular Raman calculation as well.

18.20 How do I calculate the frequency-dependent second hyperpolarizability, GAMMA?

The beta tensor can be obtained by using the input key RESPONSE, for example:

```
RESPONSE
  HYPERPOL 0.03
  DYNHYP
  ALLCOMPONENTS
END
```

In order to obtain gamma, one should calculate beta in small electric fields. Such a field can be switched on by specifying, for example:

```
System
  ElectrostaticEmbedding
    ElectricField 0.0 0.0 0.001
  End
End
```

in the AMS part of the input for an electric field of in the z-direction. The beta calculation needs to be repeated for different field directions. γ_{zzzz} can be obtained from (for example): $\gamma_{zzzz} = \beta_{zzz}(E=0.001\text{ z}) - \beta_{zzz}(E=-0.001\text{ z}) / (2 * 0.001)$

Similar relations hold for other tensor components.

The group of Lasse Jensen has implemented damped quadratic and cubic response, which gives access to many non-linear optical properties including two-photon absorption. These methods are available in ADF2017 and later.

18.21 How can I do a spin restricted open-shell calculation for the calculation of the A-tensor?

For a spin restricted open-shell calculation, save adf.rkf (TAPE21), and use the whole molecule as a fragment in a SR unrestricted calculation with the keywords:

```
scf
  Iterations 0
end
```

ADF will use the fragment density coming from the spin-restricted calculation as start-up density in the unrestricted calculation. iter 0 means that only 1 scf-iteration will be performed with the use of the fragment density (one should use the same XC-potential in both calculations of course), such that the alpha-orbital energies remain degenerate with the beta-orbitals.

18.22 How do I read data from the binary KF files (adf.rkf, TAPE21, .runkf, .rkxf, .rkf or .t21 result files)?

After a calculation with ADF, BAND, ReaxFF, DFTB etc you will have a result file (a .t21, .runkf, .rkxf, or .rkf file). These are binary files, and like all other binary files used by the ADF package they are written using the KF library. The data are organized in sections, and each section can contain variables (either real, integer, string or logical). They may be transported between different platforms, conversion is performed automatically when needed.

KF files are Direct Access binary files. KF stands for Keyed File: KF files are keyword oriented, which makes them easy to process by simple procedures. Internally all the data on KF files is organized into sections containing variables, so each datum on the file can be identified by the combination of section and variable.

All KF files can be opened using the [KFbrowser](#) GUI program:

```
$AMSBIN/kfbrowser path/to/ams.rkf
```

By default KFbrowser shows a just a curated summary of the results on the file, but you can make it show the raw section and variable structure by switching it to expert mode. To do this, click on **File → Expert Mode** or press **ctrl/cmd + e**.

KF files can be opened and read with [Command line tools](#).

For working with the data from KF files, it is often useful to be able to read them from Python. Using the [AMS Python Stack](#), this can easily be done with the [AKFReader](#) class:

```
>>> from scm.akfreader import AKFReader
>>> kf = AKFReader("path/to/ams.rkf")
>>> "Molecule%Coords" in kf
True
>>> kf.description("Molecule%Coords")
{
  '_type': 'float_array',
  '_shape': [3, 'nAtoms'],
  '_comment': 'Coordinates of the nuclei (x,y,z)',
  '_unit': 'Bohr'
}
>>> kf.read("Molecule%Coords")
array([[ -11.7770694 ,  -4.19739597,   0.04934546],
       [ -9.37471321,  -2.63234227,  -0.13448698],
       ...,
       [ 10.09508738,  -1.06191208,   1.45286913],
       [ 10.11689333,  -1.5080196 ,  -1.87916127]])
```

Tip: For a full overview of the available methods in AKFReader, see the [AKFReader API](#) documentation.

KFReader (<https://downloads.scm.com/Downloads/KFReader-20140106.zip>): C routines to read binary KF files

18.23 I get the error: NO TRANSFORMATION FOUND in a fragment-based calculation. What to do?

A possible origin of this problem is that ADF can symmetrize the input coordinates of fragments which are nearly symmetric. As a consequence, the fragment coordinates can no longer be transformed to their position in the full calculation of the complex.

The workaround is to use SymmetryTolerance 1.0e-10 (in older ADF versions SYMMETRY TOL=1.0e-10) in the calculation of the fragments, such that the coordinates in the fragments are not symmetrized.

18.24 What does the error message “BAD ETA INTEGRALS” mean?

This message shows that the numerical integration is not as accurate as required (currently tested only with spin-orbit calculations). You can force the calculation to continue using the ALLOW BADINTEGRALS input key. This will force the calculation to continue, but remember there are possible inaccuracies due to these integrals. You can probably increase the accuracy of the eta integrals by increasing the overall integration accuracy (using the integration key). One will then probably still get the BAD ETA INTEGRALS message, but this is relative to the required accuracy. One can check the accuracy (it is printed on output), and if the accuracy is good enough one can use the ALLOW BADINTEGRALS key to force the calculation to continue.

18.25 ADF will not start when the user’s login name has non-ASCII characters in it. Sometimes a message “QUICKX terminates” is printed to the logfile.

One of the reasons can be that the SCM_TMPDIR environment variable also contains non-ASCII characters and ADF cannot use it. The solution is to set the SCM_TMPDIR value to a path that does not contain non-ASCII characters, for example, C:TMP:

- Right click on My Computer
- Select Properties item in the pop-up menu
- Click on the “Advanced” tab
- Click on the “Environment Variables” button
- In the upper half under “User variables for ...”, click the New button
- Enter SCM_TMPDIR in the variable name and C:/TMP in the variable value field. Please note that the path in the variable value must not contain spaces. It is also advised to use forward slashes as a path separator instead of the backslash
- Make sure the C:TMP directory exists and is writable by anyone
- Click on the Ok button in all windows to confirm your change
- If you use the GUI, restart it so the change takes effect

18.26 What does this error mean Int. Energy with ZlmFit+LargeFragment+VoronoiGrid not implemented.

Most probably you use the INTEGRATION key for a fragment analysis and thereby using an incompatible combination of ZlmFit and Voronoi grid for fragment calculations. You should either use Voronoi + STOfit or Becke + ZlmFit (which is the default since ADF2014).

Explanation of the terms in the error: "Int. Energy with ZlmFit+LargeFragment+VoronoiGrid not implemented"

1. ZlmFit means the way the Coulomb potential is fitted. ZlmFit is the default in ADF2014 and beyond. One can also use the STOfit, using the key STOFIT. If one would use STOFIT this error would not appear.
2. LargeFragment means a fragment larger than an atom.
3. VoronoiGrid is the integration method. The VoronoiGrid will be used if one is using the INTEGRATION key. In ADF2013 and beyond the Becke grid has become the default. If one would use the default integration method in ADF, which is the BeckeGrid, this error would not appear.

Recommended is to use the BeckeGrid and ZlmFit if one has larger fragments, possibly using quality good.

Non-alphabetical

3D-RISM, 155

A

adf2aim, 317
 adf2damqt, 323
 adfnbo, 309
 adf.rkf, 439, 1392
 AIM, 315
 ALDA kernel, 175
 alternative elements, 51
 ams.rkf, 439
 AMSview, 342
 analytic second derivatives, 169
 ARH, 371
 aromaticity, 317
 A-tensor, 250
 atomic coordinates, 37
 atoms in molecules, 315
 Augmented Roothaan-Hall, 371
 automatic mode, 49

B

B1LYP, 85
 B1PW91, 85
 B2GP-PLYP, 90
 B2K-PLYP, 90
 B2NC-PLYP, 90
 B2PI-PLYP, 90
 B2-PLYP, 90
 B2T-PLYP, 90
 B3LYP, 85
 B3LYP*, 85
 Bader analysis, 315
 BAS, 20
 basic atoms, 3
 basis functions, 20
 basis set file format, 419
 basis set superposition error, 391
 basis sets, 39
 BEE, 81
 BHandH, 85

BHandHLYP, 85
 block constraints, 165
 BLYP, 81
 bond energy analysis, 23, 292, 341
 bond order, 305, 338
 Boys-Foster localization, 297
 BP86, 81
 broken symmetry, 70
 BSE, 181
 BSSE, 391

C

C8 coefficient, 225
 C10 coefficient, 225
 CAM-B3LYP, 86
 CAMY-B3LYP, 86
 Cartesian functions, 20
 CD spectrum, 204
 CDFT, 73
 charge analysis, 336
 charge hopping, 269
 charge model 5, 338
 charge transfer descriptors, 210
 charge transfer integrals, 269
 charge transport properties, 269
 CHELPG, 338
 circular dichroism, 204
 circularly polarized luminescence, 204
 CM5, 338
 collinear, 61
 conceptual DFT descriptors, 315
 constrained DFT, 73
 constrained optimizations, 165
 constrained space orbital variation, 72
 constricted variational DFT, 197
 convergence problems, 411
 core excitations, 188
 core potential, 68
 COSMO, 111
 COSMO non-electrostatic term, 114
 COSMO TDDFT, 118
 CPL, 204

cpl module, 240
create mode, 50
CSOV analysis, 72
cube files, 342
CV(n)-DFT, 197
CVDFT, 197

D

Davidson algorithm, 180
dDsC dispersion correction, 102
debug, 327
delocalized coordinates, 165
densf module, 342
density fitting, 380
dependency, 390
DFT-D, 102
DFT-D3, 100
DFT-D4, 99
DFT-MBD, 103
DFT-ulg, 103
DH-BLYP, 90
DIIS, 368
DIM/QM, 122
dipole allowed, 180
dipole moment, 339
discrete solvent RF model, 123
dispersion coefficients, 225
dispersion corrected functionals, 99
DOD-SCAN, 90
DORI, 351
DOS, 357
dos module, 356
double group symmetry, 111, 436
double-hybrid, 90
doublet energy transfer, 276
doublet-quartet excitations, 184
DRF, 123
DS1-TPSS, 90
DSD-BLYP, 90
DSD-PBE, 90
DSD-PBEP86, 90
dual descriptor domains, 315
dual descriptors, 351
dummy atom, 38

E

EDIIS, 371
EET, 276
EFG, 253
electric field (*homogeneous*), 162
electric field gradient, 253
electron mobility, 269
electron paramagnetic resonance, 250
electron smearing, 64

electron spin resonance, 250
electronic configuration, 59, 404
electrostatic embedding, 122
energy decomposition analysis, 23, 292, 341
Energy-DIIS, 371
EPR, 250
ESP-CHELPG, 338
ESP-RESP, 338
ESR, 250
ETS-NOCV, 307
evGW, 255
examples, 470
exchange-correlation, 79
excitation energies, 179
excitation energies spin-orbit, 193
excited state optimizations, 210
exciton energy transfer, 276
exciton hopping, 276
excitonic coupling, 276

F

Faraday B term, 220
FCF module, 214
FDE, 144
FDE and QM/FQ (Fp), 153
FDE energy, 151
FILE47, 309
finite nucleus, 52
fit functions, 23
fluorescence, 214
FOCDFT, 78
FOD, 323
force constants, 167, 169
FQ/QM, 134
fractional orbital density, 323
fragment files, 55
fragment mode, 53
fragment orbitals, 21
fragments, 3
Franck-Condon factors, 214
frequencies, 169
frequency scan, 169
frozen core approximation, 20
frozen-density embedding, 144
Fukui descriptors, 315
full XC kernel, 182

G

G0W0, 255
G3W2, 255
gennbo, 309
geometry optimization, 165
GGA functionals, 81
GGA-D, 102

GGA-D3, 100
 GGA-D4, 99
 GGA-MBD, 103
 ghost atoms, 51
 GPDOS, 357
 GRAC, 96
 gradients, 167
 green module, 284
 g-tensor, 252
 g-tensor LFDFT, 230
 GW, 255
 GW-Bethe-Salpeter-Equation, 181
 GW-BSE, 181

H

Hartree-Fock, 85
 HDA, 200
 Hessian, 167, 169
 HF exchange percentage, 89
 Hirshfeld charges, 336
 hole mobility, 269
 homogeneous electric field, 162
 HTBS, 81
 hybrid, 85
 hybrid functionals post-SCF, 104
 hyperfine interaction, 250
 hyperpolarizability, 163, 216

I

ICM-OS, 222
 ICM-RS, 222
 imaginary frequencies, 416
 infrared frequencies, 169
 infrared intensities, 169
 initial Hessian, 165
 interacting quantum atoms, 294
 internal coordinates, 37
 intrinsic reaction coordinate, 166
 IQA, 294
 IR frequencies, 169
 IRC, 166
 Iring aromaticity index, 317
 irreducible representation, 21, 436
 isotope shift, 169

K

KMLYP, 85
 KSSPECTRUM, 191
 KT1, 81

L

LB94, 81
 LC functionals, 86
 LDA functionals, 80

LFDFT, 226
 LIBXC, 98
 LI-DI matrix, 315
 lifetime effects, 217
 ligand field DFT, 226
 linear dependency, 390
 linear scaling techniques, 395
 linear transit, 166
 LISTb, 368
 LISTf, 368
 LISTi, 368
 localized COSMO, 152
 localized orbitals, 296
 long range corrected functionals, 86
 long range dispersion interaction, 225
 LS1-DH, 90
 LS1-TPSS, 90
 LT (*linear transit*), 166

M

M06, 86
 M06-2X, 86
 M06-HF, 86
 M06-L, 83
 magnetic circular dichroism, 205
 magnetic TDCDFT, 178
 magnetizability, 217
 MAPA, 108
 Mayer bond order, 305
 MBH, 169
 MBPT, 384
 MCD, 205
 MCD LFDFT, 231
 MCI aromaticity index, 317
 MDC, 337
 mechanical embedding, 122
 memory usage, 394
 MESA, 369
 MetaGGA, 83
 meta-GGA (*SCF*), 83
 meta-GGA functionals, 104
 meta-hybrid, 86
 MM dispersion, 99
 Mobile Block Hessian, 169
 model potentials, 96
 molecular dynamics, 166
 molecular fragments, 53
 moments of inertia, 169
 Mossbauer isomer shifts, 254
 Mossbauer quadrupole splittings, 253
 MP2, 93
 mPBE, 81
 mPW, 81
 mPW1K, 85

mPW1PW, 85
 MPW2K-PLYP, 90
 MPW2NC-PLYP, 90
 MPW2-PLYP, 90
 Mulliken population, 336, 358
 multiplet states, 425
 multipole derived charges, 337

N

Nalewajski-Mrozek bond order, 338
 NBO-analysis, 309
 NCI, 350
 NEB, 166
 NEGF, 284
 NICS, 237
 NMR chemical shifts, 231
 nmr module, 231, 251
 NMR shielding tensor, 231
 NMR spin-spin couplings, 240
 NOCV, 307
 NOCV-Hirshfeld, 307
 non-collinear, 61
 non-self-consistent Green's function, 284
 NQCC, 253
 NRVS, 255
 NSSCC, 240
 NTO, 209
 nuclear gradients, 167
 nuclear model, 52
 nuclear resonance vibrational spectroscopy, 255
 nuclear spin-spin coupling constant, 240
 nuclear-independent chemical shift, 237
 nudged elastic band, 166

O

O3LYP, 85
 OLYP, 81
 OPBE0, 85
 OPDOS, 357
 open shell TDDFT, 184
 optical rotation (*dispersion*), 217
 orbital localization, 296
 ORD, 217
 orthonormal basis, 21

P

paramagnetic NMR, 238
 partial Hessian, 167, 169
 Partial ZORA, 111
 Pauli Hamiltonian, 109
 PBE, 81
 PBE0, 85

PBE0-2, 90
 PBE0-DH, 90
 PBE-QIDH, 90
 PBESol, 81
 PDOS, 357
 periodic table, 423
 PES point character, 167
 PES scan, 166
 PETPA, 124
 phosphorescence, 214
 Pipek-Mezey localization, 297
 plasmonic CD, 126
 point charges, 162
 polarizability, 163, 214, 217
 polarizability at resonance, 217
 POLTDDFT densities, 351
 population analysis, 339
 precision, 373
 precision SCF, 367
 pseudopotentials, 68
 PW91, 81

Q

QM/FQ, 134
 QM/MM, 122, 134
 QM/QM', 122
 qsGW, 255
 QTAIM, 315
 Q-tensor, 253
 quadrupole moment, 339
 quadrupole oscillator strength, 192
 Quild, 122

R

r2SCAN-3c, 85
 Raman (*resonance*), 172
 Raman for selected frequencies, 172
 Raman intensities, 172
 Raman scattering, 172
 range-separated functionals, 86
 RA-X2C, 110
 reaction path, 166
 reduced spin-spin coupling constant, 241
 reduction of output, 335
 relativistic core potentials, 435
 relativistic effects, 106
 remove fragment orbitals, 72
 resonance Raman, 172
 response properties, 173
 restart file, 397
 restrained optimizations, 165
 rev-DOD-BLYP, 90
 rev-DOD-BLYP-D4, 90
 rev-DOD-PBE, 90

rev-DOD-PBE-D4, 90
 rev-DOD-PBEP86, 90
 rev-DOD-PBEP86-D4, 90
 rev-DOD-SCAN-D4, 90
 rev-DSD-BLYP, 90
 rev-DSD-BLYP-D4, 90
 rev-DSD-PBE, 90
 rev-DSD-PBE-D4, 90
 rev-DSD-PBEP86, 90
 rev-DSD-PBEP86-D4, 90
 rev-DSD-SCAN-D4, 90
 revPBE, 81
 revTPSS, 83
 RISM, 155
 ROB2-PLYP, 90
 ROKS, 61
 ROKS TDA-DFT, 185
 ROSCF, 61
 ROSE, 299
 rotational g-tensor, 178
 RPA, 94
 RPBE, 81
 RS functionals, 86
 R-TDA, 187

S

S12g, 81
 same-spin excitations, 187
 SAOP, 96
 SAPA, 108
 SCF, 367
 SCF acceleration method, 369
 SCF accelerators, 368
 SCF problems, 411
 Schönflies symbol, 436
 SD-SCAN69, 90
 SEDD, 351
 SEHRS, 124
 SEROA, 126
 SERS, 124
 SET, 276
 SFD-TDA, 188
 SFO, 21
 SFO population analysis, 340
 SFU-TDA, 188
 shared arrays, 394
 sigma-functional, 94
 single orbital transition, 191
 single point, 165
 singlet energy transfer, 276
 singlet-singlet excitations, 179
 singlet-triplet excitations, 179
 SM12, 118
 smeared occupations, 64

SOCME, 193
 solvent effects, 111, 118, 122, 134, 144, 155
 SOS1-PBE-QIDH, 90
 spin, 59
 spin-flip broken symmetry, 69
 spin-flip down excitations, 188
 spin-flip excitations, 185
 spin-flip up excitations, 188
 spin-orbit coupling, 111
 spin-orbit excitation energies, 193
 spin-orbit polarizability, 217
 spin-polarized calculation, 59
 spin-spin coupling constant, 240
 spin-spin Diamagnetic orbital term, 242
 spin-spin Fermi-Contact term, 242
 spin-spin Paramagnetic orbital term, 242
 spin-spin Spin-Dipole term, 242
 SSB-D, 81
 standard basis sets, 42
 state selective excitations, 189
 S-TDA, 187
 sTDA, 202
 sTDDFT, 202
 STO, 20
 STO basis sets, 40
 subspecies, 436
 subsystem DFT, 144
 subsystem TDDFT, 153
 symmetry, 21, 39, 436
 symmetry label, 436

T

Tamm-Dancoff approximation, 181
 TAPE10, 441
 TAPE13, 441
 TAPE15, 442
 TAPE21, 439, 1392
 TAPE41, 352
 TCM, 222
 TDA, 181
 TDCDFT, 177
 TDDFT, 173
 TDDFT COSMO, 118
 TDDFT SO, 193
 TD-DFT+TB, 201
 TDDFT-aas, 202
 TD-DFTB, 201
 TDOS, 357
 TET, 276
 thermodynamics, 169
 time-dependent current DFT, 177
 time-dependent DFT, 173
 total energy, 294
 TPSS, 83

TPSSH, 86
transition state, 165
triplet energy transfer, 276
troubleshooting, 410
TS (*transition state*), 165
TSRC, 165

U

UFF dispersion correction, 103
unrestricted calculation, 59
unrestricted excitations, 184
unrestricted fragments, 70
UV/Vis, 179

V

van der Waals, 99, 225
VCD, 173
VCDtools module, 362
VDD charges, 336
Verdet constant, 220
vibrational circular dichroism, 173
vibrational polarizabilities, 169, 173
vibrational Raman optical activity, 173
vibrationally resolved electronic spectra, 214
visualization, 342
volume maps, 342
Voronoi deformation density, 336
VROA, 173
VWN, 80

W

Wesolowski-Warshel FDE, 144

X

X2C, 110
X3LYP, 85
XAS, 191, 192
XC, 79
XC kernel, 175
XCFUN, 97
XES, 193
XLYP, 81
XMCD LFDFT, 231
XPS, 336
X-ray photoelectron spectroscopy, 336
X-TDA, 187

Z

Zeeman interaction, 252
zero-field splitting, 193, 253
ZFS excited state, 193
ZFS ground state, 253
Z-matrix coordinates, 37
ZORA, 109