



Scientific Computing & Modelling

ADF Release Notes

**ADF Program System
Release 2013**

Scientific Computing & Modelling NV
Vrije Universiteit, Theoretical Chemistry
De Boelelaan 1083; 1081 HV Amsterdam; The Netherlands
WWW: www.scm.com
E-mail: support@scm.com

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Introduction

This document summarizes the changes between successive versions of the ADF package, including BAND, COSMO-RS, DFTB, ReaxFF, and graphical user interfaces.

The Chapters are in reverse time order: the most recent ones come first.

This document focuses on reporting error repairs and changes in functionality or performance. Technical changes in the code may not be mentioned if they:

- have only very small effects on numerical results and/or the program's performance,
- solve bugs that let the program crash in certain circumstances, but which do not affect the outcomes in calculations that terminate normally.

Explanations of new keywords, options, etc. are brief: for more details see the User manuals. The same holds for installation comments. Generally: read the documentation! This write-up is intended to draw your attention to important changes, not to explain every detail.

ADF 2013.01

Summary ADF2013.01 improvements

ADF

- Functionality
 - range-separated xc functionals
 - DIM/QM: discrete interaction model/quantum mechanics
 - full XC kernel in excitation energy calculations
 - excitations as orbital energy differences (DFT-TS)
 - approximate spin-orbit coupled excitation energies open shell molecule
 - TDA in subsystem TDDFT with hybrid functionals
 - transport properties: green: wide-band-limit
 - charge transfer integrals with FDE
- Analysis
 - interface to the NBO 6.0 package of Prof. Weinhold
 - NCI: non-covalent interactions index
 - SEDD: single exponential decay detector
- Accuracy
 - Becke grid for numerical integration
 - density fitting with radial spline functions and Zlm's
- Speed
 - distance cut-offs in calculating Hartree-Fock exchange integrals
 - scalable SCF

BAND

- effective mass (electron/hole transport)
- GLLB-SC model potential with derivative discontinuity for band gap prediction
- Fermi surface
- optional Becke grid for numerical integration
- finite nucleus option
- density at nucleus
- various performance improvements

DFTB

- Car-Parrinello (experimental feature)
- Conjugate gradients geometry optimization
- Visualization of DFTB orbitals (only for "demo" parameters)
- Partial density of states, PDOS
- D3-BJ van der Waals dispersion correction added
- (Parallel) performance improvements
- 3OB parameters for DFTB3 method included

ReaxFF

- ReaxFF can now treat an unlimited number of atoms

- parallel scaling is greatly improved using spatial distribution
- automatic calculation scale-up by repeating unit cell in a, b, and/or c direction
- force-bias Monte-Carlo implemented for accelerated dynamics
- force field-dependent Reaxff-Ig dispersion correction

GUI

- General:
 - speed improvements when handling big systems
 - improved mouse handling for zooming and translation
 - bonds crossing cell boundaries for periodic systems
- Jobs:
 - logfile, warnings and errors in the ADFjobs window
 - display all jobs, or just the jobs in the selected directory
 - archive jobs (saves a lot of disk space)
 - cleanup jobs (remove files no longer needed)
 - synchronize jobs between machines
- Input:
 - support of most of the new features of all the computational engines
 - crystal database added with many crystals, zeolite frameworks and MOPAC solids
 - new rotate options, and control of center of mass or geometric center
- Results:
 - ADFview: improvements in the calculation of fields
 - ADFview: density and spin density shortcuts
 - ADFview: new properties (NCI, SEDD, properties at nuclei for BAND)
 - ADFspectra: view of normal modes inside the ADFspectra window
 - ADFdos: (P)DOS for DFTB calculations
 - KFBrowser; show condensed results, optionally make simple (pie/line/bar) graphs
 - KFBrowser; new export (via copy / paste) to tab separated result (easy to import in for example in Excel)

Scripting

- adfreport: export ReaxFF trajectories as PDB, xmol or gro format
- adfreport: improved support for .rxkf, .rkf and .runkf files
- adfprepare: improved support for non-ADF jobs (like ReaxFF, UFF, BAND, etc)

COSMO-RS

- simplified input for calculation of properties of multiple pure compounds
- use 1 template in ADF-GUI for COSMO-RS compound
- menu item in COSMO-RS GUI to download the COSMO-RS database ADFCRS-2010
- template in COSMO-RS GUI for Octanol-Water partition coefficient calculation

UFF

- The bonds drawn in the GUI are now accepted as input, making UFF a more robust pre-optimizer
- All UFF parameters and atom types can now be edited, making it possible to tune UFF or extent the set of atom types
- UFF manual

FlexMD

- PyMD renamed to FlexMD
- FlexMD manuals have been extended

ADF: range-separated xc functionals

Range-separated (RS) functionals make use of a modified form of the Coulomb operator that is split into pieces for exact exchange and DFT. As switching function in ADF the Yukawa potential is utilized. XCFUN, a library of approximate exchange-correlation functionals, is required

ADF: 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. DIM/QM relies on one of three descriptions of the system: Discrete Reaction Field (DRF), where the atoms interact via induced dipoles and static charge, 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

ADF: full XC kernel in excitation energy calculations

With XCFUN the full (non-ALDA) kernel can be evaluated in TDDFT excitation calculations. It can be used with GGAs (including hybrids and RS functionals) but not meta-GGAs or meta-hybrids.

ADF: excitations as orbital energy differences (DFT-TS)

Instead of the relative expensive TDDFT calculation of excitation energies, sometimes just calculating Kohn-Sham orbital energy differences may already be useful. Especially useful for core excitation energy calculations. With this method it is possible to use fractional occupation numbers in the SCF, like is used in the DFT transition state (DFT-TS) scheme

ADF: 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. The used method has some strong limitations.

ADF: TDA in subsystem TDDFT with hybrid functionals

Subsystem time-dependent density functional theory is based on the extension of the frozen-density embedding (FDE) theory to excited states. Within the TDA formulation, hybrid functionals can without modification be used for the intra-subsystem part.

ADF: transport properties: NEGF, green: 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.

ADF: charge transfer integrals with FDE

Implemented is the calculation of Hamiltonian (site energies and couplings) and overlap matrix elements with FDE-derived localized states.

ADF: interface to the NBO 6.0 package of Prof. Weinhold

An interface to NBO 6.0 version is included, which replaces the interface to NBO 5.0. The functionality remains basically the same as in previous versions.

ADF and ADF-GUI: NCI: non-covalent interactions index

The areas of non-covalent interactions (NCI) can be recognized by the a low value of the electron density coupled with a low value of RDG (reduced density gradient).

ADF and ADF-GUI: SEDD: single exponential decay detector

The single exponential decay detector (SEDD) extracts information about bonding and localization in atoms, molecules, or molecular assemblies. The only quantity needed is the electron density (calculated or experimental) and its derivatives up to the second order.

ADF: Becke grid for numerical integration

The default numerical integration method in ADF2013 is a refined version of the fuzzy cells integration scheme developed by Becke. As a result, the PES (during geometry optimization and transition state searches and numerical frequency calculations) is smoother, and the numerical noise level lower, and convergence faster. The new default grid also seems more robust in case of numerically challenging xc functionals.

ADF: density fitting with radial spline functions and Zlm's

In the Zlm fit method the total electron-density is splited 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). This makes it possible to fit more accurately, and to higher l values, than with ADF's default method, at the expense of additional CPU time.

ADF: distance cut-offs in calculating Hartree-Fock exchange integrals

Use is made of distance cut-offs for the calculation of the Hartree-Fock exchange integrals. This can reduce computation time and memory usage, especially for large molecules.

ADF: scalable SCF

The new (still experimental) ScalableSCF method typically scales much better in parallel than the default SCF procedure and it also writes less data to disk during SCF. It is not compatible with all options in ADF. This option should be very interesting to try for users with access to many processors (e.g. 128 or more per job).

BAND: effective mass

The curvature of the bands at the top of the valence band and the bottom of conduction band is calculated as a measure for the mobility.

BAND: GLLB-SC model potential

The GLLB-SC model potential models the derivative discontinuity. Usually the HOMO-LUMO gap is compared to the experimental band gap, however even with the exact functional the results would not match because the derivative discontinuity term is lacking. The GLLB-SC enables improved and fast band gap predictions.

BAND: Fermi surface

In case of a metal, BAND automatically generates a Fermi surface that can be viewed with the Band structure GUI module.

BAND: Becke grid

There is now an option to use the Becke grid in BAND, which is very similar to the implementation that is now set as default in ADF. In principle the advantage should be a smoother PES. At the current stage it is still somewhat experimental but this feature may already be very useful in case of problematic geometry optimization convergence.

BAND: finite nucleus

Supported models are Gaussian and disk. This may influence very sensitive core properties. For normal geometry optimizations this has no effect at all.

BAND: performance improvements

BAND has been applied to bigger systems and some emerging performance bottlenecks have been optimized. The changes are merely technical, the underlying algorithms being the same. In the process 10 percent of the code was removed. Many of the speed up possibilities are not activated by default, so users interested in running BAND calculations on large unit cells, are advised to study the section "Performance for large unit cells" in the BAND manual. This section gives many hints on the settings that will save a lot of CPU time depending on your hardware and calculation of interest.

DFTB: Car-Parrinello (experimental feature)

Experimental: Car-Parrinello DFTB for second order evaluation (CPBO) and molecular dynamics (CPMD). Initial serial implementation of the Car-Parrinello method.

DFTB: Conjugate gradients geometry optimization

The CG optimization is switched on by adding *method conjgrads* to the Geometry input block. The CG method should only be used if the default quasi-Newton method does not work if a system is too large, because the CG converges much slower than quasi-Newton.

DFTB: Visualization of DFTB orbitals (only for "demo" parameters)

Visualization of DFTB orbitals: NAOs used in DFTB. This feature can currently be used only with the *Demo* Slater-Koster parameter set because the latter contains a radial table for each basis function.

DFTB: Partial density of states, PDOS

The partial DOS is now calculated and visualized similar to the BAND implementation.

DFTB: D3-BJ van der Waals dispersion correction added

Grimme's dispersion correction has been added for the energies and forces of the SCC-DFTB and DFTB3 method. So far this is restricted to the molecular (nonperiodic) case.

DFTB: (Parallel) performance improvements

Parallel performance. The new version uses distributed (sparse) storage for overlap, Hamiltonian and density matrices, which makes very large parallel calculation possible.

DFTB: 3OB parameters for DFTB3 method included

The latest 3OB parameters for H, C, N, O by Elstner and coworkers for DFTB3, and other parameter sets from DFTB.org are included in the distribution and will be activated for non-profit users at no additional charge. The DFTB3 model gives a fast and accurate description for light elements.

ReaxFF: performance improvements

The ReaxFF parallelization scheme has been completely rewritten. In this version, a spacial distribution of atoms over processes has been implemented. At the same time, the global limit on the number of atoms has been removed. The per-process limit of 100,000 atoms is still in place however.

The parallel sparse conjugate gradient algorithm for solving a system of linear equations in EEM has been improved to reduce the amount of communication. In the new implementation, communication with the nearest neighbor processes only should be sufficient.

ReaxFF: improvements for restarting non-reactive calculations

The restart feature for non-reactive calculations has been improved. Now it uses the connection information found in the restart file, thus seamlessly continuing the preceding simulation.

ReaxFF new feature: automatic scaling of simulation size

Automatic scaling up: the size of your simulation can be increased by repeating the unit cell in all/any dimension(s). This can be achieved by specifying a repx, repy, and/or reptz parameter in the control file. Specifying an integer number greater than 1 will increase the simulation box in the corresponding dimension by the given factor and populate it with copies of the atoms from the original unit cell. Afterwards, the replicated atoms move independently of their origin.

ReaxFF new feature: support for London Dispersion forcefields

ReaxFF-Ig: Forcefields with London Dispersion can now be used in ReaxFF. This feature is forcefield-dependent and can thus only be used with forcefields that have been optimized with dispersion correction. For more information, see:

Liu, L., Liu, Y., Zybin, S. V., Sun, H., Goddard III, W. A., *ReaxFF-Ig: Correction of the ReaxFF Reactive Force Field for London Dispersion, with Applications to the Equations of State for Energetic Materials*, [The Journal of Physical Chemistry](#) **115** (40), 11016-11022 (2011)

The forcefield from this paper is also included in the ADF2013.01 distribution.

ReaxFF new feature: force-bias Monte Carlo

fbMC: It is now possible to combine ReaxFF MD simulations with force-bias Monte Carlo. The fbMC method can greatly accelerate MD simulations with minimal user input. For more information, see the paper by Mees et al. and references therein:

M. J. Mees, G. Pourtois, E. C. Neyts, B. J. Thijsse, A. Stesmans, *Uniform-acceptance force-bias Monte Carlo method with time scale to study solid-state diffusion*, [Physical Review B](#) **85**, 134301 (2012)

Another interesting read is Neyts and Bogaerts overview of the various techniques for combining MD and MC simulations:

E. C. Neyts and A. Bogaerts, *Combining molecular dynamics with Monte Carlo simulations: implementations and applications*, [Theoretical Chemistry Accounts](#) **132**:1320, (2012)

COSMO-RS

- simplified input for calculation of properties of multiple pure compounds
- use 1 template in ADF-GUI for COSMO-RS compound
- menu item in COSMO-RS GUI to download the COSMO-RS database ADFCRS-2010
- template in COSMO-RS GUI for Octanol-Water partition coefficient calculation

With the ADF-GUI the making of an ADF COSMO compound that can be used in subsequent COSMO-RS calculations has been simplified. With the COSMO-RS GUI it has been made easier to install and use the COSMO-RS database ADFCRS-2010. In the COSMO-RS GUI templates have been made for Octanol-Water, Benzene-water, Hexane-Water, and Ether-Water partition coefficient calculations. The solubility of a solute in more than 1 compound can be done in 1 calculation.

UFF

- The bonds drawn in the GUI are now taken as input, making UFF a more robust pre-optimizer
- All UFF parameters and atom types can now be edited, making it possible to tune UFF or extent the set of atom types
- UFF manual

GUI: General

Support for most of the new features in the computational engines

Speed

Many speed improvements have been realized when handling big systems. This is especially important for ReaxFF and other periodic systems with many atoms.

Translation and zooming in the GUI

Many users experienced difficulties when trying to translate atoms while building their system. Now the middle and right mouse button have been swapped by default. Use the right button to translate, and the mouse wheel to zoom. If you prefer the old interaction style, you can switch back via the GUI Preferences.

Periodic bonds

Bonds crossing cell boundaries for periodic systems are now displayed properly. This gives a much better view of periodic systems. Currently the only way to make such bonds is via the GuessBonds option.

External file formats

Import of MOPAC .arc files and .cif files have been added or improved, and export of trajectories to .gro, .xml or PDB trajectories has been added.

Transparent background

When saving pictures of your system, orbitals, etc, you can now opt to use a transparent background. This feature may not work on Windows.

New ADF-GUI application for Mac OS X

For Mac OS X a new application has been made to replace ADFLaunch. It works much easier, and also handles installation of your license file. The new application has also properly been signed to work without problems on Mountain Lion systems.

GUI: Jobs

Logfile, warnings and errors in the ADFjobs window

The logfile for a running job will now be shown inside the ADFjobs window. This avoids a lot of logfile windows popping up, and is more effective. Warnings and errors are also shown inside the ADFjobs window so they are much easier to spot (and harder to ignore).

All jobs, or just the jobs in the selected directory

You can toggle (with the toggle button in the right bottom corner) between the traditional folder-based view, or a global list of all your jobs.

Export and import of jobs

A command has been added to pack and unpack your jobs in a gzipped tar archive for easy distribution to others.

Archive jobs

You can now archive jobs: store part of the job files in a compressed archive. Not all files are archived, so that ADFjobs is still able to recognize the job and show its status information. If you do anything with the job,

like view results, it will be un-archived automatically. So just archive most of your jobs to save a lot of disk space!

Cleanup jobs (remove files no longer needed)

Easily remove files that are typically no longer needed

Synchronization of jobs between machines

If you work with multiple machines (desktop and laptop for example) you can synchronize jobs between them so you can pick up your work on either of those machines. You will need ssh access to both machines, so it will not work for windows.

GUI: Input

Support most of the new features

The computational engines have many new features. Most of them are supported in the Input module ADFinput. For example, the Becke grid, excitations as orbital energy differences, and so on.

Molecule database extensions

The included database with molecular structures (via the search menu in ADFinput) has been extended. Now it also contain many basic crystals, all zeolite frameworks and a list of 'MOPAC solids'. When you import a crystal the input builder will automatically switch to periodc mode.

New builder features

The builder has new rotate options. This means that 1D (e.g. carbon nanotubes) and 2D periodic systems imported from 3D cifs with artificial replication in the other dimensions, can be easily aligned along the correct axes before reducing dimensionality. Also control of center of mass or geometric center has been added.

GUI: Results

Visualize new results

Using ADFview you can now visualize properties at nuclei, calculated by BAND. Also the visualization (and calculation) of NCI and SEDD have been added. NOCV support has been extended

Field calculation improvements

When a field is calculated via ADFview, the progress dialog shows the progress for ADF, BAND and DFTB. You can also use that dialog to get more feedback about the field calculation (the densf input script and

output). When a calculation takes a lot of time, it is possible to send it to ADFjobs to run via some queue. Thus you can calculate the fields also on some remote compute cluster, if ADFjobs has been set up properly to handle that cluster. Finally, when the calculation of a field takes a significant amount of time ADFview will suggest to save the calculated field. If you do that, the next time you start ADFview those fields will already be available.

Density and spin density shortcuts

The visualization of the spin density takes several steps in ADFview. As a convenience, a shortcut has been added to do this with just one menu command.

Normal mode visualization

Now ADFspectra has an improved fast view of normal modes, inside the ADFspectra window. Use the cursor keys to move through the different normal modes, and to increase or decrease the amplitude.

DOS (and partial DOS) for DFTB

The ADFDos module can now also show the DOS and partial DOS for DFTB results.

Results browser

The KFBrowser has been extended. It could already be used to view any data item on the binary result files (KF files). However, most of these data items are rather technical and not that useful for normal users. Now the KFBrowser has two modes: expert and non-expert. The new non-expert mode is the default. It shows again data from the KF files, but only those data items that will be useful to normal users. In the display the names and output has been adjusted so that it should be convenient. Users can select any piece of information and show it in a graph (bar, line or pie). The results shown can be also copied in a tab-separated format, and pasted into for example Excel for further processing.

Scripting

The adfreport command has been extended to have much better support for .rxkf, .rkf and .runkf files, in addition to the .t21 result files. If you run it with the -h flag and specify a result file, the help information will be extended with a list of information that actually is present on the result file. And export of ReaxFF trajectories to PDB, xmol or gro format has been added.

The adfprepare tool has improved support for non-ADF jobs (like ReaxFF, UFF, BAND, etc)

ADF 2012.01

Summary ADF2012.01 improvements

ADF

- Functionality
 - transport properties: non-self-consistent Green's function calculation
 - zero-field splitting (ZFS) ground state due to spin-orbit coupling
 - ESR g-tensor and A-tensor: perturbative spin-orbit coupling
 - paramagnetic NMR chemical shifts
 - state selective optimization excitation energies
 - VSCRF (vertical excitation self-consistent reaction field)
 - SCRF and a protein environment
 - XC functionals: revTPSS, HTBS, Grimme-D3-BJ, dDsC
- Analysis
 - metaGGA and metahybrid energy decomposition analysis
 - improved energy analysis hybrids
 - AIM critical points and bond paths
 - NBO analysis unrestricted
- Accuracy
 - SCF convergence method LISTi
 - improved optimizer for minima and Transition States

BAND

- Optimizations: lattice vectors, spin-orbit coupling
- Calculation of phonon dispersion curves and related thermodynamic properties
- Critical points for the QT-AIM topological analysis
- Interpolation of the band structure for smooth plots
- Fully analytical NMR shielding tensor
- Static homogeneous electric field
- XC functionals: Grimme-D3-BJ, GGA+U, HTBS, revTPSS, and TB-mBJ
- Speed-ups

DFTB

- Major update
- Method
 - Self-consistent charge (SCC) and third-order (DFTB3) self-consistent charge
 - Dispersion correction
- Functionality
 - Evaluation of periodic and non-periodic systems
 - Optimization of lattice parameters
 - Molecular dynamics with Velocity Verlet; Berendsen and Scaling thermostats
 - Phonons evaluation
 - Speed-ups and reduced memory consumption
 - Code parallelization
- Analysis
 - Density of States, band structure

ReaxFF

- Non-reactive iterations
- Threshold for counting hydrogen bonds

GUI

- All input modules are merged into one single, integrated GUI
- DFTB, UFF, and MOPAC pre-optimization
- User interface redesign
- Search options: panels, documentation, and database of molecules
- Phonon spectra, vectorfields, tensor visualization
- KF browser added

- speed-up and other improvements

COSMO-RS

- COSMO-SAC implementation
- Ternary mixture, Composition Line, Flash points
- MOPAC PM6 COSMO files

FlexMD

- New module FlexMD, python interface
- MD simulations in the canonical and the micro-canonical ensemble
- Multi-scale MD simulations
- Biased MD simulations

Documentation

- Merging manuals
- Merging tutorials

ADF: transport properties: non-self-consistent Green's function calculation

The density of states (DOS) and transmission of molecules connected to semi-infinite contacts can be calculated. The calculation is based on the non-self-consistent Green's function method. At the moment this is an expert option.

ADF: zero-field splitting (ZFS)

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 spin-spin coupling. In the present implementation only the spin-orbit coupling term is included.

ADF: ESR g-tensor and A-tensor: perturbative spin-orbit coupling

The ESR g-tensor and A-tensor can be calculated with a perturbative inclusion of spin-orbit coupling. It was already possible to calculate the ESR g-tensor and A-tensor in which spin-orbit coupling is treated self-consistently.

ADF: 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. Because of the dependence on the g-tensor, prediction of paramagnetic NMR (pNMR) shifts is not straightforward. A paper describes in detail how to calculate pNMR contact chemical shifts and pNMR pseudo-contact chemical shifts, using the ADF program, but this procedure is not documented in the ADF manual.

ADF: state selective optimization excitation energies

In this scheme a guess vector for the orbital transition has to be provided. An overlap criterion is used to follow the wanted eigenvector.

ADF: VSCRF (vertical excitation self-consistent reaction field)

VSCRF is a method of accounting for the effect of the solvent environment (and possibly a macromolecular environment) on the energy of absorption/emission transitions between electronic states.

ADF: SCRF and a protein environment

The ability to include a classical representation of a macromolecular environment, such as a protein around an enzyme active site, has been added to SCRF (self-consistent reaction field).

ADF: hybrid, metaGGA and metahybrid energy decomposition analysis

For hybrids, metaGGA's, and metahybrids the calculation of the Pauli repulsion is implemented, also if one is simulating an unrestricted fragment. In addition for hybrids the contributions of exact exchange to the orbital interactions are divided amongst orbital symmetries.

ADF: SCF convergence method LISTi

The LISTi method has been implemented. A nice feature of LISTi is that the algorithm used in it scales better in parallel.

ADF: improved geometry and Transition State optimizer

The geometry optimizer for minima and saddle points (Transition States) has been improved. It is more stable and converges more quickly.

ADF and BAND: AIM critical points and bond paths

The calculation of critical points of the density and bond paths (which can be visualized with the GUI) has been added.

ADF and BAND: XC functionals

Grimme-D3-BJ (ADF and BAND) and dDsC (only ADF) are MM dispersion corrections.

ADF and BAND: HTBS is a GGA, revTPSS is a metaGGA.

BAND only: LDA+U and GGA+U are intended to solve the band-gap problem of traditional DFT, by using, in its simplest form, an extra parameter U.

BAND only: TB-mBJ is a model potential, which also tries to solve this band-gap problem.

BAND: Optimizations: lattice vectors, spin-orbit coupling

Band currently has a numerical implementation of the forces that act on the lattice vectors. The effect of spin-orbit coupling can be taken into account in the calculation of forces.

BAND: Calculation of phonon dispersion curves and related thermodynamic properties

Atoms vibrate about their equilibrium positions, giving rise to lattice vibrations called phonons. Band can calculate phonon dispersion curves within standard harmonic theory, implemented with a finite difference method. Within the harmonic approximation we can calculate the partition function and from that thermodynamic properties such as the specific heat and the free energy. This implementation can also handle 1D and 2D periodic systems.

BAND: Interpolation of the band structure for smooth plots

Band has an option to interpolate the band curves for the path through the Brillouin zone.

BAND: Fully analytical NMR shielding tensor

The NMR has been improved to calculate analytically the derivative with respect to the nuclear magnetic moment and external magnetic field.

BAND: Static homogeneous electric field

For systems of 1D and 2D periodic symmetry it is possible to specify an external electric field.

BAND: Speed-ups

Fast overlap, fast dot product. Faster gradients for COSMO solvation model, faster generation of COSMO points, faster spin-orbit code.

DFTB: Self-consistent charge (SCC) and third-order (DFTB3) self-consistent charge

The new version of DFTB supports Self-Consistent Charge (SCC) evaluation, allowing to treat molecular systems where intermediate charge transfer has a determinant contribute. Third order evaluation is also available to accommodate for charge dependent Hubbard parameter, granting additional flexibility in the self consistent procedure, and a refined evaluation of the coulomb term between partial charges involving hydrogen, thanks to an improved gamma function specific for this element. Non Self-consistent evaluation is also available for improved evaluation speed when intermediate charge transfer effects can be neglected.

DFTB: Dispersion correction

To account for long-range interaction component of the total energy, empirical Universal Force Field dispersion correction with C6/C12 potential is integrated in the result of the SCC evaluations.

DFTB: Molecular dynamics with Velocity Verlet; Berendsen and Scaling thermostats

DFTB includes a molecular dynamics engine based on the Velocity Verlet algorithm. It also includes two thermostats: a Berendsen thermostat (operating either locally on the per-atom kinetic energy, or globally on the total kinetic energy of the system) and a scaling thermostat. The molecular dynamics engine allows checkpointing and trajectory sampling, as well as specification of initial velocities either random, zero, or user-defined.

DFTB: Evaluation of periodic and non-periodic systems

Both periodic and non-periodic systems can be treated in a nonSelf-consistent and Self Consistent Charge method. Third order is not supported for periodic systems. Single point, geometry optimization (via QuasiNewton method), molecular dynamics, and phonons evaluation are available with the periodic code. Geometry optimization can be performed on the lattice parameters. Band structure and density of states are provided, and easily accessible through the GUI Interface.

DFTB: Performance improvement

The code has been revised and improved for speed and memory occupation. Parallelization and use of pseudo-diagonalization techniques allow a relevant speed up. Available physical memory constraints the size of the systems that can be analyzed.

ReaxFF: Non-reactive iterations

First run a number of non-reactive iterations in a MD run. This can easily be set in the ReaxFF-GUI

ReaxFF: Threshold for counting hydrogen bonds

Introduce an energy threshold for hydrogen bonds counted in hbond in ReaxFF. The default abs value is 0.1 kcal/mol and can be changed via hbthr control parameter.

GUI: merge of ADFinput, BANDinput, and ReaxFFinput

All input modules, including new DFTB input are merged into one single, integrated GUI for seamless switching between programs and visualization.

GUI: DFTB, UFF, Mopac

Major improvement in selection of options, possibility to do 1D, 2D, and 3D periodic calculations.

GUI: User interface redesign

The left menu in ADFinput now selects the type of job (ADF, BAND, DFTB, MM, Mopac, Open Babel, QM/MM, Quild, ReaxFF, UFF) to be generated. Settings made in other main types will be ignored in your job.

GUI: Search options: panels, documentation, and molecules

Search in ADFinput finds keywords in ADFinput panels and in ADF User's documentation. Search in ADFinput also finds molecules from a database of 35000 molecules. This includes the 1892 molecules from the COSMO-RS database.

GUI: Phonon spectra, vectorfields, tensor visualization, AIM

Phonon spectra can be visualized.

VectorFields added in ADFview, calculated fields now can calculate the gradient of any scalar field. For example, you can make a calculated field to calculate Electric field (the gradient of the Potential). Next add a Vector Field to visualize the Electric field.

Via the Properties menu in ADFview, you can now visualize tensor result if they are available.

Visualization of AIM critical points and bond paths in ADFview.

GUI: KF browser added

A mostly undocumented feature is the KF browser. With the KF browser it is possible to browse a kf file, such as a .t21 or a .runkf file.

GUI: speed-up and other improvements

- improvement accuracy of GuessBonds
- possibility to save camera positions
- stereo effects
- edit geometry by sliders, smallest group changes
- save and manage structures commands added
- QM/MM: protein handling, improved Amber types
- ADFjobs: job monitoring
- speed-up

PyMD: New python interface for adaptive QM/MM and metadynamics

PyMD is a python package providing flexible multi-scale molecular dynamics (MD) simulations using the energy and force evaluation methods made available by the ADF suite. The package offers the following features:

- MD simulations in the canonical and the micro-canonical ensemble, using force evaluations from:

- ADF
- BAND
- DFTB
- MOPAC
- REAXFF
- UFF
- The external package NAMD
- Multi-scale MD simulations:
 - Within the IMOMM scheme
 - Using link-atoms
 - With more than two different resolutions
 - Adaptively changing the high/low resolution partitioning (adaptive QM/MM)
- Biased MD simulations:
 - Applying constraints
 - Using metadynamics
 - Through an interface with the PLUMED library for free energy calculations

COSMO-RS: COSMO-SAC implementation

The ADF COSMO-RS program can calculate activity coefficients using the COSMO-SAC model. If experimental values are not specified then the pure compound vapor pressure will be approximated using the COSMO-RS method, and not using the COSMO-SAC method. Thus only the activity coefficients are calculated according to the COSMO-SAC method. The COSMO-SAC parameters were not reoptimized for use with ADF COSMO result files.

COSMO-RS: Ternary mixture, Composition Line, Flash points

Ternary mixture (VLE/LLE)

The COSMO-RS module can automatically calculate properties of a ternary mixture, by calculating these properties for a number of different compositions.

Solvents s1 - s2 Composition Line

The COSMO-RS module can linear interpolate between the compositions of solvent 1 and solvent 2, which both could be mixtures, and calculate properties, like activity coefficients, and excess energies.

Flash points

The COSMO-RS module can calculate the flash point of a mixture. The COSMO-RS module, however, does not calculate or predict the flash point of pure compounds.

COSMO-RS: MOPAC PM6 COSMO files

With the ADF-GUI it is simple to do a MOPAC COSMO calculation. Some COSMO-RS parameters were reoptimized for MOPAC PM6 COSMO result files.

COSMO-RS: Technical

Mass fractions and molar fractions can be used. The Gibbs-Helmholtz equation is used to calculate the excess enthalpy of a mixture. The Clausius-Clapeyron equation is used to calculate the enthalpy of vaporization. With the ADF-GUI COSKF files (.coskf) are created automatically in an ADF COSMO calculation. In the COSMO-RS GUI buttons to run and kill a property calculation have been added. Accuracy settings can be adjusted.

Documentation

Separate Properties document (NMR, EPR, van der Waals dispersion coefficients, Franck-Condon factors), Analysis document (Preparing plot data, plotting, DOS, NBO, AIM), Utility document (Scripting with ADF, binary KF files, atomic Dirac program), Theory document (Multiplet energies), and Basis sets document now part of the ADF manual.

All separate GUI tutorials (for ADF, BAND, DFTB, MOPAC, ReaxFF, and COSMO-RS) combined in one GUI tutorials document. All separate GUI reference manuals (ADF, BAND, DFTB, ReaxFF, and COSMO-RS) combined in one GUI manual. ADF-GUI quick reference manual also merged in GUI manual.

ADF 2010.02

Summary ADF2010.02 improvements

Apart from some minor bug fixes, this release contains:

ReaxFF (including GUI)

ReaxFF is now available (including GUI). ReaxFF is a program for modeling chemical reactions with force fields.

MOPAC

MOPAC2009 is now bundled with ADF. MOPAC is a semiempirical molecular orbital package. Users do not need to worry about installing MOPAC.

BAND: bug fixes

This version is advised to all BAND users, for reasons of memory usage and a frozen core check.

ReaxFF (including GUI)

ReaxFF is a new program for modeling chemical reactions with force fields based upon the reactive force field method of van Duin and coworkers. See: [A.C.T. van Duin, S. Dasgupta, F. Lorant, F and W.A. Goddard III J. Phys. Chem. A 105, 9396 \(2001\)](#). SCM has significantly optimized the original code in our implementation of this method. Memory bottlenecks have been removed, and the code has been parallelized. Systems consisting of a 3D box of multiple molecules totaling tens of thousands of atoms can now be modeled.

It includes parameters for many elements not included in traditional force fields, such as a number of transition metals. ReaxFF has been used over the past decade in various studies of inhomogeneous reactive systems, including solvent environments, interfaces, and molecules on metal and metal oxide surfaces.

A summary of ReaxFF's features:

- molecular dynamics and minimizations using reactive force fields
- model reactants, intermediates and products for systems of up to tens of thousands of atoms in a 3D box
- [Packmol](#) builder for setup of complex systems of differing molecules
- define different temperature regimes, pressure constraints, bond constraints, et cetera
- analyze changing molecular composition during a reactive dynamics run

MOPAC: included in distribution

The standard MOPAC2009 binaries (from Stewart Computational Chemistry) are included in the distribution.

To use MOPAC, start ADFinput and go to the Mopac panel on the right hand side. The MOPAC license will be taken care of automatically, provided you have a MOPAC license via SCM.

For more information on MOPAC, see the [OpenMOPAC](#) web site.

BAND: bug fixes

This version is advised to all BAND users. One issue was that too much memory was used in the gradient part of the code, which could lead to crashes on some platforms. Also the frozen core check was disabled in the original 2010.01 release.

ADF 2010.01

Summary ADF2010.01 improvements

ADF

- Functionality
 - Excited state (geometry) optimizations
 - Vibrationally resolved electronic spectra
 - VROA: (Resonance) vibrational Raman optical activity
 - 3D-RISM: 3D Reference Interaction Site Model
 - Calculation of charge transfer integrals made easy (transport properties)
 - Transition State Reaction Coordinate (TSRC)
 - Grimme's DFT-D3 Functionals
 - ADIIS to solve problematic cases for SCF convergence
 - MCD C terms related to spatially degenerate states
 - Hybrids for CD spectra
 - Select range of excitation energies
 - Subsystem TDDFT: coupled FDE for excitation energies
 - Polarizability in combination with spin-orbit coupling
 - NBO analysis: EFG and NMR
- Accuracy
 - Gradients and frequencies ZORA improved
 - Numerical stability (meta-)hybrids and Hartree-Fock improved
 - Possibility to use a different fit set or add extra diffuse fit functions
 - COSMO cavity construction numerically made more stable
- Memory
 - Shared arrays on shared memory systems in case of parallel calculations

ADF-GUI

- Speed
- Bond Style
- Menu commands improved
- Copy-Paste between GUI modules
- Paste XYZ or SMILES in molecule editor
- Multiple curves in graphs
- Support for most (new) ADF features

BAND

- COSMO solvation model
- NMR shielding tensor
- Grimme D3 functional: empirical dispersion
- Divide and Fit method: better scaling with system size
- Direct option: on-the-fly evaluation of basis functions
- FitType

BAND-GUI

- Menu commands improved
- Copy-Paste between GUI modules
- Paste XYZ in molecule editor
- Support for most (new) BAND features

COSMO-RS

- The COSMO-RS database ADFCRS-2010 has been created, eliminating the need for time consuming DFT calculations for over 1800 common molecules
- A fast approximation introduced for COSMO-RS calculations has been implemented
- The COSMO cavity construction in ADF has been made more numerically stable
- The ADF-GUI now has easier to use recommended settings to produce more accurate COSMO result files
- The COSMO-RS GUI has been improved for easier usage with many compounds

ADF: Excited state (geometry) optimizations

The possibility to do excited state geometry optimizations is implemented. 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. Possible run types are:

- Geometry optimization
- Frequency analysis with numerical second derivatives: (analytical second derivatives (ANALYTICALFREQ) are not possible).
- Linear transit
- Transition state search
- IRC calculations may be possible but this possibility has not been tested yet.

ADF: Vibrationally resolved electronic spectra

To calculate vibrational effects on the electronic excitations (Uv/vis, X-ray), one needs to do a frequency calculation both at the ground state as well as the excited state of interest. Next Franck-Condon factors need to be calculated for the transition between the two electronic states, which can be done with the FCF program. These Franck-Condon factors can then be used to predict the relative intensities of absorption or emission lines in the electronic spectra. Note that the Herzberg-Teller effect is not taken into account.

ADF: (Resonance) vibrational Raman optical activity (VROA)

A method is implemented to calculate both on- and off-resonance vibrational Raman optical activities (VROAs) of molecules using time-dependent density functional theory.

ADF: 3D Reference Interaction Site Model (3D-RISM)

The three-dimensional reference interaction site model with the closure relation by Kovalenko and Hirata (3D-RISM-KH) provides the solvent structure in the form of a 3D site distribution function for each solvent site. It enables, at modest computational cost, the calculations 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 search, with the molecular solvation described from the first principles. The method yields all of the features available by using other solvation approaches.

ADF: Calculation of charge transfer integrals made easy (transport properties)

ADF does not calculate charge transport properties. However, it can provide input parameters, such as charge transfer integrals, that are needed in approximate methods that model these 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. The calculation of these charge transfer integrals has been made easy.

ADF: Transition State Reaction Coordinate (TSRC)

The possibility to specify a reaction coordinate for transition state search is added. This feature is especially useful when an accurate Hessian is not available. One can now specify a reaction coordinate along which the transition state is sought for. Such a reaction coordinate can consist of one or more distance, valence or dihedral angle, or just a combination of vectors on certain atoms.

ADF: Grimme's DFT-D3 Functionals

Stefan Grimme's latest dispersion correction is implemented. Grimme and his coworkers at the Universität Münster called this new parameterization DFT-D3.

ADF: ADIIS to solve problematic cases for SCF convergence

A-DIIS is implemented such that one can solve problematic cases for SCF convergence. ADIIS performs similar to the Energy-DIIS scheme but it does not require calculation of the total energy.

ADF: MCD C terms related to spatially degenerate states

C terms related to spatially degenerate states, i.e. breaking of degeneracies can be calculated.

ADF: hybrids for CD spectra

CD spectra can now also be calculated with Hartree-Fock or hybrids.

ADF: Select range of excitation energies

One can reduce the computational costs of, for example, core excitation energies, by using some selection criteria on the used occupied and virtual orbitals. This can also be used in case of spin-orbit coupling. 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, for example, only the core electrons are excited. Another possibility is to restrict 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.

ADF: Subsystem TDDFT: coupled FDE for excitation energies

The theory of coupled excited states for subsystems (subsystem TDDFT, coupled FDE) is implemented in ADF. This theory allows to treat the mutual response of several subsystems, including the ones that are considered environment.

ADF: Polarizability in combination with spin-orbit coupling

Spin-orbit ZORA polarizability is implemented.

ADF: NBO analysis: EFG and NMR

The calculated EFGs and NMR chemical shifts, and NMR spin-spin coupling constants can be analyzed in terms of Natural Bond Orbitals (NBOs) and Natural Localized Molecular Orbitals (NLMOs).

ADF: gradients and frequencies ZORA improved

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, order of magnitude: less than 0.001 Angstrom. In ADF2010 this difference is reduced to order 0.0001 Angstrom. In ADF2010 also the calculation of analytical frequencies has improved in case of QZ4P basis sets and heavy elements, like uranium.

ADF: Numerical stability (meta-)hybrids and Hartree-Fock improved

The calculation of Hartree-Fock matrix elements has been made more stable numerically.

ADF: possibility to use a different fit set or add extra diffuse fit functions

One might want a larger fit set than is present on the basis file, this is now possible. It is also possible to add extra diffuse fit functions.

ADF: COSMO cavity construction numerically made more stable

The COSMO cavity construction has been made more stable numerically, by merging close lying COSMO surface points, and by reducing the dependence of the results on coincidental close lying integration points with COSMO surface points

ADF: Shared arrays on shared memory systems in case of parallel calculations

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 is not the same as distributed arrays.

ADF-GUI: Speed

The speed of rendering big systems (many atoms and bonds) has been greatly improved. This also makes displaying of normal modes etc more efficient.

This is very important when you are working with proteins or many solvent molecules for example.

ADF-GUI: Bond Style

The drawing style for bonds has been changed, and looks much better now. And draws faster ...

ADF-GUI: Menu commands improved

Some parts of ADFinput are now much easier to find. In addition to the pop-up menus you now have equivalent menus on top of the window (Select, Atoms, Bonds).

The Atom Inspector panel now is accessible via the Atom Details menu command.

ADF-GUI: Copy-Paste between GUI modules

Now you can select your molecule (or part of it), copy it, and paste it in any GUI module. Thus not only in the window from which you copied it (that was already possible), but you can paste also in another window. For example, between different ADFinput windows, or from BANDinput to ADFinput, and so on.

ADF-GUI: Paste XYZ or SMILES in molecule editor

If you have the XYZ coordinates of your molecule somewhere (including the atom type as usual), you can just copy that and next paste it in the molecule editor. The corresponding atoms will be created automatically. This is very convenient to copy structures from other sources.

You can also copy a SMILES string and paste it. ADFinput will use OpenBabel to convert it to xyz, and paste the result. This works for many SMILES strings, though for complicated structures OpenBabel does not seem to produce the proper results.

ADF-GUI: Multiple curves in graphs

When displaying graphs of results in ADFmovie, you now can have multiple curves in a graph (for example, different angles shown in the same graph).

ADF-GUI: Support for most (new) ADF features

Most important new ADF features are supported, like TSRC, excited state geometry optimizations, Franck-Condon spectra. ...

BAND: COSMO solvation model

The conductor like screening model is now available in BAND. The same surfaces are available as in the ADF program (adapted for periodic symmetry).

BAND: NMR

The NMR shielding tensor can now be calculated with band.

BAND: Grimme's DFT-D3 Functionals

Stefan Grimme's latest dispersion correction is implemented. Grimme and his coworkers at the Universität Münster called this new parameterization DFT-D3.

BAND: fit method

Band used to do global fitting of the density. There is now an alternative call Divide and Fit, which scales better with system size. It also makes use of Shared Arrays, which further reduces the memory footprint.

BAND: direct option

Normally band stores basis and fit functions on file. There is now the alternative choice to calculate them on the fly. This reduces the disk IO, and increases the CPU time. The overall elapsed time may become less or more, depending on the type of calculation.

BAND: flexible fit specification

You can select from the data base a fit set independently from the basis set. For instance, you can use QZ4P fit functions with a DZ basis.

BAND-GUI: Menu commands improved

Some parts of BANDnput are now much easier to find. In addition to the pop-up menus you now have equivalent menus on top of the window (Select, Atoms, Bonds).

BAND-GUI: Copy-Paste between GUI modules

Now you can select your molecule (or part of it), copy it, and paste it in any GUI module. Thus not only in the window from which you copied it (that was already possible), but you can paste also in another window. For example, between different ADFinput windows, or from BANDinput to ADFinput, and so on.

BAND-GUI: Paste XYZ in molecule editor

If you have the XYZ coordinates of your molecule somewhere (including the atom type as usual), you can just copy that and next paste it in the molecule editor. The corresponding atoms will be created automatically. This is very convenient to copy structures from other sources.

BAND-GUI: Support for most (new) BAND features

Most important new BAND features are supported, like NMR.

COSMO-RS: COSMO-RS Database ADFCRS-2010

The COSMO-RS Database ADFCRS-2010 contains 1892 compounds, mostly solvents and small molecules. This database consists of ADF COSMO result (.coskf) files, which are results of ADF quantum mechanical calculations using COSMO, with settings suitable for use in our COSMO-RS module. The geometries have been optimized with ADF. We expect the database to make the COSMO-RS functionality much easier and faster (the time-consuming DFT step is already done ..) to use.

COSMO-RS: Fast approximation introduced for COSMO-RS calculations

In the 1998 COSMO-RS model each segment of the molecular surface has a charge density of σ_v , but also a second charge density σ_v^\perp , which is a descriptor for the correlation between the charge density on the segment with its surrounding. In the original ADF COSMO-RS implementation this was treated as a 2-dimensional problem, in the fast approximation this is effectively reduced to 1-dimension. Starting from COSMO-RS 2010 this fast approximation is now the default. This approximation reduces the computation time, especially in cases of more than 1 compound.

COSMO-RS: Accuracy ADF COSMO result files improved

The recommended settings for ADF COSMO calculations have become more accurate: TZP small core basis set (for all $Z \leq 36$), TZ2P small core basis set for Iodine (for all $Z \geq 37$), the relativistic scalar ZORA Hamiltonian, and an integration accuracy of 6. The use of the Becke Perdew exchange-correlation functional did not change. The COSMO cavity construction has been made more stable numerically.

COSMO-RS: GUI improved to handle many compounds

The COSMO-RS GUI has been improved for easier usage with many compounds. The visualization of the COSMO surface with ADFview has been simplified. Extra examples have been added.

ADF 2009.01

Summary ADF2009.01 improvements

ADF

- Exchange-correlation functionals
 - Gradients and numerical frequencies with hybrid xc potentials (geometry optimization, TS, IRC, LT, numerical frequencies)
 - Hybrids for excitation energies and NMR chemical shifts. PBE0 hybrid for NMR spin-spin couplings
 - meta-GGA's (M06-L, TPSS) and meta-hybrids (M06, TPSSh) during the SCF and optimizations
 - exact exchange optimized effective potential method (OEP)
 - Hybrid functionals with user-defined percentage of HF exchange
 - Dispersion-corrected functionals for heavier elements (Cs-Rn)
- Spectroscopic properties
 - Resonance Raman implementation using excited-states finite lifetime
 - Magnetic Circular Dichroism (MCD), A, B, and C terms
 - Verdet constant and Faraday B term
 - Mössbauer spectroscopy
 - Perturbative spin-orbit coupling in excitation energies
 - COSMO in Time-Dependent DFT
 - Nuclear Resonance Vibrational Spectroscopy (NRVS)
- SCF, potential energy surface, general
 - Self-Consistent Reaction Field (SCRF) method to describe environment effects via MEAD electrostatics program
 - Frozen density embedding (FDE) energy calculation
 - Finite size nuclear charge distribution for core properties
 - Energy analysis: Natural Orbitals for Chemical Valence (ETS-NOCV) for comprehensive energy and bonding analysis
 - Energy-DIIS and ARH to solve problematic cases for SCF convergence
 - Mobile Block Hessian (MBH) method for fast frequency calculations and transition-state searches
 - Improvements in multi-level QUILD program including GUI support for ONIOM-type jobs
 - Spin-flip method for converging broken-symmetry systems
 - Block constraints to freeze internal degrees of freedom of (less important) parts of a molecule but allow movement of the block with respect to the rest of the molecule.

ADF-GUI

Editing protein structures (from PDB files) in ADFinput; adding a box of solvent molecules around a solvated molecule.

Support for multi-level calculations by letting the user define different regions in the molecule. For each region the computational method (DFT, MM, DFTB, MOPAC) can be selected and the appropriate input for the (internal or external) program can be set up via the ADF-GUI. This also includes, as a simple case, using ADF-GUI to set up and run a MOPAC2009 calculation, provided it has been installed separately.

The partial (electronic or vibrational) Density-Of-States (DOS) can be visualized interactively to show contributions to the spectrum of user-selected atoms.

OpenBabel has been included in the distribution for guessing bonds and UFF pre-optimizations, and SYMMOL makes symmetrizing molecules much easier. Usability improvements include sequential execution of series of calculations on desktop machine ("queueing") and error reporting for failed jobs.

BAND

BAND now contains the same fast Bader Atoms-In-Molecules implementation as ADF. It can be used to obtain Bader atomic charges for periodic systems. Dispersion-corrected xc functionals were implemented for

an accurate description of weak interactions in organic solids, zeolites, and molecule-surface interactions. The revTPSS meta-GGA functional (recently proposed by Perdew et al. as new "workhorse" xc functional) is available for accurate energies. Several other (meta)-GGA's can be used for geometry optimizations and transition state searches. The Electric Field Gradient (EFG) can now be calculated for solids in addition to molecules.

BAND-GUI

A new powerful builder enables constructing complicated periodic geometries, by picking the appropriate space group and using predefined special symmetry positions. A solid can be cut in various ways to create a slab for true two-dimensional periodic calculations. Files in .cif format can be imported, or pick a structure from a small library of standard systems.

The Electron Localization Function (ELF) is calculated and visualized to aid in understanding chemical bonding. Scanning Tunneling Microscopy (STM) images can be calculated and visualized with or without bias. The visualization support for spin-unrestricted calculations has been improved, including the band structure.

DFTB

Several parameter files have been added in the ADF distribution to perform density functional tight binding calculations with the DFTB program.

ADF: gradients and numerical frequencies with hybrids

Forces and numerical frequencies are now available for self-consistent calculations with hybrid and meta-GGA xc functionals. This can be used to study potential energy surfaces (geometry optimization, TS, IRC, LT, numerical frequencies). Note that hybrid functionals are much slower than GGA's, so we do not recommend them for default usage.

ADF: excitation energies and NMR with hybrids

Excitation energies and NMR calculations can now also be done with an admixture of HF exchange. The choice of functionals for the NMR spin-spin coupling part is limited.

ADF: meta-GGA's and meta-hybrids during SCF and optimizations

Forces and numerical frequencies are now available for self-consistent calculations with some meta-GGA xc functionals (TPSS and M06-L), and meta-hybrids (TSSh, M06, M06-2X, M06-HF). This can be used to study potential energy surfaces (geometry optimization, TS, IRC, LT, numerical frequencies). Note that an accurate integration may be needed for the M06 functionals, thereby increasing the calculation time.

ADF: exact exchange optimized effective potential method (OEP)

OEP has been implemented. As the results often reduce to Hartree-Fock, the practical usefulness may be limited at present.

ADF: hybrids with user-defined percentage of HF exchange

This enables the user to study how the HF exchange percentage influence the results.

ADF: dispersion-corrected functionals for heavier elements

Prof. Grimme kindly provided (yet unpublished) parameters also for the elements in the row Cs-Rn.

ADF: other updates XC functionals

Starting from ADF2009.01 the default PBE functional uses LDA PW92, instead of LDA VWN, and uses for the GGA part routines provided by Burke.

New GGA-potentials: PBEsol, SSB-D. New post-SCF GGA energies: RGE2, revTPSS.

ADF: resonance Raman using excited-states finite lifetime

The previous resonance Raman implementation (still available) was restricted to cases with one dominant excitation. The new implementation should be more widely applicable and more user-friendly.

ADF: magnetic circular dichroism (MCD), A, B, and C terms

All terms for MCD are now available. Visualization in the GUI is available for part of them.

ADF: Verdet constant and Faraday B term

May require a post-processing step to obtain numbers that can be compared to experiment. Contact SCM for details.

ADF: Mössbauer spectroscopy

The electron density at the nuclei is calculated and could be used for the interpretation of isomer shifts in Mössbauer spectroscopy (usually requires fit to experimental values).

ADF: perturbative spin-orbit coupling in excitation energies

Spin-orbit excitation energies are already available in ADF. This method offers a far less time-consuming, although approximate, alternative method.

ADF: COSMO in Time-Dependent DFT

The COSMO model can now be used also in the excitation energy code to find solvent-induced shift in absorption spectra, etc.

ADF: nuclear resonance vibrational spectroscopy (NRVS)

A partial vibrational Density-Of-States (PVDOS) has been implemented. It is only useful via the ADF-GUI, where atoms can be selected by the user, to view only the part of the vibrational spectrum related to those atoms. This is useful for analysis of NRVS spectra in bioinorganic chemistry for NRVS-active nuclei.

ADF: self-consistent reaction field (SCRF)

SCRF (Self-Consistent Reaction Field) is a method of accounting for the effect of a polarizable solvent on the quantum system. The solvent is modeled as a dielectric continuum. This method by Bashford, Noodleman and coworkers requires the MEAD electrostatics C++ program by Bashford. For technical linking reasons, it is not included in the ADF distribution on all platforms. Contact SCM for details.

ADF: FDE energy calculation

The calculation of the FDE energy is implemented as the sum of the energy of the active, embedded system and the interaction energy 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.

ADF: finite size nuclear charge distribution

A spherical Gaussian nuclear charge distribution model has been implemented in ADF. Nuclear finite size effects can have large effects on hyperfine interactions (ESR A-tensor, NMR spin-spin coupling) if heavy atoms are involved.

ADF: natural orbitals for chemical valence (ETS-NOCV)

Building on ADF's energy decomposition, this scheme combines charge, bond order, and energetic analysis in a single framework. The energy of a chemical bond is often determined by a limited set of pairs of NOCV's. This option is graphically supported in ADFview, where the (weighted pairs of) NOCV's can be inspected.

ADF: energy-DIIS and ARH

An alternative, energy-guided, DIIS method, and the new Augmented Roothaan Hall (ARH) have been implemented to deal with certain types of poorly converging SCF cycles, including cases with small but finite energy gaps.

ADF: mobile block Hessian (MBH)

By subdividing a molecule into an "active site" and a set of internally frozen blocks that may move with respect to the active site, the MBH method achieves considerable computational savings in calculating frequencies for large molecules, at a modest loss in accuracy.

ADF: multi-level Quild improvements including GUI support

QUILD has become much more user-friendly because of GUI support for multi-level calculations in ADFinput. QUILD now supports symmetry, and can in principle deal with any external program.

ADF: spin-flip method for broken symmetry

For broken-symmetry calculations, one often converges the easy high-spin state first and then attempts to converge the more cumbersome states. The spin-flip method, possibly together with the MODIFYSTARTPOTENTIAL option now supported in the GUI, makes it much easier to converge all the relevant spin configurations.

ADF: block constraints

Related to the MBH method, ADF can now keep internal degrees of freedom for user-defined blocks frozen during geometry optimizations and numerical frequency calculations. These blocks are allowed to move with respect to the rest of the molecule. Currently the main application is in combination with MBH frequency calculations.

ADF-GUI: partial DOS and NRVS

The ADFdos utility and GUI support for it have been improved, so ADF can now also provide partial Density-Of-States plots. BAND could already do this. Similar functionality is now available in ADF for IR spectra, showing only contributions of selected atoms.

ADF-GUI: improvements solvents, proteins, symmetrization

It is now possible to edit structures imported from PDB files. One can also add a box of solvent molecules around a system. Finally, symmetrizing molecules has been simplified by use of the SYMMOL utility.

ADF-GUI: support multi-level calculations

The user defines regions in the molecule first, and then prepares an input for each region via different tabs. Each region can be dealt with via different methods and even different programs. The QUILD program is used.

ADF-GUI: run DFTB, MM, MOPAC, OpenBabel

ADF can also be used to set up and run DFTB, MM, or MOPAC2009 jobs. MOPAC needs to be installed separately. OpenBabel is included in the distribution to guess bounds, perform UFF pre-optimizations, and for some other tasks.

ADF-GUI: job queueing on desktop machine

Define a set of calculations, use the "Sequential queue" in ADFjobs to run all jobs one after the other, and return after the weekend to inspect the results. Previously only immediate execution was possible, with poor performance in case of multiple simultaneous jobs.

BAND: fast Bader AIM charges

The grid-based Bader Atoms-In-Molecules (AIM) method already available in ADF has now also been implemented in BAND to calculate AIM atomic charges.

BAND: revTPSS and dispersion-corrected functionals

The dispersion-corrected functionals should improve description of weak interactions in systems such as zeolites and organic solids, graphene, etc. The revised TPSS meta-GGA has recently been proposed by Perdew as a new workhorse functional. BAND currently has an energy-only implementation.

BAND: electric field gradient (EFG) for solids

EFG calculations could already be done in ADF. Now also available in BAND in a very similar implementation.

BAND-GUI: solid/surface builder with support for all space groups

The first hurdle in performing a periodic structure calculation is building the geometric structure. That has now become much easier in BAND, via an advanced builder that supports all space groups, and knows about symmetry positions. Certain standard structures are also available in a small library.

BAND-GUI: import of .cif files

If you have a geometry on file in .cif format, you can now import it in BANDinput.

BAND-GUI: ELF, STM images, other properties on any grid

The visualization options of 3D data fields have been extended significantly. The Electron Localization Function (ELF) and STM images (with or without bias) can now be visualized, also on a user-defined grid.

BAND-GUI: improved support unrestricted calculations

Certain limitations on visualizing results of spin-unrestricted calculations have been solved.

BAND-GUI: visualization of Brillouin Zone

In the bandstructure program there is now a 3D visualization of the path through the Brillouin zone.

DFTB: several parameter files included in distribution

A limited number of DFTB parameter files have been included in the ADF distribution itself. For these elements, one can now do DFTB calculations without the need for downloading parameter files externally.

ADF 2008.01

Summary ADF2008.01 improvements

ADF

Ultrafast grid based method for Bader's analysis; life time effects in (dynamic) polarizabilities; magnetizability; new implementation for ADF QM/MM calculations, which can handle large molecules; new optimization branch is now the default for geometry optimizations, TS, and LT; calculation of Franck-Condon factors between two vibrational modes; inclusion of MM dispersion-corrected functionals made easy; calculation of total energy (work in progress); module *adfpref* is added to facilitate scripting of proper adf jobs; module *adfreport* makes it easier to get results using scripts.

ADF-GUI

Preoptimization with DFTB or MOPAC. Visualization of NBOs in ADFview added. Easier to set up Raman calculations. Support for most new features.

BAND

Transition state searches; constraints in geometry optimizations; numerical frequencies; ESR g-tensor and A-tensor; Meta-GGA during SCF and analytical gradients; SZ basis set; Histogram-like DOS.

BAND-GUI

Support for new features in BAND (except for Meta-GGA's). A new module, BANDdos, allows the visualization of DOS.

COSMO-RS

A first implementation of COSMO-RS in ADF. The COSMO-RS (COnductor like Screening MOdel for Realistic Solvents) method allows the prediction of properties of pure liquids and liquid mixtures,

DFTB

A DFTB program has been added for density functional tight binding calculations,

ADF: Bader's analysis

A fast grid based method for Bader atomic property calculations is implemented. Such calculations can be used for relatively big systems (hundreds of atoms). The default calculation produces atomic electron density populations, charges, density Laplacian, dipole moments and quadrupole moments.

ADF: QM/MM

A new QM/MM implementation is available as an alternative to the existing one, which is faster, more robust, and less memory-demanding for big systems. At the moment this new implementation should be used in combination with the Amber force field only.

ADF: lifetime effect, magnetizability

A new implementation of TDDFT offers some unique features, namely lifetime effects and the calculation of (dynamic) magnetizabilities.

ADF: Franck-Condon Factors

The *fcf* module is an auxiliary program which can be used to calculate Franck-Condon factors from two vibrational mode calculations. Franck-Condon factors are the squares of the overlap integrals of vibrational wave functions. Given a transition between two electronic, spin or charge states, the Franck-Condon factors represent the probabilities for accompanying vibrational transitions. As such, they can be used to predict the relative intensities of absorption or emission lines in spectroscopy or excitation lines in transport measurements.

ADF: MM dispersion-corrected functionals

A new implementation of MM dispersion-corrected functionals is based on the paper by Grimme and is extremely easy to use. This feature is also supported by the ADF-GUI.

ADF: improved optimization now default

The new improved optimization method can be used (and is default) in geometry optimizations, transition state searches, and (new) in (linear) transit calculations.

ADF: Speed-ups

Faster calculation of bond energy during geometry optimizations. Linear scaling and other speed-ups in NMR calculations (NMR and CPL codes). Parallel diagonalization using Scalapack.

ADF: output, files

By default the SFO MO coefficients and SFO overlap matrix are no longer printed on standard output.

Changed the way scratch files are handled. The master will create its logfile and TAPE13 files in the CWD (current working directory) but place all other files in its scratch directory. For all tasks: if SCM_TMPDIR is not defined at all then the scratch sub-directories will be created in CWD.

Densf

The module *densf* can now read grid as list of points. It can calculate density gradient and Hessian of the SCF density (exact or fitted) and frozen core density. It is now also possible to calculate Laplacian on the total SCF density (exact or fitted).

Bugfix in SCF Coulomb potential display in ADFview (was a bug in densf).

ADFprep: scripting

The module *adfprep* is intended to facilitate scripting: it makes it very easy to construct proper adf jobs from within a script. This module can be used, for example, to run the same type of job on various molecules, or to change input settings such as basis set choice or numerical integration accuracy.

ADFreport: reporting results

The module *adfreport* is intended to facilitate scripting: it makes it very easy to get results calculated by *adf* in your own script. The results are taken from a .t21 result file. The results are available as an HTML file, a tab-separated file, or on standard output for use in other scripts. In this way, one can quickly compare calculate values across a set of calculations, as well as specified pictures, such as HOMO and LUMO orbitals.

ADF-GUI: GUIPrefs module added

The preferences for all GUI modules are now combined and handled by the GUIPrefs module. Selecting 'Preferences' from the menu (currently the SCM menu, that might change) will start this module.

ADF-GUI: adfjobs

In ADFjobs the Tools/Prepare menu can be used to generate sets of jobs with different options. This is a GUI to the *adfprep* program.

Fix in algorithm to get job ID when submitting with ADFjobs: now works with LoadL.

Resizing ADFjobs: job name will use additional space, which is useful if you have jobs with long names. ADFjobs search fields combined.

ADFjobs already had a short-cut: double click on a job and it will open either in ADFinput or in ADFtail. This is now even more convenient: you get the same effect by clicking once on the job button (on the left side).

ADFjobs may dynamically import queues from remote systems.

ADF-GUI: other improvements

Atom numbering in the ADF-GUI and BAND-GUI now starts at 1.

DFTB and MOPAC2007 are supported for preoptimization in the ADF-GUI. For these programs one needs to do additional installations from third parties.

A new Raman panel has been added to make it easier to set up raman calculations (both full and range scan). Also ADFspectra has been fixed to handle raman spectra when symmetry is used.

Visualization of NBOs in ADFview added. In ADFinput you can enable calculating them in the Orbitals panel. When they are present on a TAPE21 result file, you can also visualize the Boys localized orbitals and the NLMO's from the NBO analysis in ADFview.

ADF-GUI can use lines to show bonds. You can also change the bond coloring: the colors of the atom types will be used.

Capped-Bonds-Only visualization for molecule added.

Show scalar values by atomic radii in GUI. Color legend added when atoms are colored by scalars.

Cube file export in ADFview added.

ADFmovie: export to .amv file of current movie added.

ADFLevels Show Interaction modified.

In ADFinput, ADFmovie, ADFview and BANDinput, show multiple atom properties (name, charge, radius etc) at the same time. Also the updating of the displayed information has been fixed.

BAND

- Transition state search
- Numerical determination of Hessian
- Constraints in geometry optimization
- ESR A-tensor and g-tensor
- Meta GGA during SCF and analytical gradients
- A SZ basis
- Histogram-like DOS: no peaks can be missed, improvement in speed

It is now possible to calculate vibrational frequencies of atoms in unit cell by means of finite difference method.

The ESR A-tensor is implemented within the nonrelativistic and scalar relativistic spin-polarized Kohn-Sham scheme. The ESR g-tensor is implemented using a spin-restricted two-component approach.

The DOS is now calculated on the fly, preventing an old problem that sometimes more nodes were required to perform this task. Normally the DOS was evaluated at a grid of energy values with separation Δ using an exact delta function. Plots thus produced looked quite rough and narrow peaks can be missing entirely. It is more convenient to integrate the dos over each energy interval ΔE . This leads to a more comprehensible DOS. Very narrow peaks show up as a peak of 1 electron (or multiples of that, depending on degeneracy).

BAND-GUI: New BANDdos module

A new module, BANDdos, allows the visualization of the density of states (DOS), and has many options to show a partial DOS.

BAND-GUI: other improvements

The BAND-GUI now supports the following features: Transition state search; Numerical determination of Hessian (including visualization); Constraints in geometry optimization; ESR A-tensor and g-tensor; single-zeta (SZ) basis.

Zooming and Translation added in BANDstructure.

COSMO-RS

The COSMO-RS method was implemented in ADF. The COSMO-RS (CONductor like Screening MOdel for Realistic Solvents) method allows the prediction of properties of pure liquids and liquid mixtures, such as:

- activity coefficients
- solubilities
- partition coefficients
- excess energies
- boiling points
- vapor-liquid diagrams

The new module includes a Graphical User Interface for user-friendly job set up and output visualization. The use of COSMO-RS module in ADF is described in the ADF COSMO-RS Manual and the ADF COSMO-RS GUI tutorial.

DFTB

The Self-Consistent Charge Density-Functional Tight-Binding (SCC-DFTB) method is implemented in ADF in a separate module. DFTB is a semi-empirical method based on DFT. It is much faster, although more approximate, than a normal DFT calculation. The DFTB program requires parameter files to be installed for all pair-wise combinations of atoms in a molecule. Unfortunately, parameters are not available for some elements, but calculations for many common molecules should be possible.

ADF 2007.01

Summary ADF2007.01 improvements

ADF-GUI

A new module, ADFjobs, facilitates remote job submission and management for ADF and BAND jobs. Other ADF-GUI improvements: atomic data (geometrical) shown, export of movies, energy graphs, import/export of cube files, usability and design improvements.

BAND-GUI

BAND-GUI now contains a crystal and surface builder.

BAND

BAND can now perform geometry optimizations on periodic systems, has improved speed, and contains several extensions to its Time-Dependent DFT module.

ADF

ADF contains improved methods for geometry optimizations, transition state searches, and SCF convergence. Vibrational Circular Dichroism and geometry optimizations with spin-orbit coupling have been implemented. A parallel Windows version is introduced. The MO6 xc energy functional is available. A number of efficiency improvements, and important and less important bug fixes have been applied.

ADF-GUI: New ADFjobs module

ADF2007.01 is the first ADF release containing in the GUI a module called ADFjobs, which enables ADF users to easily manage their ADF and BAND (and other) jobs. You can use ADFjobs to keep an overview of your jobs, to quickly access old jobs, to run jobs locally and remotely, and to keep track of running jobs. Finally, it provides a convenient launcher of the other ADF-GUI or BAND-GUI modules.

ADF-GUI: Other Graphical User Interface (ADF-GUI) improvements

The most important improvements and changes for the ADF-GUI are:

- ADFjobs: remote job control
- Improved usability and design
 - Improved look of buttons and icons
 - ADFinput: runscript simplified, reorganization left panel
 - ADFinput: reorganization left panel (most important input options)
- Visualization of results:
 - ADFview: support for cube file
 - ADFview: display atom info, bond lengths, angles
 - ADFmovie: movies (MPEG)
 - ADFmovie: graphs
 - ADFmovie: live update
- Support for most new options

ADF: Improved Optimization in delocalized coordinates

Parameters and algorithms have been improved for geometry optimizations in delocalized coordinates. This means that fewer steps are needed, especially for weakly bound or floppy systems and strict convergence demands. The optimization in delocalized coordinates can also be used in Transition State searches.

ADF: Frequency scan, Raman

Raman intensities can now be calculated for a range of frequencies, leading to drastic reductions in computation time.

A frequency scan can now also be done after analytical frequencies, which can remove doubt on imaginary frequencies.

ADF: Transition State searches: partial Hessian and improved NEB

A partial Hessian can be calculated, which is fast to calculate for large molecules compared to the full Hessian. This means that the 'active atoms' can be treated exactly, the rest of the Hessian can be calculated with a semi-empirical estimate.

The Nudged-Elastic-Band (NEB) implementation has also been improved and should converge in fewer steps now.

ADF: Spin-orbit gradients

Gradient calculations for the spin-orbit formalism have been implemented. Therefore, you may now calculate harmonic frequencies (numerically) and do geometry optimizations and transition state searches including spin-orbit coupling.

ADF: Vibrational Circular Dichroism (VCD) spectra

ADF can now calculate and visualize VCD spectra.

ADF: Environment modelling - Frozen Density Embedding (FDE)

Huge restructuring of the code for frozen density embedding (FDE) calculations. Basic functionality remains the same.

ADF: Environment modelling - QUILD

The QUILD program has been developed for enabling calculations through multi-level approaches, in which different computational treatments are used for different regions of the system under study. This is achieved by making the definition of the regions flexible, i.e. there is no need to have a layered structure as in the

ONIOM approach. An arbitrary splitting of the total system into different regions is permitted with, therefore, possibly overlapping regions; this resembles a quilt, hence the name of the program. The different treatments currently possible are based on either quantum mechanics (QM) or force field molecular mechanics (MM).

ADF: New SCF convergence option

For problematic SCF convergence, a new experimental NEWDIIS option is now available. It has shown promise in some very recent test calculations.

ADF: MO6 xc functional

The Zhao - Truhlar MO5 and MO6 class xc energy functionals have been implemented in post-SCF manner.

BAND-GUI: Various Graphical User Interface (BAND-GUI) improvements

The most important improvements and changes for the BAND-GUI are:

- ADFjobs - also works for BAND jobs
- Crystal and Surface builder
- Support for geometry optimization

BAND: Geometry optimization for periodic structures

Geometry optimizations are now possible for one-, two-, and three-dimensional periodic structures, using a simple Cartesian optimization scheme. The start-up Hessian is unit matrix, no constraints are possible yet. The geometry can be optimized in the non-relativistic and scalar relativistic ZORA case.

BAND: Time-dependent DFT extensions

The TDDFT implementation has been extended such that it can be used to calculate the dielectric function for metals and that effects of spin-orbit coupling can be calculated. The Vignale-Kohn functional is supported.

BAND: Linear scaling and speed-ups

New defaults: Tails, nonorthogonalSCF, needed for large jobs

BAND: New TZP basis, improvements for lanthanide basis sets

Some fixes for lanthanide elements. New TZP basis sets for all elements.

ADF 2006.01

Introduction

ADF2006.01 is the first ADF release containing a graphical user interface for BAND: BAND-GUI. The ADF graphical user interface has been improved. Faster, more capable, and bugs fixed.

ADF2006.01 contains new functionality - including hybrid functionals during the SCF and analytic second derivatives, efficiency improvements, and a variety of important and less important bug fixes.

BAND Graphical User Interface (BAND-GUI)

ADF2006.01 is the first ADF release containing a graphical user interface for BAND.

BANDinput enables also inexperienced ADF-BAND users to easily create BAND jobs. You can use BANDinput to define your periodic structure (geometry), and to set details of your BAND job using an easy-to-use graphical user interface. BANDinput will generate the complete job script for you. This script takes care of running BAND. You can also use BANDinput to run these script files on your local machine in the background. BANDinput is very similar to ADFinput.

ADFview displays volume data, such as the electron deformation density and orbitals using the BAND .runkf file. (ADFview is also used in the ADF-GUI).

BANDstructure shows a plot of the electronic band structure.

ADFTail shows the progress of a BAND (and ADF) calculation.

BOB shows the output generated by BAND (and ADF).

ADF Graphical User Interface (ADF-GUI) improvements

The most important improvements and changes for the ADF-GUI are:

- fragment analysis supported
- easy building of complicated metal-ligand compounds: many standard structures and ligands built-in
- linear transit support in ADFinput and ADFmovie
- protein QM/MM calculations with PDB files (pdb2adf interface)
- .adf files are included in the \$ADFHOMe/examples/adf directory
- simplification selecting NMR nuclei for users
- visualization of spin-orbit coupled calculations in ADFlevels, ADFview, ADFspectra
- additional tutorials to explain the new features

Other important improvements and changes for the ADF-GUI are:

- add structure to all selected atoms
- popup menu on atom with many options
- properties only task
- improve the usability of the templates (now presets)
- color coding to warn you that you changed input fields
- .adf files are included in the \$ADFHOMe/examples/adf directory
- select picture resolution
- tip of the day

- layout improvement: more space for your molecule

Hartree-Fock and hybrids in the SCF

The implementation in ADF of the calculation of exact exchange (Hartree Fock exchange) during the SCF, which is also needed for the hybrid functionals, is based on work by Watson et al. J. Chem. Phys 119: 6475 (2003). Implemented are Hartree-Fock, B3LYP, B3LYP*, B1LYP, KMLYP, O3LYP, X3LYP, BHandH, BHandHLYP, B1PW91, MPW1PW, MPW1K, PBE0, and OPBE0. The use of the DEPENDENCY key is necessary at the moment, (and sometimes the ADDDIFFUSEFIT key). Not (yet) available for geometry optimizations, TS, IRC, LT, NMR, EPR g-tensor, TDDFT, frozen cores.

Analytic second derivatives inside ADF

The functionality of the analytic second derivatives program SD has been moved inside the ADF program. In ADF one needs to use the AnalyticalFreq block keyword. Besides the LDA potential, one can now also use the GGAs BP86, PBE, RPBE, revPBE, BLYP, OLYP, and OPBE. A bug has been fixed for unrestricted calculations. Because this method is much faster and also seems more robust than numerical frequency calculations, the analytic second derivatives are now the new default in the ADF-GUI.

Frozen-Density Embedding

In the orbital-free frozen-density embedding (FDE) formalism, the environment of an embedded subsystem is accounted for by means of the embedding potential depending explicitly on electron densities corresponding to the embedded subsystem (e.g., a solvated molecule) and its environment (e.g., solvent). This could be called DFT/DFT embedding.

Spin-Orbit coupled TDDFT

The relativistic TDDFT formalism, including spin-orbit coupling, is implemented for closed-shell molecules with full use of double-group symmetry. This two-component TDDFT formalism has the correct nonrelativistic limit and affords the correct threefold degeneracy of triplet excitations.

Resonance Raman

According to a the time-dependent picture of resonance-Raman (RR) scattering, the relative intensities of RR scattering cross sections are, under certain assumptions, proportional to the square of the excited-state energy gradients projected onto the ground-state normal modes of the molecule. Such excited-state gradients can be computed numerically by ADF's VIBRON module.

MM dispersion

Method to add an MM empirical correction to DFT to get accurate van der Waals dispersion forces and energies. The method requires expertise as it needs various empirical parameters, such as atomic polarizabilities, atomic C_6 -coefficients, atomic radii, and a damping function.

Further ADF improvements and changes

- Basis key recognizes ghost atoms
- Relativistic molecule does not require TAPE12 anymore, TAPE12 is only needed in create run
- Relativistic Ghost atoms do not require TAPE12 anymore
- Multi-step smearing option and Averill-Painter method for difficult SCF convergence
- Defaults maximum number of atoms 10000
- Nuclear electric quadrupole and magnetic moments updated
- Many new predefined solvents for COSMO calculations

Property improvements

Simplification selecting NMR nuclei for users, relevant for EPR, NMR, and CPL.

BAND BasisDefaults key

New BasisDefaults key, which obsoletes the explicit specification of basis and fit sets in the input for a BAND calculation (similar to the Basis key in ADF). Makes BAND input files much shorter and easier to understand and modify.

Further BAND improvements

- Plotting options for the deformation density and orbitals
- Slightly improved fragment analysis
- Band structure plots along the edges of the Brillouin zone
- Improvements for large BAND calculations, such as bug fixes for large unit cells

Maxmemoryusage removed

Use of dynamic allocation for all arrays in all programs instead of partially using a static array of which the size was controlled with MAXMEMORYUSAGE. MAXMEMORYUSAGE has no effect anymore. Instead use for example vectorlength to reduce the size of a calculation if needed.

Automatic conversion of the binary KF files

Added automatic conversion for files with different byte order and/or integer size. Also added kfwrappers for writing KF files. In practice one can now copy for example the binary TAPE21 from one platform to another, without needing conversion steps using \$ADFBIN/dmpkf and \$ADFBIN/udmpkf.

ADF 2005.01

Introduction

ADF2005.01 contains new functionality, efficiency improvements, and a variety of important and less important bug fixes.

The ADF graphical user interface has been improved. Faster, more capable, and many bugs fixed.

ADF Graphical User Interface (ADF-GUI) improvements

The ADFinput module shows better images (using OpenGL), and the molecule builder is more capable (symmetry, fragments, detailed control over angles, bond lengths, ..).

The ADFview module now is based on OpenGL, so that your graphics hardware is used to provide high quality pictures which you can rotate interactively. You can also visualize results from TAPE21 without running DENSF first. Cut planes, transparent surfaces, and simultaneous viewing of surface and molecule are now available. Pictures can be saved in standard graphics file formats.

ADFmovie also utilizes OpenGL to provide nice and fast movies.

ADFspectra now can also do Raman and CD spectra, has more options to control axes and peak shapes, and can save the spectra.

ADFlevels is a new module that you can use to visualize energy levels and molecular orbital interaction diagrams.

Discrete Reaction Field environment model

The Discrete Solvent Reaction Field (DRF) model is a hybrid Quantum mechanical and Molecular Mechanics (QM/MM) model using polarizable MM atoms, which is implemented in ADF.

Bond orders

The calculation of Nalewajski-Mrozek bond-orders has been implemented.

Excitation energies

Excitations for open shell molecules are now available, including spin-flip excitations. The calculation of core excitation energies is improved. The time-dependent current-density-functional (TDCDFT) theory is implemented.

Faster gradients

Improved performance in geometry optimizations and numerical frequency runs due to a new implementation of the calculation of the gradients that now use linear scaling techniques. Especially important for large molecules.

Delocalized coordinates

Delocalized coordinates can be used in geometry optimizations and transition state searches. For large or floppy systems this may reduce the number of required steps.

Nudged Elastic Band (NEB) method for transition state search

Calculation of the reaction path and transition state search using Climbing-Image Nudged Elastic Band method.

Frequency calculations

Symmetric displacements can be used in frequency calculations, with an option to compute only IR-visible frequencies.

New XC potentials

Including KT1, KT2, XLYP, mPBE, exchange-correlation potentials and energies. Including OPBE0, X3LYP, in exchange-correlation energy functionals.

Bug fix off-diagonal part NMR shielding tensor

The 2004.01 and older versions of the NMR module does not always calculate the off-diagonal part of the NMR shielding tensors correctly. This has been fixed in the ADF2005.01 version.

Basis sets

The TZ2P+ basis set is now available also for the lanthanides ($Z=57-70$), only in the ZORA directory. These basis sets are nearly identical to ZORA/TZ2P except for a better description of the f-space (4 f-functions instead of 3).

Augmented basis sets are available, for use in time-dependent density functional calculations. These are augmented SZ, DZ, DZP, TZP, TZ2P non-relativistic basis sets for H-Kr. They are named ASZ, ADZ, ADZP, ATZP, and ATZ2P, respectively. They are devised by Prof. Del Chong for use in TDDFT calculations, especially for the reasonable accurate calculation of excitation energies, with a relatively small basis set.

EPR: SOO contribution to the g-tensor

The spin-other-orbit contribution to the g-tensor can be computed with the EPR module.

LDA potential in analytic second derivatives program SD

Besides the $X\alpha$ -potential, SD now also works with the LDA-potential (VWN), for both closed-shell and open-shell systems. The efficiency of SD has been improved.

pdb2adf

The pdb2adf utility was written to read a PDB file, which contains the atomic coordinates of a protein structure, and transform it into an ADF inputfile, particularly for use with QM/MM calculations. Previously in Contributed Software. Several bugs have been fixed.

Physical constants updated

Updated physical constants to the latest CODATA recommended values, see also <http://physics.nist.gov>.

ADF 2004.01

May 2004

Introduction

ADF2004.01 contains both new functionality and a variety of important and less important bug fixes. Two important new modules are added to the ADF Graphical User Interface: ADFspectra and ADFmovie.

Platforms

New platform: HP Itanium2 with HP-UX.

Also new is a fast PC Linux version based on the Intel ifc compiler, which leads to very fast ADF2004 executables for Xeon and Opteron that can outperform ADF2003 by a factor of two or even more. The same is true for the improved Windows version, which no longer requires the Cygwin Unix emulator to be installed. The new Windows version is much easier to install and more intuitive to use.

2 GB limit for Pentium Linux solved.

ADFspectra

This module reads information from TAPE21 and displays different types of spectra that were calculated by ADF: Density-of-States (DOS), infrared, and optical spectra. One can select a peak with a mouse click. This will then result in additional information on that peak. In the case of an infrared spectrum, ADFmovie - the second new module, will start up automatically to show the nuclei moving back and forth according to the normal mode of vibration that corresponds to the selected peak.

ADFmovie

This module shows moving nuclei. This is useful for visualization of molecular vibrations in combination with the ADFspectra module above. It can also be used (by attaching a logfile from a running ADF calculation) to monitor the progress of an ongoing geometry optimization.

Chiral optical properties

Chiral optical properties were implemented by Dr. Autschbach in ADF's Time-Dependent DFT code: Circular Dichroism and Optical Rotatory Dispersion (CD and ORD). The implementation is fully parallel, can be applied to large molecules, and is very simple to use.

Meta-GGA and hybrid xc energy functionals

By efficiently using ADF's fit functions, an initial beta release for a post-SCF implementation of hybrid functionals, such as B3LYP, is available. The first test results show encouraging agreement with literature data and the feasibility of using this option on molecules up to at least 50 atoms. Further improvements and speed-ups are planned. New nonempirical meta-GGA functionals have also been added and often outperform even the most popular hybrid functionals.

New XC potentials

Including OLYP, OPBE, BLAP3, OLAP3 exchange-correlation functionals.

SIC potential

The Perdew-Zunger (PZ) self-interaction energy correction (SIC) with the Krieger-Li-Iafrate (KLI) approximation to the self-interaction corrected optimized effective potential (OEP) is implemented. In ADF the Foster-Boys localization procedure is used.

Improvements in grid generation

Better convergence in geometry optimizations. A few important bugs have been fixed related to the generation of the numerical integration grid for certain types of molecular geometries. As a result, certain geometry optimizations now converge smoothly in 10 iterations whereas no convergence was reached in ADF2003.

Geometry optimizations: new Hessian update and constraint options

New possibilities to conveniently apply nonstandard types of constraints (e.g. a linear combination of two constraints, or an initially unsatisfied constraint) will become available. New Hessian update methods have also been implemented. Both improvements have greatly improved geometry optimization convergence in certain, previously problematic, cases.

Smoothing of gradients

Improved convergence in geometry optimizations and accuracy in frequency runs can be obtained with the smoothing subkeyword in the geometry block key. The idea is to reuse as much information as possible from the numerical integration from a previous geometry cycle such that the remaining error due to numerical integration is only systematic, and not random.

Interface to NBO package

Dr. Autschbach, SCM, and Prof. Weinhold have collaborated to prepare a simple input file generator for the GENNBO program of Prof. Weinhold's Natural Bond Orbital (NBO) 5.0 package:

<http://www.chem.wisc.edu/~nbo5>

The GENNBO executable will be included in the ADF distribution and enabled via the license file for all those who buy an NBO manual from either the NBO authors or from SCM.

Expectation value S^2

In ADF2004.01, the expectation value of S^2 will be printed in unrestricted calculations. This allows one to check the amount of spin contamination in the final result.

Spin-Orbit Coupling

After a Spin-Orbit coupled calculation an SFO analysis is printed in case of one scalar relativistic fragment. Implementation of the collinear approximation and the noncollinear approximation for unrestricted Spin-Orbit coupled calculations (symmetry NOSYM).

ESR

In a Spin-Orbit spin unrestricted relativistic calculation (collinear approximation) the program will compute the g-tensor and the Nuclear Magnetic Dipole Hyperfine interaction (A-tensor). There may be more than one unpaired electron.

Faster analytic second derivatives

The SD program for analytic second derivatives calculations has been optimized significantly. For medium-sized and large molecules without symmetry the new SD implementation (work by Dr. Wolff, Perth, Australia) should be several times faster than ADFs current finite difference implementation for the second derivatives. The speed-ups are achieved by parallelization, use of distance effects and use of symmetry.

Parallelization NMR and CPL programs

The NMR and CPL (for NMR spin-spin coupling constant calculations) programs have been parallelized. Serial bottlenecks with unfavorable scaling with system size were also removed. These improvements make NMR calculations on much larger molecules conveniently accessible. (Work by Dr. Autschbach.)

Major speed-ups for Fock matrix calculation

By a few subtle but important changes, the calculation of the Fock-matrix during the SCF has been made more efficient, saving some time for all types of calculation, especially those on large molecules. Usage of special compiler flags improves the situation much further (e.g. using SSE2 instructions for Xeon and Opteron machines). (Work by Dr. van Hees.)

Time-dependent DFT code in BAND

Algorithmic improvements lead to speed-ups by more than a factor of two for large TDDFT calculations in BAND. The speed-up becomes even more significant for systems with many atoms in the unit cell.

TAPE10

TAPE10 can be saved from a parallel run. This is important, especially for model potentials like SAOP, or SIC potentials. Property programs, like NMR and EPR, often do not know about these potentials, but sometimes need them.

DENSF

The DENSF program will be able to calculate more different types of data fields in the ADF2004 release, such as the Electron Localization Function (ELF). The new data fields can then be visualized with ADFview.

ADFview

Most, if not all, reported bugs were fixed. The speed of ADFview has been considerably improved, making rotations of the pictures much more convenient.

ADFinput

All reported bugs have been fixed.

Other

TDDFT: other definition polarizability anisotropy

SCF Levelshift: other defaults

PRINT OrbPopER: other defaults

BAND and ZORA: improved numerical integration grid

rm wild cards removed in examples

Name element 110 Ds (Darmstadtium) instead of Uun

ADF 2003.01

March 18, 2003

ADF2003.01 is the first ADF release containing a graphical user interface: ADFinput.

Apart from that, this release is identical to the ADF2002.03 release.

ADF 2002.03

December 6, 2002

Introduction

ADF2002.03 contains both new functionality and a variety of important and less important bug fixes. There have also been some technical changes, related to the directories where ADF puts its files. We recommend all users to read the parts of the rewritten Installation Manual which deal with directories. The Installation Manual also contains additional advice for tuning ADF.

Platforms

As a new platform, SCM will provide also ADF executables for PC Linux with MPICH. Ports to various other new platforms are being prepared and will be announced in the News section of the web site when ready.

BAND

The BAND code now includes the Time-Dependent DFT code from the Groningen group, which enables the calculation of frequency-dependent dielectric functions for one-dimensional and three-dimensional systems. BAND further contains confinement and distance cutoff options. These help to make large BAND calculations significantly faster and reduce the amount of I/O. The confinement option can further help to prevent problems with linear dependency in large basis sets.

QM/MM and AddRemove model

The AddRemove model, from Marcel Swart, has been made ready for standard usage and documented more fully in the QM/MM User's Guide. The AddRemove model is a new coupling model to connect the QM and MM regions. First results with geometry optimizations look very promising.

Basis sets

Prof. Del Chong has devised two improved large basis sets for ADF that become available with ADF2002.03. The TZ2P+ basis set is available for the transition metals Sc-Zn only ($Z=21-30$). These basis sets are nearly identical to TZ2P except for a better description of the d-space (4 d-functions instead of 3). An improved even-tempered (ET) basis set has also been devised by Del Chong. It is named ET-pVQZ and available for the elements H-Kr. Because of smaller basis set superposition errors, the Et-pVQZ basis is to be preferred over the current ET-QZ3P and ET-QZ+5P basis sets. Further details are given in the README files in the basis set directories.

Modified way of working with temporary directories

The Installation Manual gives the details and the preferred settings related to this change.

Bug fix Z-matrix geometry optimization

An important bug that occurred in previous versions during geometry optimizations using internal (Z-matrix) coordinates has been fixed. This bug occurred when certain angles passed through 180 (or 0) degrees, leading to slow convergence, or no convergence at all. Some other less crucial bugs have been fixed in the calculations of the gradients.

Bug fixes numerical grid generation

Several bugs have been fixed which led, for certain exceptional geometries, to internal inconsistencies in the build of the numerical integration grid, causing the program to stop. The corresponding error messages included: HULL31, HULL33, SPHERE TOO LARGE, BAD CORE INTEGRAL, ERROR1 PLGIRR, and others.

Other bug fixes

The possibility to use only STO functions in BAND without Numerical AOs has been restored.

The use of point charges in EPR for calculations of Nucleus-Independent Chemical Shifts has been fixed.

An inconsistency in the reordering of point charges of symmetric molecules has been fixed.

A small inconsistency in the symmetry treatment of the EPR/NMR program in case of frozen core has been corrected as well as another small bug related to the spin-orbit treatment in this code.

The option `adf -h` has been restored.

The value of the parameter `MXNR14` has been increased in the QM/MM code to avoid problems in exceptional geometries.

Some minor issues with the treatment of the `BASIS` key have been solved.

A bug in running geometry optimization with the nondefault `DISK BASIS` option has been solved.

Problematic geometry optimizations for certain small highly-symmetric geometry optimizations in COSMO calculations has been solved by using all integration points by default in such calculations.

A bug in the rotational part of the thermal analysis in frequency calculations has been fixed that occurred for certain symmetric molecules.

A bug in the Multipole-Derived charge analysis, leading to an error message `Internal Error Stein`, has been fixed by handling singular matrices differently.

The possibility to print a limited number of MOs has been restored.

An inconsistency in the use of length units between `densf` and `cntrs` has been solved.

Utility `udmpkf` has been fixed to work on all platforms.

`ADFview` can now handle unrestricted orbitals and it can handle very long lists of orbitals and other properties.

And some other minor bugs.

ADF 2002.02

8 July, 2002

Introduction

ADF2002.02 is a minor upgrade of ADF2002.01, including primarily the first release of the ADFview module, for visualization of ADF output, of the graphical user interface as new functionality. ADFview is available on all platforms on which ADF is supported.

Platforms

For the first time a Windows version of the ADF package is released with ADF2002.02. It requires the Cygwin Unix emulator to be installed. The Windows version has the same functionality as ADF on other platforms.

COSMO

A bug in the COSMO implementation for ADF2002.01 release was fixed. Users who regularly use the COSMO functionality are advised to install ADF2002.02 as soon as it becomes available for their platform.

Densf

The densf interface was considerably simplified. This has been done to radically simplify the use of the ADFview module. Data on a grid can now be very easily obtained. The ADFview tutorial shows how this is done.

ADF 2002.01

28 February, 2002

Introduction

ADF2002.01 is a major upgrade of ADF2000.02, including much new functionality.

Platforms

Versions for the following platforms have been generated:

Compaq Alpha running Tru64 Unix

HP

NEC IA64 with linux and MPI

IBM Power3, Power4, AIX4, AIX5 with PVM

SGI running IRIX64 6.5 and 6.2

PC linux (Pentium III, Pentium IV, Athlons) with PVM

A complete list of currently supported platforms is available on our web site.

Input generation

A BASIS keyword has been introduced which removes the need for a separate specification of atomic preparatory calculations (Dirac runs and Create runs). This makes the ASCII input files much more compact. Please check the Examples document and ADF User's Guide for further details.

Property Programs

The CPL program, written by Jochen Autschbach in the group of Tom Ziegler, is now available for the calculation of nuclear spin-spin coupling constants that play a role in NMR. Relativistic effects can be included (ZORA and spin-orbit). An EPR/NMR program written by S. Patchkovskii, based on an earlier version by G. Schreckenbach has also been made available by the Calgary group. Its functionality partially overlaps and partially exceeds existing functionality of the NMR and ESR options within the ADF package. Steve Wolff's implementation for analytic second derivatives is made available in the SD program. This implementation is currently still slow and the traditional implementation in ADF, using finite difference techniques is still recommended for the time being.

For more information, please consult the Properties document and the examples.

XC functionals

The asymptotically correct GRAC and SAOP xc potentials have become available. They tend to give improved results over LB94 and BP for response property calculations. For the energy xc functional, many

modern (meta)GGA functionals have been implemented in a post-SCF fashion. They can all be printed simultaneously. Their accuracy improves significantly on traditional GGAs for the standard G2 test set.

Linear Scaling and Parallelization

Linear scaling techniques have been combined with the parallelization in ADF to give improved efficiency for SCF and TDDFT calculations on (very) large molecules.

QM/MM

Efficiency improvements have been implemented in the QM/MM program part. This enables QM/MM calculations on many thousands of atoms. To make this practically accessible, additional tools are needed to build an input file conveniently. These will be made available separately when ready.

Basis sets

All basis sets in the database have been thoroughly tested. Some have been adapted if this was deemed necessary after unsatisfactory results in our diatomic tests. The new basis sets are called SZ-TZ2P instead of I-V as we consider the new names more descriptive. In addition, large basis sets, such as ZORA/QZ and the even-tempered basis sets designed by Prof. Del Chong in the ET directory are made available. Basis sets with diffuse functions are also available in the ET subdirectory. Please check the Basis Sets document to find details on the test results and on the changes.

Errors Repaired

A bug in the Bond Energy Decomposition has been repaired.

A problem with the levelshift option in the SCF has been solved

A problem with hanging BAND jobs was solved

Some bugs related to the COSMO option were solved

Memory leaks in the QM/MM implementation were removed

Dependence of DISK BASIS calculation on input order of atoms solved

Error exits generated for attempts to do certain open-shell property calculations

Linux executables statically linked to avoid problems with different versions for glibc and other libraries

Problem in print routine for quadrupole polarizabilities solved

Timeout parameter adapted to enable larger jobs with some load imbalance on parallel machines

Treatment of equivalent nuclei in NMR calculations

Problems with dmpkf and udmpkf utilities (remove parallel information from output)

Several other minor bugs.

ADF 2000.02

17 July, 2000

Introduction

ADF2000.02 is a very minor upgrade of ADF2000.01, primarily to include versions for more platforms.

Platforms, Licenses

Versions for the following platforms have been added:

Compaq Alpha running Linux

Cray-C90

Cray-T3E

HP

NEC SX5 (should also run on SX4, which we have not yet verified)

SGI running IRIX64 6.4

SUN

A complete list of currently supported platforms is available on our web site.

Utility Programs and Scripts

On some systems the program may find that the license file is 'CORRUPT'. The Installation manual discusses the possible causes. A possible reason that was recently found is that the line breaks between the different records in the license file may contain (invisible) <CR> (carriage-return) characters. These can be removed by the (new) utility fix_license, which will be put into your \$ADFBIN directory by the installation procedure. See the Installation manual for details.

Errors Repaired

The PW91 correlation implementation contained an error that may have affected some calculations using the PW91 functional, in particular for calculations with BAND.

ADF 2000.01

17 May, 2000

Introduction

ADF2000.01 is an upgrade of ADF1999.02. It cures a few problems in ADF1999 and new functionality has been added. The fact that the new release is coined '2000' does not signal a major difference with respect to the ADF1999.x series. We simply name the versions after the year of release.

Runtime control, Installation

The PVM 'ARCH' on SGI systems to use with the ADF package has been changed from 'SGI64' to 'SGI6'. Please note carefully, that this is different from the usual (default) settings that may be present on your system (often: SGI64 or SGIMP64). This implies that you may need to install another PVM version.

Platforms, Licenses

At the time of writing we have prepared only executables of ADF2000.01 for a few platforms. Others will be added successively. At all times, the web site provides a survey of currently available versions.

Documentation, Examples, Database

We have extended the Examples document to include more sample runs. The new functionality QMMM (in ADF) is described in a completely separate (and new) QMMM manual. The corresponding description in the ADF User's Guide is brief and mainly points to the QMMM manual.

The organization of sample runs, in the \$ADFHOMe/examples/ directory has been changed. Each sample run has now its own (sub) directory, containing the run script and the output file.

A few new basis sets have been added for Cm with 5d core, in the database directories II/ and IV/

Functionality

The QM/MM (Quantum Mechanics / Molecular Mechanics) functionality is available to treat large systems by handling a 'core' part by the first-principles and accurate QM approach, while the remainder is treated by a force-field based approximation (MM). QMMM cannot yet be used in combination with a Frequencies run. In a Linear Transit run with QMMM, only the QM atoms may define the LT parameters of the path to scan.

ZORA-NMR

NMR chemical shifts and the advanced ZORA relativistic methodology can now be combined. ZORA-NMR may give a marked improvement over the traditional Pauli relativistic NMR results.

BAND has acquired a new Fragments feature to analyze results, in particular Density-of-States data, in terms of fragment orbitals rather than elementary basis functions.

Utility Programs

No new utility programs yet. Some of them are in development and parts (or all) of their code may already be contained in the package, but without documentation and without support. We're working on them and will inform you when they are ready for usage.

Performance, Precision, Technical

In some cases we found that the accuracy of the ADF numerical integration grid fell somewhat below expectation, sometimes resulting in a warning or error abort 'INACCURATE ETA INTEGRALS' or 'BAD ETA INTEGRALS'. To solve this, a few technical parameters in the grid generator have been adjusted. For a given accuracy parameter (the input key `Integration`) this will produce more points (roughly 10%) than was the case in ADF1999, with a corresponding increase in computing time but yielding more stability, robustness and reliability.

ADF calculations with *large* numbers of *point charges* (most of them far away from the real molecule) were very slow, due to a very large number of (mostly redundant) numerical integration grid points. This has been cleaned up, resulting in a significant gain in speed for such calculations.

Representation, Results

In the SFO / MO analysis output section a list of MOs has been inserted with a population breakdown in terms of the SFOs.

Errors Repaired

The Compaq release of ADF1999 failed on any substantial calculation, due to an overflow of the stack. Although this was not due to an error in the program, being a Compaq specific problem, we have solved it by reprogramming the involved routines.

The COSMO implementation in ADF1999 contained several major errors. Usually they 'only' caused the program to crash. Occasionally, the problems affected also the numerical results in a calculation that terminated normally. All problems in this functionality that we have encountered have been repaired; all related errors that were reported to us now run correctly.

IRC calculations often failed to proceed correctly, either by quickly going astray or by convergence problems with the point-by-point geometry optimizations. Another error that could show up was a sudden swap of coordinates, resulting of course in an energy jump and failure to produce anything meaningful.

Volume maps generated with Cerius2 were (almost) a factor 2 wrong in size. (The program mixed up bohr and angstrom units of length). The error was, in fact, not in the Cerius2 software but in the *densf* utility program in ADF, so to repair it you have to download the new version of *densf*.

ESR calculations with LDA for the XC functional failed to compute the A-tensor (hyperfine splitting) in a scalar-relativistic spin-unrestricted calculation.

There were a few deviations from the correct symmetry in NMR tensor results. Most of the discrepancies have been solved; the remaining deviations are a few orders of magnitude smaller than before and (probably) related to insignificant numerical issues.

A few minor inaccuracies and (small) numerical errors in relativistic NMR calculations have been corrected. The effects are believed to be small and often insignificant.

The list of atomic coordinates in Z-matrix format in the logfile could have incorrect atom *numbering* indices, depending on the order of atoms in the input file.

ZORA relativistic calculations sometimes failed with error abort 'SORXR error'

The following error aborts have also been repaired:

'Error 4 Polyhe',

'no convergence bounds'

'TOO MANY TRIES. HULL32'

'inconsistent merge of edges'

'point edge. HULL32'

We have treated the error abort 'BAD ETA INTEGRALS' and the related warning 'INACCURATE ETA INTEGRALS' by tuning the internal precision control in the numerical grid generator. Most of the cases should be cured. Please report any persisting ones.

Relativistic calculations involving ghost atoms in the molecule failed, for instance in a Basis Set Superposition Error calculation.

There was an error in the computation of IR intensities for certain point group symmetries. This resulted in the following message in the logfile: 'WARNING: INFRARED INTENSITIES WRONG'

A computation with an Icosahedral system with an atom in the symmetry point produced garbage results, due to an error in the numerical integration grid around the central atom.

Note: ADF does not support I and I(h) symmetry, but the system may itself have that symmetry (in which case you may run it in, for instance, D(5h) symmetry). The error did not depend on what subgroup symmetry you actually used, only on the fact that the true symmetry is Icosahedral *and* that it has an atom in the center.

In a spin-unrestricted calculation the printout of one-electron energies for the second spin were (often) wrong.

A particular numerical instability occasionally caused a further slowdown of SCF convergence (or even failure) in BAND for systems with very slow convergence anyway.

Computations on very large molecules sometimes failed with the message 'TOO MANY POINTS. PLGOUT'

RESTARTDOS in BAND sometimes failed (due to non-initialized variables)

Known, but Unsolved Errors

Due to a complicated numerical problem, resulting in loss of precision for certain integrals, calculations with very steep functions (typically, using ZORA basis sets) may fail on Cray systems with the error message 'singular sfit matrix'. We have analyzed and understood the cause and are working on a repair.

Cerius2 fails to display orbitals computed in a relativistic Spin-Orbit calculation. This is not really a bug: it has simply not been implemented (for good reasons) yet. We are considering to work on this for a future release.

Miscellaneous

Much more of the ADF sources have been made available (for those who have a license including source code). Released are now major parts of the Time-Dependent DFT, NMR, and Spin-Orbit routines, as well as scattered others.

A few data arrays related to the frozen cores in ADF were written to TAPE21 with one (redundant) element too many. This has been corrected. Consequently, ADF1999, which also *reads* the redundant array element will fail to read an ADF2000 TAPE21 file. It will abort upon an attempt to read this redundant element.

With the Define key you can assign values (or functions) to identifiers and then use these identifiers rather than numerical data for, say atomic coordinates. Usage of one-character identifiers is not recommended and easily leads to unintended (and sometimes unnoticed) mistakes in the input file. To 'protect' against such situations, 'loud' warnings are issued in standard output as well as in the logfile as soon as you 'Define' one-character variables.

ADF 1999.02

30 June, 1999

Introduction

ADF1999.02 is a minor upgrade of ADF1999, primarily to solve a few installation problems and to extend the number of supported platforms. For several platforms already supported by ADF1999 no executables have been replaced. The source code at the web site corresponds to ADF1999.02

There is also new functionality: ESR properties. However, to use this you don't need to download ADF1999.02, as the functionality already exists within ADF1999. It is documented now in the ADF User's Guide. If your current ADF1999 license file denies you access to the ESR feature, contact us for an upgrade of the license file.

Platforms

ADF1999.02 supports Compaq (DEC) platforms. Note carefully that default settings for the maximum stack size on your Compaq station may be insufficient to run ADF1999. See the README at the download page.

The ADF1999 version for the IBM RS6K has been replaced to cure a few installation problems. Contrary to the first release of ADF1999, we now have only one RS6K version, which should be usable for all users with Fortran compilers 3.2.5 or higher. Unfortunately we cannot support yet older versions of the Fortran compiler.

In addition, we have placed at the web site the MPI executable for the IBM SP. The script to properly run an MPI version is rather system dependent, and you will probably have to modify the standard run script (\$ADFBIN/start) for the MPI version.

Documentation, Examples, Database

Description of TAPE21 contents in the User's Guide updated: was rather incomplete. Description of TAPE13 (checkpoint file) added.

Functionality

ESR properties can be computed with ADF1999. See the ADF UsersGuide. Keywords: ESR and QTENS.

ADF 1999

18 May, 1999

Introduction

ADF 1999 involves a significant enhancement of functionality to include solvent effects, excitation energies, (hyper) polarizabilities, NMR chemical shifts and the ZORA relativistic formalism, to mention a few major extensions. Technically, the program has been 'upgraded' from the Fortran77 to the Fortran90 language. This implies that, in order to compile the program, you must have a Fortran90 compiler. However, we have also started to distribute complete executables, so the need to compile the program by your self is reduced.

The extended functionality, new language features and other technical matters have made it unavoidable that the format of the TAPE21 output file had to be changed. This implies that the TAPE21 files of ADF2.3 and ADF1999 are technically not compatible, i.e. you cannot hook up a version 2.3 TAPE21 file as a fragment file to a calculation with ADF1999. However, the logical content is largely identical. You may verify this by making an ASCII dump of the files, using the KF utilities. The logical compatibility means that privately developed tools that access TAPE21 files through the KF library procedures should work with the 1999 version as well (using the KF library of the 1999 release, of course), or may need only minor adjustments.

The 1999 release has focused on a significant increase in functionality compared to ADF2.3 and we believe this is a major step forward. However, we appreciate and acknowledge the fact that there is room for improvement in the area of speed, memory, IO, and disk usage and we will give this aspect more attention in the near future.

Runtime control, Installation

With version 2.3 we introduced the run-script 'start'. This was convenient, if not necessary for the control of parallel calculations. The script still exists but we have now 'soft-linked' each of the program names (adf, band, densf, ...) to this particular script in \$ADFBIN. This means that you can call 'adf' and thereby in fact invoke the 'start' script. The program name that you actually use in the command is passed to 'start' as the main argument. As a result, usage is simpler now and has the form

```
$ADFBIN/adf -n4 <in > out
```

This replaces the (still available) 2.3 variety

```
$ADFBIN/start -n4 adf <in >out
```

See also the Installation manual and the Examples document. Take a look at the sample runs for the new format used in practice.

Technical note: since the names 'adf', et cetera are now used as soft-links to the start script, the program *binaries* have acquired other names: adf.exe, band.exe, and so on, in \$ADFBIN.

We are shifting the distribution from using ftp accounts (as we did up to release 2.3) to downloading from our web site: <http://www.scm.com> (starting with release 1999). All users will get password-protected access to the web site with their old ftp account data (user name and password). This will, we hope, make downloading easier for you.

The ftp facility remains in place, but only to *upload* files for error reports.

We have introduced a few more (UNIX) environment variables that should be defined when running programs of the ADF suite, in particular - but not only - when running in parallel. We recommend that you define these variables in your login script (.cshrc if you run C-shell). Consult the Installation manual for details.

Control of parallelization features at the first line of the input file has been disabled. All parallelization is now controlled by environment variables and by the -n flag to the program execution scripts. See the Installation manual.

Platforms, Licenses

Due to difficulties (i.e. compiler bugs) in several Fortran90 compilers as they were distributed by hardware vendors we had a hard time to create versions of ADF 1999 for all the platforms that we wish to support. Unfortunately, we have not sorted out all the problems yet. As a consequence, we are distributing only a few (major) platform types now and will follow up as soon as possible with the other ones. Please contact us (by email to: support@scm.com) if the now-distributed-platform types cause any difficulties on your machine.

Support for IBM RS6K running AIX3 has to be discontinued, unfortunately, for lack of a suitable Fortran90 compiler.

Documentation, Examples, Database

New all-electron basis set files up to Kr (type I through V in the database directory)

Several polarization functions have been changed in type III, IV and V basis sets, after extensive tests with calculations on small molecules.

For S: the exponential decay factor of the *d*-type polarization function changed from 1.5 to 2.1.

For Si: *d*-function exponent changed from 1.35 to 1.75; *f*-function exponent changed from 2.0 to 1.9

For Cl: *d*-exponent changed from 1.65 to 2.0; *f*-exponent from 2.5 to 2.0

For Al: *d*-exponent changed from 1.2 to 1.6; *f*-exponent from 1.8 to 1.75

A few basis sets with (too) large frozen cores have been declared obsolescent. They have been moved to a new 'Old' directory in the database. This applies to heavy elements (Hf ... Hg).

Some keywords for BAND were not documented in the BAND User's Guide. The list has been completed.

The database contains also files that are used for the Cerius2-ADF interface developed by SCM (based on the older version created by MSI for ADF2.x).

Functionality

Response properties can now be calculated, based on an implementation of Time Dependent DFT (TDDFT). For closed shell systems you can compute frequency dependent (hyper) polarizabilities, Van der Waals coefficients (see also the utility program DISPER), excitation energies and Raman intensities.

NMR chemical shifts are computed with a new utility program NMR. See the Utilities manual for an input description.

Solvent effects (COSMO model) are available. See the ADF User's Guide for a description of input parameters (keyword SOLVATION).

The ZORA relativistic option is available in ADF. This is a major improvement over the (still available) Pauli approach. See the ADF User's Guide for details. ZORA requires special basis sets. The ZORA basis sets are, exactly as for the non-ZORA sets, organized in subdirectories I, II, III, IV and V for increasing flexibility. All ZORA basis sets are in the \$ADFHOME/atomicdata/ZORA/ directory of the ADF database.

BOB: the Basic Output Browser has been included in the package, to enable a quick scan of the (potentially large) standard output file. See the Utilities documentation.

The SlaterDeterminants key has been introduced to enable the computation of multiplet states. See the Theory document for a discussion.

Atomic coordinates can be input (ADF) with MOPAC format. ASCII output files can be generated with coordinates in MOPAC and/or XYZ and/or MOL format.

The SCF Level-Shift option has a new sub-option to turn the level shifting off as soon as the SCF error drops below a user-set threshold. This may, occasionally, improve the convergence rate when the final stages of the SCF may only slow down by the level shifting technique.

The AUFBAU option to the OCCUPATIONS key has been disabled. The KEEPORBITALS parameters have somewhat changed. ElectronSmearing is suppressed in more cases and should be understood as *only* a trick to achieve SCF convergence in an intermediate calculation, for instance during a geometry optimization.

Utility Programs

NMR: computes NMR chemical shifts, using a TAPE21 file from ADF.

DISPER utility program to compute Van der Waals dispersion coefficients. It requires files from one or two preceding ADF calculations using Time Dependent DFT.

BOB: the Basic Output Browser allows you to quickly scan the standard output file for important data.

(All utility programs are described in the Utilities manual)

Performance, Precision, Technical

The energy decomposition in a single-point run (and at the end of an optimization) and the energy calculation during optimization / Linear Transit / ... runs were not exactly identical in version 2.3, with discrepancies in the order of 0.01eV. Analysis revealed that a different handling of fit-related inaccuracies caused the difference and that, in fact, a slightly more accurate correction for the fit-error could be used in either case. Both algorithms have accordingly been improved and now give the same results.

Differences with ADF2.3 results (regarding this aspect) should be fairly small: 0.01eV or less. They may be larger when rather inaccurate fit sets are used.

Single-Point runs with single-atom fragments that were computed in ATOM symmetry now also use *exact* rather than *fit* densities for the computation of the electrostatic interaction between the fragments. This eliminates any fit-related error from that energy term.

The parallel execution sometimes failed when file permissions or machine-access settings prevented the ADF run scripts to copy (fragment) files from one host to another. We have solved this by implementing in the code an automatic transfer of (file) data through the parallel message passing facility *if the kid processes do not have the same file as the parent*. This will cause a few seconds delay in the very early phase of the program, because parallel message passing of a fair amount of data is relatively slow. At the other hand, it has reduced the run-script-controlled copying of data files and makes the procedure more robust.

A serious slow-down of BAND in the final stage of the calculation, usually accompanied by one of more logfile messages 'BROKEN ELSTAT LOOP' (occurring during the processing of electrostatic interactions) has been cured.

The continuation code in the usage of block-type keys with arguments has been changed from the double plus character (++) to the ampersand (&). The old format is still supported, but not recommended.

User comments in the input file start with the exclamation mark (!) instead of the double colon (::). The old format is still supported. The exclamation mark is recommended.

Representation, Results

BAND cohesive energies are (by default) with respect to spin-restricted atoms. This has been different in BAND0.5; it was changed in a later version, but not stated correctly in the manual.

Energies in Linear Transit path points (ADF) included Hamiltonian terms that the user did not specify on input (in particular: relativistic). This has been changed.

ASCII output files can be generated with MOL and/or MOPAC and/or XYZ style coordinates, see the new FILE key.

The ADF logfile contains lists of Cartesian coordinates (not in a single point run). The number of displayed digits has been extended from 4 to 6 (to better preserve symmetry properties). Internal (Z-matrix) coordinates are now displayed also in the logfile if a Z-matrix structure has been given in the input file.

Errors Repaired

Bond energies (ADF) in LARGE molecules with COMPOUND fragments, or with single-atom IONIC fragments could be wrong (errors up to 1eV or more!) as a result of incorrectly ignoring electrostatic monopole interactions over larger distances. If you have done such calculations with ADF2.3 we recommend that you carefully check the results, and if feasible compare the data against calculations that use neutral single-atom fragments and/or against ADF1999. For the latter, please be aware that other improvements may also cause some (smaller) differences in results.

DENSF went wrong when higher virtual orbitals were processed while at least one lower one was skipped, producing incorrect data for the higher orbitals.

Frequency calculations (ADF) in T(D) symmetry with a large number of atoms and/or a large number of basis functions could cause overflow of data arrays, resulting in (often) an error abort, depending on what other data were overwritten exactly.

The Level Shifting procedure sometimes processed data incorrectly, leading to unintended changes in orbital energies during the SCF. Usually, this was rather counter-productive in terms of convergence speed although it did not affect the final density and related properties like the energy.

A frequency run could not start by using the TAPE21 file from a non-frequency run as a restart file (to pick up converged geometry data, for instance)

Parallel execution on SGI Power Challenge (maybe also Origin2000) failed when using more than 14 CPUs.

Mulliken populations in BAND did not always reflect the crystal symmetry correctly.

The ORBPOP key didn't work in BAND.

Symmetry breaking by an homogeneous electric field (ADF) was not handled correctly for the infinite symmetries D(lin), C(lin) and ATOM.

Linear Transit variables would change in the wrong direction when the FIRST reference to it has a negative sign in the input file.

The following error messages have been analyzed and (hopefully) cured:

'wrong index block read'. Note that this error may also show up when a fragment calculation failed and you incorrectly try to use the resulting fragment file. Usually, however, such attempt will give another error: 'Wrong Superindex' or something similar.

'no vectors in mergev'. This was a numerical threshold problem.

'Lowdin is not a linear combination of ETAS'. This error occurred when the Create database file contained core orbital expansion sets for higher *l*-values, while no corresponding core orbitals were actually present.

Usage of PW86 or PW91 XC functionals could result in a core dump. Cause: use of uninitialized variables. Fortunately, this occurred in terms that weren't used anyway, so if the computation completed successfully, the results should be fine. On some machines, however, processing the uninitialized variables resulted in a crash.

Miscellaneous

Relativistic ADF calculations require preparatory DIRAC calculations for the involved atoms, to create a TAPE12 file with relativistic potentials. Contrary to ADF2.3 you must now also run DIRAC for atoms that don't have a frozen core at all, such as Hydrogen, because the TAPE12 file of the 1999 release contains not only the *core* potential and density but also the (relativistic) *total* atomic potential and density. This also implies that the TAPE12 files from release 2.3 must not be used in release 1999.

Moreover, relativistic ADF calculation now *must* use a relativistic TAPE12 file (prepared with DIRAC). In ADF2.3 you could use a non-relativistic TAPE12 file, or no *a priori* generated TAPE12 file at all (and get incorrect results) without even a warning from the program.

Default for the input key DIRECTIONALSCREENING (for the BAND code) has been set to 'true'.

Symmetry tolerance default (ADF) was documented as 1e-3 Angstrom, but was implemented as 1e-3 bohr. The documentation reflected the intention and the implementation has accordingly been corrected.

ADF 2.3 / BAND 1.0

May 7, 1997

Runtime control

To solve a couple of problems with the parallel execution of our programs on certain platforms, a run-control script has been included in the package, called *start*, which is placed by the installation procedure in the \$ADFBIN directory. We recommend using this script always, also for the serial version. For parallel (PVM) versions you *have* to use it. This applies to executing all programs of the ADF suite (*adf*, *band*, *densf*, ...). See the Installation manual and the *adf* User's Guide for comments and instructions. All Example runs have been adapted to use the script, providing you with an easy-to-copy illustration of how to use it (easy!).

Please let us know if you have any problems with it. Parallel programs are by far not yet a standard thing and controlling what precisely happens on the various nodes is very machine dependent. We strive of course to make our setup as portable and robust as possible, but comments and suggestions are always welcome to help us improve things.

The new setup with the script 'start' assumes the existence of an environment variable (*nscm*). This is not necessary, but it makes it easier to set / adjust the defaults for parallel calculations. See the manuals (Installation, User's Guide).

Installation, Platforms

Serial (non-parallel) versions could encounter problems in the linking due to missing external statements.

SUN: missing library-*resolve* specification could lead to failure of the installation / link.

NEC-SX4 version available. Only the serial version has been tested so far. Work on the parallel (PVM) version is on its way.

Installation parameters for BAND on the Cray-T3E led to too many open files during the calculation and hence to a program abort. We are still testing the T3E version. Please let us know your experiences, if any...

On SGI *irix64* an additional compiler flag '-64' was needed for some older levels of the operating system to avoid linking in 32-bit object code. Also, the -O3 optimization level is now completely suppressed and replaced by -O2. This should not affect efficiency very much, while it does circumvent a couple of compiler bugs (!).

Documentation, Examples

The Installation Manual and User's Guide (for *adf*) contain a description of and remarks about the (new) method to run the programs of the *adf* suite, using the unix script *start* which is delivered with the *adf* package.

Functionality, Options

Parsing of expressions in input, previously applicable everywhere except in the data blocks of certain keys, has been changed into: only applicable for a specified list of keys, see the User's Guide. This does not imply a lot of change in practice, but merely reflects a different approach as regards the generality of the feature.

The change was triggered by a previous error, that the program incorrectly 'parsed' and hence corrupted symmetry labels of double-group symmetry groups in the input file.

Bugs, Errors

On DEC and SGI (irix64) platforms, a failure could occur due to wrong data types in some calling sequences (only in parallel versions).

An error about 'SPHERE TOO LARGE' could happen due to numerical round-off problems.

'ILLEGAL DET. MATGEN' error abort fixed.

'MARKER ERROR' at the end of the SCF procedure, more precisely in module COREPS, could happen for molecules with large basis sets.

Date_and_time on HP was not activated correctly, leading to 'TODAY' and 'NOW', rather than correct date and time information in the logfile.

Due to numerical noise, diagonalizations and vector set orthonormalizations could yield inexact results, in some cases detected by the program as a fatal error.

ADF 2.2.1

February 28, 1997

Installation, Platforms, License

There were a few problems with installing ADF2.2 that we've fixed in ADF2.2.1:

A runtime error occurred on SGI running IRIX6.1, probably due to a compiler error. The problem is circumvented in the new release.

Checking the license file could fail if the domain name as picked up by the license control module was empty.

Suppressing the usage of C code altogether could fail due to a linking problem (calls to the C modules were runtime suppressed but not eliminated from the source code, so that the linker reported unsatisfied externals).

ADF 2.2

Installation, Platforms, License

Added to the supported platforms: Pentium_Linux, cray_t3e, rs6000_aix3.

License-file info now also printed when running with a license file that not includes the machine on which the run is attempted. Previously, you had to remove the license file first; otherwise the program would abort with a message 'Invalid License'.

Installation on a SUN using C-code could fail (due to a typo in one of the C-routines).

Installation on sgi 64 bits (R8000 or higher) could fail due to problems with linking in lexicographical routines from the standard library.

We recommend that before you install the package you define the environment variable TESTBIN. This is used from now on in all sample runs to specify the directory in which the executables are located. Previously the sample runs addressed ADFBIN. You may, therefore, set TESTBIN equal to ADFBIN.

Documentation, Examples

The documentation has not changed significantly, the most relevant issues being the remarks about the LB94 functional (ADF User's Guide) and the memory-usage control in DOS, DENSF, CNTRS (Utilities).

Two sample runs are provided for BAND (input and output files) in \$ADFHOMe/examples/band.

The BAND documentation incorrectly stated the availability of standard example runs in the code: these have been disabled.

Functionality, Options

The LB94 DFT functional is not suitable for geometry optimization (generally: not for the computation of gradients, hence also not for Frequencies). This is now documented in the User's Guide. In the program an attempt to use the LB94 option in combination with energy gradients will now fail, unless the internal check is disabled with the ALLOW key.

Bugs, Errors

Installation (compile)-time adjustment of (maximum) memory usage didn't function: the pertaining parameters were rigidly defined within the binary part of the distributed code. Run-time adjustments of memory parameters worked OK.

In some cases ADF wouldn't recognize the true symmetry, finding a lower one instead.

Error abort 'wrong nr of points' repaired.

Calculations that used a TAPE21 (or TAPE13) restart file from a SinglePoint run in a Geometry Optimization failed (because the program assumed the restart file to contain optimization-type data).

Parallel versions on DEC or SGI machines with LARGE memory (more than 2Gb) could fail (due to incorrect memory addressing).

LinearTransit runs without degrees of freedom for optimizations in each LT point aborted with a 'KF error' message.

LinearTransit runs print a survey of the energy along the LT path when the scan is completed. This energy included only the terms used for the computation of gradients, not any post-SCF terms for instance or any correction terms to improve the estimate of the bonding energy. This applied also to the storage of such energy data in the LT section on TAPE21.

The printout of Dipole Moment values along an LT path, at the end of the run, was incorrect. The Dipole Moment values printed in the RESULT sections at the end of each of the restricted optimizations along the LT path, were correct.

Geometry Optimization runs with a dummy atom sometimes failed with an error message 'wrong nr removed'.

An error about 'ERROR1 PLGIRR' could occur due to too sloppy thresholds in an internal numerical precision test.

Calculations on a molecule that was *close to* a higher symmetry than actually detected by the program sometimes failed with an error message 'ERROR 1. SYTABL'.

The program evaluated 'mathematical expressions' also in parts of the input file where it was not supposed to do so. This led to errors when supplying, for instance, OCCUPATION numbers for double-group symmetries with labels that end with an asterisk (*).

Unrestricted LinearTransit runs failed with a 'KF' error message like 'non-existing variable'

Due to the allocation of unnecessarily large arrays the program could run out of memory in relatively small calculations on platforms where character-type data are not dynamically, but statically allocated. In particular: Cray platforms.

Utility Programs

Maximum memory usage can now also be adjusted (run-time) for DOS, DENSF, CNTRS. See the Utilities manual.

DOS utility program wouldn't execute on some systems (sgi, ...) with an error message like "no atom pairs" or something similar.

ADF 2.1

Installation, Platforms, License

Part of the package includes binary code (object files) for a few minor modules, and for license-control software. This has increased the size of the whole package since for each of the supported platforms separate object files are incorporated.

The supported platforms are each represented by a subdirectory within \$ADFHOME/Install.

For UNIX platforms not available there, contact us (email: support@scm.com). The issue here is not that the program would not be portable on other platforms, but only that we haven't yet generated the required object files for them.

The program controls license matters by reading and checking a *license file*. If you don't have a license file yet, don't worry: just install the program and run it. It will stop and print out information that we need to generate your license file. E-mail (or fax) this info to us.

Be aware that at installation time, although you don't need to have the license file yet, you must know *where* the license file will be put (the installation script will ask you for the "name" of the license file). This must be a place accessible by all people that are going to use the program.

The installation script has been revised.

READ THE INSTALLATION MANUAL!

Database, Basis sets

New basis sets: W.4d, Xe.4p, Ni_d9.2p and Ni_d9.3p: in II and IV.

The Ni_d9 basis sets are tuned to the d9 configuration of the isolated Ni atom. The other Ni basis sets (without _d9 suffix) are more suitable for the d8 configuration. Both sets can be applied in Ni-containing molecules. The differences are not very large, but the more appropriate choice in an actual situation may improve the basis set quality somewhat.

New basis sets with various frozen core levels and relatively large fit sets (larger fit sets also for the old basis sets) are available now for La through Rn.

All-electron basis sets are available, in the directory \$ADFHOME/atomicdata/AE. However, the data base files here have no fit sets with them so you cannot use them directly in a CREATE run. Standard fit sets, as used in the other database files, cannot be used because they would be highly inadequate and lead to incorrect results. The generation of fit sets suitable for a particular basis set is not a trivium. The all-electron basis sets are being made available only for experimentation purposes, not to be used as a "standard". We intend of course to generate fit sets for them, but other issues have higher priority.

Documentation, Examples

Major parts of the ADF documentation are already available on the WorldWideWeb. This will be extended in the near future.

The documents EXAMPLES and APPLICATIONS have been combined into the new (more extensive) EXAMPLES document. A few more sample runs have been incorporated to cover new functionalities. The "old" sample runs have been renamed.

Functionality, Options

All restart facilities available, including cases such as: use the Hessian from a Frequencies run in a follow-up optimization or TS search.

LinearTransit and Frequency runs can be carried out in parts, using the restart facility to control the continuation. The number of steps to be done in one particular run is controlled with the ITERATIONS subkey (in the GEOMETRY block), which may have a second argument (for the LT run).

Frequency calculations can be carried out with constraints (for instance, to study the vibrational modes of a more-or-less rigid fragment w.r.t. a metal surface).

Spin-Orbit relativistic option available: only in SinglePoint runs.

Orbital Localization (Boys-Foster method) available. Localized orbitals can also be addressed by DENSF (preparation for plotting or 3D maps).

New XC functionals: Xonly (pure LDA exchange), LYP (Lee-Yang-Parr), BLYP (same, but combined with Becke88 exchange corrections), PW86 (Perdew-Wang formulas of their 1986 paper).

XPS: The one-electron energies of the Core Orbitals in the final SCF field are computed and printed, in the RESULTS output section. Absolute values may not be very accurate (because the core orbitals are not self-consistently relaxed in the SCF field), but differences between e.g. the 1s orbitals of distinct Carbon atoms should be fair and hence provide a good estimate of (differences in) chemical shifts.

The AUFBAU principle in geometry optimizations etc. will by default be applied in the same way as for the start-up geometry (a few SCF cycles, occupations frozen thereafter). Used to be: only applied in first geometry. This feature can be tuned with the (new) option AUFBAU2 to the key OCCUPATIONS.

ElectronSmearing has been largely suppressed: only applicable in optimizations (incl. TS searches), but not in the final geometry.

The symbol for an "Alternative Element" can also be Gh (rather than J).

The atomic mass can also be specified (to override default values) for "normal" chemical elements: this used to be possible only for J-type elements.

DFP (Davidon-Fletcher-Powell) Hessian update scheme available in TS search (was available already in optimizations).

Performance, Precision, Technical Matters

Dynamic allocation of memory has been implemented. Installation-defined workspace sizes are now only defaults which can be adjusted by input-keys. No need anymore to compile differently-sized program versions. It also improves in a general way the efficiency of memory usage.

Default (automatic) values for Numerical Integration precision have been increased AND now depend on the runtime (high default value for Frequencies, for instance).

Minor modifications in the Numerical Integration grid generator, leading to higher standard precision within the atomic core regions. This may result in slightly (but not essentially) different outcomes.

The electrostatic interaction energies, and their derivatives w.r.t. nuclear displacements, were computed from the fitted (i.e.: approximate) densities. An evaluation using the exact densities has been implemented. This generally leads to somewhat different results. The so-corrected inaccuracies in the old version are larger for atoms that had relatively inaccurate fit sets in their database files.

The SCF convergence criterion is relaxed during the intermediate cycles of optimizations. This reduces (usually) the total execution time. In some cases it may lead to using one or two geometry cycles more. This feature (a secondary SCF criterion) is controllable with the (extended) CONVERGENCE option to the SCF key. The (new) key FULLSCF can be used to suppress the feature altogether.

Optimization and TS search strategies have been modified to solve stability problems and improve robustness (geometry convergence sometimes failed after initial progress towards the minimum; TS searches very often failed to converge by randomly walking around the TS point).

Calculated energy gradients are adjusted to eliminate spurious components of rigid motions. This used to be treated in a slightly different way in Optimizations versus Frequency calculations. As a result, the computation of Frequencies in a previously optimized geometry could issue warnings that "GRADIENTS IN THE EQUILIBRIUM ARE NOT SMALL".

A new key DEPENDENCY has been introduced to handle numerical problems with very large basis sets that contain diffuse functions. It should not be necessary/useful to apply it to the standard basis sets provided with the package.

Presentation, Results

Standard output has been restructured a bit to separate the distinct main parts more clearly: general characterization of the run, building info (fragments, basis sets), computational progress, and results. These main sections are controllable with PRINT keys.

PRINT keys/options EIGSFO and EIGCFSFO have been removed. A general (EPRINT) option SFO is available to address all SFO-related output switches.

For hints to suppress large parts of printed output see the User's Guide.

Printed Voronoi Charge analysis: results are printed with opposite sign wrt ADF2.0: a net total negative charge (electrons!) is now printed negative. Previously: positive (i.e.: effectively counting the number of electrons). In addition, the "Voronoi Deformation Density" is printed, in the last column of the table.

In a Frequencies run the computed Force Constants Matrix is by default printed on standard output.

Bugs, Errors

Calculations on linear molecules performed in finite ("broken") symmetries used incorrect numerical integration schemes in some special cases.

SFO populations in spin-unrestricted calculations were incorrect for spin-A (the spin-B values were printed both for spin-A and for spin-B).

Constrained optimization in Cartesian coordinates could go wrong when the molecule was rotated by the program to adjust the input coordinates to symmetry-related orientation requirements.

In O(h) symmetry f-type atomic basis functions were treated incorrectly. The effects are (in all cases that we verified) minor.

LinearTransit runs failed when *all* non-transit coordinates were kept frozen AND non-local (GGA) XC-options were used.

The PW91 functional implementation had a few numerical problems leading in some cases to ridiculous (and obviously wrong) values. Application of PW91 in UNRESTRICTED calculations often failed.

Recognition and treatment of point group symmetries D(2h) and D(2d) often went wrong. C(s) occasionally also caused difficulties.

The calculation of Frequencies for a linear molecule specified with finite ("broken") symmetry failed (error message: WRONG NR OF RIGIDS).

The key REMOVEFRAGORBITALS failed when ALL orbitals of a fragment irrep were removed.

When the LevelShift SCF-option was used the printed one-electron orbital energies were not corrected (and hence included the LevelShift value).

The dipole moment was incorrect in an UNRESTRICTED calculation that was executed in PARALLEL mode.

The LevelShift option didn't function correctly for spin-B (in an unrestricted calculation).

On some machines and in some applications the program would abort with an error message like "STEBZ ERROR". Some (hopefully all) of these cases have been cured. Please notify us when this error still occurs: we have not been able to REPRODUCE some of the reported errors, so we are not sure that we've traced all underlying causes.

Miscellaneous

Input coordinates used to be adjusted so as to place the center-of-mass in the origin. This is applied now only as far as necessary to match symmetry-related orientation requirements.

Installation defaults for the maximum numbers of atoms, basis functions, et cetera are increased considerably and should accommodate large calculations without adjustment. See the Installation manual.

A new key INCLFILE is available to store for instance personal preferences for standard input items in a separate file and link that to an actually used input, rather than typing in all the preference values each time again.

The SAVE key options has been extended to enable saving scratch files (for instance).

The counting of free (optimization) variables has been modified so as to make them be strictly ascending along the input list of atomic coordinates. This affects the selection of a specified coordinate to focus on in the initial phase of a TS search.

We will start including a list of ADF-related publications (by users) in the standard documentation of the package. This list will (by necessity) not be complete but is meant primarily as a starting point for (other) users to access literature related to their own research. We therefore invite you to send us a reprint of publications with a brief accompanying note containing a one-line characterization of the publication and the program's relevance for it and two or three keywords.

Utility Programs

DENSF documentation has been upgraded (was rather unclear and in some cases incomplete or incorrect). Printed output gives a summary of invoked items. Values of the electrostatic potential had the wrong sign.

Documentation of KF utilities (pkf, dmpkf) improved to clarify usage and results.

New utility program DOS: for the generation of density-of-states type information: Total as well as different kinds of Partial (gross-, overlap-, ...) density-of-states data.

ADF 2.0 / 2.0.1

Installation

The UNIX Installation procedure has been modified. The script "configure", which previously had to be executed with as argument the name of the platform on which the installation takes place, is now executed without argument. It is interactive and starts a dialogue with the user about various installation issues.

Read the Installation manual.

Special attention is required for the installation of a PARALLEL version of ADF. As message passing libraries both PVM and MPI are supported, but virtually all testing has been done with PVM. We strongly recommend therefore PVM. PVM is public domain software and has to be installed separately before you install the PVM version of ADF.

Read the Installation manual carefully!!

Documentation

The Installation manual has been thoroughly revised, in particular with an eye on the parallelization options.

Additional documentation has come available:

"Applications": a discussion of special applications of ADF the description of which would not fit well in the User's Guide. In this release "Applications" contains only a discussion of the BSSE (Basis Set Superposition Error).

"Utilities": description of auxiliary programs and utilities that are part of the ADF package. One of these programs is a utility to generate density, potential, orbital values on a user-specified grid (e.g. for plotting).

The User's Guide has not been changed in a very fundamental way but the modifications are so many that it is undoable to summarize them here.

Functionality and Options

Relativistic (Scalar, Pauli formalism) geometry optimization.

In geometry optimizations an initial guess of the Hessian is computed from a Force Field (previously: set to diagonal unity). This results in most cases in faster geometry convergence. More importantly: a Transition State search can now be started directly, without first computing the Hessian by way of a Frequencies run.

Hirshfeld and Voronoi analyses of atomic/fragment charges.

Atomic coordinates can be input in a new format "ZCART": Cartesian coordinates with Z-matrix structure. This can be used to apply optimization in internal coordinates while input is given in Cartesians.

Density Functional options extended: Perdew-Wang-1991 formulas for exchange and/or correlation, and the Perdew-Wang-1986 formulas for exchange.

Performance, Precision, and Technical Issues

ADF has been parallelized. For installing a parallel version read the Installation manual.

The Direct SCF feature has been extended from fit functions to (also) basis functions. This gives a considerable reduction of disk access. The keyword controlling this is DISK (used to be DIRECTSCF).

The internal handling of files has been totally revised. This has made other developments (now and in the future) much easier. One of the (negative) consequences is that the old files are incompatible with ADF2.0: any TAPE21s etc. from ADF1.1 can not be used in ADF2.0.

Better use is made of symmetry in geometry optimizations, giving significant speedups for molecules with high symmetry.

Processing of basis and fit functions and the computation of (Fock) matrix elements takes distance effects into account, so as to speed up the calculation by not computing negligible contributions. Technical details can be set with TAILS.

The DIIS (Direct Inversion in the Iterative Subspace) approach has been implemented for geometry updates in optimizations and TS searches. This supplements the usual Newton-type strategy and in most cases improves the convergence behavior.

Numerical Integration precision is (optionally) self-adapting during geometry optimizations.

Interpolation method of frozen core data from the core tables has been improved. Same for interpolation of Electrostatic interaction terms in geometry optimizations. In both cases the improvements are minor.

Solved Bugs

fragments computed in C(lin) or D(lin) fragment symmetry could not be used in molecules with C(lin) or D(lin) symmetry: the results were wrong or the program crashed.

An error in the computation of energy gradients has been detected and repaired. This played hardly a role in most cases, but was significant in the presence of large frozen cores.

A1 frequencies were not computed in T(d) and O(h) symmetries.

A small error in the Fit-Correction terms in the bond energy has been detected and repaired. Effect on energy very system dependent, usually (much) smaller than 0.1 eV.

Labels of T1.u and T2.u subspecies in O(h) symmetry have been interchanged to match the most often encountered assignment of labels in the literature.

"SELECTED" optimization was not recognized (resulting in complete variation of all coordinates) if the type of coordinates was specified explicitly by the OPTIM subkey in the GEOMETRY block.

The LevelShift option (key: SCF) did not work correctly.

Miscellaneous

Restarts of geometry optimizations etc. have temporarily been disabled. The same holds for the computation of frequencies with restricted degrees of freedom. Both are related to the new file system and the fact that we are still fine-tuning the new file structure. The disabled options will be re-enabled in the next release.

For several keywords the units in which input is interpreted has been made absolute, independent of the units used for atomic coordinates input. This applies for instance to EFIELD (homogeneous Electric Field). Read the User's Guide carefully. Such changes in units are notified in bold face in the User's Guide.

Several keywords have been modified somewhat as regards suboptions defaults. See the User's Guide, in particular for the keywords GEOMETRY, SCF, OCCUPATIONS, CHARGE.

The key ELECTRONS has become obsolete. It can still be used, but will be removed in the next release. Its functionality is represented by OCCUPATIONS and CHARGE.

Atomic masses stored in the database have been adapted. They used to be isotope-averaged values. Now they correspond to the most abundant isotope. This affects frequencies (not much).

PRINT options have been added to completely suppress certain types of information on output. See the PRINT options FRAG and SFO.

Description of the ZORA relativistic option has been removed from the User's Guide. The ZORA formalism is still in development and the currently available basis sets in the ADF data base are not suitable for this approach: results can absolutely not be trusted.

All-electron basis sets have been added to the database. However, the files do NOT contain fit sets and hence cannot be used as such in a Create run. We do not yet have fit sets that are adequate for the all-electron basis sets. Using the standard fit sets from the other (frozen-core) data base files is NOT recommended.