

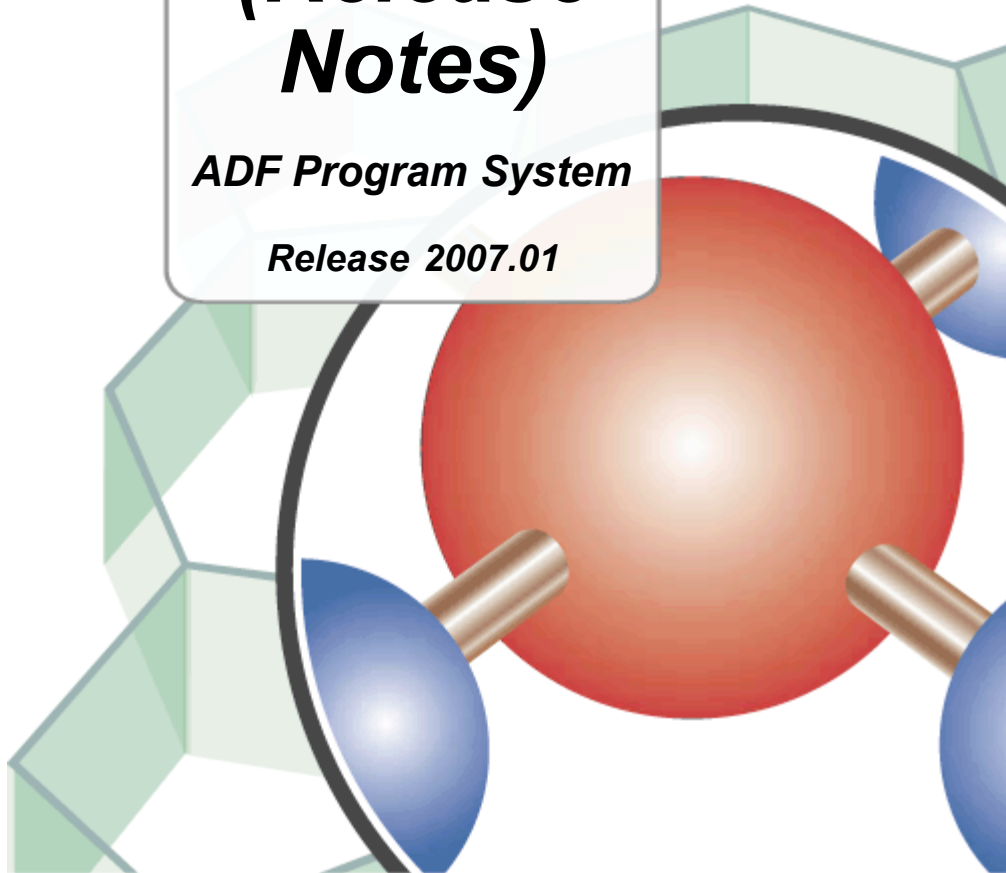


Scientific Computing & Modelling

ADF Updates (Release Notes)

ADF Program System

Release 2007.01



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This document summarizes the changes between successive versions of the ADF package, including BAND, property and utility programs, 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.

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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, ZORA cannot be used.

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.

Parallellization 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 Localisation 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 about '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. Were 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 Users Guide. 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` Users 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_iris64 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 Users 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 abort '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 abort '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 triviality. 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 behaviour.

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.