



Scientific Computing & Modelling

ADF 2014 Release Notes

**ADF Program System
Release 2014**

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Introduction

This document summarizes the changes between the last version of the ADF package (2014) with the previous version (2013). This includes changes in ADF, BAND, COSMO-RS, DFTB, ReaxFF, and GUIs (graphical user interfaces).

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.

To find out what changed in older versions, please see the previous [Release notes](#).

ADF

DFT-MBD dispersion corrected XC functional

The MBD@rsSCS method is implemented. MBD@rsSCS is designed to accurately describe long-range correlation (and thus dispersion) in finite-gap systems, including at the same time a description of the short-range interactions from the underlying DFT computation of the electronic structure. MBD@rsSCS includes both screening effects and treatment of the many-body vdW energy to infinite order, and employs a range-separation (r_s) of the self-consistent screening (SCS) of polarizabilities and the calculation of the long-range correlation energy. It has been parametrized for the elements H-Ba, Hf-Rn, and for the functional PBE and PBE0.

A. Tkatchenko, R.A. DiStasio Jr., R. Car, M. Scheffler *Accurate and Efficient Method for Many-Body van der Waals Interactions*, [Physical Review Letters](#) **108**, 236402 (2012)

A. Ambrosetti, A.M. Reilly, Robert A. DiStasio Jr., A. Tkatchenko, *Long-range correlation energy calculated from coupled atomic response functions*, [Journal of Chemical Physics](#) **140**, 18A508 (2014)

Intensity selected excitation energies

Use only those single orbital transitions, which are pairs of an occupied and virtual orbital, as guess vectors, for which the oscillator strength of the single orbital transition is larger than a threshold.

NMR spin-spin couplings with subsystem DFT

The calculation of NMR spin-spin couplings has been made possible in case of FDE.

Distance difference restraints in optimizations

Charge model 5

The charge model 5 (CM5) uses the Hirshfeld analysis in combination with a parametrization to yield atomic charges that can accurately reproduce dipole moments obtained from experimental results.

Improved density fitting with radial spline functions and Zlm's

The default density fitting scheme changed to ZlmFit instead of STO fit. The ZlmFit has been improved compared to the previous release. It has been included for almost all properties. It is possible to use locally a better fit (and grid), for example, for the active site in a molecule. Note that possibly not all options for frozen density embedding are working correctly, in which case one should use STO fitting.

M. Franchini, P.H.T. Philipsen, E. van Lenthe, L. Visscher, *Accurate Coulomb Potentials for Periodic and Molecular Systems through Density Fitting*, [Journal of Chemical Theory and Computation](#) **10**, 1994 (2014)

NMR chemical shifts: spin-orbit gauge correction term, unscaled ZORA

In the ADF2008.01 version a bug was introduced in the spin-orbit part of the calculated chemical shielding, which caused the calculated chemical shielding to be gauge dependent. This has been solved by including a spin-orbit gauge dependence term.

There is gauge dependence if the scaled ZORA method is used in the calculation of NMR chemical shieldings. Therefore the default method for NMR chemical shielding calculations is changed to use the unscaled ZORA method.

In case of hybrids one should use all electron basis sets if one wants to calculate NMR chemical shieldings. The use of frozen cores and hybrids gives gauge dependent results for the NMR chemical shieldings, therefore the NMR program will stop in this case.

Much smaller TAPE21 (.t21) result files

For analytical frequencies calculations the ADF result file (TAPE21 or .t21) is much smaller, especially for big systems.

GPGPU (CUDA) implementation for selected bottlenecks

A number of algorithms has been ported to CUDA, including evaluation of matrix elements by numerical integration on a grid. Using CUDA speeds up calculation of the Fock matrix for LDA and GGA functionals significantly. Also the performance of the energy gradients (forces) and analytical second derivatives (vibrational frequencies) is improved this way. Executables containing the GPU code (currently only for 64-bit Linux) will be available on request.

The paper by Hans van Schoot and Luuk Visscher describing the implementation and some benchmark results will be published early 2015.

Local quality

You now can have atom dependent (local) quality for fit and grid. Via ADFinput you can easily set this up using regions.

Distance cut-offs for Hartree-Fock exchange integrals changed

Stricter settings for distance cut-offs in calculating Hartree-Fock exchange integrals have been implemented.

Scalable SCF: better parallelization and less memory

A new SCF algorithm has been implemented, Scalable SCF. It scales more favorably with CPUs and also enables the study of larger systems through reduced memory usage. Scalable SCF is the default and is switched off for features for which it is not supported.

COSMO runs in parallel

The continuum solvation model COSMO now also runs in parallel, making it much faster on the typical machine.

RamanRange: include A1 representation to the list of Raman-active ones

BAND

Changed defaults

- NUMERICALQUALITY concept. Now the precision of all key algorithms can be controlled with a simple Quality key, and the overall NUMERICALQUALITY sets the default for these. Similar in spirit to the old Accuracy keyword. Does not affect the basis set or model Hamiltonian.
- Fit method: ZlmFit (was STO fit). This has two advantages, namely that the performance scales much better with system size, and secondly that the accuracy can be systematically improved (or worsened). Although the STO fit was quite accurate, especially when using the QZ4P fit, this was not so for the Lanthanide and Actinide series, for which the standard STO fit sets lacked functions with extra high l to describe partially filled f shells. Finally the screening function is no longer needed to calculate the Coulomb potential. This is now obtained via a proper summation of the multipole terms. The screening was inefficient with stretched unit cells, and not so accurate when having a dipole in the z -direction in a slab or linear chain calculation.
- Grid: Becke grid (was Voronoi grid). The advantage is that the error of the Becke grid is more smooth as a function of geometry, thus stabilizing geometry optimizations.
- KSpace: use a regular grid with a possibly different mesh per direction. The underlying algorithm is unchanged, namely the quadratic analytical tetrahedron method. The default sampling now depends on the size of the lattice vectors: the bigger the real space lattice, the smaller the number of k -points.
- Confinement: at lower levels of NUMERICALQUALITY use smooth confinement, for better localization of the basis functions. In principle this changes a bit (the radial behavior of) the basis set.
- Direct: no more reading/writing of basis functions from/to the disk. Does not affect the results.
- For NMR, and Response calculations the old defaults are used. The same is true for systems with cylinder symmetry.

Non-collinear spin

When doing a spin-orbit coupled relativistic calculation, it is now possible to use a non-collinear magnetization density. Normally the z -component of this vector is used as the polarization density in the non-relativistic XC functional. In the non-collinear model the size of the vector is used as spin-polarization.

LISTi and LISTb SCF convergence accelerators

For systems that are difficult to converge there is now the alternative to use the LISTi method. Typically this reduces the number of cycles needed to reach convergence, however it is quite a bit more expensive per SCF step, because an extra density fitting step is needed.

Significantly smaller RUNKF files

The number of matrices stored on the result file has been reduced to what is really needed for restarts. For k -points that are real only the real part of the matrices is stored.

Local quality

It was already possible to specify basis sets per atom. Now also the grid for numerical integration and the density fitting can be configured to be better for some atoms and worse for others. In the region of interest

you can use a good basis set and an accurate numerical grid and density fit, while using a simple basis set and reduced accuracy for the rest of the system.

DZP basis set

Like ADF, band now also has a DZP basis set. It is defined not for all elements, and it defaults to the TZP basis if it is not available for an element. The DZP basis set gives much better geometries than the DZ basis. It is however not advised for adsorption of organic molecules on transition metal slabs, because the TM atoms will be described with a TZP basis and the molecule with a DZP basis. This imbalance may lead to an artificial deformation of the slab.

DFTB

TD-DFTB excitation energies

DFTB now allows excited state calculations for molecular systems using single orbital transitions as well as time-dependent DFTB. Singlet-singlet as well as singlet-triplet excitations can be calculated. A filter can be used to reduce computational costs, for example by using only single orbital transitions that have a minimal oscillator strength. The PRIMME library is used for finding the lowest eigenvalues of a matrix with the Davidson method.

R. Rürger, E. van Lenthe, Y. Lu, J. Frenzel, T. Heine, and L. Visscher, *Efficient Calculation of Electronic Absorption Spectra by Means of Intensity-Selected TD-DFTB*, J. Chem. Theory Comp., submitted. Manuscript available on [arXiv](#).

Constrained optimizations

Geometry optimizations can be constrained with constraints for the distance between two atoms, an angle defined by three atoms, or a dihedral angle defined by four atoms.

QUASINANO2013.1 parameters

The QUASINANO2013.1 set of DFTB parameter files available in the ADF package are designed by Mohammad Wahiduzzaman et al. contains parameters for a large part of the periodic table (no f-elements). Note that the QUASINANO2013.1 set only contains the electronic part of the interaction, so that only the spectrum for a given geometry can be calculated, but no total energy, and thus also no forces. These parameters can be used in TDDFTB calculations, for example.

M. Wahiduzzaman, A.F. Oliveira, P.H.T. Philipsen, L. Zhechkov, E. van Lenthe, H.A. Witek, T. Heine, *DFTB Parameters for the Periodic Table: Part 1, Electronic Structure*, [Journal of Chemical Theory and Computation](#) **9**, 4006 (2013)

Density matrix purification and sparse matrix algebra

An alternative way to compute the density matrix corresponding to a given Hamiltonian is by means of the density matrix purification method. This method scales linearly with the system size when the Hamiltonian matrix is sparse and the HOMO-LUMO gap is large enough. This makes it especially useful for modeling large insulator or semi-conductor systems.

Conductance

The conductance program has been added. It is a program to calculate coherent transport in extended junctions consisting of two semi-infinite electrodes separated by a molecule using the DFTB method combined with the nonequilibrium Green's Function (NEGF) formalism.

Faster MOPAC

MOPAC has been made much more efficient by using mkl libraries and parallelization. For larger molecules, calculations can be up to two orders of magnitude faster than with previous MOPAC versions.

J.D.C. Maia, G.A.U. Carvalho, C.P. Manguiera, S.R. Santana, L.A.F. Cabral, and G.B. Rocha, *GPU Linear Algebra Libraries and GPGPU Programming for Accelerating MOPAC Semiempirical Quantum Chemistry Calculations*, *J. Chem. Theory Comp.* **8**, 3072-3081 (2012)

ReaxFF

Changes in the dihedral angle and conjugation terms

To solve a discontinuity problem at small bond orders for torsion angle and conjugation contributions the formula for $f(\text{BO})$. These terms correspond to expressions for f_{10} (eq. 10b) and f_{12} (eq. 11b) in the "ReaxFF: A Reactive Force Field for Hydrocarbons", J. Phys. Chem. A 2001, 105, 9396-9409 paper. The new expression for each term in f_{10} is now $[1 - \exp(-2 * \lambda_{23} * \text{BO}^2)]$ and in f_{12} it is now $\sin(\text{BO} * \pi/3)^4$. The new expressions ensure correct asymptotic behavior for the $dE/d\text{BO}$ for $\text{BO} \rightarrow 0$

Grand canonical Monte-Carlo (GCMC)

The GCMC as describe in two papers by Senftle et al. has been included as a tool with ReaxFF.

Thomas P. Senftle, Randall J. Meyer, Michael J. Janik and Adri C.T. van Duin, *Development of a ReaxFF potential for Pd/O and application to palladium oxide formation*, *J. Chem. Phys.* **139**, 044109 (2013)

Thomas P. Senftle, Adri C.T. van Duin, Michael J. Janik, *Determining in situ phases of a nanoparticle catalyst via grand canonical Monte Carlo simulations with the ReaxFF potential*, *Catalysis Communications* **volume 52**, 5 July 2014, Pages 72–77

Monte-Carlo force-field parameter optimization

An easy to use parallel optimization method for force-field parameters has been added. The method is based on the paper by Eldhose Iype et al.

E. Iype, M. Huetter, A.P.J. Jansen, S.V. Nedeia, C.C.M. Rindt, *Parameterization of a Reactive Force Field Using a Monte Carlo Algorithm*, *J. Comp. Chem.* **34**, 1143-1154 (2013)

GUI

Conformers

The ADF-GUI does have some basic support for handling conformers. This includes the generation of conformers, the refinement of conformers using different theoretical methods, and the calculation of properties like spectra (UV/Vis, IR, NMR, and others). These spectra are the weighted spectra of the individual conformers, typically using a Boltzmann weighting.

The different conformers to handle are stored in a .sdf file. This .sdf file is a standard SDF file, with the calculated energy in the title for each conformer. It also contains information were to find calculation results for the individual conformers, if present. The ADF-GUI uses RDKit to generate conformers, and to align and match conformers.

If you want to calculate something using the conformers of your molecule:

- Generate and view the conformers (and thus the .sdf file that contains them)
- Refine the structures of the conformers, for example with ADF (this gives a new .sdf file)
- Calculate the spectrum of interest for selected conformers
- View the Boltzmann averaged spectrum

A tutorial has been added to explain the conformers handling.

ADFinput support of new features, local quality, smaller files

There are many small changes to ADFinput to support all the new features in ADF, BAND, DFTB, MOPAC and so on. One of these features is to enable the automatic gzipping and gunzipping of KF files, in particular the t21 result file. This will reduce the size of the .t21 files significantly.

Editing of big systems with multiple molecules is now a little easier: you can use Regions to group molecules when moving them using the slider. This makes it much easier to move for example solvent molecules with respect to some surface.

Another important change is the support for the Numerical quality option in ADF and BAND. This includes the option to set the numerical quality (Becke integration, Zlm fit and basis set quality) per region.

ADFjobs ssh multiplexing

The use of ssh multiplexing (connection sharing) has been implemented in the ADFjobs. When used interaction with remote machines is typically much faster, and only a few ssh connections per remote machine are used. To use set the SCM_SSH_MULTIPLEXING environment variable. Note it only works with OpenSSH (thus NOT on Windows).

ADFspectra: Conformers handling, improved units handling

ADFspectra now can calculate averaged spectra for conformers. It also remembers its position and size on screen, and it remembers the units used per spectra type.

ADFmovie: improved ReaxFF and SDF support

ADFmovie can now read sdf files (currently mainly used for examining conformers). For ReaxFF result files the option to show / hide molecules of some type has been added, and the Molecules dialog is much easier to use.

ADFview new tools: Multilso, Clipping plane, diverging colormap, Dipole vector, Tensors

In ADFview the Multilso visualization option has been added. When used, multiple isosurfaces of the same field are created, colored by isovalue. When used with transparency or with a clipping plane this gives a much better view how a scalar field changes than a single isosurface. Please check out the tutorials!

Also a diverging color map has been introduced. For most properties it works better than the old style color map (rainbow) that is still available.

Finally, the dipole moment and several tensor properties can be visualized.

ADFoutput search and speed

ADFoutput now has a search field at the bottom, and is much faster when displaying large files.

UFF: new UFF4MOF

The UFF program now comes with UFF4MOF parameters for Metal-Organic Frameworks by M.A. Addicoat et al.

Matthew A. Addicoat , Nina Vankova , Ismot Farjana Akter , and Thomas Heine, *An extension of the Universal Force Field to Metal-Organic Frameworks*, [J. Chem. Theory Comput.](#) **10 (2)**, 880-891 (2013)

Scripting

Adfreport and adfprep both support much better BAND, MOPAC and DFTB in addition to ADF jobs. See the Scripting example in the ADF examples directory.

Adfreport and adfprepare now handle geometries from LT or IRC steps on a .t21 result file, as well as .sdf files and .cry files. This may be used to run single point calculations for the converged LT or IRC geometries, for example to see how orbitals change along the path.

The Prepare tool in ADFjobs also supports this (but more conveniently you can turn this on in ADFinput).

The scripting tools are also used to actually perform the conformer calculations. It takes only a few lines of shell scripts to set up calculations for all conformers. This is done by ADFinput automatically, but you may wish to have a look at the saved .run file to see how one may use adfprep and adfreport.

COSMO-RS: COSMO-SAC 2013-ADF

A new parametrization for COSMO-SAC has been included. In our COSMO-RS module, activity coefficients can be calculated according to this new COSMO-SAC 2013-ADF method, which includes a dispersion contribution in the mixture interaction.

Pure compound properties are not calculated according to the COSMO-SAC 2013-ADF method yet

R. Xiong, S. I. Sandler, and R. I. Burnett, *An Improvement to COSMO-SAC for Predicting Thermodynamic Properties*, *Ind. Eng. Chem. Res.*, **53**, 8265–8278 (2014).

Source code and compiling

- Configure has changed, check Install/configure -h for details.
- Compiling is now done with foray: python based parallel build system instead of yam
- Fortran source code consists of .f90 files instead of .d90 files which have to be preprocessed
- Default MPI version is now IntelMPI for Windows and Linux

License file request and installation

When starting a GUI module or any software (ADF, BAND etc) a script will verify that a license is available. If not, a dialog is present where the user can request a license.

The script contacts the SCM license server, possibly creating a license file, and/or returning a license file. If a license file is returned, it is installed automatically.

The old way of generating license info and installing license files received via email is also still available.

Changes in older versions

To find out what changed in older versions, please see the previous [Release notes](#).