

Using ADF: Some Comments and Examples

Michael Patzschke
Institut für Nukleare Entsorgung
Forschungszentrum Karlsruhe
Germany
`michaelp@chem.helsinki.fi`

02.06.2006

Abstract

A short introduction to ADF and its utilities is given. Advantages of ADF are highlighted. Two small input examples are given.

Outline

1. ADF Features
2. Internal And External Tools
3. The Fragment Analysis
4. Some Hints And Tricks
5. Relativistic Effects
6. Valence-Electron Methods
7. QM/MM Methods
8. Two Small Examples
9. Conclusions

ADF Features

- Amsterdam Density Functional ('pure DFT', no hybrid functionals, but ...)
- Spin restricted and unrestricted LDA,GGA's and meta-GGA's
- Newest Version : 2006.01
- 2005.01 includes : Single Point calculation, Geometry Optimization, Transition States, Frequencies and thermodynamic properties, Tracing a Reaction Path, Computation of any electronic configuration, Excitation energies, Oscillator strengths, Transition dipole moments, (Hyper)polarizabilities, Van der Waals dispersion coefficients, TDDFT, NMR chemical shifts and spin-spin coupling constants, QM/MM, COSMO, Tools for analyzing the results
- The main programme ADF is well parallelised and linear scaling techniques are in use
- ADF uses the full molecular point-symmetry group to speed up calculations (also non-Abelian groups)
- Basis sets up to quadruple- ζ quality are available for all elements of the periodic table up to E118
- Some properties are calculated with external programs: cpl, eprnmr, nmr, sd, disper

- ★ cpl : NMR spin-spin couplings
- ★ eprnmr : More or less obsolete, only Pauli
- ★ sd : Analytical first and second derivatives, only VWN or X- α , not recommended at the moment
- ★ nmr : Chemical shift (ZORA, Pauli, spin-orbit)
- ★ disper : Computes van der Waals coefficients up to C₁₀
- KF command-line utilities to edit TAPE files:
 - ★ pkf : Summary of TAPE file
 - ★ cpkf : Copies part of a TAPE file
 - ★ dmpkf : Converts TAPE file to ASCII format
 - ★ udmpkf : Convert ASCII-TAPE file to binary
 - ★ (dirac: Calculates relativistic potentials for atoms)
- Good graphical user interface, ADF-GUI, available (costs extra)
- Peculiarity 1 : Uses STO's rather than GTO's, fragment approach, may lead to problems when comparing energies
 - ★ Slater-type orbitals:

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{n-l} e^{-\zeta r} \quad (1)$$

Correct behaviour at the centre (electron cusp) and at large distance. Two centre inte-

grals difficult to solve analytically.

★ Gauss-type orbitals:

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \varphi)r^{2n-2-l}e^{-\zeta r^2} \quad (2)$$

Wrong behaviour at the centre (no cusp) and at large distance. Two centre integrals very easy to solve analytically.

- Peculiarity 2 : Fragment approach, only bonding energies between fragments are computed, no total energies
- Peculiarity 3 : ADF stores information like densities and molecular orbitals in binary TAPE files (architecture dependent)
- Very good documentation and commented input examples are available on the ADF homepage (<http://www.scm.com/>)

Tools - Internal and External

- Charges : Mulliken, Multipole fit, Voronoi, Hirshfeld
- Hirshfeld :

$$q_i = Z_i - \int \frac{\rho_i^{at}(r)\rho^{mol}(r)}{\sum_i \rho_i^{at}(r)} dv \quad (3)$$

Z_i nuclear charge, $\rho_i^{at}(r)$ spherically averaged ground-state atomic density of atom i in the molecule, $\rho^{mol}(r)$ molecular electron density.

- Voronoi : Polyhedra are constructed around fragments (e.g. the atoms) of a molecule, so that every point in a polyhedron is closer to the fragment than to any other fragment. These charges are not very useful as such but the change in charge upon formation of the molecule (VDD) agrees often closely with Hirshfeld charges.
- Bonding situation : Fragment analysis and different bond orders are automatically computed. Both are available for bonds between atoms and bigger fragments.
- Bonding situation, external tools : Interfaces for Baders AIM code and Weinholds NBO code exist. Licenses for NBO have to be bought separately

- MO's and Densities : Best to use the GUI. Almost all external programs need the ADF utilities.
- External tools: DGrid, Basin, NBO, Molekel, gOpenMol
- DGrid is a very useful free tool for calculating different properties like the electron localisation function, densities, spin densities, gradient of the density and more. Contact the author Miroslav Kohout for more information (kohout@cpfs.mpg.de), or have a look at <http://www.cpfs.mpg.de/ELF/> . The DGrid program works well together with gOpenMol

Fragment Analysis

- ADF calculations are done by first calculating the fragments (atoms or groups) and then calculation of the molecule defines by the fragments
- The fragment approach is natural for chemists, as they use to think of molecules made up from atoms or groups.
- Bonds between fragments can be analyzed, several theoretical methods exist
 - ★ Morokuma-Kitaura Decomposition
 - ★ Reduced Variational Space Analysis
 - ★ Symmetry Adapted Perturbation Theory (SAPT)
 - ★ Ziegler-Rauk (improved by Baerends) (DFT)
- Ziegler-Rauk : Bond formation in three steps
 1. Bring the fragment from infinite distance to final position, i.e. form a superposition of $\rho_A + \rho_B$ ($\Delta E = \Delta V_{\text{elstat}}$)
 2. Combine ρ_A and ρ_B to a wave function for the molecule, allowing only for Pauli-relaxation. ($\Delta E = \Delta E_{\text{Pauli}} = \Delta V_{\text{Pauli}} + \Delta T^0$)
 3. Relaxation of the system to its final ground state. This step involves mixing of orbitals. ($\Delta E = \Delta E_{\text{orbital-interaction}}$)

- Steps [1] and [2] are sometimes combined to a term called 'steric interaction'
- Some discussion about the meaning of the different terms exist, see e.g. F.M. Bickelhaupt and E.J. Baerends, "Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry" In: Rev. Comput. Chem.; Lipkowitz, K. B. and Boyd, D. B., Eds.; Wiley-VCH: New York, 2000, Vol. 15, 1-86.

Some Hints And Tricks

- As many centre integrals involving STO's are hard to solve analytically, ADF used a numerical method for the purpose. The integrals are calculated on a grid. The grid size can be changed by the user. Different types of calculations require different grid sizes. Numerical frequencies e.g. require a much tighter grid than single point calculations!
- Many different functionals are available in ADF. Self consistently it can only use LDA and GGA functionals. Hybrid functionals (containing Hartree-Fock exchange), SIC (self interaction corrected functionals) and meta-GGA's are available a posteriori. Special functionals for special types of calculations are available (for example functionals for excitation energy calculations)
- Molecular coordinates can be given in xyz form, as z-matrices or as delocalised coordinates
- Convergence can be slow sometimes, Fermi heating (also known as electron smearing) can be used. The so converged calculation can be used as a starting point for a new calculation without smearing. Different parameters to speed up convergence can be set. Here is an example that works quite well for actinides:

```
Occupations Keeporbitals=1000 Smearq=0
```

```
SCF
```

```
  Iterations 500
```

```
  mixing 0.5
```

```
  diis N=0
```

```
  lshift 1
```

```
End
```

- ADF has good restart capabilities. Restarts can be performed using the data from the TAPE21 file. If the job crashed, this file may be incomplete. In that case the TAPE13 file can be used.

Relativistic Effects I

- Dirac equation:

$$(c\alpha \cdot \hat{\pi} + \beta mc^2 - \phi + V_{ee})\psi = E\psi \quad (4)$$

- "Das traurigste Kapitel der modernen Physik ist und bleibt die Diracsche Theorie ... Um mich nicht weiter über ihn (Dirac) zu ärgern, sollte ich mich mit etwas gänzlich anderem befassen." (W.Heisenberg to W.Pauli)

- Elimination of the small component:

$$\hat{H}_D^{esc} = V + \frac{1}{2m}\sigma\hat{\pi} \left(1 + \frac{E - V}{2mc^2}\right)^{-1} \sigma\hat{\pi} \quad (5)$$

- Expansion of

$$K = \left(1 + \frac{E - V}{2mc^2}\right)^{-1} \approx 1 - \frac{E - V}{2mc^2} \quad (6)$$

leads to Pauli or Breit-Pauli Hamiltonian

- It is singular at the nucleus

- Only usable as perturbation
- Problem : Neglect of $E - V$ compared to $2c^2$ not valid in a central potential
- Is available in ADF, but it is strongly recommended to use ZORA (see below)

Relativistic Effects II

- Elimination of the small component in a slightly different way:

$$\hat{H}_D^{esc} = V + \frac{c^2}{2mc^2 - V} \sigma \hat{\pi} \left(1 + \frac{E}{2mc^2 - V} \right)^{-1} \sigma \hat{\pi} \quad (7)$$

and expansion of

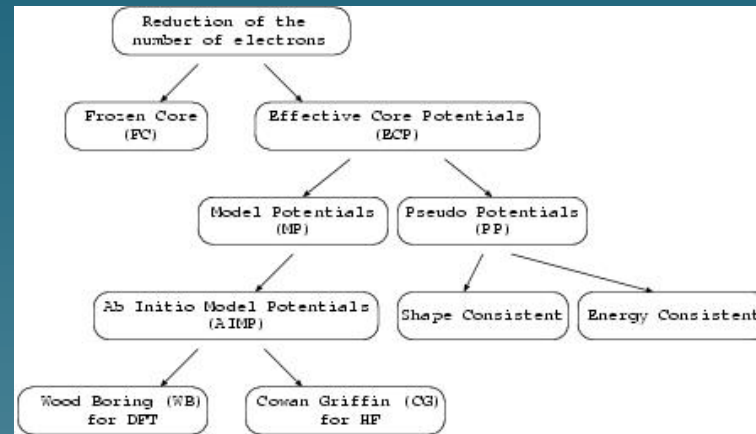
$$K' = \left(1 + \frac{E}{2mc^2 - V} \right)^{-1} \quad (8)$$

leads to ZORA and FORA which circumvents some problems of Breit-Pauli

- ZORA can be used variationally (FORA not)
- Has no singularities at the nucleus
- Is bounded from below up to Z=136
- Ignores effect of picture change (core states)
- Is available in ADF and should be used to treat relativistic effects
- For relativistic open-shell calculations two approaches are available, the collinear and the non-collinear approach. The latter is recommended

- If ZORA calculations are performed, special (ZORA) basis sets should be used
- If the frozen core approximation is used with ZORA, a relativistic frozen core for the atoms has to be generated. For this the helper routine 'dirac' is available.

Valence-Electron Methods



- Chemically the valence electrons are most important
- Different methods to treat only the valence electrons have been developed
- Best way: All electron calculations on the atoms, in the molecule keep the core orbitals frozen (unrelaxed) as they will not change to much. This is known as the frozen-core approach and it is integrated in ADF. Therefore no ab-initio model potentials (AIMP) or effective core potentials (ECP) are available in ADF. The size of the frozen core can be chosen, different basis sets for different frozen cores exist for all elements up to E118 (apart from H and He of course).

QM/MM Methods

- ADF can do QM/MM in the IMOMM and AddRemove coupling scheme
- Amber95 and Sybyl forcefield are available
- Force field parameters are adaptable
- Search for minima and transition states possible
- Utility pdb2adf creates an ADF input file from a pdb file
- The GUI helps very much with QM/MM input (e.g. choosing the QM region, adding solvent)

Some Small Examples

- Well documented sample inputs can be found in `$ADFHOME/examples/adf`
- First example of a geometry optimisation:

```
$ADFBIN/adf -n $NUMPROCS << eor
```

```
ATOMS
```

```
  H   .0000   .0000   .0000
```

```
  Br  .0000   .0000  1.4140
```

```
End
```

```
Basis
```

```
  Type DZ
```

```
  Core Large
```

```
End
```

```
XC
```

```
  GGA Becke Perdew
```

```
End
```

```
Geometry
```

```
End
```

```
End input
```

```
eor
```

- ★ Atoms are given here cartesian coordinates.
- ★ In the Basis section the basis set (double- ζ in this case) and the size of the frozen core are set
- ★ In the XC section the exchange and correlation functionals are set (see the manual for a list of available functionals)
- ★ The appearance of a Geometry section tells ADF to optimise the geometry, further parameters can be given here
- Second, slightly more elaborate, example:

```
$ADFBIN/dirac -n1 < $ADFRESOURCES/Dirac/Au.4d > $SCM_TESTOUTPUT
```

```
mv TAPE12 t12.rel
```

```
$ADFBIN/adf -n $NUMPROCS << eor  
Create Au $ADFRESOURCES/ZORA/TZ2P/Au.4d
```

```
Relativistic scalar zora  
CorePotentials t12.rel
```

```
End Input  
eor
```

```
mv TAPE21 t21.Au
```

```
$ADFBIN/adf -n $NUMPROCS << eor
```

```
Title Au2 relativistic optimization: scalar ZORA

Integration 6.5

Atoms Zmat
  Au 0 0 0
  Au 1 0 0 2.5
End

Fragments
  Au t21.Au
End

XC
  GGA Becke Perdew
End

Relativistic scalar ZORA
CorePotentials t12.rel

Geometry
  convergence grad=1e-4
End

End Input
eor
```

★ First the program dirac is used to create the frozen-core file t12.rel

- ★ Then the atomic fragments are defined with a simple ADF run on the atom, the TAPE21 file is saved (here as t21.Au)
- ★ A ZORA calculation is performed, therefore the appropriate ZORA basis set must be used
- ★ Then the geometry optimisation is performed, the geometry is given in z-matrix format this time

Conclusions

- Pro's
 - ★ ADF is fast and well parallelized
 - ★ Different basis sets for all elements available (FC)
 - ★ It offers a lot of functionality, especially analysis tools
 - ★ Very good support
- Con's
 - ★ SCF-convergence for fragments and numerical Hessians can be difficult to achieve
 - ★ Missing analytical Hessians
 - ★ Generating MO plots is rather tedious without the GUI
 - ★ Input philosophy needs getting used to
 - ★ Basis set comparison with other programs is difficult