Investigating Chemical Bonding with ADF

Winter School on Modeling Chemical and Biological (Re)Activity – MCBR

IIIT Hyderabad

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Structure

About ADF

- Stands for **A**msterdam **D**ensity **F**unctional. Developed by Scientific Computing & Modelling (SCM) based in Amsterdam, the Netherlands. Originating in the 1970s.
- Quantum chemistry program for many tasks.
- Relativity: ZORA scalar relativistic and spin-orbit coupling
- All-electron basis sets for Z=1-118: no artifacts from ECPs
- Spectroscopy: NMR, UV/Vis, IR, Raman, X-ray, ESR, CD, Mössbauer, ...
- Many chemical analysis tools: fragments, **energy decomposition**, **EDA**-**NOCV**, (P)DOS, AIM, ELF, NCI, SEDD, NBO
- XC functionals: GGA, (range separated) hybrid, (hybrid)metaGGA, dispersion-corrected (D3-BJ, dDsC)

About ADF

Advantages

- Many quantum-chemical tools implemented
- Relativistic effects included via ZORA
- Easy and intuitive syntax
- Good powerful GUI (ADFView)

Disadvantages

- Slow geometry optimization
- Sometimes cryptic error messages
- Sometimes serious convergence problems

General Syntax

```
Title h2o

xc (Functional)
 lda vwn
 gga becke perdew
end

charge 0

atoms
O          0.000000    0.000000    0.033961
H          0.000000   -0.766097    0.630503
H          0.000000    0.766097    0.630503
end

FRENKING-BASIS TZ2P+ (Basisset)
...
```

General Syntax

`...`
`!symmetry C(2V)` *(Symmetry and Comment symbol !)*

`!occupations` *(Occupations Block and Comment symbol !)*
`!A1`
`!B2`
`!end`

`scf` *(SCF Options)*
` iterations 300`
` converge 0.00000100 0.00100000`
`end`

`integration 7.0 7.0` *(Integration Grid)*

`end input`

A Little Bit of Theory

How does an EDA work?

1. A system A—B is cut into 2 (or more) fragments along an interesting bond: A—B $\rightarrow$ A and B.
2. The fragments are calculated each seperately in a certrain electronic state (only singlepoints, no optimization!)
3. The fragments are then overlapped again in the geometry which they had in the complete system AB but are not allowed to interact with each other: A + B $\rightarrow$ A$|$B
4. The electrostatic attraction between the fragments is calculated quasi-classically (ΔE_{elstat}).

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A Little Bit of Theory

How does an EDA work?

1. The wavefunctions are allowed to overlap. The resulting wavefunction has to been antisymmetrized which increases the energy (ΔE_{Pauli}).
2. The orbitals of the fragments are allowed to relax and electrons get redistributed to achieve the electronic state of the complete system. This lowers the energy again (ΔE_{orb}).
3. ΔE_{orb} can be decomposed into different contributions $(\sigma, \pi, \ldots)$ via symmetry or EDA-NOCV.
4. In addition to the intrinsic energy, the preparation energy ΔE_{prep} has to be considered for the right dissociation energy: $-D_e = \Delta E_{int} + \Delta E_{prep}$

A Little Bit of Theory

Energy Components

- Decomposition of binding energy into different contributions.
- ΔE_{int}: Total intrinsic interaction energy between two (or more) fragments.
- ΔE_{elstat}: Attractive, quasi-classical electrostatic interaction between the electrons and the nuclei.
- ΔE_{Pauli}: Repulsive energy between electrons of the same spin. Comes from the antisymmetrization of the wavefunction.
- ΔE_{orb}: Comes from the relaxation of the fragment orbitals (mixing). Most interesting contribution to ΔE_{int} for a chemist.

Important Files and Commands

- **filename.in**: Input file.
- **filename.out**: Output file.
- **filename.t21**: Binary output file. Can be opened with ADFView.
- `source /home5/paul/scripts/subrc.sh`: First command which has to be executed to get all necessary scripts.
- `subadf filename.in`: Submit a calculation onto the cluster.
- `myq`: See your jobs in the queue.
- `myq -a`: See all jobs in the queue.
- `qdel job-number`: Delete a job.

Crash Course: ADFView

- To change appearance: Use the big SCM button in the top left corner.
- To plot an orbital: Properties → HOMO.
- To change shown orbital: Click on orbital name at the bottom.
- To change appearance of orbitals: Click on 'Isosurface Double' and then on 'Show Details' and change for example the opacity, etc.
- Very special feature of ADFView: You can open multiple fragments (new switch appears under the picture). Useful for finding overlapping fragment orbitals.

Singlepoint Calculation of H_2O

Try it out

- Copy `/home5/paul/input-files/1-basics/1.1.h2o_s/h2o-adf.in` to your home directory and submit the calculation with `subadf h2o-adf.in`

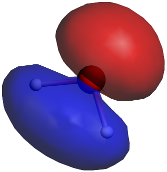
Familiarize yourself with the output

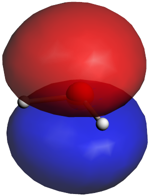
1. Search for the symmetry and look at the orbital occupations (SFO)!
2. How is the energy defined? Where do you find it?
3. Open the .t21 file with ADFView and look at the HOMO, the HOMO-1 and the LUMO! Save pictures of it as .png files!

Singlepoint Calculation of H_2O

Familiarize yourself with the output

1. Search for the found symmetry: C_{2v}
2. Look at the orbital occupations: *4e$^-$ in A1, 2e$^-$ in B2 and 2e$^-$ in B1 orbitals. Total of 8e$^-$. Note: Only valence electrons are included!*
3. Where do you find the energy? How is it defined? *The energy is given at end of the file and is given relative to the atomic ground states of the single atoms.*





Geometry Optimization of H_2

To optimize a system, include this block in the input

```
geometry
converge grad=1e-4
end
```

Try it out

- Copy and submit `/home5/paul/input-files/1-basics/1.2-h2_o/h2-adf-opt.in`
- Find the optimized structure at the end of the file.

DIY: Geometry Optimization of H_2O

DIY

- Guess a reasonable structure for water and optimize it with ADF.

EDA of H_3B–CO

Performing an EDA

1. Optimize the whole system.
2. Copy the coordinates of the optimized structure into two singlepoint input files. Use the ! to comment the respective fragment out. Submit the calculations. You should obtain two .t21 files.
3. Prepare an EDA input file, use the optimized geometry, declare which atom belongs to which fragment and specify the paths to the .t21 files.
4. Look into the newly obtained .epa file for your EDA results. Use ADFView to understand which interaction is which.

EDA of H_3B–CO

Using the Comment Symbol

```
atoms
B           0.000000    0.000000   -1.329393
H           0.586074    1.015110   -1.647361
H           0.586074   -1.015110   -1.647361
H          -1.172149    0.000000   -1.647361
!C          0.000000    0.000000    0.179517
!O          0.000000    0.000000    1.322604
end
```

EDA of H_3B–CO

The EDA Input File

```
Title h3b-co-EDA

xc
 lda vwn
 gga becke perdew
end

charge 0

atoms
B          0.000000    0.000000   -1.329393 f=f1
H          0.586074    1.015110   -1.647361 f=f1
H          0.586074   -1.015110   -1.647361 f=f1
H         -1.172149    0.000000   -1.647361 f=f1
```

EDA of H_3B–CO

The EDA Input File

```
C          0.000000     0.000000     0.179517 f=f2
O          0.000000     0.000000     1.322604 f=f2
end

FRENKING-BASIS TZ2P+

fragments /home/paul/workshop/2-da-eda/2.1-h3b-co_eda
f1 h3b-adf.t21
f2 co-adf.t21
end
```

EDA of H_3B–CO

The EDA Input File

```
scf
 iterations 300
 converge 0.00000100 0.00100000
end

integration 7.0 7.0

end input
```

EDA of H_3B–CO

Try it out

- Copy the input files from `/home5/paul/input-files/2-da-eda/2.1-h3b-co_eda/`
- Submit the fragment files and change the path to the .t21 files in the eda input file which you submit afterwards.

Check your results

1. Have a look at the .epa file.
2. Use ADFView with the fragment .t21 files to determine which orbital contribution is which.

EDA of H_3B–CO

The .epa file

```
                                 kcal/mol
                               ----------
Total Bonding Energy:              -50.20
                               ----------
Total Pauli Repulsion:             151.70
Total El.stat. Interaction:        -73.84
Total Orbital Interactions:       -128.07
Orbital Interactions:
A1:                                -90.93    ( 71.00%)
A2:                                  0.00    ( -0.00%)
E1:                                -37.14    ( 29.00%)
 36.57 % Elst. Interaction //  63.43 % Orb. Interaction
```

EDA of H_3B–CO

A1 (σ–type donation)

E1 (π–type back donation)

EDA of H_3B–CO

The Bonding Situation

- Quite strong donor–accpetor bond ($\Delta E_{int} = –50.2$ kcal/mol).
- Attractive interactions dominated by the orbital term (63.4%).
- Largest contribution to orbital term: σ–type donation (71%).
- Nevertheless: Notable π–type back donation (hyperconjugation): –37.1 kcal/mol.

EDA of $W(CO)_6$

Try it out

- Copy the input files from `/home5/paul/input-files/2-da-eda/2.2-w-co6_eda/`
- Submit the fragment files and change the path to the .t21 files in the eda input file which you submit afterwards.

Check your results

1. Have a look at the .epa file.
2. Use ADFView with the fragment .t21 files to determine which orbital contribution is which.

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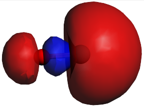
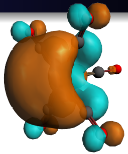
EDA of $W(CO)_6$

The .epa file

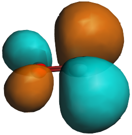
```
                                   kcal/mol
                                 ----------
Total Bonding Energy:                -49.61
                                 ----------
Total Pauli Repulsion:               118.94
Total El.stat. Interaction:          -89.84
Total Orbital Interactions:          -78.70
Orbital Interactions:
A':                                  -57.50    ( 73.06%)
A":                                  -21.20    ( 26.94%)
 53.30 % Elestat. Interaction //  46.70 % Orb. Interaction
```

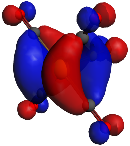
EDA of $W(CO)_6$



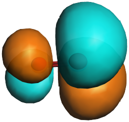


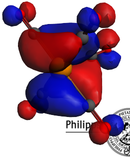
A' (σ–type donation)





A' (π–type back donation)





A'' (π–type back donation)

EDA of $W(CO)_6$

The Bonding Situation

- Quite strong donor–accpetor bond ($\Delta E_{int} =$ –49.6 kcal/mol).
- Largest contribution to orbital term: A' (73.1%) (includes σ **and** π because of C_s symmetry!)
- A" contribtion: –21.2 kcal/mol (only π)

DIY: EDA of HF

DIY

- Guess a reasonable structure for HF and optimize it with ADF.
- Perform an EDA with H^+ and F^- as fragments in a C(LIN) symmetry.
- How large is the σ and the π contribution?

DIY: EDA of HF

The .epa file

```
                                      kcal/mol
                                    ----------
Total Bonding Energy:                  -380.98
                                    ----------
Total Pauli Repulsion:                    0.00
Total El.stat. Interaction:            -241.55
Total Orbital Interactions:            -139.43
Orbital Interactions:
SIGMA                                  -113.67    ( 81.52%)
PI:                                     -25.76    ( 18.48%)
DELTA                                     0.00    ( -0.00%)
PHI:                                      0.00    ( -0.00%)
 63.40 % Elstat. Interaction //  36.60 % Orb. Interaction
```

Unrestricted Fragments

The fragoccupations block in the EDA file

`fragoccupations` *(begin block)*
`f1` *(fragoccupations for fragment 1)*
`S 1//1` *(occupations for S: α electrons//β electrons)*
`P 3//0` *(occupations for P: α electrons//β electrons)*
`subend` *(end of sub block)*
`f2` *(fragoccupations for fragment 2)*
`S 1//1`
`P 0//3`
`subend`
`end`

Unrestricted Fragments

Why so complicated?

- Unpaired electrons in ADF are treated as semi-unrestricted: $1e^- = \frac{1}{2}\alpha e^- + \frac{1}{2}\beta e^-$
- To overcome this you have to tell ADF in the final EDA calculation which electrons should have which spin. Otherwise, your results will be meaningless.

Unrestricted Fragments

Remember!

1. If you are breaking bonds homolytically, you **need** to specify the spins in the fragoccupations block.
2. Investigate the occupations of the fragment singlepoint calculations (output, ADFView) and note the occupations of the orbital. Depending on the symmetry they can be denoted S, P, D ...; A1, B1, B2 ...; A', A"; etc.
3. Decide which fragment should be be occupied by α electrons and which are occupied by β electrons.
4. If you are having only doubly occupied orbitals you don't need to do this.

EDA of N_2

Try it out

- Copy the input files from `/home5/paul/input-files/3-es-eda/3.1-n2_eda/`
- Submit the fragment files and change the path to the .t21 files in the eda input file which you submit afterwards.

Check your results

1. Have a look at the .epa file.
2. Use ADFView with the fragment .t21 files to determine which orbital contribution is which.

EDA of N_2

The .epa file

```
                                    kcal/mol
                                  ----------
Total Bonding Energy:                -240.23
                                  ----------
Total Pauli Repulsion:                802.21
Total El.stat. Interaction:          -312.79
Total Orbital Interactions:          -729.65
Orbital Interactions:
SIGMA                                -478.74    ( 65.61%)
PI:                                  -250.91    ( 34.39%)
DELTA                                   0.00    ( -0.00%)
PHI:                                    0.00    ( -0.00%)
 30.01 % Elstat. Interaction //  69.99 % Orb. Interaction
```

The occupations block

The occupations block in the fragment singlepoint file

```
occupations  (Start of the occupations block)
A1 2 1       (Occupations of the A1 orbitals)
B1 2         (Occupations of the B1 orbital)
B2 1         (Occupations of the B2 orbital)
end
```

Examples for occupation numbers

- All occupation numbers can be summed up: A1 2 2 2 = A1 6
- All occupation numbers can be summed up even with unpaired electrons: A1 2 2 2 1 = A1 7
- To leave an orbital empty use a 0: A1 2 2 0 2 2. Summing up still works (= A1 4 0 4)
- Some irreducible representations (E1, etc.) are fully occupied with 4 (or more) electrons. In these cases a 2 means half occupied.

EDA of C_2H_4

Try it out

- Copy the input files from `/home5/paul/input-files/3-es-eda/3.2-c2h4_eda/`
- Submit the fragment files and change the path to the .t21 files in the eda input file which you submit afterwards. Note the fragoccupations block!
- Also: Comment the occupations block in the fragment files and submit them again. What occupation does ADF choose?

Check your results

1. Have a look at the .epa file.
2. Use ADFView with the fragment .t21 files to determine which orbital contribution is which.

EDA of C_2H_4

The .epa file

```
                                  kcal/mol
                                ----------
Total Bonding Energy:              -191.19
                                ----------
Total Pauli Repulsion:              281.01
Total El.stat. Interaction:        -182.05
Total Orbital Interactions:        -290.15
Orbital Interactions:
A1:                                -210.81    ( 72.66%)
A2:                                   0.00    ( -0.00%)
B1:                                  -9.53    (  3.28%)
B2:                                 -69.81    ( 24.06%)
 38.55 % Elstat. Interaction //  61.45 % Orb. Interaction
```

EDA of GaMe

Systems with unpaired electrons

- Use the following lines in the head of the file for a molecule in the triplet state (2 unpaired electrons):
- `unrestricted`
  `charge 0 2` *(2: Number of unpaired electrons)*

EDA of GaMe

Try it out

- Copy the input files from `/home5/paul/input-files/3-es-eda/3.3-c2h4_eda/`
- Submit the geometry optimization file and copy the optimized coordinated into the fragment files and the eda input file. Change the path to the .t21 files in the eda input file which you submit afterwards. Note the occupations and the fragoccupations block!
- Also: Comment the occupations block in the fragment files and submit them again. What occupation does ADF choose?

Check your results

1. Have a look at the .epa file.
2. Use ADFView with the fragment .t21 files to determine which orbital contribution is which.

EDA of GaMe

The .epa file – not finished!

```
                                    kcal/mol
                                  ----------
Total Bonding Energy:                -184.58
                                  ----------
Total Pauli Repulsion:                201.90
Total El.stat. Interaction:           -97.37
Total Orbital Interactions:          -289.11
Orbital Interactions:
A':                                  -285.67     ( 98.81%)
A":                                    -3.44     (  1.19%)
 25.19 % Elstat. Interaction //  74.81 % Orb. Interaction
```

DIY: EDA of C_2F_4

DIY

- Perform an EDA of C_2F_4 as fragments in a C(2V) symmetry. Use the geometry of C_2H_4 as a starting point.
- How large is the σ and the π contribution?

DIY: EDA of C_2F_4

The .epa file

```
                                    kcal/mol
                                  ----------
Total Bonding Energy:                -187.25
                                  ----------
Total Pauli Repulsion:                303.65
Total El.stat. Interaction:          -179.84
Total Orbital Interactions:          -311.06
Orbital Interactions:
A1:                                  -216.94     ( 69.74%)
A2:                                    -0.55     (  0.18%)
B1:                                   -11.35     (  3.65%)
B2:                                   -82.23     ( 26.44%)
 36.63 % Elstat. Interaction //  63.37 % Orb. Interaction
```

ΔE_{orb} as a Criterion for the Best Fragment Occupation

The problem: Many electronic configurations are possible for the fragments

- Singlet vs triplet!
- Ionic vs covalent!
- Electron-sharing vs donor–acceptor!

Using ΔE_{orb} as a Criterion:

- A highly negative value of ΔE_{orb} means: A lot of electron density has to be moved in order to have the electron distribution as in the complete molecule.
- The closer ΔE_{orb} is to Zero the better the model is to the physical reality.

DIY: EDA of HF (homolytically vs heterolytically splitting)

DIY

- Perform an EDA of HF with H and F as fragments in C(LIN) symmetry.
- Compare the value of ΔE_{orb} with the EDA of the heterolytically split HF.

DIY: EDA of HF (homolytically vs heterolytically splitting)

The .epa file

```
                                     kcal/mol
                                   ----------
Total Bonding Energy:                 -181.83
                                   ----------
Total Pauli Repulsion:                 392.36
Total El.stat. Interaction:            -85.40
Total Orbital Interactions:           -488.79
Orbital Interactions:
SIGMA                                 -314.32    ( 64.31%)
PI:                                   -174.46    ( 35.69%)
DELTA                                    0.00    ( -0.00%)
PHI:                                     0.00    ( -0.00%)
 14.87 % Elstat. Interaction //  85.13 % Orb. Interaction
```

DIY: EDA of HF (homolytically vs heterolytically splitting)

Note:

ΔE_{orb} provides only a guideline to the best fragmentation, but which fragmentation you choose in the end is determined by chemical intuition and the problem which you are trying to solve. In this case, a $H^+ + F^-$ fragmentation makes no sense as we are looking at a gas phase environment where only homolytical bond breaking will occur.
If some (polar) solvent would be included, this fragmentation would be the more sensible choice.

A Brief Introduction into the EDA-NOCV (**N**atural **O**rbitals for **C**hemical **V**alence)

- The orbital terms of molecules with no symmetry cannot be decomposed with the standard EDA.
- In short: The EDA-NOCV observes the **electron flow** when overlapping the fragments to come the final electron distribution.
- The electron flow is calculated via NOCVs. Each NOCV has a eigenvalue v assigned to it which shows how many electron are being moved into or out of the NOCV. The NOCVs are paired according to their eigenvalues and are then called NOCV pairs.
- NOCV pairs can be superimposed and are then called deformation densities. These are used to assign contributions of the orbital term to certain orbital interactions of the fragments in a compact way.
- In the deformation densities, the electrons flow from **red** → **blue**.

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How to Perform an EDA-NOCV

Necessary steps:

1. Perform all the steps similar to the ones in the standard EDA
2. Add the following lines to the EDA input:

```
symmetry NOSYM
ETSNOCV
PRINT ETSLOWDIN
```

3. For electron-sharing bonds use: `ETSLOWDIN-unrestricted`

How to Perform an EDA-NOCV

Interpretation of the results:

1. Open the output and look for the 'SFO decomposition of Delta rho k'. Here the energy contributions to the orbital are ordered by their eigenvalues.
2. Visualize the deformation densities with ADFView: 'Properties', 'HOMO', 'NOCV Def Densities'. Change contour value to 0.005 (or similar values) to see something.
3. Use the deformation densities to assign the contributions up to a certain cut-off energy (say, 3 kcal/mol).

EDA-NOCV: H_3B–NH_3

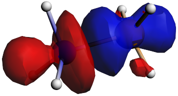
Try it out

- Copy the input files from `/home5/paul/input-files/5-eda-nocv/5.1-h3b-nh3_eda-nocv`
- Submit the fragment files and change the path to the .t21 files in the eda input file which you submit afterwards. Note the additional lines!

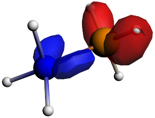
Check your results

1. Have a look at the .epa file.
2. Use ADFView with the eda .t21 file to determine which eigenvalue belongs to which orbital contribution. Look into the output and determine the amount of donation and back-donation.

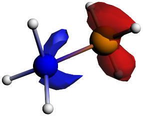
EDA-NOCV: H_3B–NH_3



$v = 0.5630$
ΔE = -77.2 kcal/mol



$v = 0.1909$
ΔE = -4.8 kcal/mol



$v = 0.1468$
ΔE = -3.7 kcal/mol

DIY: EDA-NOCV: C_2H_4

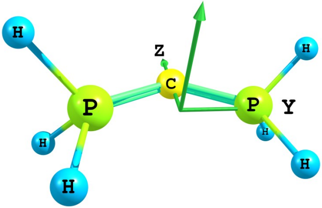
DIY

- Perform an EDA of C_2H_4 with CH_2 as fragments in C(2v) symmetry.
- Perform an EDA-NOCV in addition to the EDA and see if you get the same values for the donation and the back-donation.
- **Note:** You will get deformation densities for the α **and** the β-electrons when viewing the orbitals. In a simple case like this, it is sufficient to only look at one type (α) as the corresponding β-electrons are just the symmetrical equivalents.
- **Hint:** Be sure to check the right lines in the output: First, all the α-electrons are listed, then the β-electrons and lastly the sums (α + β-electrons). Doublecheck if the sums are calculated right. When in doubt, add α and β contributions by hand.

DIY: EDA-NOCV: Carbone

DIY

- Use `.../5-eda-nocv/5.3-carbone_eda/geom.xyz` as a start geometry.
- Perform an EDA-NOCV of the carbone $C(PH_3)_2$in C(2v) symmetry. The fragments are C ($s^2p_\perp^2p_{||}^0p_\sigma^0$) and $(PH_3)_2$.
- How large are the contributions for donation and back-donation?



Here: $p_\perp$ = x-axis, $p_{||}$ = y-axis, p_σ = z-axis.

DIY: EDA-NOCV: Carbone

Results:

- σ: –312.3 kcal/mol
- $\pi_{||}$: –190.4 kcal/mol
- $\pi_{\perp}$: –61.4 kcal/mol

Thanks

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