



Scientific Computing & Modelling

# Teaching in ADF - BSc exercises

**ADF Program System  
Release 2014**

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These teaching exercises have been designed by Célia Fonseca Guerra and have been used to teach BSc. computational chemistry courses at the Vrije Universiteit Amsterdam.

## **Discounted teaching-only licenses; free 30-day evaluation**

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## **Teaching exercises**

# Exercise 1: Tutorial and Basis sets

## Objective Exercise 1

In this exercise you will learn to use the Graphical User Interface (GUI) of the Amsterdam Density Functional (ADF) program and learn about basis sets, which determine the accuracy but also the computation time of the calculation.

### 1.1 How to work with a quantum chemical program

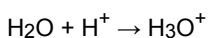
A good start to get an idea how to use the ADF-GUI is to watch the [Tutorial Videos](#). Watch Tutorial 1 (geometry optimization of ethanol) and Tutorial 3 (vibrational frequencies of ethane). After watching these, go to the [Tutorial page](#), and perform Tutorial 1 yourself.

### 1.2 Benchmarking: Choice of the basis set

To determine whether a basis set will achieve satisfactory results we can look at the following criteria:

- Compare with experimental results. The results will be close to identical when the basis set is optimal
- Compare with high level ab initio calculations. Again, the larger the agreement, the better the basis set.
- When neither results are available, a different strategy is called for. We will perform the calculation with increasingly larger basis sets, until the property we are interested in is no longer affected by extending the basis (basis set convergence).

In this exercise we will calculate the proton affinity (PA) of water with different basis sets. The definition of the PA of water is the energy released (positive quantity!) in the following reaction:



Draw a water molecule in ADFinput and repeat the following procedure with basis sets SZ, DZ, DZP, TZP, TZ2P and QZ4P:

- Perform a geometry optimization, use for the XC potential GGA BP
- Collect the following geometrical data in a table: the O-H distance, the H-O-H angle and the energy
- Calculate the proton affinity for water for each basis set. In order to do this you will have to calculate the energy of  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  as well.

Note that the set-up and analysis of multiple calculations can be automated (see Tutorial 10, basis sets for  $\text{NH}_3$ ).

## Questions Exercise 1

- For which basis set has the bond length, bond angle and proton affinity converged?
- Which basis set would you choose when you are interested in the geometry of a large molecule? Why?

- You have measured the proton affinity of lysine in the laboratory, but you do not know whether this corresponds to the carbonyl group or the amino-group. Which basis set would you choose to determine this? Why?

Make a report in which you also answer these question (length of report max 2 pages).

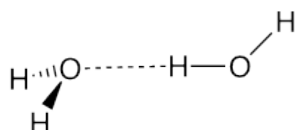
## Exercise 2: Choosing a Density Functional

### Objective Exercise 2

How to choose the right functional for DFT calculations on your system? There are many different exchange-correlation functionals available. Typically, we need a benchmark against which to compare. Either previously published DFT calculations that perform well for similar systems, an experimental value, or a high-level *ab initio* calculation on a model system. In this exercise we will test different functionals for the geometry of the water dimer.

### 2.1 Hydrogen Bonding

Normally, we look up in the literature which approximation of the exchange-correlation functional we should use for our chemical problem that we want to investigate. In this exercise you are going to perform your own benchmark for hydrogen bonds. You will do this for different functionals. The system that you will benchmark is the water dimer:



The hydrogen bond energy and length depends on the employed basis set and functional in the calculation. From [exercise 1](#) we know that the TZ2P basis set is a choice that will produce reliable results.

- Start ADFinput and create the water dimer. Optimize this geometry with the following functionals: GGA BP, BLYP-D, BLYP-D3, B3LYP and two other functionals which you can choose by yourself. Write down the hydrogen bond length and the total energy. Note that, like with basis sets, calculations with various functionals may be set up and analyzed at once using the adfprepare and adfreport tools. Useful if you need to do this more often in the future.
- Also determine the total energy of an isolated water molecule, use this result to determine the hydrogen bond energy.

### Question Exercise 2

The highest level *ab initio* calculations predict an O-O distance of 2.92 Å and a hydrogen bond energy of -21.05 kJ/mol (Phys. Chem. Chem. Phys., 1999, 1, 3073-3078). Which functional would you choose for hydrogen-bonded systems?

Make a report (max 1 page) in which you also answer this question.

## Exercise 3: Performing an NMR Calculation

### Objective Exercise 3

In this exercise you will learn how to perform NMR chemical shift calculations with ADF.

### 3.1 Hydrogen Bonding

NMR is a widely used technique to identify chemical compounds, but sometimes calculations are needed to interpret the results. In this exercise you will learn how to perform NMR calculations. This will be done for ethane, ethene and ethyne.

- a. Start with optimizing these molecules on the GGA BP/TZ2P level. Perform an NMR calculation on these optimized structures. You can do this by choosing 'NMR' in the 'properties' tab, and select one proton for which you want to calculate the NMR shielding. Make sure that both isotropic shielding constants and full shielding tensor are going to be printed. In the main menu set core to 'None' and perform a single point calculation.
- b. The chemical shift ( $\delta$ ) of a molecule 'A' with reference to TMS (tetramethylsilane) can be determined by also calculating the NMR properties for TMS and then to subtract the chemical shift of 'A' from that of TMS:  $\delta(\text{TMS}) - \delta(\text{A})$ . Draw and optimize TMS at the same level (BP/TZ2P) and calculate the chemical shift of an H atom, as in **a**.

### Questions Exercise 3

- What is the  $^1\text{H}$  chemical shift of ethane, ethene and ethyne with TMS as a reference?
- Are these calculated chemical shifts in agreement with experiment? You can find experimental NMR results in elementary organic textbooks and scientific papers.

Make a report (max 1 page) in which you answer these questions.

# Exercise 4: Symmetry in Calculations

## Objective Exercise 4

In this exercise you will learn how to discover symmetry with the ADFGUI and how symmetry can be exploited to speed up calculations.

### 4.1 Rotation axis

Draw a methane molecule in the ADFinput window and symmetrize the structure by clicking on the asterisk at the bottom. Optimize the structure at the GGA BP/DZP level.

- Are all the bond lengths identical? How many  $C_3$  axes does methane have and can you describe them? (A  $C_3$  axis leaves the molecule unaltered when rotating over  $120^\circ$ )
- Now replace a hydrogen atom by a chloro atom, again symmetrize and optimize. Are all bond lengths identical now? How many  $C_3$  axes does this molecule have?
- Now replace a second hydrogen atom by another chloro atom. Symmetrize and optimize once more. How many  $C_3$  axes can you find?

### 4.2 Formaldehyde

Create a formaldehyde molecule in ADFinput, symmetrize and optimize at the GGA BP/DZP level.

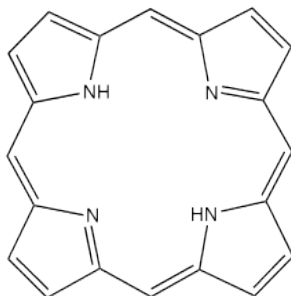
- How many mirror planes does formaldehyde have? Can you describe them?
- Use ADFview to look at the HOMO of formaldehyde. Are they symmetric or antisymmetric in the mirror planes you found earlier?
- What about the HOMO-1?

### 4.3 Cost of calculation and nodal planes in orbitals

- Create a benzene molecule and do not presymmetrize this time. Click on the tab 'Details', then click on 'Symmetry' and set 'Symbol' to 'Nosym'. Optimize the benzene molecule at the GGA BP/TZ2P level. Take notice of the elapsed time, this will be displayed in your logfile.
- Now symmetrize and set 'Symbol' to 'Auto'. This means that ADF makes use of the symmetry of the molecule and therefore should be faster. Is this indeed the case? Which symmetry group does ADF employ for benzene?
- A nodal plane is a plane in an orbital in which the probability to find an electron equals zero. The 'phase' of the orbital on the two sides of this plane will be of opposing sign (in ADF indicated as opposing colors).
- Now look at the two highest occupied  $\pi$  orbitals (HOMO), and the second highest (HOMO-1), as well as the two lowest unoccupied (LUMO) and the second lowest unoccupied  $\pi$ -orbitals (LUMO+1). How many nodal planes do these orbitals have? Which trend do you see?

### 4.3 Porphine

A lot of porphyrins are derived from porphine, also in biology it is an important substance. It has the following structure:



- Create a porphine molecule. To do this, use the structure tool, in ADFinput and select metal complexes. Select porphyrins and adjust this structure. Symmetrize, perform a single-point calculation (GGA BP/DZP level) and have a look at the orbitals.
- Does this molecule have mirror planes? Can you describe them? The molecule is situated in one plane and the principle axis is perpendicular to this. How many degrees do you have to rotate to arrive at exactly the same situation? What is the principle axis of this molecule?
- Now remove the protons from the two nitrogen atoms. Set the total charge to -2. Again perform a single-point calculation at the GGA BP/DZP level. What is the principle axis now?
- Use ADFview to look at the orbital corresponding to the lone pairs on the nitrogen atoms. What are the energy levels?

## Report Exercise 4

Make a report (max 2 pages) in which you address the questions in **4.1-4.3**.



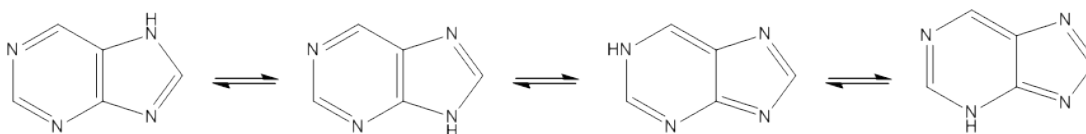
## Exercise 5: Tautomers in Gas Phase and in Water

### Objective Exercise 5

In this exercise you will employ chemical analysis tools (interpret atomic charges and molecular orbitals) to compare tautomers of biologically relevant molecules in the gas phase and in the aqueous phase.

### 5.1 Purine tautomers

Purine itself is not a naturally occurring substance but a lot of its derivatives are, for instance the DNA bases adenine and guanine but also caffeine. There are four possible tautomeric configurations:



In this exercise we will try and find out which tautomer is the most abundant one.

- Create the purine anion molecule in the ADFinput window. Perform a geometry optimization at the GGA BP/DZP level. Determine the Mulliken and VDD charges of the different nitrogen atoms. Use ADFlevels and ADFview to look at the orbitals of this molecule, especially the ones highest in energy. Can you find orbitals with lone pair character on the nitrogen atoms?
- Calculate the energy of all four tautomers at the GGA BP/DZP level via a geometry optimization calculation. Collect results for the gas phase as well as for the condensed phase. To perform a calculation in water, choose in your ADFinput window in the tab Model the option Solvation. Then choose for Solvation Method the option COSMO and as solvent you can now choose water.

#### Questions

- What is the order of stability of the tautomers? Is there any difference between gas phase and water?
- Looking at atomic charges of the anion, is it possible to make a prediction on which tautomer is most likely to occur? Are there differences between your VDD and Mulliken results?
- If you look at the orbital pictures of the anion, especially the ones with lone pair character, what would you predict on the order of stability of the tautomers? (Hint: Protonation involves donation of electronic charge from the lone pair on a nitrogen to the empty orbital of a proton. So what nitrogen do you expect to be most reactive?)

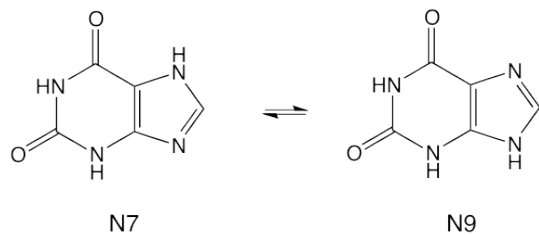
### 5.2 Xanthine N7 or N9

The ratio of occurrence between two substances can be calculated with the following formula:

$$\frac{N_1}{N_2} = e^{-\frac{E_2 - E_1}{kT}}$$

where  $E_2$  and  $E_1$  are the energies of the different substances, and  $k$  is the Boltzmann constant.

Employing this formula, calculate the ratio between two Xanthine tautomers (N7 and N9) in water at  $T=298.15$  K (Standard temperature - default in ADF). Also comment on the deviation in your prediction knowing that the accuracy of DFT is about 1 kcal/mol.



## Report Exercise 5

Make a report (max 2 pages), answering the questions and describing what you have done. Comment on your results.