Scientific Computing & Modelling

Teaching with ADF - MSc exercises

ADF Program System
Release 2014

Célia Fonseca Guerra designed these exercises to teach the two week HRSMC computational chemistry course, for teaching at the Masters level. In the second week, the students design and run their own mini project, and present their results to each other.

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Teaching exercises

Exercise 1: Tutorial, basis sets and molecular orbitals

Objective Exercise 1

In this exercise you will learn to use the Graphical User Interface (GUI) of Amsterdam Denisty Functional (ADF).

## 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 basis set convergence. We will perform the calculations with different basis sets. When enlargement of the basis set hardly influences the outcome, there is 'convergence of the basis set', and we can conclude that the quality of the basis set is sufficient.

1.2a 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:

$$H_2O + H^+ \rightarrow H_3O^+$$
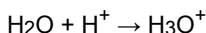
Draw a water molecule in ADFinput and repeat the following procedure with basis sets SZ, DZ, DZP, TZP, TZ2P and QZ4P:
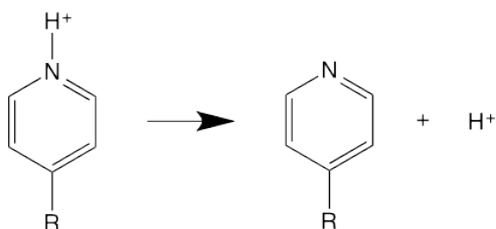
- Perform a geometry optimization, use the BP86 XC potential (choose BP from the GGA dropdown menu)
- Collect the following geometrical data in a table: the O-H distance, the H-O-H angle and the energy
- Calculate the proton affinity for water for each basis set. In order to do this you will have to calculate the energy of H^+ and H_3O^+ as well.

Note that the set-up and analysis of multiple calculations can be automated with ADFprepare and ADFreport (see Tutorial 10, basis sets for NH_3).

Questions Exercise 1.2a

- For which basis set(s) are the bond lengths, bond angles, and proton affinity converged?
- Which basis set would you choose when you are interested in the geometry of a large molecule? Why?

1.2b In this exercise we will calculate the proton affinity (PA) of pyridine (see Figure with R=H) with a variety of basis sets. The definition of the PA of pyridine is the energy change in the following reaction:

Draw a pyridine in ADFinput, or use the search function to find it. Repeat the following procedure for the basis sets SZ, DZ, DZP, TZP, TZ2P and QZ4P: (or use ADFprepare)

- Perform a geometry optimization for C_5H_5N and $C_5H_5NH^+$, using the BP GGA xc-functional.
- Calculate the PA for pyridine with the different basis sets. Note that you will need to include the energy of the proton as well, which you still have from the previous exercise. Determine also the C-N bond length in pyridine. For which basis set have the proton affinity and the C-N distance converged?
- Increase the PA of pyridine with a substituent R. Do the same with another substituent to lower the PA. Try to rationalize your findings with atomic charges and the energy level of the lone pair of the substituted pyridine. (Use ADFview and choose Properties/HOMO, which will give you the energy in atomic units. Choose Properties/Atomic Info/Voronoi Deformation Charge for the atomic charges).

1.3 Carbanions: Molecular orbitals

A carbanion is a reactive intermediate in organic chemistry. Calculate the proton affinities of the following systems at the BP/TZ2P level of theory for R=H, F, Br, CCH and CN. (Use the star-shaped symmetrize button).
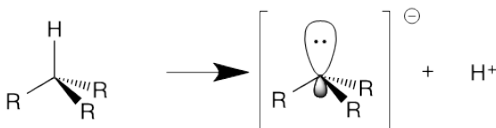
Try to rationalize your findings with the atomic charges on the central carbon atom and/or the energy levels of the HOMO. Another way to rationalize reactivity is to investigate the percentage of $2p_z$ on the central carbon atom in the highest occupied orbitals. For the latter use ADFoutput and go to the "List of all MOs, ordered by energy, with the most significant SFO gross populations". You can easily find this with Properties/'% SFO per orbital' and then scroll a bit down. (SFO stands for symmetry-adapted fragment orbital and in this calculation the fragments are atoms.)

Background information:

F. M. Bickelhaupt, H. Hermann, G. Boche, Angew. Chem. Int. Ed. **45**, 823-826 (2006)
S. C. A. H. Pierrefixe, C. Fonseca Guerra, S. J. M. van Stralen, J. N. P. van Stralen, F. M. Bickelhaupt, Angew. Chem. Int. Ed. **48**, 6469-6471 (2009)

Exercise 2: Tautomerization and rotation barriers in gas phase and solvent

Objective Exercise 2

Learn how to include solvent effects and how to perform linear transits.

2.1 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:
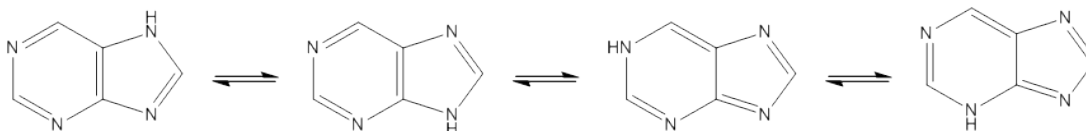
In this exercise we will try and find out which tautomer is the most abundant one.

a. Create the purine anion molecule in the ADFinput window. Perform a geometry opitimization 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?
b. Calculate the energy of all four tautomers at the GGA BP/DZP level via an geometry optimization calculation. Collect results for the gas phase as well as for the condensed phase.
To perform a calculation in water, choose Model → Solvation in your ADFinput window. Then choose COSMO as solvation method and water as Solvent

Questions 2.1
- What is the order of stability of the tautomers? Is there any difference between gas phase and water?
- Looking at atomic charges, 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, 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?)

2.2 Rotation barrier of biphenyl

To calculate the rotation barrier of a bond, we make use of a Linear Transit to scan the potential energy surface. Draw biphenyl (use the search option), select the dihedral angle C6-C1-C7-C12, and set it to zero.
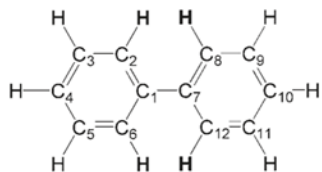
Set your basis set to DZP and Integration accuracy to 5.0. Go the tab Model → Geometry Constraints and Scan , and set the Number of transit points: to 10. Select the dihedral angle, click on the + next to it, and set the first value to 0° and the last to 90°. Note that scanning in 10 steps from 0 to 90° entails steps of 10°.

When the calculation has finished, select ADFmovie and take the highest energy value as the barrier. Redo the calculation with dichloromethane (DCM) as a solvent. Is it necessary to include the solvent?

Background information:

J. Poater, M. Solà, and F. M. Bickelhaupt, Chem. Eur. J. **12**, 2889-2895 (2006)
J. Poater, J. J. Dannenberg, M. Solà, and F. M. Bickelhaupt, Int. J. Chem. Model. **1**, 63-78 (2008)
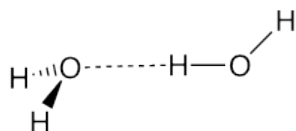
Exercise 3: Choosing a density functional; S_N2 reaction profiles

Objective Exercise 3

Awareness of accuracy due to functional, finding stationary points of SN2 reactions, and making predictions on the reaction rate.

3.1 Hydrogen Bonding

In this exercise we will investigate different functionals. We will do this by performing calculations on a water dimer:


The hydrogen bond energy and length is dependent 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.

   a. Start ADFinput and create the water dimer. Perhaps you want to pre-optimize this with UFF and symmetrize it (Cs).
   Optimize the water geometry with the following functionals: BP, BLYP-D3(BJ), B3LYP and two other functionals of your choice. Write down the hydrogen bond length and the total energy (or use adfprepare and adfreport).
   Note that for the shallow butterfly mode geometry optimization may not converge fully with this large basis set. Adding diffuse functions in the fit (in the Details → Accuracy input panel) may help in this case.
   b. Determine the bond energy of a single water molecule with the same molecules to determine the hydrogen bond energy in the water dimer.

The highest 'ab initio' calculations show 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?

3.2 S_N2 reactions

In an S_N2 reaction a lone pair from a nucleophile attacks an electron deficient center and bonds to it, expelling a leaving group. For instance, the anion Cl- can attack CH_3Cl. The reaction profile looks like:
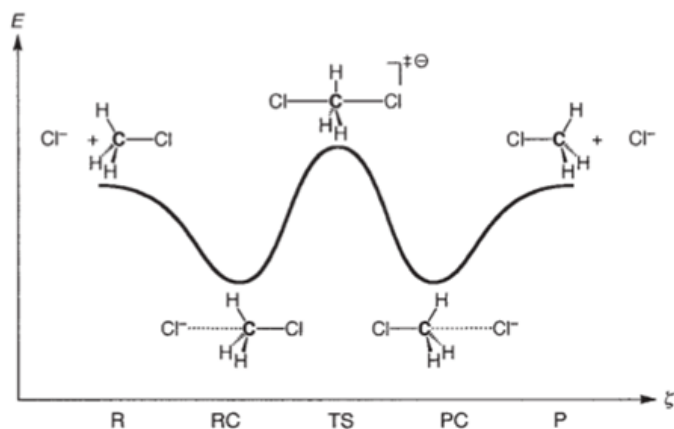
On the x-axis along the reaction coordinate ζ the stationary points are abbreviated R = Reactants, RC = Reactant Complex, TS = Transition State, PC = Product Complex and P = Products. The y-axis corresponds to energy. In this exercise we will calculate a series of reaction barriers and employ a frequency analysis to validate whether we are really dealing with minimum energy structures resp. transition state structures. Note: the optimization process could require more opt-cycles than the included into the default input file.

Questions Exercise 3

a. How would you distinguish a minimum energy structure (e.g. an RC) from a transition state structure (TS) based on a frequency analysis, i.e. which conditions must be satisfied? What would you define as the reaction barrier? If you would have to compare a series of reactions and predict which reaction most likely takes place, which features would you take into account?

b. Optimize the structure of the Reactant complex at the OLYP/TZ2P level. Perform a linear transit at the same level to obtain an approximate reaction path over the transition states between reactants and products. Select Linear transit in the main menu. Select 'Geometry Constraints and Scan' from the Model menu. Select two atoms to add a distance constraint. Write the initial and the final atomic distances of the linear transit. Then, use ADFmovie to look at the results and plot the energy graph. Click on the View tab and select 'converged geometries only'. Does it look like the energy profile depicted above

c. Calculate the energies of all stationary points on the reaction coordinate for the S_N2 reaction Cl- @ CH3Cl at the OLYP/TZ2P level. All minima structures can be found with a 'Geometry Optimization'. However, the TS is located at a 'saddle-point' on the PES landscape obtained in the previous linear transit obtained in part b. This structure can be found with a 'Transition State Search' in the main menu.

d. Perform a frequency analysis on the stationary points you found in part c. Start with importing the geometry in ADFinput, and set 'Preset' to 'Frequencies'. When the calculation has finished you can look at the results with ADFspectra. By clicking on a certain peak in the IR spectrum you can look at the vibration corresponding to that peak. If you look at the imaginary frequency vibration of the TS structures, what do you see and how would you interpret this?

e. Redo this procedure, but now replace the Cl atoms with Br.

f. Also determine the stationary points for the S_N2 reaction Cl- @ SiH3Cl. Note: the reaction profile can be different for different reactions.

g. What could be the physical cause why the reaction profiles of S_N2 @C and S_N2 @Si are different? Calculate how many times the S_N2 reaction with Cl is faster or slower compared to the S_N2 reaction with Br. Hint use the Arrhenius equation and assume that the prefactors A are identical for both reactions.

h. The transition states in this S_N2 reaction are special cases because they are symmetric. Therefore, a much faster way of finding the transition state is by imposing D_{3h} symmetry. Optimize

the TS for both the nucleophile and leaving group being respectively F-, Cl-, Br-, and I-. Redo the same calculations at the BP86/TZ2P and B3LYP/TZ2P level and use a benchmark paper with post-Hartree-Fock ab initio calculations (coupled cluster) to choose the best V_{xc}. (Also comment on the difference in time between the functionals).

Background information:

A. P. Bento, M. Solà, and F. M. Bickelhaupt, J. Comput. Chem. **26**, 1497-1504 (2005)
A. P. Bento, M. Solà, and F. M. Bickelhaupt, J. Chem. Theory Comput. **4**, 929-940 (2008), Erratum
A. P. Bento and F. M. Bickelhaupt, Chem. Asian J. **3**, 1783-1792 (2008)

Exercise 4: Energy decomposition analysis and MO interaction diagrams

Objective Exercise 4

To learn about energy decomposition analysis (EDA) and molecular orbital interaction diagrams.

4.1 Tutorial

Before starting this exercise, you can learn how to do fragment calculations with the advanced ADF tutorial. In these fragment calculations you divide your molecular system into chemically meaningful fragments.

4.2 Fragments

In this exercise we want to understand the donor-acceptor interactions between NH_3 and BH_3:
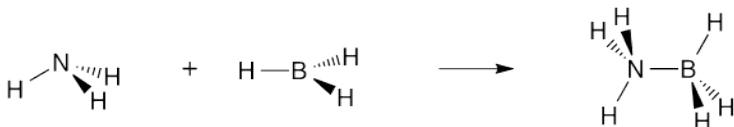
Before starting to analyze the interaction you have to get acquainted to the fragments. Optimize the structures of NH_3 and BH_3 at the BP/TZ2P level of theory and analyze the HOMO and LUMO of the two molecules. Use ADFview to view the orbitals of the HOMO and LUMO of both molecules. Rationalize which donor-acceptor interactions will be possible and write down the total energy of NH_3 and BH_3 because you will need it in the next part.

4.3 Donor-acceptor interactions in the complex

The next step is to analyze the chemical interaction between the two fragments. For that purpose, you first optimize $H_3B \cdots NH_3$ at the BP/TZ2P level of theory. Then import the coordinates and start the fragment analysis calculation. The MO diagram can be visualized with ADFlevels. This MO diagram contains the donor-acceptor interactions, but also the Pauli repulsion, that is the repulsive interaction between occupied orbitals of NH_3 and BH_3. Read the following intermezzo before proceeding.

Bonding Energy Analysis

The bond energy ΔE_{bond} of the complex $H_3B \cdots NH_3$ is defined as:

$$(1) \quad \Delta E_{bond} = E_{complex} - E_{BH3} - E_{NH3}$$

where $E_{complex}$ is the energy of the optimized complex and $E_{NH3/BH3}$ is the energy of the optimized NH_3/BH_3 fragment.
The overall bond energy ΔE consists of two major components:

(2) $\Delta E_{bond} = \Delta E_{prep} + \Delta E_{int}$

In this formula, the preparation energy ΔE_{prep} is the amount of energy required to deform the separate fragments NH_3 and BH_3 from their equilibrium structure to the geometry that they acquire in the complex. The interaction energy ΔE_{int} corresponds to the actual energy change when the prepared fragments (that is in the geometry of the complex) are combined to form the complex.
The interaction energy in the donor-acceptor systems can be examined in the framework of the Kohn-Sham MO model using a quantitative energy decomposition analysis (EDA), which divides the interaction energy into electrostatic interaction, Pauli repulsive orbital interactions, and attractive orbital interactions:

(3) $\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared (i.e. deformed) fragments and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction ΔE_{oi} in any MO model, and therefore also in Kohn-Sham theory, accounts for charge transfer (i.e., donor-acceptor interactions between occupied orbitals on NH_3 with unoccupied orbitals of BH_3, including the HOMO-LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment).
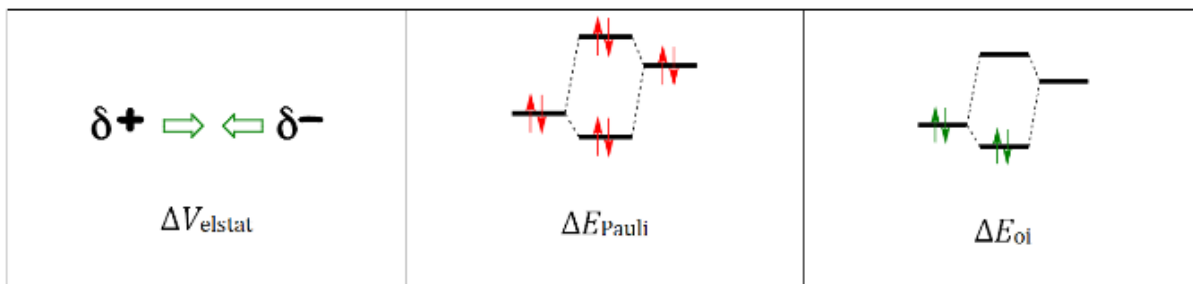
With the MO-diagram and the SFO gross populations, you will be able to analyze an orbital of the complex in terms of the fragment orbitals. Of which fragment orbitals is the HOMO-2 composed? Look at the output in the "List of all MOs, ordered by energy, with the most significant SFO gross populations". Can you pinpoint what is Pauli repulsion and what is the donor-acceptor interaction in the HOMO-2 of the overall system? Calculate the bond energy of equation (1) and get the terms of equation (3) from the output.

4.4 σ-donation and π backdonation in a metal-ligand complex

Calculate which energy term is larger for Pd-CO: σ-donation or π backdonation? Does the Voronoi charge of Pd confirm this observation in the energy terms? Use for you calculation C(lin) symmetry, this makes it easy to spot what is σ and π interaction.

Background information:

C. Fonseca Guerra, F. M. Bickelhaupt, J. G. Snijders and E. J. Baerends, Chem. Eur. J. **5**, 3581-3594 (1999)
U. Radius, F. M. Bickelhaupt, A. W. Ehlers, N. Goldberg, R. Hoffmann, Inorg. Chem. **37**, 1080-1090 (1998)

Exercise 5: NMR calculations

Objective Exercise 5

Learn how to perform NMR calculations

5.1 NMR basics

NMR is a widely used technique to identify chemical compounds. In this exercise you will learn how to perform NMR calculations. As a quick start we will look at the calculation of proton chemical shifts for ethane, ethene and ethyne.

  a. Start with optimizing these molecules at the GGA BLYP/TZ2P level. Perform an NMR calculation on these optimized structures. You can do this by choosing 'NMR' in the 'properties' tab, and after selecting all protons (pick a proton and choose 'select atoms of the same type' in the select menu) clicking the + button in the NMR shielding field. Make sure that both isotropic shielding constants and full shielding tensor print buttons are selected to get the full output. In the main menu set core to 'None' and perform a single point calculation. Look first at the simulated NMR spectrum in the Spectra module and locate also the NMR section in the text output file. This section provides information about the different contributions to the shielding tensor.
  b. The chemical shift (δ) of a molecule 'A' with reference 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: $\delta(TMS) - \delta(A)$. What is the chemical shift of ethane, ethene and ethyne with reference TMS? Do you need to perform a calculation of TMS as well? And if you had chosen a different basis set or functional?
  c. Are these calculated chemical shifts in agreement with experimentally derived results? Experimental results can be found in about every elementary organic chemistry textbook, in many scientific papers and in databases accessible via the internet.

5.2 NMR and hydrogen bonding

In this exercise we will investigate the chemical shift of C2 of the adenine base in the gas phase and in a solvent. We will do this by performing calculations for adenine unpaired and paired with thymine:
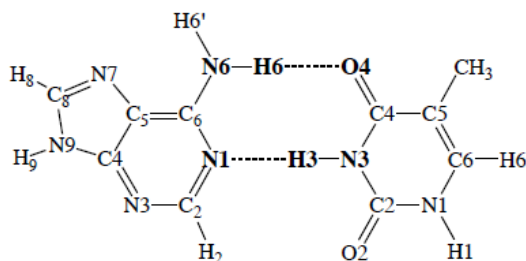
When calculating the chemical shift, different aspects have to be taken into account. Adenine can be paired or unpaired. The solvent has to be taken into account and protonation might change the chemical shift. The adenine base can be drawn by using the DNA utility (do not forget the hydrogen atom at N9). Optimize the structure at the BP86/TZ2P level of theory.

a. Perform an NMR calculation on these optimized structure. You can do this by choosing 'NMR' in the 'properties' tab, and select the C2 atom for which you want to calculate the NMR shielding. In the main menu set core to 'None' and perform a single point calculation.
b. Now start your investigation on the shift of C2 by protonation at N1, N3 and N7. Which site of protonation influences the NMR value more?
c. Investigate the influence by pairing with thymine or making one hydrogen bond with water. The AT pair is in the DNA drawing tools.
d. The last influence to be investigated is the solvent. Perform a NMR calculation on adenine in a solvent. In the 'Model' tab, you choose solvation and the Solvation method "COSMO". The perform an NMR calcultion on Adenine in water and in DCM. Do you think that you also have to optimize the structure in the solvent before doing the NMR calculation or can you just take the gas-phase structure?

Background information:

M. Swart, C. Fonseca Guerra, and F. M. Bickelhaupt, J. Am. Chem. Soc. **126**, 16718-16719 (2004)

Exercise 6: Excitation energies

Objective Exercise 6

Learn how to perform TDDFT calculations

6.1 TDDFT basics

Being able to calculate excitation energies is important for the study of various photochemical processes. The easiest and most common use of TDDFT is to calculate vertical excitation energies at an optimized structure. This corresponds reasonably well with the absorption maxima measured in UV/Vis spectra if you take care to chose an appropriate basis set (use of an augmented basis set with additional diffuse functions is often necessary) and functional. More advanced (and time-consuming) is the optimization of the structure of a molecule in its excited state. This will provide you with information about the fluorescence frequency. We will look at both aspects for the trans-1,3-butadiene molecule, which is small enough to keep the calculations manageable for a teaching exercise. To speed up the calculation we also use a rather small basis set.

1. The molecule is contained in the ADF molecules library (search for butadiene) but to have the precise minimum for this level of theory we will first optimize the structure for the ground state. After optimization, calculate the vibrational frequencies. Look at the structure and verify that the C-C and C=C bond distances are as drawn.
2. Choose the Single Point calculation mode and specify 10 "Singlet Only" excitations in the Excitations/CD part of the Properties tab. This will activate the TDDFT module and make it calculate the lowest spin-allowed transitions. Run the calculations and choose Spectra from the SCM menu. You will now see a simulated UV spectrum in which the sharp transitions are artificially broadened by convolution with a Gaussian function. Click axis to change the units to nm, for this molecule the wave length of maximum absorbance is 217 nm and you should get a value that is pretty close to this. To see the nature of the excitation, you can point your mouse on the transitions and visualize the orbitals involved in the transition. How would you qualify the first transition (e.g. $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, Rydberg, charge-transfer).
3. We'll now optimize the structure of the first excited state to get an estimate of the fluorescence frequency. Set the calculation mode to Geometry Optimization and specify in the Properties/ Excited State Geometry section which excitation you want to optimize on. Here you need the symmetry label of this excitation, which can be found in the output obtained in b. If you start from the previous input, make sure to reduce the number of excitations calculated as we only need one. What is the Stokes' shift (difference between absorption and fluorescence maxima)? What happened with the C-C and C=C bondlengths and is this what you expected from the nature of the excitation?

6.2 TDDFT pitfalls

In the previous exercise we looked at a molecule for which the results with a small basis set and a standard GGA functional already come out quantitatively correct. We will now also consider more difficult cases that require more advanced functionals and/or basis sets.

1. We take the ethene molecule to show the importance of diffuse functions and the functional in three different calculations. To be able to easily compare results, make sure that you choose three different names for the calculations so that you can look at all spectra simultaneously. We start by calculating all allowed vertical excitation energies with the BP/DZP functional combination. Use the spectra and viewer modules to verify that the most intense transition is the $\pi^* \rightarrow \pi^*$ ($^1B_{1u}$)

transition (or use the text output viewer and use the Response Properties menu to directly jump to the section of interest, there you will find all relevant information as well). Then switch the basis set to ATZ2P and look again at the spectrum. You see that it looks quite different with a peak that was previously slightly above the $\pi \rightarrow \pi^*$ transition now coming clearly separated at lower energy. If you look at the orbitals involved in this transition you can see this is transition to a Rydberg orbital, an orbital that could not be represented well in the small basis and hence came out at a too high energy. While the basis set is now adequate, we still have a problem because a GGA does not describe Rydberg orbitals well. This can be remedied by choosing the SAOP functional that was designed to better treat Rydberg orbitals and properties (e.g. polarizabilities) influenced by the diffuse orbitals. Switch the functional to SAOP, while keeping the ATZ2P basis. What happens with the two transitions mentioned earlier? Coupled cluster benchmark calculations give a vertical transition values for the $^1B_{1u}$ and $^1B_{3u}$ transitions of 7.9 and 7.2 eV, respectivey. How well does this fit the TDDFT values?

2. Another problem that you may encounter is related to charge-transfer excitations. LDA and GGA functionals can not "detect" a large movement of charge and will underestimate the exchange interaction. The result is that charge-transfer excitation appear at much too low energies. A simple, brute force remedy is to mix in Hartree-Fock exchange and use a hybrid functional. We will here look at intramolecular charge-transfer, but the problem also occurs for intermolecular charge-transfer. As we need to move the charge over some distance to best see the effect, we need to take a sizeable molecule. The p-nitroanaline molecule (contained in the searchable ADF molecules library) is one of the smallest systems to clearly observe the effect.
Calculate the lowest excited states with BLYP, B3LYP and BHandHLYP and note the change in excitation energy upon increasing the amount of exact exchange (BLYP has none, BHandHLYP has 50%). Note also the increase in computer time, and remember to only use B3LYP or similar hybrids if you really need them. A lot of effort has gone into determining the amount of exchange in these approaches, but no universal solution has emerged and the "best" amount is quite system specific. A somewhat better solution is to use a range-separated or local hybrid functional, which are available in ADF2013.

Background information:

A recommended recent review on TDDFT for non-specialist: C. Adamo and D. Jacquemin Chem. Soc. Rev. **42**, 845 (2013)