

Exercises ("Werkcollege") 1: getting started

The objective of this exercise is to become familiar with the graphical user interface (GUI) of the Amsterdam Density Functional program (ADF). ADF is a quantum chemistry program that calculates the properties of chemical structures with Density Functional Theory (DFT).

At the end of every (set of) werkcollege we ask you to write a small report answering the question asked in the werkcollege. You will be graded on the basis of these reports.

Please hand in the report before **Friday May 8th (23:59)** by handing it in during the werkcollege or sending it to R.E.Bulo@uu.nl and J.M.Boereboom@uu.nl.

1. Becoming familiar with ADF

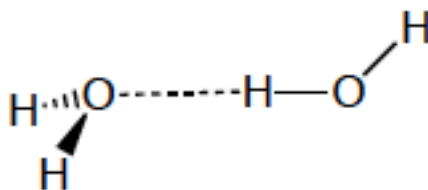
A good starting point is to use the GUI of ADF is to have a look at the tutorial videos on <http://www.scm.com/Videos/>. Please watch Tutorial 1: Geometry optimization of ethanol.

The next step is to do a tutorial yourself. On the website of Scientific Modeling and Computing (www.scm.com) you can find many tutorials. We recommend you to follow Tutorial 1, which you can find on: http://www.scm.com/Doc/Doc/GUI/GUI_tutorial/page1.html.

Before you run the calculations save the calculations as `filename.adf` select the interactive queue by clicking the `Queue` tab in `ADFJobs` and selecting `Interactive`, after selecting the `Queue` you can run the calculation by clicking the `Job` tab and selecting `Run`. ***It is advised to always select the Interactive queue before running a calculation.***

2. Hydrogen bonding

In this exercise we will perform calculations on a water dimer:



- Start `ADFInput` and create the water dimer. Optimize this geometry with the `GGA_PBE` functional and a `TZP` basis set. Save the calculation as `water_dimer.adf` and run the calculations. Write down the hydrogen bond length and the total energy.
- Determine the total energy of an isolated water molecule; use this result to determine the hydrogen bond energy.

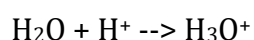
3. Benchmarking: Choice of basis set

The basis set determines in how many degrees of freedom the calculation is performed. That means that the larger the basis set, the more accurate the results, but at a higher cost of computing time.

In order to determine whether a basis set will achieve satisfactory results we can benchmark it by looking at the following criteria:

- We compare our computational results with experimental results. The results will be close to identical when the basis set is optimal (This is only true if the level of theory is adequate).
- We compare our computational results with high level *ab initio* calculations. Again, the better the agreement, the better the basis set.
- When there are no experimental or *ab initio* results available, however, we have to rely on a different strategy; we will redo the calculations with different basis sets. When the enlargement of the basis set hardly influences the outcome, there is a so-called '**convergence of basis set**', and we can conclude that the quality of the basis set is sufficient.

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



Now draw a water molecule in ADFInput and repeat the following procedure for the basis sets: SZ, DZ, DZP, TZP, TZ2P, QZ4P.

- Perform a geometry optimization with the GGA PBE XC functional
- Collect the following geometric information in a table: the O-H distance, H-O-H angle and the energy
- Calculate the proton affinity for water within the basis set. In order to do this you will have to calculate the energy of H^+ and H_3O^+ as well (tip: ADF does not allow you to perform a calculation on a proton. The energy of a proton is the energy required to remove an electron from the H-atom).

Answer the following questions:

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

Make a report in which you answer the questions of exercise 2 and 3 (length of the report max. 2 pages).

Please hand in the report before **Friday May 8th (23:59)**

Exercises "Werkcollege" 2: continuum solvation

The objective of this werkcollege is to become familiar with an implicit model to include solvation and to extract partial charges. The implicit solvation model that we will use in this werkcollege is the Continuum Solvation Model (COSMO). We will test the effect of this model on the stability of charged systems.

Moreover, we are going to look at the relative stability of chemical structures upon rotation of a dihedral angle.

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the question asked in this werkcollege.

Please hand in the report before **Monday May 18th (23:59)** by handing it in during the werkcollege or sending it to R.E.Bulo@uu.nl and J.M.Boereboom@uu.nl.

1. Partial charges and solvation model

So far, all the calculations we have performed took place in the gas phase, meaning that we perform the calculations in vacuum. In this exercise we will use a model to incorporate solvents. This implicit model (we will not draw explicit solvent molecules) represents the solvent by means of their dielectric constant, which is a good approximation of the long-range interaction of the solvent.

In this exercise we will have a look at the partial charges of different atoms in a molecule (i.e. these determine nucleophilic/electrophilic centers of a molecule). Moreover, we will look at the effect of the continuum solvation model (COSMO) on these partial charges and on the stability of charged systems.

a. NH_4^+

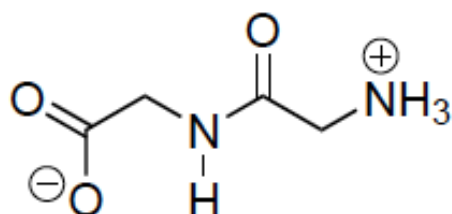
Perform a geometry optimization with the PBE functional and the COSMO model for a TZP basis set. In order to select the implicit solvation model go to the `model` tab and click on `solvation`, select the COSMO model as `solvation method` and use water as a solvent.

What are the partial charges of the nitrogen and hydrogen atoms (use an average value) for this calculation. Look at the Mulliken population analysis and the Hirshfeld charge analysis. Also calculate the Mulliken and Hirshfeld charges with the DZ, DZP, TZ2P and basis set (It is not necessary to re-optimize the geometry, you can do single-point calculations to determine atomic charges). Tip: you can select the charge analysis from the `properties` tab in the output to jump directly to the relevant section of the output file. Which analysis do you trust more and why?

Recalculate NH_4^+ in the gas phase for TZP basis set (PBE functional). What is the effect of a polar protic solvent like water on the stability of NH_4^+ ?

b. Zwitterion: Diglycine

Perform a geometry optimization of diglycine (see figure) in the gas phase with the LDA functional and a DZP basis set. Go to the details tab and click on geometry convergence. Set the Gradient convergence to 0.01 hartree/Angstrom and the Radial convergence to 0.05 Angstrom. We do this to reduce computational time. Please note that generally these settings are not sufficient to obtain reliable results, and should only be used as a last resort and if you know what you are doing (in this case it was tested that even with these settings, the outcome of the calculations is the desired outcome). In order to be able to calculate enough geometry iterations, it is needed (for ADF on Windows machines) to set number of geometry iterations to 100, this can also be done in the geometry convergence sub-menu.

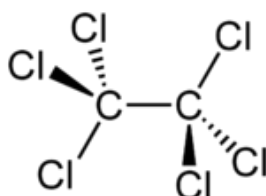


Have a look at the change of geometry during the geometry optimization with ADF View, what do you notice?

Perform a geometry optimization of diglycine in water (with the COSMO model) selecting the same settings as for the gas phase calculation. Again, have a look at the change of geometry during optimization, what happens now? What does that mean for the stability of charged systems in polar protic solvents (like water)?

2. Rotational barrier of hexachloroethane

To calculate the rotation barrier of a bond, we make use of a Linear Transit to scan the potential energy surface. Draw hexachloroethane and set a Cl-C-C-Cl dihedral angle to zero.



Choose Linear Transit and then go to the model tab and select Geometry Constraints and Scan. Select the dihedral angle and set the first value to 0° and the last to 180°. Note that you will do the scan in 10 steps. You can use the LDA functional and a DZ basis set. Do not forget to set number of geometry iterations to 100.

What is the most stable configuration? And what is the transition state?

In order to obtain the energy of the different Linear Transit points it is best to search in the logfile for:

```
Bond Energy      -1.04174499 a.u.  
Bond Energy      -28.34732363 eV  
Bond Energy      -653.70 kcal/mol  
Bond Energy at LINEAR TRANSIT point: 10 = -1.041745
```

Then plot these energies with excel or a similar program of your liking.

Replace the Chlorine atoms by other halogen atoms. What would you expect to happen with the barrier height? Compare the barrier heights of this calculation with that of hexachloroethane and comment on the findings.

Please hand in the report before **Monday May 18th (23:59)** by handing it in during the werkcollege or sending it to R.E.Bulo@uu.nl and J.M.Boereboom@uu.nl.

Exercises "Werkcollege" 3: spin states

This werkcollege deals with spin states, of electrons as well as of nuclei. The objective of the first part is to learn how to compute energies of higher electron spin states. Up till now, we have only done spin "restricted" calculations, where we force the molecules to have *closed shell* singlet character. In this werkcollege we will also perform calculations on unrestricted *open shell* spin-systems, such as triplet and *open shell* singlet states.

Furthermore, we will compute NMR chemical shifts that can be compared with experimental results. The spin states of nuclei cannot be dealt with directly, because we treat the nuclei as classical particles. Instead, we deal with the effect of a magnetic field on the electron density: shielding. In order to compare that with experimental results we have to calculate the chemical shifts relative to a reference: tetramethylsilane (TMS).

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions. Please hand in the report before **Friday May 29th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to R.E.Bulo@uu.nl and J.M.Boereboom@uu.nl. If you choose to send in a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

1. Spin contamination of molecular hydrogen

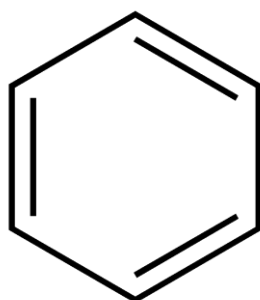
In this exercise we will look at the binding energy of molecular hydrogen at different bond lengths.

- a. Calculate `Single point` binding energies of molecular hydrogen for bond lengths of 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 3.0, and 3.5 Å at the PBE/TZP level with a small frozen core.
- b. Repeat all single point calculations for the Triplet and open shell Singlet states. In order to perform a Triplet calculation please set `unrestricted` to `yes` and set `Spin polarization` to 2.0 (2 more α electrons than β electrons). Performing (broken symmetry) open shell Singlet calculations is a bit more complex. The calculation needs to start from a representative asymmetric guess density, to avoid a collapse of the spin densities to the symmetric (closed shell) state. Set `unrestricted` to `yes`, but leave `Spin polarization` on 0.0 (an equal number of α and β electrons). Click on `Spin` and `occupation` under the `Model` tab, select one of the hydrogen atoms, add `Modify start potential` and set `Alpha` to 0.0 and `Beta` to 1.0. Now select the other hydrogen atom and add `Modify start potential` again, set `Alpha` to 1.0 and `Beta` to 0.0. In order to get the desired result we also need to change a few setting in `SCF convergence details` under the `Details` tab. Set `Mixing` to 0.03 and set `Electron smearing`, `Initial` and `Electron smearing`, `final` both to 0.0. Finally click on `Symmetry` under the `Details` tab and set `Symbol` to `NOSYM`.

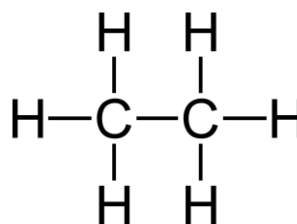
- c. Plot the binding energies of the restricted closed shell calculations, the Triplet calculations, and the unrestricted closed shell calculations as a function of the bond length.
- d. Compute the energy of a hydrogen atom in the doublet state (Spin polarization = 1.0). Compare the energy to the energies of the hydrogen molecule at large distances. What do you expect? What do you see?
- e. The computed open shell Singlet is not a pure spin state. This is reflected in the value of the S^2 matrix. Tabulate the expectation value of the Total S^2 (S squared) matrix for the unrestricted calculation. Compare the values with the plot of the binding energies of question c. What other spin states are mixed in? How do the contributions of those other spin states change with changing H-H distance?

2. Nuclear Magnetic Resonance (NMR) calculations

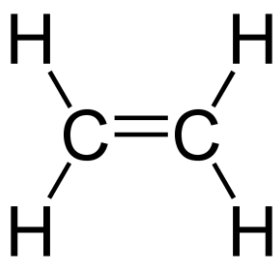
NMR is a widely used technique to identify chemical compounds. In this exercise you will learn how to compute chemical shifts. This will be done for benzene, ethane, ethene (ethylene) and ethyne (acetylene).



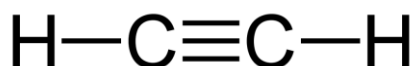
Benzene



Ethane



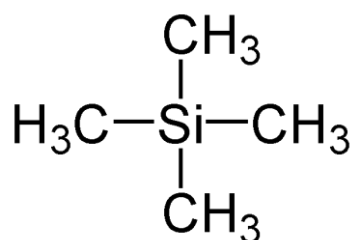
Ethene (Ethylene)



Ethyne (Acetylene)

- a. Start with optimizing these molecules at the GGA BP/TZ2P level. Perform an NMR calculation on the 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 the isotropic shielding constants and full shielding tensor will be printed. Set Frozen core to None in the Main tab and perform a single point calculation.

- b. To obtain the chemical shift (δ) of a molecule 'A' versus the reference of TMS (tetramethylsilane) one also needs to compute the NMR properties for TMS, and then subtract the chemical shift of 'A' from that of TMS: $\delta(\text{TMS}) - \delta(\text{A})$. What is the chemical shift of ethane, ethene (ethylene), and ethyne (acetylene) relative to the TMS reference? TMS also needs to be optimized at the same level of theory as the other molecules, why? Please make sure that the TMS starting structure is already reasonable by using the pre-optimization tool (please note that TMS is tetrahedral).



Tetramethylsilana (TMS)

- c. Are these calculated chemical shifts in agreement with experimentally derived results? Experimental results can be found in almost every elementary organic textbook, and in many scientific papers.

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions.

Please hand in the report before **Friday May 29th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to R.E.Bulo@uu.nl and J.M.Boereboom@uu.nl.

If you choose to send a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

Exercises "Werkcollege" 4: UV/VIS, IR, Raman

This werkcollege deals with electronic excitations, Infrared absorption, and Raman spectroscopy. The objective of this werkcollege is to learn how to compute IR/Raman Spectra of molecules and to visualize the normal modes, which give rise to the specific peaks of these spectra. Furthermore, we will compute excitation energies, which can be used to construct a UV-Vis spectrum of a molecule. Lastly, we will learn how to compute the geometry of the first excited state, which is useful to calculate the fluorescence frequency of a molecule.

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions. Please hand in the report before **Friday June 5th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to **F.M.F.deGroot@uu.nl** and **J.M.Boereboom@uu.nl**. If you choose to send in a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

1. Infrared absorption of greenhouse gasses

In this exercise we will calculate the absorption (IR) spectra of different greenhouse gasses. In order to assess the greenhouse potential of a molecule it is important to look for absorption in the so-called IR atmospheric window (between 800 cm^{-1} and 1400 cm^{-1}), where there is no absorption from water or carbon dioxide. From benchmarks it is known that the simple LDA functional reproduces the IR frequencies and intensities of a reference calculation (MP2) quite well. Therefore, we will take this functional and a TZP basis set in this exercise.

- f. Create a water molecule and optimize the geometry with the LDA functional and a TZP basis set. After optimization, perform a frequencies analysis by selecting `Preset: Frequencies`. Start `ADFSpectra` and tabulate the absorption maxima and their intensity.
- g. Repeat the calculation for carbon dioxide, again tabulating the absorption maxima and their intensity. You should find one absorption in the IR atmospheric window, but with zero intensity. Looking at the normal mode of this vibration explain why it has zero intensity.
- h. For carbon dioxide we will also perform a Raman calculation. Which modes do you expect to have intensity in a Raman spectrum? Explain this with the selection rules of IR and Raman spectroscopy. In order to perform Raman calculations select `Preset: Frequencies`, go to the `Properties` tab and select `Raman`, `VROA` then select `Calculate: Raman Full`. Do the results from the calculations agree with your theory?
- i. Now consider nitrous oxide (N_2O) and methane, gases that are known to be potent greenhouse gases. Do you indeed observe significant absorptions in the calculated IR atmospheric window?

- j. Other important greenhouse gases are chlorofluorocarbons. Find out what is meant by CFC11, CFC21, CFC12, etc. and choose one such molecule to calculate its IR absorption spectra. Describe the normal modes that give rise to the most intense absorptions in the IR atmospheric window.

2. Electronic excitations

Being able to calculate excitation energies is important for the study of various photochemical processes. The easiest and most common of TD-DFT 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 choose an appropriate basis (often also diffuse functions are needed, which are in augmented basis sets) and functional. More advanced is the optimization of the structure of the molecule in its (first) excited state. This will provide you with information about the fluorescence frequency.

In order to keep the calculations not too time-demanding we choose here just a TZP basis set and the BP functional.

- d. Draw trans-1,3-butadiene, and optimize the geometry. Tabulate the carbon-carbon bond lengths, do these indeed reflect the C-C and C=C bond lengths character you have drawn?
- e. In order to calculate the excitation energy, do a Single Point calculation selecting Excitations, CD under the Properties tab. Specify Type of Excitations: SingletOnly and choose Number of excitations: 4. If you go the Spectra module you can see a simulated UV-Vis spectra, note that the transitions are artificially broadened by convolution of a Gaussian function. Click on the axis to change the units of the excitation on the x-axis. The maximum absorbance of this molecule is around 217 nm, how does your calculation agree with experiment? What are the orbitals involved in the first excitation (tip: if you point your mouse to on the transitions you can visualize the orbitals by clicking on the orbital transition with the largest percentage in the green field that appears when hovering over the excitation)?
- f. Now, optimize the geometry of the first excited state to get an estimate of the fluorescence frequency. First we need to find out what the symmetry is of the lowest excitation (this can be found in the output file of **b**). Set Preset : Geometry optimization and go to Excited State and Geometry under the Properties tab. Fill the symmetry you just found in under Excitation: _____. If you start from the previous input, please make sure that you reduce the number of excitations to 1. What is the Stokes shift? What happened to the C-C and C=C bond lengths and is this what you expected on the basis of the nature of the excitation?

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions.

Please hand in the report before **Friday June 5th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to **F.M.F.deGroot@uu.nl** and **J.M.Boereboom@uu.nl**. If you choose to send a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

Exercises "Werkcollege" 5: chemical reactions

This werkcollege deals with chemical reactions. The objective of this werkcollege is to learn how to find the reaction profile of S_N2 reactions in order to make predictions on reaction rates.

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 potential energy surface looks like the profile sketched in Figure 1.

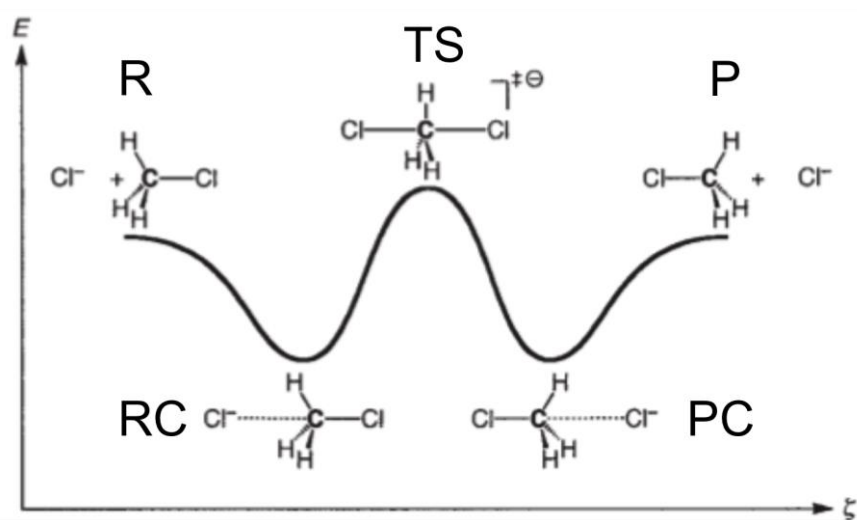


Figure 1: Sketch of the potential energy surface of an S_N2 reaction

On the x-axis along the reaction coordinate ζ , all stationary points are abbreviated; R stands for reactants, RC for reactant complex, TS for Transition state, PC for product complex, and P for products. The y-axis correspond to the energy.

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions. Please hand in the report before **Monday June 15th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to F.M.F.deGroot@uu.nl and J.M.Boereboom@uu.nl. If you choose to send in a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

1. S_N2 reaction profiles

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 or transition state structures.

- k. How would you distinguish a minimum energy structure (for example a Reactant complex) from a transition state structure (TS) based on a frequency analysis? What would you define as the reaction barrier?
- l. First optimize the structure of the Reactant complex of Figure 1 at the GGA:BP/TZP level. Please make sure that you set the number of geometry optimizations to 100.
- m. In order to get an idea of the reaction profile of Figure 1, you can perform a Linear transit calculation. Start from the optimized geometry of **b**. It is best to freeze the Cl—C—Cl angle to 180°. In order to do this go to Geometry constraints and scan under the Model tab and select the Cl—C—Cl atoms and add the angle constraint. Now select the Cl and C atoms and add the distance constraint, now set the linear transit for this distance constraint from 3.9 Å to 1.8 Å. Set the number of transit points to 8. Plot the energy of the transit points. You can do that in the ADFMovie module, select Optimized Geometries Only from the View tab.
- n. Now also calculate the energy of the stationary points of the reactants and transition state from Figure 1. Minima structures can be found by a geometry optimization. A transition state, however, is located at a 'saddle-point' on the potential energy landscape. This structure can be found with a Transition State Search in the main menu, it is advised to start with the guess of the transition state of question **c**. It might be useful to add the Cl—C distance as the reaction coordinate in Transition State Search under the Model tab.
- o. Perform a frequency analysis for the reactants, reactant complex, and transition stationary points. Does this agree with your theory of question **a**? If you look at the imaginary frequency vibration of the TS structure, what do you see and how would you interpret this?
- p. Redo this procedure (**c** (optional), **d** and **e**), but now replace Cl atoms with Br. 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* of both reactions are identical).

At the end of this werkcollege we ask you to write a small report (max 2 pages) in English answering the supplied questions. Please hand in the report before **Monday June 15th (23:59)**, either during the werkcollege as a paper version or as a digital file sent to F.M.F.deGroot@uu.nl and J.M.Boereboom@uu.nl. If you choose to send a file by email, please make sure that in the subject of the email at least the acronym TDFT is placed so that we can archive these emails appropriately.

Exercises "Werkcollege" 6: X-ray absorption

This werkcollege deals with x-ray excitations,. The objective of this werkcollege is to learn how to compute X-ray spectra of molecules and to visualize the spectral shapes.

Please note that for this werkcollege you **do not have to hand in a report**.

1. X-ray absorption of amino acids

In this exercise we will calculate the x-ray absorption spectra (XAS) of amino acid molecules. The energy of the absorbed x-ray photon is used to excite a core electron to an empty orbital.

- q. Create an amino acid molecule of your choice (tip: if your computer is not really fast choose one of the smaller amino acids) and optimize the geometry with the GGA:BP functional and a TZP basis set. It is important to set `Frozen Core` to `none`.
- r. X-ray absorption can be calculated with TDDFT similar to an optical excitation. It is necessary to define the correct excitations for the XAS calculation. One method to select them is to select the energy range for the excitation. You first have to search for the 1s core level states of all elements other than hydrogen. The binding energy of 1s states is higher than 100 eV. Search the 1s binding orbitals for carbon, nitrogen and oxygen in the output file and write down the energies in eV and in Hartree (tip: In order to find the energies it might be helpful to `reset zoom` in `ADFLevels`).
- s. Calculate the XAS spectrum for all non-hydrogen atoms (carbon, nitrogen, and oxygen). Select `Preset: Single Point`, and select `Excitations,CD` from the `Properties` tab. Set `Type of excitations` to `SingletOnly`. Go to `Select Excitations` from the `Details` tab and select `Modify Excitation`. Now give the energy range of the `Occupied orbital energies` (-0.5 Hartree to +0.5 Hartree with respect to the different core level binding energies that you found in **b**. (*3 calculations in total*)). Explain which core orbitals are participating in the peaks in the XAS spectrum.

Exercises "Werkcollege" 7: band structures

This werkcollege deals with band structures. The objective of this werkcollege is to learn how to use the BAND suite of ADF, and to become familiar with the properties of solids.

Please note that for this werkcollege you **do not have to hand in a report**. The understanding of Exercise 2, however, can be useful for the exam.

1. Tutorial of the band structure of NaCl

In this werkcollege we are going to use BAND. BAND is a suite of the ADF program that performs periodic DFT calculations. Therefore, BAND allows for proper modeling of 1D (chains) and 2D (surfaces) of solids.

Although BAND is part of the ADF graphical user interface, the input required for calculations is a bit different than the normal (molecular) suite of ADF. It is therefore advised to follow a Tutorial on the band structure of salt, which can be found on: http://www.scm.com/Doc/Doc2014/GUI/GUI_tutorial/page108.html.

2. Band structure of CO molecules in 1D, and 2D

In this exercise we will calculate the band structure of CO in 1 dimension and 2 dimensions.

- t. Optimize a CO molecule in with the normal (molecular) suite of ADF at the GGA:RPBE/TZP level. What is the bond length after optimization?
- u. Go to the BAND suite (click on the yellow ADF to change to band), and set the `Periodicity` to `None`, then draw a CO molecule. In order to set the correct distance and orientation of the CO molecule we will move to `Coordinates` in the `Model` tab. The C atom should be positioned at the origin and position the O atom on the z-axis at a distance that you found in a (tip: O should be at $(0,0,r)$, where r is the bond length).
- v. In order to calculate the band structure of CO in 1 dimension, set the `Periodicity` to `Chain`, and make sure that the lattice distance is set to 3.0\AA . In order to change this distance go to `Lattice` in the `Model` tab. Perform a `single point` calculation at the GGA:RPBE/TZP level. Plot the band structure and determine the nature of the four highest orbitals (σ , π , etc.).
- w. Now we are going to calculate the band structure of CO in 2 dimensions, set the `Periodicity` to `Slab` and make sure that the lattice distance is set to 3.0\AA , and perform a `single point` calculation at the GGA:RPBE/TZP level. Again plot the band structure. Is it the same as the graph given above? Explain the parameter given on the x-axis? Explain the k-dependent energies of the HOMO and the LUMO.
- x. The band structure of CO depends on the lattice distance between the different CO molecules. Change the lattice distance from 3.0 to 2.5\AA . Again, perform a `single point` calculation and compare the band structure with that of **d.** and with that of experiment (Figure 1). What happens to the band

structure when changing the lattice distance? How well do your calculations compare with experiment?

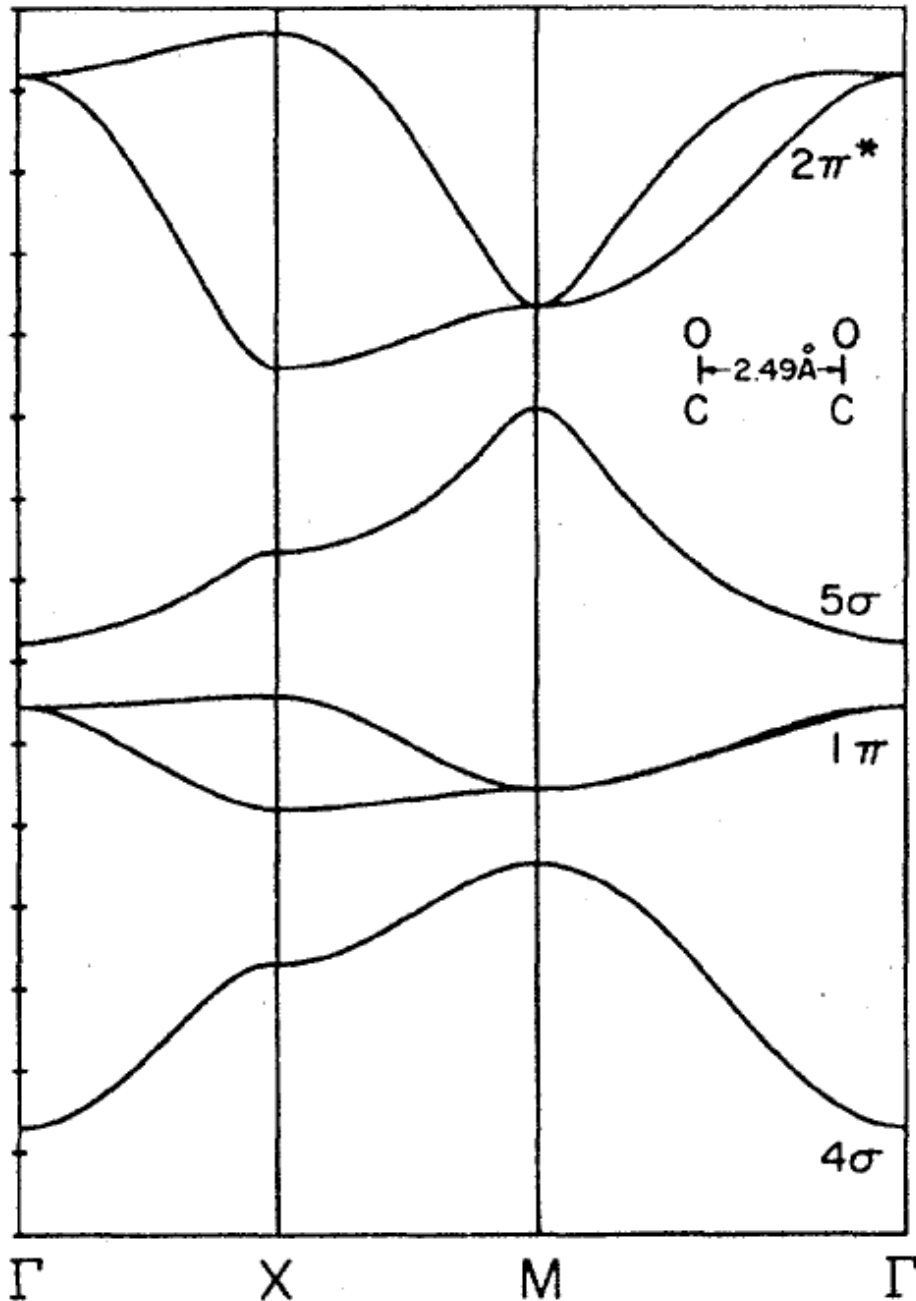


Figure 1: Band structure of CO molecules in 2 dimensions with a lattice distance of 2.49 Å. The labels Γ , X, M correspond to the number of the k-point on the x-axis of the band structure figure from ADF, where $\Gamma=1$ X=3 M=2 k-points.