Worksheet 1: Quantum chemistry and simple models

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Contents

General remarks

- Deadline for the report is **Wednesday, 2 May 2018, 13:00**

- In this worksheet, you can achieve a maximum of 20 points.

- The report should be written as though it would be read by a fellow student who attends the lecture, but does not do the tutorials.

- To hand in your report, send it to your tutor via email.

  – Miriam Kohagen (`mkohagen@icp.uni-stuttgart.de`)

- Please attach the report to the email. For the report itself, please use the PDF format (we will *not* accept MS Word doc/docx files!). Include graphs and images into the report.

- The report should be 5–10 pages long. We recommend using LaTeX. A good template for a report is available online.

- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

In this worksheet, you will first tackle a couple of theoretical task concerned with simple quantum chemistry model Hamiltonians. Secondly, you will perform several quantum chemical calculations using Hartree-Fock. The simulations will be performed using the software package ORCA.

All files required for this tutorial can be found in the archive `templates.zip` which can be downloaded from the lecture's homepage.

2 Short questions - short answers (4 points)

> **Task** (5 points)
>
> Answer the following questions:
>
> - What is the Born-Oppenheimer approximation?
> - What is the adiabatic approximation?
> - What are the simplifications of the Hartree-Fock approach?
> - What is the so-called Hartree-Fock limit?

3 Hückel approximation for benzene (6 points)

Benzene is a cyclic hydrocarbon with the chemical formula C_6H_6. The structure is planar due to six sp^2 hybridized carbon atoms which means that the electrons in the π-orbitals are largely delocalized. This results in two stable mesomeric conformations as shown in Fig. 1.
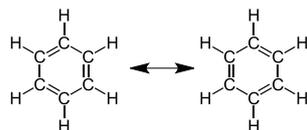
Figure 1: Chemical structure of benzene with mesomeric conformations.

An analytical approach for the calculation of the energy eigenvalues is given by the Hückel approximation.

The Hückel approximation has the following characteristics:

- Is applicable for conjugated hydrocarbons
- Only π-electrons are considered, σ-electrons are ignored
- Uses linear combination of atomic orbitals for the determination of the molecular orbitals (LCAO-MO)

- Uses orthonormal basis set, i.e., overlap integrals $S_{kl} = \delta_{kl}$

Schrödinger equation and atomic orbitals

Task (1 point)
Expand Ψ into relevant atomic orbitals and write down the corresponding Schrödinger equation.

Matrix equation

Task (3 points)
Write an explicit matrix representation for the Schrödinger equation with the following characteristics and orbitals: • Diagonal elements of the Hamilton matrix are given by α, and coupling terms between neighboring elements (*only*) by β Solve the equation for the energy eigenvalues and compare the total energy of benzene to that of ethene.

Energy eigenvalues (HOMO and LUMO representation)

Task (2 points)
• Draw the energy eigenvalues in an energy plot and distribute the electrons. Determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).   • Draw the molecular orbital (MO) diagram and denote the orbitals by $\pm$ notation.

4 Quantum chemical calculations using Orca (10 points)

4.1 Running the simulations

On the desktop PCs in the ICP CIP pool you can add Orca to your local environment by issuing the following command:

```
$> export PATH=/group/allatom/orca-2.9.1:$PATH
```

Afterwards, you should be able to simply run the `orca` executable.
You can run any Orca input file by issuing a command like:

```
$> orca <INPUT_FILE> &> <OUTPUT_FILE>
```

where already the redirection of standard and error output to the <output> file is included. Please note, that you do not have to redirect the output, but you will get a lot of screen output if you do not.
The user manual can be found online:
`http://rossi.chemistry.uconn.edu/chem5326/files/OrcaManual_2_9.pdf`
Example input files and input geometries are provided in the `templates.zip` archive. After unpacking of the archive, a couple of directories should have been created:

- `hydrocarbons` - one input file for Hartree-Fock calculations for the benzene dimer with the minimal basis set STO-3G and geometries for ethene, and 1,3-buta-diene

- `water` - input file for the geometry optimization in the gasphase and input files for one calculation with a plate capacitor

Please note, input files has to be adapted.

Hints

- You can use programs like MOLDEN or VMD to visualize your systems. A copy of these programs is also installed on the CIP pool computers. Please note so in your hand-in.

4.2 Quantum chemical energy of unsaturated hydrocarbons

Benzene is the prototypical aromatic hydrocarbon. You already calculated the stabilization energy of benzene using Hückel's molecular orbital theory, compared to the simple, unsaturated hydrocarbon compound ethene. Now, you will essentially perform the same calculation, but on a higher theoretical level, without semi-empirical assumptions.
As a first step, you will have to minimize the energy of each input structure with respect to its geometry (colloquially called "geometry optimization") using different basis sets. Geometry optimizations are necessary to obtain representative energies as different methods can give different potential energy surfaces. You should now investigate

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how multiple, conjugated double-bonds affect the geometry and energies of unsaturated hydrocarbons, and compare to the cyclic compound benzene.

Task (3 points)

- Perform geometry optimizations for ethene, 1,3-buta-diene, and benzene using different basis sets (STO-3G, 6-31G*, 6-31G**, 6-311++G**).

- Analyse structural parameters, like carbon-carbon bond lengths, and angles and compare the energies. Explain the differences in the energies for different basis sets.

- Calculate the stabilization energy due to the aromaticity in benzene. Compare this value to what you obtained in the Hückel-MO calculations.

Hints

- You can use VMD to analyse structural properties, like bond lengths, angles, and dihedrals. Labels for the latter quantities are created by enabling different selection modes for the mouse in the VMD main window under `Mouse→Label`. The so created labels can be analysed under `Graphics→Labels→Graph`.

Hückel MO theory is attractive because of its simplicity and general support of chemical intuition. However, the theory also has its limitations, e.g., it cannot describe multiple interacting, but non-bonded molecules. Hence, it simply cannot describe the interaction of two stacked benzene molecules, as they are only bound by van-der-Waals interactions. Ab initio quantum chemical methods are more general and should in principle be capable of describing arbitrary chemical compounds. Nevertheless, many theories are approximate to some degree, either in the theory itself, or in its application. We will now investigate one theory (Hartree-Fock) and its description of the benzene dimer at its minimum energy configuration. We will come back to this in a subsequent worksheet and use also DFT and MP2.

Task (2 points)

- Calculate the stabilization energy of the benzene dimer at the given geometry with Hartree-Fock.

- Explain the observed differences.

4.3 Polarization energy of a water molecule

Another simple model is the so-called "Drude-oscillator" model which describes the response to an electric field. The corresponding inducible dipole moment is represented by a charge on a harmonic spring. The model is commonly used in molecular simulations

(to which we will come later in more detail) to explicitly treat polarizability. The energy E_{pol} needed to induce a dipole moment μ in the Drude oscillator is given by:

$$E_{\text{pol}} = \frac{1}{2}\alpha E^2 \tag{1}$$

where α is the dipole polarizability and E the electric field. In principle, we need to work with tensorial and vectorial quantities for α and E. However, we will only focus on the z-direction. Think about why this makes sense in the setup that we are using. Our aim in this part of the exercise is to examine how well eq. 1 describes quantum-mechanical reality.

At first, we take a look at a single water molecule embedded in a continuum solvent, representing liquid bulk water. You will study how the liquid influences the single water molecule, in terms of energy and structure, and also to get an idea of the electric fields present in a dense liquid. You can find the input for the gas phase simulations in the `templates.zip` archive. First check the Orca manual for the keyword needed to perform the calculation with an implicit water model. Here, Cosmo should be used. The dipole moment is calculated automatically. Check the manual for the keyword needed to calculate the polarizability.

Task (2 points)

- Perform geometry optimizations with and without implicit solvent ("Cosmo") for a single water molecule.

- Analyse geometry, energy, dipole moment, and polarizability in both cases.

- Extract the electric field acting on the water molecule.

We now have a good starting guess for the electric field in liquid water. By applying various external electric fields, we can now investigate the range of validity of the Drude-oscillator model. Therefore, you are going to perform a number of energy calculations with varying field strength. In Orca, this can be done by putting the water molecule between two plates of a plate capacitor. It is an approximation, but the field we get is homogeneous enough for our purpose. The field strength can be varied by choosing different charges on the plates of the capacitor. Take a look at the file called pointcharges.pc. The first row contains the charges, the second, third and forth, the x-, y- and z-coordinates, respectively.

Task (3 points)

- Perform several calculations with applied electrical fields of varying strength for a single, isolated water molecule (field along the z-axis).

- Calculate the polarization energy and compare with the Drude-oscillator model.

- Calculate and compare dipole moments for both Drude dipole and water molecule.

- Explain deviations from the simple Drude-oscillator model at high field strengths.

Hints

- Energies obtained with Orca applying a plate capacitor also include the interaction energies of the charges of the capacitor with each other.