Worksheet 5: Quantum chemistry and simple models

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Contents

General Remarks

- Deadline for the report is **Monday, 3 July 2017, 12:00 noon**

- 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 doesn't do the tutorials.

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

  - Frank (`fuhlig@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, density functional theory, and many-body perturbation theory. The simulations will be performed using the software package CP2K.

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

2 Short Questions - Short Answers (5 points)

> **Task** (5 points)
>
> Answer the following questions:
>
> - What is the Born-Oppenheimer approximation?
>
> - What are the simplifications of the Hartree-Fock approach?
>
> - What do the Kohn-Sham equations describe?
>
> - When is it useful to use DFT compared to Hartree-Fock? Give reasons for your choice.

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.
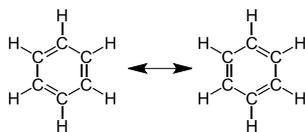

Figure 1: Chemical structure of benzene with mesomeric conformations.

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

The Hückel approximation has the following characteristics:

- Applicable for conjugated hydrocarbons

- Only π-electrons are considered, σ-electrons are ignored

- Usage of linear combination of atomic orbitals for the determination of the molecular orbitals (LCAO-MO)

- 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 ethylene.

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 wave function schematically and denote the orbitals by $\pm$ notation.

4 Quantum chemical calculations using CP2K(10 points)

4.1 Installing CP2K

You can download CP2K from its git-repository:

```
$> git clone https://github.com/cp2k/cp2k
```

You can build an OpenMP-parallelized version of CP2K as follows:

```
$> cd cp2k
$> wget goo.gl/4jO56j -O libint.sh && chmod +x ./libint.sh
$> ./libint.sh
$> wget goo.gl/Fr3xek -O myCP2K.sopt
$> sed -i s#'LOCAL_LIBINT'#"${PWD}/extra_libs/libint/lib"#g myCP2K.sopt
$> mv myCP2K.sopt cp2k/arch/
$> cd cp2k/makefiles
$> make ARCH=myCP2K VERSION=sopt
```

This assumes that you have the GNU compiler collection (gcc/gfortran), and basic linear algebra packages installed (LAPACK, BLAS). If everything goes well, the final executable `cp2k.sopt` will be located under `cp2k/exe/myCP2K`.

Hint

- You can supplement the make command with the `-j <NCPUS>` option, where <NCPUS> is to be substituted by the number of parallel processes used to build CP2K.

- If you desire advanced features, examine the other architecture files included in the CP2K distribution. They are however not necessary for this tutorial.

4.2 Running the Simulations

On the desktop PCs in the ICP CIP pool you can add CP2K to your local environment by issuing the following command:

```
$> export PATH=/group/sm/2017/tutorial_05/cp2k/exe:$PATH
```

Afterwards, you should be able to simply run the `cp2k.sopt` executable. In case you installed CP2K in a different location, change the path in the above command accordingly to the location of the executable. You can run any CP2K input file by issuing a command like:

```
$> cp2k.sopt <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.

Example input files and input geometries are provided in the `templates.tar.gz` archive. After unpacking of the archive, a couple of directories should have been created:

- `hydrocarbons`

    - `inputs` - input files for DFT and MP2 calculations
    - `structures` - geometries of hydrocarbon complexes

- `polarization energy` - input files and input geometry

which contain all the necessary files for running the calculations. Please note, input files may need adapting, especially in the `&GLOBAL` section, before plainly running them.

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.

4.3 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 ethylene. 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"). This is necessary to obtain representative energies as different methods can give different potential energy surfaces. You should now investigate 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 ethylene, 1,3-buta-diene, 1,3,5-hexa-triene, and benzene.

- Analyse structural parameters, like carbon-carbon bond lengths, and angles.

- 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 a few theories and their description of the benzene dimer at its minimum energy configuration. As our high-level reference, we choose Møller-Plesset perturbation theory in 2nd order (MP2). The gold-standard for these kinds of systems is coupled-cluster theory with doubles and perturbative triples, but is too expensive for us to calculate.

Task (2 points)

- Calculate the stabilization energy of the benzene dimer at its equilibrium geometry with Hartree-Fock, Møller-Plesset perturbation theory (2nd order), and density functional theory.

- Explain the observed differences.

- Collect information on the time needed for each calculation, and rationalize the differences.

4.4 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 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. The polarization energy given in the CP2K output is not the one corresponding to our definition in eq. 1. The output value CP2K corresponds to $-4E_{\text{pol}}$.

Task (2 points)

- Perform geometry optimizations with and without implicit solvent 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. The field strengths should lie between 0.005 $\text{E}_\text{h}/(\text{ea}_0)$ and 0.45 $\text{E}_\text{h}/(\text{ea}_0)$.

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

- You can run the calculations for the different field strengths in the same directory to make use of previous initial guesses.

- Energies obtained with CP2K with an applied external field also include the interaction of the field with the charge density. You can assume that this is well represented by the dipole–electric field interaction.