Worksheet 1: Quantum chemistry and simple models

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General remarks

- Deadline for the report is **Wednesday, 1 May 2019, 13:00**.

- In this worksheet, you can get **a maximum of 15 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: Maofeng Dou (mdou@icp.uni-stuttgart.de).

- For the report, please use the **PDF format** (unfortunately, MS Word doc/docx files are not accepted) and include graphs and images. We recommend using LATEX. A good template for a report is available online.

- The report should be **4–8 pages long**.

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

1   Introduction

In this worksheet, you will first tackle a few theoretical tasks related to simple quantum chemistry m odel Hamiltonians. You will also perform several quantum chemical calculations using Hartree-Fock. The simulations will be performed using the software package CP2K. 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 (4 points)

- Q1: What is the Born-Oppenheimer approximation?

- Q2: What is the adiabatic approximation?

- Q3: What are the simplifications of the Hartree-Fock approach?

- Q4: 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 orbitals are largely delocalized. This results in two stable 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 the wavefunction 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.
>
> Solve the equation for the energy eigenvalues and compare the total energy of benzene to that of ethene.

4 Quantum mechanical calculations using Orca (5 points)

4.1 Running the simulations

1). Prepare files for simulation

The files required include a structure file (xyz format), input file (.inp).

Examples are provided in the templates.tar archive. After unpacking the archive, a couple of files, named **benzene.xyz**, **benzene_dimer.xyz**, **bu-**

tadiene.xyz, **ethene.xyz**, **ethene.inp**, and **benzene_dimer.inp**, should have been created.

3). Run Orca

The Orca program is istalled at directory **/group/allatom/orca-2.9.1**. Run Orca executable by typing:

/group/allatom/orca-2.9.1/orca input.inp &> output.out

Here, input.inp and output.out is the name of the input and output file, respectively. Please note, that you do not have to redirect the output, but you will get a lot of screen output if you do not.

Hit:

- It is better to define /group/allatom/orca-2.9.1/orca as environment variable in the bashrc under your account.

- Please note: input files has to be adapted

The manual for Orca can be found here:
`http://rossi.chemistry.uconn.edu/chem5326/files/OrcaManual_2_9.pdf`

4.2 Quantum chemical energy of unsaturated hydro-carbons

Benzene is a 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"). Geometry optimizations are 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 ethene, 1,3-buta-diene, and benzeneusing different basis sets (STO-3G, 6-31G*, and 6-31G**).

- Analyse structural parameters, like carbon-carbon bond lengths, and an-gles and compare the energies. Explain the differences in the energies fordifferent basis sets.

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

Hits

- You can use VMD or VESTA 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 $\longrightarrow$ Labels. The so created labels can be analysed under Graphics $\longrightarrow$ Labels $\longrightarrow$ 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.

Task (2 points)

- Optimize the geometry of the benzene dimer (π-stacked) at different separation distance, plot the curve of total energy versus separation distance and find the distance with lowest total energy.

- Calculate the binding energy of the benzene dimer at the optimized distance.