

Worksheet 2: Density Functional Theory (DFT)

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Contents

1	Introduction	2
2	Short Questions - Short Answers (7 points)	2
3	Local spin-density approximation and Thomas-Fermi energy of hydrogen atom (5 points)	3
4	Quantum chemical calculations using Orca (8 points)	3
4.1	Quantum chemical energy of benzene from density functional theory (DFT)	4
4.2	Calculation of the basis set superposition error (BSSE) for the benzene dimer using DFT	6

General Remarks

- Deadline for the report is **Monday, 24 May 2021, 23:59**.
- 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.
 - Azade Yazdan (ayazdan@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** people.

1 Introduction

In this worksheet, you will first tackle a couple of theoretical tasks concerned with the density functional theory.

All files required for this tutorial can be found in the archive `templates.zip`, accessible from the exercises' homepage on ILIAS.

2 Short Questions - Short Answers (7 points)

Task

(7 points)

Answer the following questions:

- What do the Hohenberg-Kohn theorems state?
- How is the system treated and described in the Kohn-Sham DFT?
- Compare DFT to the Hartree-Fock method and explain when is it useful to use DFT compared to Hartree-Fock?
- What is the main difference between LDA and GGA density functionals?
- What is the self-interaction error?
- Why regular LDA- or GGA-type density functionals cannot describe long-range van der Waals type interactions?
- What is the major advantage of using Kohn-Sham equations instead of pure DFT equations?

3 Local spin-density approximation and Thomas-Fermi energy of hydrogen atom (5 points)

The local spin-density (LSD) approximation introduces a new variable to our density functional, namely the spin density $m(\mathbf{r})$. The spin density is defined as the difference between individual densities for α and β spin as $m(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$. Introducing spin densities allows for a more complete description of the physics in our systems. It is also necessary to correctly describe systems with unpaired electrons, i.e., radicals like the hydrogen atom. The corresponding kinetic energy is defined as:

$$T_s[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2\right) \phi_{i\sigma}(\mathbf{r}), \quad (1)$$

where $\phi_{i\sigma}$ are spatial parts to the spin orbitals $\psi_i(\mathbf{r}s) = \phi_{i\sigma}(\mathbf{r})\sigma(s)$ and the $\sigma(\mathbf{r})$ are spin eigenfunctions. Here and throughout the text, we use atomic units.

We write for convenience $T_s^0[\rho] = T_s[\frac{1}{2}\rho, \frac{1}{2}\rho]$. The superscript 0 indicates completely paired spin densities, i.e., $m(\mathbf{r}) = 0$ everywhere. This kinetic energy is, however, not generally equal to the exact Kohn-Sham kinetic energy $T_s[\rho]$, $T_s[\rho] \neq T_s^0[\rho]$. A specific example is the case of an odd number of electrons.

For all of our following calculations, we use the Thomas-Fermi density functional. It is one of the earliest density functional theoretical descriptions available. The Thomas-Fermi kinetic energy density functional T_{TF} for an electron density $\rho(\mathbf{r})$ (without spin) is given by:

$$T_{\text{TF}} = C_{\text{F}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}, \quad \text{with} \quad C_{\text{F}} = \frac{3}{10} (3\pi^2)^{2/3}. \quad (2)$$

Task (5 points)

- Derive the general formula for the kinetic energy functional in terms of kinetic energies for the spin-unpolarized case: $T_s[\rho^\alpha, \rho^\beta] = \frac{1}{2} T_s^0[2\rho^\alpha] + \frac{1}{2} T_s^0[2\rho^\beta]$.
- Use the Thomas-Fermi kinetic-energy density functional as an approximation to $T_s^0[\rho^{\alpha/\beta}]$ and calculate the kinetic energy of a hydrogen atom within the local density approximation and the local spin-density approximation. Note that for the 1s ground state of the hydrogen atom $\int \rho_{1s}^{5/3} d\mathbf{r} = 0.1007$. Compare your value to the exact value for the hydrogen atom.

4 Quantum chemical calculations using Orca (8 points)

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 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. You do not have to redirect the output, but you will get a lot of screen output if you do not.

The user manual for the Orca version installed on the CIP Pool machines was already included in the files for the previous worksheet on ILIAS.

Some files are provided in the `templates.zip` archive. After unpacking of the archive, a couple of directories should have been created:

- **benzene** - output files of the geometry optimizations of the dimers. Please note, the output files come from a newer version of Orca than you are using. Keywords for certain options can be different.

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.
- On most Linux distributions there already is an `orca` command, which is a screen reader and **not** the quantum chemistry program.

4.1 Quantum chemical energy of benzene from density functional theory (DFT)

Benzene is the prototypical aromatic hydrocarbon.

You already investigated the benzene dimer at its minimum energy configuration and calculated the stabilization energy with Hartree-Fock in the first worksheet. We will now investigate two more 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

(5 points)

- Starting with the benzene monomer, perform geometry optimization with DFT and MP2 methods; use the PBE functional with the 6-31G** basis set. Check out the manual for the corresponding keywords.
- Using the output files for the geometry optimization of the benzene dimer in the **templates.zip** archive, calculate the stabilization energy of the benzene dimer at its minimum energy configuration with MP2 and DFT methods.
 - Look inside each file to find out which method, functional and basis set have been used. You will find two output files for HF; if you examine the last lines in these two files, you should be able to find their relation.
 - In case you would like to perform these calculations yourself, make sure to use the 'verytightSCF' option in your optimization. You can then compare your results to those in the provided output files.
- Repeat the first point (geometry optimization of the benzene monomer) with the DFT and MP2 methods, this time with applying a dispersion correction with Becke-Johnson damping; use the same basis set and functional as point one above. Check out the manual for further details and the corresponding keywords. The output file of the geometry optimization for the dimer, with the dispersion correction, can be found in the **templates.zip** archive. Why a dispersion correction has to be applied to obtain reasonable results here?
- Determine the distances between the rings for all calculations.
- Explain the observed differences in the stabilization energies and in the distances. Take also the result of the Hartree Fock calculations from the first worksheet into account.
- Collect information on the time needed for the monomer calculations, and rationalize the differences. Such info can be found at the end of your output file for each calculation.

Hints

- For more details about the dispersion energy problem in DFT check out 'A Chemist's Guide to Density Functional Theory', Wolfram Koch and Max C. Holthausen, 2nd Edition (page 236) Wiley-VCH. A scan of this chapter is provided.
- 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**.

4.2 Calculation of the basis set superposition error (BSSE) for the benzene dimer using DFT

In the following task you will calculate the basis set superposition error (BSSE) for the benzene dimer.

Task	(3 points)
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- Explain in your own words what the BSSE is and why it occurs. How does the BSSE behave in dependence of the size of the basis set?
- Write down the equation for the counterpoise correction of the benzene dimer.
- Calculate the BSSE for the **stabilization energy of the benzene dimer** and the **corrected stabilization energy** using the DFT method with the dispersion correction of Becke-Johnson damping, PBE functional and 6-31G** basis set. Check out the manual for the corresponding keywords and an example at the 'Counterpoise correction' section.
 - If you are not able to run the calculation as suggested in the manual in one input file, you can simply do each section in a separate input file, and at the end do the calculations yourself.