

Worksheet 6: Density functional theory and ab initio molecular dynamics

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General Remarks

- Deadline for the report is **Monday, 17th 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 tasks concerned with density functional theory. Secondly, you will perform several ab initio molecular dynamics simulations of water clusters and examine their vibrational spectra, and properties. 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:	
<ul style="list-style-type: none">• What is the main difference between LDA and GGA density functionals?• What is the self-interaction error?• Which minimum output frequency is needed to describe a vibrational mode of 3000 cm^{-1}?• Why can regular LDA- or GGA-type density functionals not 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 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 Ab initio molecular dynamics simulations of small water clusters (10 points)

In this exercise, you will perform several simulations of small water clusters. You will use the density-functional tight-binding approximation to calculate forces for the molecular dynamics integrator.

All simulations are performed with CP2K. CP2K is an open-source ab initio molecular dynamics software package available at <https://www.cp2k.org/>. You can either use the computers in the ICP CIP pool or install CP2K on your own computer.

Download the archive `templates.tar.gz` from the lecture website. After unpacking, you will find different files and directories in the included directory:

- `setup/`: directory containing input file templates
 - `md.inp`: general input file to be used for molecular dynamics
 - `geoopt.inp`: general input file to be used geometry optimizations
- `data/`: directory containing parameter files needed for simulations

The data directory contains parameters for the DFTB calculations. This directory (or a symbolic link to it) needs to be present in the directory where you run the calculations. Symbolic links can be created by:

```
$> ln -s <TARGET> <LINK_NAME>
```

The online, input reference for CP2K is available at <https://manual.cp2k.org/>. Please note that this reference manual merely contains the available input options, but not detailed information on the involved algorithms. The relevant references are, however, linked in the corresponding sections. All input is structured into sections that start with `&SECTIONNAME` and end with an `&END`. All sections can contain further subsections and keywords.

4.1 Installing CP2K

In case you are doing these exercises in the computer pool of the Institute for Computational Physics, skip this section and use the pre-installed version of CP2K. Otherwise, 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/cp2k/arch
$> wget goo.gl/M5JYhr -O myCP2K.sopt
$> cd ../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:

```
$> export PATH=/group/sm/2017/tutorial_06/cp2k/exe:$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.

First we start by constructing our input geometries. You can be creative and use any method that comes to mind except copying from existing structures. After that, inspect the input files and modify them to include the geometries you just created. Note that algorithms and their parameters in the input files do not need to be changed.

Task

(4 points)

- Create input structures for a water monomer and a water dimer. Explain how and why you chose that path.
- Perform geometry optimizations for each of the structures to obtain input structures for the molecular dynamics simulations. How much do the optimized structures differ from your input structures, and your expectations.
- What is the potential energy of the hydrogen bond in your water dimer?
- Run several simulations of the water dimer at different temperatures. Select a temperature for your final production simulation. Explain your choice.

The timestep for the molecular dynamics is set to 0.5 fs which is small enough to allow accurate integration of Newton's equations of motion and large enough to achieve

reasonable sampling. The only input parameters you are supposed to change are the temperature used for thermostating and the total number of integration steps. In the preceding task, you determined a temperature for your final production runs. Run simulations for both water monomer and dimer at that temperature and use these trajectories for your final analysis and to answer questions in the next subsection. Increase the run time at least ten-fold compared to the values in the to you provided input files. This should suffice to achieve reasonable sampling.

Hints

- You can use programs like MOLDEN or AVOGADRO to build and visualize your systems. A copy of MOLDEN is also installed on the CIP pool computers in the CP2K directory.
- In case you suffer a critical lack of creativity, you can download reasonable input structures from: <http://www-wales.ch.cam.ac.uk/~wales/CCD/anant-watc1.html>. Please note so in your hand-in.

4.3 Analysis of the ab initio molecular dynamics simulations

In the following tasks, you will analyse the simulation data in various ways. Only use the part of the simulation that is equilibrated. You can judge the relaxation by trends seen in the potential energy of the simulation.

Energy and geometry

After running the molecular dynamics simulation, CP2K will have generated several output files. `MD-pos-1.xyz` contains the corresponding trajectory, `MD-1.ener` the relevant energies of your system during the MD. The latter file contains a header line denoting the contents of the individual columns.

Task	(2 points)
<ul style="list-style-type: none">• Determine the mean, potential energy of the hydrogen bond and compare the value to the one obtained in the geometry optimizations.• Determine and compare structural properties of the water dimer at finite temperature to the one obtained in the geometry optimizations.	

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`.

Infrared spectroscopy

The infrared, vibrational spectrum can be obtained from molecular dynamics simulations. The necessary information is the total dipole moment of the simulated system. Your CP2K simulations should have produced a corresponding output file called `DIPOLE.out`. The classical approximation to the infrared absorption cross-section α is:

$$\alpha(\nu) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \sum_{j=x,y,z} \left| \int_0^{\tau} dt \exp(-i\nu t) \frac{d\mu_j}{dt} \right|^2, \quad (3)$$

where μ_j are the cartesian components of the system's dipole moment.

Task

(4 points)

- Determine the infrared spectra of the water monomer and dimer. Plot the absorption cross-section α in dependence of the wavenumber in cm^{-1} .
- What is the origin of the individual vibrations?
- Explain the differences in the obtained monomer and dimer spectra and their origins.

Hints

- You can perform numeric differentiation and Fourier transforms efficiently with `NUMPY`.