Worksheet 2: Properties of water from quantum mechanical and atomistic simulations

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General remarks

- In this worksheet, you can get **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: 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 **5–10 pages long**.
- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

In this worksheet, you will first tackle several theoretical tasks related to water molecule. After that, you will run quantum mechanical calculations of a water monomer and dimer using CP2K. In the third part, you simulate liquid water using GROMACS and run various analyses on the simulation data to investigate the properties of water.

2 Short questions - short answers (4 points)

In this section, you will answer few questions related to the fundamental properties of water. Please use your own words to answer the questions.

Tasks (4 points)

- Q1: Why is a water molecule polar?
- Q2: What is a hydrogen bond?
- Q3: What are the values for the H-O-H angle in water and the typical distance of a hydrogen bond (not O-H bond)?
- Q4: What are the main differences between SPC, SPC/E, and TIP3P water models?

3 Quantum mechanical calculation of water (8 points)

In this section, you will calculate the water monomer and dimer using different funcitonals as implemented in CP2K. The input files and structure files are in the directory named cp2k.

3.1 Quantum mechanical calculation of water

In this section, you will first calculate the water dimer and analyse the structure properties (e.g., bond length) and partial charges of water.

Tasks (2 points)

- Perform simulations of water dimer using PBE funcitonals with and without van der Waals corrections, compare the O-H and hydrogen bond lengths calculated using different functionals.
- Present the Hirshfeld charges of O and H in water monomer calculated using different functionals.

Notes:

- The Hirshfeld charges will be printed to the output file (.out) of CP2K with key words "Hirshfeld Charges" after each calculation.
- A input example is provided in the directory named cp2k.
- For van der Waals correction, we will use Grimme D3 approach and an input example is provided for PBE functional.

3.2 *Ab initio* molecular dynamics simulation of water dimer

In the following tasks, you will perform *ab initio* molecular dynamics simulation of water dimer using PBE functional with van der Waals Grimme D3 correction and analyse the simulation data from your production runs. Only use the part of the simulation that is equilibrated. After running the molecular dynamics simulation, CP2K will have generated several output files. The water-pos-1.xyz contains the corresponding trajectory and the water-1.ener file the relevant energies of your system during *ab initio* molecular dynamics simulation. The latter file contains a header line denoting the contents of the individual columns.

Tasks (3 points)

- Run test simulations of the water monomer and dimer at different temperatures, e.g., 100 and 300 K for some steps (e.g., 2000-3000 steps). Select a temperature for your final production simulation (e.g., with steps about 10000). Explain your choice.
- Determine the mean potential energy of the hydrogen bond of water dimer. Do the same for only the input structures and compare the two values
- Determine and compare the hydrogen bond length of the water dimer at finite temperature to the one given as input structure.

3.3 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 of dipole moment, e.g., water-dipole.out. The classical approximation to the infrared absorption cross-section α is:

$$\alpha(\nu) = \lim_{\tau\to\infty} \frac{1}{\tau} \sum_{j=x,y,z} \left| \int_0^\tau dt \exp\left(-it\nu\right) \frac{d\mu_j}{dt} \right|^2, \tag{1}$$

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

Tasks (3 points)

- Compute and plot the absorption cross-section α in dependence of the wavenumber (wavenumber is in the unit of cm^{-1}.)
- Explain the differences in the obtained monomer and dimer spectra and their origins.

4 Atomistic simulation of water (8 points)

In this section, you will perform several simulations of water with different water models using GROMACS, which is a freely available at `www.gromacs.org`. You can either remote access the computers in the ICP CIP pool or install GROMACS on your local computer. The source code of GROMACS can be download at `http://www.gromacs.org/Downloads`.

4.1 Files required for simulation

In the gromacs directory, you will find the follow files required for simulation and analysis:

- **conf.gro**: pre-equilibrated water structure with 216 solvent molecules which can be visualized the system using VMD.
- **grompp.mpd**: parameters for the simulation
- **topol.top**: topology file for the water simulations including a link to the force field parameters
- **index.ndx**: file needed for the analyses

4.2 Running the Simulations

In this section, we will perform simulation of water using different water models.

Task (1 point)

- Perform simulations of water at 300K for 500 ps (with time step of 2 fs) using SPC, SPC/E, and TIP3P water model, respectively.

The water model can be defined through keywords `#include "XXX.itp` in the the **topol.top** file, for example `#include "spc.itp"` , `#include "spce.itp"` and `#include "tip3p.itp"` for SPC, SPC/E, and TIP3P water model, respectively.

In order to have the required GROMACS commands available in your terminal, execute the following command:

```
source /group/allatom/gromacs-4.6.7/bin/GMXRC
```

and then call the GROMACS preprocessor grompp via:

```
grompp
```

If grompp completed without errors, the simulation can be started with

```
mdrun -v
```

The system will then be simulated for 500 ps with a time step of 2 fs at 300 K.

4.3 Analysis

In the following tasks, you will analyze the simulation data in various ways using a variety of tools in GROMACS.

1. Radial distribution function

The radial distribution function (RDF), which gives the local structure information of the liquid water, can be computed by typing the command:

```
g_rdf -n index
```

Tasks (2 points)

- Compute the RDFs of the systems you have simulated.
- Compare the RDFs of the different water models and interpret the results (peaks, distances between peaks, differences between water models).

2. Hydrogen bond analysis

Hydrogen bonding is essential in liquid water and influences many of the water properties.

Task (1 points)

- Run the hydrogen bond analysis for the different water models and calculate the average number of hydrogen bonds per water molecule.

The number of hydrogen bonds within the simulated system can be determined via

```
echo -e "0\n0" | g_hbond
```

3. Mean square displacement and diffusion coefficient

In three-dimensional space, the diffusion coefficient D can be calculated from the mean square displacement (MSD) function

$$\langle \Delta r^2(t) \rangle = 6Dt$$

for large enough t. You can calculate the MSD using GROMACS with

```
g_msd -n index
```

Tasks (4 points)

- Compute the MSD for each of the different water models.
- Have a look at the output files msd.xvg for the different water models and compare them. What are the differences? Can you identify the diffusional ($\langle \Delta r^2(t) \rangle \propto t$) and the ballistic regime?
- Determine the fitting range that GROMACS uses and check if it is a sensible choice for you analysis. If not, adapt the options to the `g_msd` command.