Worksheet 3: QM/MM methods and *ab initio* molecule dynamics

Maofeng Dou, Kartik Jain, and Maria Fyta

Institute for Computational Physics, University of Stuttgart

April 2019

General remarks

- Deadline for the report is **Wednesday, 29 May 2019, 13:00**.
- In this worksheet, you can get **a maximum of 22 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 calculate a couple of theoretical task concerning quantum-mechanics/molecular mechanics (QM/MM) and *ab initio* molecule dynamics using CP2K. The files required for this tutorial can be found in the archive templates.zip which can be downloaded from the lecture's homepage.

Note

- In the worksheet 1 and 2, the ready-to-use structure and input files are provided. In this worksheet, only the basic parameters in the input files are provided, you are asked to add the key parameters for different tasks yourself.
- For the report, it is highly recommend to include more details, for example, the optimized structure at each adsorption site. Even your final results is not accurate, you still get some points as long as you calculation process/step is correct.

2 Run CP2K

2.1 Prepare input files

The basic files required for simulation include input file (.inp), basis-set file (BASIS_MOLOPT), pseudopotential file (GTH_POTENTIALS). Example is provided in the templates.zip archive, which includes

- libs, it contains BASIS_MOLOPT, GTH_POTENTIALS and dftd3.dat (for van der Waals D3).
- qmmm, it contains input file (qmmm.inp) for QM/MM simulation, structure of water molecule (water.xyz) to be adsorbed on Au surface, and Au.pot (data for Au described by embedded atom model).
- water_monomer, it contains input file (md.inp) for *ab initio* molecule dynamics simulation and structure of water monomer (water_monomer.xyz).
- water_dimer, it contains input file (md.inp) for *ab initio* molecule dynamics simulation and structure of water dimer (water_dimer.xyz).

you should modify the input files like the lattice parameters, MM_INDEX according to your structure.

For details of the input and output parameters, please refer to the CP2K manual:

`https://manual.cp2k.org/#gsc.tab=0`
Note: please choose the version 5.1

2.2 Run CP2K

The CP2K excutable (named cp2k.sopt) is installed at directory:
/group/allatom/cp2k/cp2k-5.1/exe/icp2.

```
cp2k.sopt -i input.inp -o output.out
```

3 QM/MM simulation using CP2K (10 points)

We already calculated the interaction of benzene-benzene and graphene-graphene using Hartree-Fock and DFT with van der Waals, respectively. In some cases, e.g., surface adsorption, we may be more interested in some parts, e.g., the adsorbate. However, the rest of the system is still too important to be ignored.. QM/MM is one of the options for such system.

In this section, you will use additive QM/MM approach to calculate the water molecule adsorbed on Au surface, where the water molecule and Au will be treated at QM (using PBE functional) and MM level (using emmbeded atom model (EAM)), respectively.

Tasks (3 points)

- Optimize the structure of one water molecule adsorbed on the (100) surface of Au using QM/MM where the interactions between Au and water are treated using Lennard-Jones potential.
- Calculate the adsorption energy of water molecule on the (100) surface of Au using QM/MM approach.
- Analyze the structures (e.g., O-H bond length, H-O-H bond angle, and Au-O and/or Au-H bond length) and properties (e.g., electron density, DOS and dipole moment) of the adsorbed water molecule. Understand the origin of the differences compared the free-standing water molecule.

Notes:

- For the slab of the Au (100) surface, it is recommended to create a 2×2 supercell with at least **4 atomic layers**.
- To optimize the water at Au surface, in principle, you should analyze all the possible adsorption sites and configurations to find the most stable ones. In this work, to avoid heavy and repeating calculations, it is suggested to calculated the most possible adsorption sites, like ontop and bridge sites. If you already know some global optimization methods, you are free to choose global optimization methods to find the most stable sites and configurations.
- It is recommended to keep the Au atom fixed during your relaxation.

In the above calculations, the interaction between Au and water molecules are treated using Lennard-Jones potential. Now, we will introduce the interactions which are ignored in the last task to understand the origin and differences of those interactions.

Tasks (7 points)

- Repeat the procedures in the above task but including electrostatic interactions between Au and water molecule. This can be done by setting image charge on Au atoms.
- Repeat the processes in the above task but with two layers of Au treated at QM level. **Note, due to memory issue, this task mostly can not be done on desktop, so, it recommended to understand to input parameters. Calculations and associated report for this task are not mandatory**.
- Compare the differences of the dipole moment, electron density and DOS calculated from two/three approaches and explain why.

In this worksheet, you are asked to use ASE (Atomic Simulation Environment) to prepare the structures of Au surface and water molecule adsorbed on the Au surface. The homepage of ASE is `https://wiki.fysik.dtu.dk/ase/`.

If you are comfortable with other program, you are free to choose other methods to create the surfaces and adsorbate on the surfaces.

3.1 Install ASE

It is recommended to installing ASE through Anaconda distribution, which can be downloaded from here `https://www.anaconda.com/distribution/`. Please choose the 3.x version.

Once the Anaconda is installed, simply type **conda install -c conda-forge ase** from the terminal to install ASE.

3.2 Create surface using ASE

There are two ways to create surfaces of a given crystal. One is to use to build-in function in ASE to create common surfaces, e.g., (100), (111), and (110), of common crystals like FCC and BCC. The other approach is to use the **surface** function in ASE to create non-common surfaces of a give crystals. We will use the second approach.

- Download the crystal structure of Au (materials-id: mp-81) from Materialsproject database: `https://materialsproject.org/`
- Read the structure file (e.g., .cif format) using *ase.io.read* function. `https://wiki.fysik.dtu.dk/ase/ase/io/io.html#ase.io.read`
- Create a slab of the (100) surface of Au using the surface function in ASE. The length of the vacuum layer in the slab should be **at least 12 Å**. To save computational time, please choose **4 atomic layers**. The detail instruction is here: `https://wiki.fysik.dtu.dk/ase/ase/build/surface.html#create-specific-non-common-surfaces`, please refer to the section of *"Create specific non-common surfaces"*.
- Make a $2 \times 2 \times 1$ supercell of the created slab. The details of how to make supercell in ASE is `https://wiki.fysik.dtu.dk/ase/ase/build/tools.html`, please refer to the function *"ase.build.make_supercell"*.

3.3 Add water molecule on the surface

- Read the structure of water molecule from the water.xyz file provided.
- Using the function *"ase.build.add_adsorbate"* to add water molecule on the (100) surface of Au. `https://wiki.fysik.dtu.dk/ase/ase/io/io.html#ase.io.read`.
- Manipulate the molecule if need, e.g., rotation. **Note: if the molecule is out-side of your slab box, please use *wrap* function or shift your molecule**.

- Write out the structure (in the format of .xyz) using *ase.io.write* function.

3.4 Run simulation using CP2K

Once the structure files been created, put them into the directory you wish and change the value of the COORD_FILE_NAME in qmmm.inp to the path and name of your structure file. Please do not forget to change the lattice parameters and MM_INDEX.

4 *ab initio* molecule dynamics of water (12 points)

In this section, we will calculate the water monomer and dimer using *ab initio* molecule dynamics. The input files and structure files are already provided. Since the computational time (about 13 hours for each simulation) will be larger compared to that of the QM/MM, the input parameters are already optimized, you only need to modify the parameters, like temperature, number of steps, and structures, in the .inp file.

Task (1 points)

- Run test simulations of the water dimer at different temperatures, e.g., 100 and 300 K for some steps (e.g., 2000 steps). Select a temperature for your final production simulation (e.g., with steps about 10000). Explain your choice.
- Run a simulation for the monomer at the same temperature..

4.1 analysis

In the following tasks, you will analyse the simulation data from your production runs 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.

After running the molecular dynamics simulation, CP2K will have generated several output files. water-pos-1.xyz contains the corresponding trajectory, water-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 (3 points)

- 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 structural properties (e.g., Hydrogen bond) of the water dimer at finite temperature to the one given as input structure.

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.

Task (8 points)

- Read the output file of the dipole moment and shortly explain why is a water molecule polar?
- Compute and plot the absorption cross-section α in dependence of the energy of in dependence of the wavenumber (wavenumber is in the unit of cm^{-1}.)
- What is the origin of the individual vibrations?
- Explain the differences in the obtained monomer and dimer spectra and their origins.