

Day 2: Hands-on Tutorial session: First Principles Molecular Dynamics

Molecular dynamics of molecule and solid systems using
FHI-aims code.

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1 Overview

First principles molecular dynamics is a powerful tool to explore the properties of matter at the atomic scale[1]. It allows us to peek into the movement of the materials with atomic resolution in length and femtosecond resolution in time via a "computational experiment". With the help of statistical mechanics tools, we can then take the movement as input to predict the macroscopic properties of matter.

The goal of this tutorial is to explore two systems with the first principles molecular dynamics function built into the FHI-aims code[2]. The first one is a molecular system, the Zundel cation, which plays an important role in the proton diffusion mechanisms[3]. The second one is an organic-inorganic hybrid perovskite which is a promising materials for photovoltaics[4].

2 Tasks

- Run first principles molecular dynamics simulation for the Zundel cation ($H_5O_2^+$) using the NVE ensemble. Visualize the molecular dynamics trajectory. Explore the total energy, temperature, and HOMO-LUMO gap fluctuation. Analyze the trajectory to get the vibrational density of states and identify the peaks on the plot.
- Run first principles molecular dynamics simulation for the MAPbI₃ organic-inorganic hybrid perovskite solid system with NVE ensemble. Visualize the molecular dynamics trajectory. Explore the total energy, temperature, and the electronic bandgap fluctuation.

3 First Principles Molecular Dynamics of the Zundel cation($H_5O_2^+$)

3.1 Input File Preparation and Job Submission

Go to the folder.

```
Day2_tutorial/1_md_H5O2+
```

Check geometry.in file. How many atoms do we have in the file?

In the control.in file, we have these keywords define the physical properties of the system. What do they mean?

```
xc      pbe
spin    none
relativistic  none
charge  1.
```

To run first principles molecular dynamics, we add these keywords in the control.in file. What do they mean?

```
MD_MB_init      300
MD_run           2      NVE
MD_time_step     0.0005
```

Check the job submission script myjob.sh for the SLURM workload manager system.

```
#!/bin/bash
#SBATCH -p workshop
#SBATCH --job-name=aims
#SBATCH --ntasks-per-node=44
#SBATCH --nodes=1
#SBATCH -c 1
#SBATCH --reservation=workshop
#SBATCH --time=0-04:00:00

export SLURM_JOB_RESERVATION=workshop
module purge
module use markreed/modules_dogwood
module load intel/19.4
module load mvapich2-2.3.5/intel.19.4
export MV2_USE_THREAD_WARNING=0
ulimit -s unlimited
AIMS=/nas/longleaf/home/sryatunc/2021Hybrid3/Intel_compile/aims.201231.scalapack.mpi.x
home='pwd'
mpirun $AIMS > aims.out
```

Run this command to submit the job.

```
SBATCH myjob.sh
```

Use this command to check whether the job is running.

```
squeue -u workshop*
```

Note: This job is expected to run for ~20 mins to finish.

3.2 Visualize the trajectory

After the calculation finished, run this command to extract the first principles molecular dynamics trajectory into a XYZ file.

```
perl create_xyz_movie.pl aims.out > aims.xyz
```

Copy the aims.xyz file back to your local machine (Two steps copy to the hub then from the hub to your local machine). Using jmol to visualize it. What do you see?

3.3 Analyze the "total energy vs time", "temperature vs time", and "HOMO-LUMO gap vs time" plots

Check and run the three scripts to see what they are doing.

```
bash get_total_energy.sh
bash get_temperature.sh
bash get_gap.sh
```

Do you see the three new files generated? Move them back to the local computer and use a 2D plotting software (GNUplot, xmgrace, excel, originlab,...) to visualize them.

```
data_time_ps_totalenergy_eV
data_time_ps_temperature_K
data_time_ps_homolumogap_eV
```

How large are the fluctuations for the total energy, temperature, and the HOMO-LUMO gap? Are these expected?

3.4 Vibrational density of states

Using Travis^[5] (<http://www.travis-analyzer.de/>) to analyze the trajectory to get the vibrational density of states (also called power spectrum). What is the mathematical formula of the vibrational density of states?

Check and run this command.

```
bash get_vibrational_DOS.sh
```

We will get this file.

```
power_spectrum_global.csv
```

Use a 2D plotting software to visualize the first two columns of this file for the vibrational density of states. How many peaks are there on the plot? What is the meaning of these peaks?

3.5 Repeat the Analyzing Steps with a Longer Trajectory

Go to the folder.

```
Day2_tutorial/1_md_H5O2+_prerun_20ps
```

This is a much longer 20ps trajectory for the same system prepared. Repeat the steps in sections [3.2,3.3,3.4](#). Are the plots the same or different comparing to the short trajectory?

Why do we need a long trajectory? How long is enough for the trajectory?

4 First Principles Molecular Dynamics of the Organic-Inorganic Hybrid Perovskite MAPbI₃

4.1 Input File Preparation and Job Submission

Go to the folder.

```
Day2_tutorial/2_MAPI_48atoms
```

Check the geometry.in file and see what the structure looks like. What is the different of this structure compared to the previous system?

We will use the same control.in and job submission script files for this system as in the previous example.

Note: This job is expected to run for ~20 mins to finish.

4.2 Visualize the trajectory

Run this command to extract the first principles molecular dynamics trajectory into a XYZ file.

```
create_geometry_zip.pl aims.out
```

Copy the geometries.zip file back to your local machine. Using jmol to visualize it. What do you see and how the MD trajectory of MAPbI₃ is different from the molecular system Zundel caion.

4.3 Analyze the "total energy vs time", "temperature vs time", and "bandgap vs time" plots

Use the same tools as you used for the previous example to plot and check the total energy and temperature fluctuation during the simulation time. Are these expected? Are you convinced that you got a converged MD trajectory?

Plot the bandgap fluctuation vs. time. What do you see? How do you relate this theoretical prediction to experiments?

4.4 Repeat the Analyzing Steps with a Longer Trajectory

Go to the folder.

```
Day2_tutorial/2_md_MAPI_48atoms_prerun_2ps
```

This is a much longer 2ps trajectory for the same system prepared. Repeat the steps in sections [4.2,4.3](#). Are the plots the same or different compared to the short trajectory?

Why do we need a long trajectory? How long is enough for the trajectory?

References

- [1] Dominik Marx and Jürg Hutter. *Ab initio molecular dynamics: basic theory and advanced methods*. Cambridge University Press, 2009.
- [2] Volker Blum, Ralf Gehrke, Felix Hanke, Paula Havu, Ville Havu, Xinguo Ren, Karsten Reuter, and Matthias Scheffler. Ab initio molecular simulations with numeric atom-centered orbitals. *Computer Physics Communications*, 180(11):2175–2196, 2009.
- [3] Evgenii S Stoyanov, Irina V Stoyanova, and Christopher A Reed. The structure of the hydrogen ion (haq+) in water. *Journal of the American Chemical Society*, 132(5):1484–1485, 2010.
- [4] Yasuo Shirai Akihiro Kojima, Kenjiro Teshima and Tsutomu Miyasaka. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 131(17):6050–6051, 2009.
- [5] M Brehm, M Thomas, S Gehrke, and B Kirchner. Travis-a free analyzer for trajectories from molecular simulation. *The Journal of Chemical Physics*, 152(16):164105, 2020.