Day 1 : Introduction to AIMD and PIMD

Aug 2018

In today's exercise, we perform ab-initio molecular dynamics (AIMD) and path integral molecular dynamics (PIMD) using CP2K[**?**]. We will use the Zundel's cation i.e $H_5O_2^+$ as our prototype for all calculations. Each exercise is planned to introduce the different features of CP2K to perform DFT-based AIMD/PIMD simulations.

1 Exercise 1. Determination of the CUTOFF

CP2K uses the plane-wave basis set to represent the electronic charge density and Gaussian basis set for the Kohn-Sham orbitals. The QUICKSTEP[**?**] module of CP2K uses a multigrid system to map wide Gaussians on a coarser grid and narrow Gaussians on a smoother grid. Further, electronic density is always mapped on the finest grid. On the implementation level, this aspect is taken care of in the subsection DFT of section $FORCE\_EVAL$. The keyword CUTOFF defines the plane-wave cutoff for the finest level of the multigrid system. The higher the plane-wave cutoff, the finer is the grid and calculations are numerically more accurate.

To begin with today's exercise, login to the HPC cluster OCuLUS from your laptop using the password credentials provided. Each participant has a working directory which is same as the participant's name.

(a) Read the input file *Zundel.inp* provided to you.

(b) The information about the cutoff is provided by the user in subsection MGRID of the section of $FORCE\_EVAL$. In the input file provided, the cutoff is given as 100 Ry.

(c) Without modifying the input file, use it to run CP2K on the HPC.

(d) Read the output file generated and locate the section titled SCF WAVE-FUNCTION OPTIMIZATION in the end. Check the "Total energy" obtained after completion of SCF cycle. You should also examine the total charge den-

sity on the grids. The number of electrons is obtained by summing over all grid points.

(e) Now, rerun the input after modifying the CUTOFF values as 250 and 400.

How did the value of Total energy change for each calculation? Based on the value of Total energy obtained and CPU time taken, can you decide what should be the value of CUTOFF?

(f) Now, we will use a different BASIS SET i.e. SZV-MOLOPT-GTH-SR instead of DZVP-MOLOPT-GTH-SR. In section SUBSYS make the modifications accordingly and determine how is the CUTOFF affected by the change in BASIS SET.

2 Exercise 2. Using POISSON SOLVER in AIMD

In this exercise, we will make small modifications in the input of Ex. 1 so as to reduce the overall time required for the SCF cycle. SCF is the most important and time-consuming step of DFT-based simulations.

(a) Insert a subsection POISSON[?] in section DFT of the input file of Ex.1, as shown below,

&POISSON
PERIODIC NONE
   POISSON_SOLVER   WAVELET
&END POISSON

(b) Don't forget to change the periodicity of the CELL in the SUBSYS section also to NONE.

The section SUBSYS in the input has the dimensions, topology, and periodicity of the simulation cell. In previous calculations, a large simulation box was used to avoid electrostatic interaction between the mirror images. We can now reduce the cell dimensions to a small value and perform our calculations again.

(c) Check the output file *Zundel.out* generated. Did you get any warnings during SCF convergence?

(d) The warnings displayed are due to the non-zero density at the cell boundaries. We should increase the cell dimensions to a more optimal value and rerun CP2K. Check again for the warning flags. You can also check the effective CPU time taken and compare with the earlier calculations of Ex.1.

3   Exercise 3. BOMD of Zundel Cation

In this exercise, we will perform a Born-Oppenheimer MD simulation of Zundel's cation using CP2K.

(a) We will change the RUN_TYPE in section GLOBAL from ENERGY to MD in our input file.

(b) Further, we insert a section MOTION after the end of the GLOBAL section as shown below.

```
&MOTION
 &MD
      ENSEMBLE NVT
      STEPS 20
      TIMESTEP 0.5
      TEMPERATURE 100.0
      TEMP_TOL 200
   &THERMOSTAT
      REGION MASSIVE
      TYPE CSVR
   &CSVR
      TIMECON 10
   &END CSVR
   &END THERMOSTAT
&END MD
&END MOTION
```

(c) We will perform the MD using this input. Study the energy file with name $Zundel - 1.ener$ generated at the end which provides the energy and net CPU time taken for each step.

(d) Now, we will modify the input further and replace the input USE_GUESS with ASPC for the EXTRAPOLATION keyword. Increase the steps to 100 and rerun the simulation. You will note that the effective CPU time consumed is reduced. We will analyze the trajectory generated for g(r) in the next exercise.

4   Exercise 4.   PIMD of Zundel Cation using CP2K

In this exercise, we will illustrate the nuclear quantum effects on the proton delocalization in Zundel cation. We will perform PIMD using CP2K and then calculate radial distribution function using VMD.

(a) Modify the input file of the previous exercise and change the RUN_TYPE

in section GLOBAL to PINT[**?**] from MD. Further, remove the complete subsection MD of section MOTION.

(b) Insert a subsection PINT in section MOTION as shown below,

```
    &PINT
        PROPAGATOR PIMD
        P  4
        NUM_STEPS  100
        TEMP  100.0
        T_TOL  50.0
        DT  0.50
        NRESPA  1
        TRANSFORMATION  NORMAL
        HARM_INT  EXACT
&END PINT
    &PRINT
        &RESTART ON
         BACKUP_COPIES 1
        &END RESTART
        &RESTART_HISTORY OFF
        &END RESTART_HISTORY
    &END PRINT
```

(b) Now we will run the input using CP2K.

(c) Next we determine the g(r) using VMD from the trajectories obtained from Ex.3 and the present calculation. What differences do you expect in g(r)?

References

[1] Lippert, G., J. Hutter, J. & Parrinello, M. A hybrid Gaussian and plane wave density functional scheme Mol. Phys. **92**, 477-487 (1997).

[2] VandeVondele, J. , Krack, M., Mohamed, F., Parrinello, M., Chassaing, T. and Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. Comput. Phys. Commun. **167**, 103 (2005).

[3] Genovese, L; Deutsch, T; Neelov, A; Goedecker, S; Beylkin, G. Efficient solution of Poisson's equation with free boundary conditions. J. Chem. Phys. **125**, 074105 (2006).

[4] Ceriotti, M; Parrinello, M; Markland, T; Manolopoulos, D. Efficient stochastic thermostatting of path integral molecular dynamics. J. Chem. Phys. **133**, 124104 (2005).