Laboratory 5
CPMD
Car-Parrinello Molecular Dynamics

Lesson	Information covered	Time to complete
CPMD Input file	Creating simple input file for CPMD.	45 minutes
Geometry Optimization for isolated water molecule.	Geometry optimization and vibrational analysis using 5x5x5 box size and PBE functional.	45 minutes
Molecular Dynamics for isolated water molecule.	Molecular Dynamics simulation at temperature 298K. Vibrational spectrum.	90 minutes

Creating simple input file for Car-Parrinello Molecular Dynamic (CPMD).

You can find online manual for CPMD on **www.cpmd.org**. CPMD input consists of a series of lines in an ASCII text file. The basic structure of a CPMD input file includes several different sections. Each section starts with a special keyword and ends with a special keyword:

```
&CPMD

...

&END
&DFT

...

&END
&SYSTEM

...

&END
&ATOMS

...

&END
```

Input file for geometry optimization.

Go to Your directory in directory tree list. If You do not have one create it by typing:

```
cd ~/
mkdir your_directory_name
cd your_directory_name
```

Create and open an empty file. This file will be your input file for all runs:

```
vi file.inp
[ESC] :wq
```

Now look through the manual for **vi** editor how to manipulate the text by this tool. Your task is to create input file for one water molecule optimization scheme for CPMD. You are going to use parameters shown below: Cubic box size of 5.0 x 5.0 x 5.0 , energy cutoff 70Ry and PBE functional.

First of all you need to download CPMD software on your maschine. Please store all script and programs in directory:

```
cd /home/design/bin
```

Now download needed code from the server by using scp protocol (be sure that you are now in a correct directory).

```
scp -r ekola@156.17.103.199:~/bin/* .
password: e7k7o7l7a7
```

After previous steps now the program CPMD is placed in **bin** directory at your home directory as a *cpmd.static.x* and *cpmd.intel.x*. You must check which of this two executables will work with your maschine. In the same directory you can find the file **script** which will be use to start the job and the file **fourier.x** which will be use to calculate autocorrelation function of total dipole moments to generate vibrational spectrum. In directory PSP few selected psudopotentials are stored for PBE functional.
Now copy a runing script file and needed psudopotentials (oxygen and hydrogen) to your directory wher you will run your job:

```
cp /home/design/bin/script /home/design/your_directory_name
cp /home/design/bin/O_*psp /home/design/your_directory_name
cp /home/design/bin/H_*psp /home/design/your_directory_name
```

Here in your working directory once again open the file **file.inp** and put there following text:

```
! Geometry optimization H2O
!
&CPMD
  OPTIMIZE GEOMETRY XYZ
  CENTER MOLECULE
  HESSIAN SCHLEGEL
  STORE
    500
  STRUCTURE BOND ANGLES
  MAXSTEP
     100000
&END

&DFT
 FUNCTIONAL PBE
&END

&SYSTEM
   ANGSTROM
   SYMMETRY
    CUBIC
   CELL ABSOLUTE DEGREE
    5.0 5.0 5.0 90.0 90.0 90.0
   CUTOFF
    70.0
&END

&ATOMS
*O_MT_PBE.psp   KLEINMAN-BYLANDER
  LMAX=P
   1
     -0.050300    -0.455200    -1.635200
*H_MT_PBE.psp  KLEINMAN-BYLANDER
  LMAX=S
   2
     -0.020700    -0.443200    -0.672900
      0.121400     0.455200    -1.877100
&END
```

Save the file **:wq** Do the backup of all your data:

```
mkdir BACKUP
cp * BACKUP
```

Try to run a CPMD code with your input file:

```
./script.sh file.inp
```

If there are some errors try to fix them. When the CPMD will finish the geometry optimization, the last optimize structure (xyz) is in the file **GEOMETRY.xyz**. Open this file with molden4.2 by taping **molden4.2 GEOMETRY.xyz**. Check the bond lenghts and angle. Now copy the whole data to seprate directory:

```
mkdir OPTIMIZATION
cp * OPTIMIZATION
```

Molecular Dynamics at temerature 298K - RESCALING

The next step is to check the average value of electrons kinetic energy - to set up then the thermostat on them. To do so, you need to change the input file. Go to the **file.inp** and change the content. Now You are going to run ab initio molecular dynamic at temperature of 298K with rescaling temperture if it is not in the range of 250-350K. You are restarting coordinates and wavefunction from previous run.

```
! Molecular Dynamics at 295K with rescaling
!
&CPMD
  MOLECULAR DYNAMICS CP
  RESTART WAVEFUNCTION COORDINATES LATEST
  HESSIAN SCHLEGEL
  TRAJECTORY SAMPLE XYZ
   1
  TEMPERATURE
    298
  TEMPCONTROL IONS
   298   50
  TIMESTEP
    3.0
  STORE
    50
  STRUCTURE BOND ANGLES
  MAXSTEP
     500
  SUBTRACT COMVEL ROTVEL
   10
&END

&DFT
 FUNCTIONAL PBE
&END

&SYSTEM
   ANGSTROM
   SYMMETRY
    CUBIC
   CELL ABSOLUTE DEGREE
    5.0  5.0  5.0    90.0   90.0   90.0
```

```
   CUTOFF
    70.0
&END

&ATOMS
*O_MT_PBE.psp   KLEINMAN-BYLANDER
  LMAX=P
   1
     -0.050300    -0.455200    -1.635200
*H_MT_PBE.psp  KLEINMAN-BYLANDER
  LMAX=S
   2
     -0.020700    -0.443200    -0.672900
      0.121400     0.455200    -1.877100
&END
```

Try to run a CPMD code with your input file:

```
./script.sh file.inp
```

After the run try to locate in output file **file.out** somewhere at the end, the average value of electron kinetic energy. Write down this value. Now when you now the kinetic energy of electrons you are able to run molecular dynamic with Nose-Hoover thermostat. Before this new run, save the data in new directory.

```
mkdir TEMPCONTROL
cp * TEMPCONTROL
```

Molecular Dynamics at temerature 298K - EQUILIBRATION

Now change input file **file.inp** to look similar like the example below. This is the equilibration period before proper run. Important: Instead of **xxx** put before obtained value of electron kinetic energy.

```
! Molecular Dynamics at 298K production RUN
!
&CPMD
  MOLECULAR DYNAMICS CP
  RESTART WAVEFUNCTION COORDINATES LATEST
  HESSIAN SCHLEGEL
  TRAJECTORY SAMPLE XYZ
   1
  TEMPERATURE
    298
  NOSE IONS MASSIVE
   295   3020
  NOSE ELECTRONS
   xxx   15000
  TIMESTEP
    3.0
  STORE
    100
  STRUCTURE BOND ANGLES
  MAXSTEP
     1500
  SUBTRACT COMVEL ROTVEL
   10
```

```
&END

&DFT
 FUNCTIONAL PBE
&END

&SYSTEM
   ANGSTROM
   SYMMETRY
    CUBIC
   CELL ABSOLUTE DEGREE
    5.0   5.0   5.0    90.0   90.0   90.0
   CUTOFF
    70.0
 &END

 &ATOMS
*O_MT_PBE.psp   KLEINMAN-BYLANDER
  LMAX=P
   1
     -0.050300    -0.455200    -1.635200
*H_MT_PBE.psp  KLEINMAN-BYLANDER
  LMAX=S
   2
     -0.020700    -0.443200    -0.672900
      0.121400     0.455200    -1.877100
&END
```

After the equilibration run make a new directory and copy there your data:

```
mkdir MASSIVE
cp * MASSIVE
```

Molecular Dynamics at temerature 298K - the RUN

Now you are ready to perform production run. Open the file **file.inp** and change it:

```
! Molecular Dynamics at 298K
!
&CPMD
  MOLECULAR DYNAMICS CP
  RESTART WAVEFUNCTION COORDINATES LATEST
  RESCALE OLD VELOCITIES
  DIPOLE DYNAMICS SAMPLE
   5
  HESSIAN SCHLEGEL
  TRAJECTORY SAMPLE XYZ
   1
  TEMPERATURE
    298
  NOSE IONS
   295   3020
  NOSE ELECTRONS
   xxx   15000
```

```
  TIMESTEP
    3.0
  STORE
    1000
  STRUCTURE BOND ANGLES
  MAXSTEP
     15000
  SUBTRACT COMVEL ROTVEL
   10
&END

&DFT
 FUNCTIONAL PBE
&END

&SYSTEM
   ANGSTROM
   SYMMETRY
    CUBIC
   CELL ABSOLUTE DEGREE
    5.0   5.0   5.0    90.0   90.0   90.0
   CUTOFF
    70.0
 &END

 &ATOMS
*O_MT_PBE.psp   KLEINMAN-BYLANDER
  LMAX=P
   1
     -0.050300    -0.455200    -1.635200
*H_MT_PBE.psp  KLEINMAN-BYLANDER
  LMAX=S
   2
     -0.020700    -0.443200    -0.672900
      0.121400     0.455200    -1.877100
&END
```

This run will take at least one hour on standard maschine. During this time you should track in **ENERGIES** file how the temperature (third column) and Hamiltionian Energy (sixth column) is varying during the simulation. The Hamiltionian Energy sould be stable to the fourth-fifth digit. There should be no increase of electron kinetic energy (second column) observed. In a file **TRAJEC.xyz** the whole trajectory of the run is stored in a format of xyz. During the production run you have a time do do some test. Please check how the time needed to perform one molecular dynamic step increases when you change box size from 5.0 x 5.0 x 5.0 to:

- 6.0 x 6.0 x 6.0
- 7.0 x 7.0 x 7.0
- 8.0 x 8.0 x 8.0
- 9.0 x 9.0 x 9.0
- 10.0 x 10.0 x 10.0

To perfome the test create separate directory for each run:

```
mkdir 6 7 8 9 10
cd MASSIVE
cp * ../6
cp * ../7
cp * ../8
cp * ../9
cp * ../10
cd ../6
vi file.inp
```

Now change the appropriate lines in the input file - increase the box size (CELL) and change the total numbers of step (MAXSTEP) to 2. Two steps of molecular dynamics are enough to estimate needed time for per step. When the input file is ready start the run:

```
./script file.inp
```

From file.out or from ENERGIES file extract time per step. Now go to directory 7 and reapeat previous steps - change input, start run, extract time. When all simulations are done, prepare a plot showing time per step vs. box length. The next plot is the time per step vs. volume of the box. Knowing that the minimum box size for simulation is calculated as a size of the molecule plus 3 free space in each direction estimate the minimum box size for our system. Base on this box size estimate the time we need to spend to do 15000 steps. Is the box size we are using in this exercice sufficient?

Now go back to our normal run. Look through the results. Compare them with the previous one from gaussian at 0K. After the run is complited in the file DIPOLE you have the total dipole moment of the system. Based on this data you are abel to calculate vibrational spectrum. Beacause the run was very short do not expect to get very accurate spectrum. Create a vibrational spectrum with **fourier.x** program. To do so, tape

```
./fourier.x
```

and give the answer for all questions. Now plot your vibrational spectrum (1st and 5th column) and compare it with previous results from HyperChem and Gaussian.