

10.675 Assignment #5

due 11/23/04

In the last problem set, you learned how to run CPMD on NCSA supercomputers. Now in this problem set, you will use CPMD to study the dynamics of a proton transferring among water molecules (H_9O_4^+). And you can compare what you observe with the literature report (*Nature*, vol. **397**, 1999, 601).

1. The input file (H9O4) can again be copied from the directory: /u/ac/hairong/public
It is also enclosed at the end of this document. Make sure to have the potentials for H and O in your potential path. They can be obtained from the above directory too: H_BLYP.PP30 and O_BLYP_glue
2. Now you need to fill up the xyz coordinates for the atoms (marked as yellow in the attached file). As in the previous problem sets, use GaussView to do this. (You can refer to the figure at the end of this document for the geometry of H_9O_4^+ system.) To save the allocated hours on NCSA, optimize the geometry in Gaussian 03 first. (This will be helpful for the convergence of your CPMD calculations.) Then, copy the xyz coordinates from the log file to the H9O4 input file you got in step 1.

[Note: Make sure to set the charge for your system to +1 during your calculation]

3. As you might have noticed, there are many keywords in the &CPMD section. But notice that only those that start with capital letters are valid. In order to run a MD simulation, you have to run a wavefunction optimization first. (We already did geometry optimization by Gaussian in step 2.) To do that, you need to change 3 things, as below:

```
MOLECULAR DYNAMICS      -> mOLECULAR DYNAMICS
RESTART WAVEFUNCTION LATEST -> rESTART WAVEFUNCTION LATEST
oPTIMIZE WAVEFUNCTION    -> OPTIMIZE WAVEFUNCTION
```

After you have performed the wavefunction optimization, you can change the above three keywords back to run an MD simulation.

4. After running MD, the code will generate a file called MOVIE in your working directory. Be careful that if you have run MD a couple of times, the MOVIE file might contain separators between various appended sections. Also since you have some limit for the space in your home directory, it might be better to move your previous MOVIE files to your scratch directory (/scratch/users/*username*). Now copy the executable file MOV2xyz.x from /u/ac/hairong/public, and use it to generate MOVIE.xyz file from data in MOVIE file. Basically, what you need to do is:

```
./MOV2xyz.x MOVIE & (put 13 atoms in each frame)
```

A new file called MOVIE.xyz will then be generated in the same directory. This is the one that we will use to visualize the dynamics.

5. Now you are ready to watch the movie if your computer has VMD (Visual Molecular Dynamics) or similar program to visualize the dynamics of proton transferring among water molecules. In

your solution, give some representative snapshots of your dynamic simulation results, and compare to the literature report. [A small tip: To visualize more clearly, you can change **Graphics->Representations->Drawing Method** to “DynamicBonds”.]

If your computer does not have that, it is free to download online:

<http://www.ks.uiuc.edu/Research/vmd/>

Input file for CPMD simulation (do not forget to fill the part marked in yellow)

```
&CPMD
MOLECULAR DYNAMICS
RESTART WAVEFUNCTION LATEST
oPTIMIZE WAVEFUNCTION
oPTIMIZE GEOMETRY
rESTART WAVEFUNCTION LATEST
rESTART WAVEFUNCTION COORDINATES LATEST
CONVERGENCE
  0.00001 0.0001
STORE
  100
MAXSTEP
  50
ODIIS
  5
GDIIS
  3
QUENCH BO
TEMPERATURE
  300
TEMPCONTROL IONS
  300 30
TIMESTEP
  4.0
MOVIE
  10
EMASS
  400
&END

&SYSTEM
ANGSTROM
SYMMETRY
  1
CELL
  10.0 1.0 1.0 0 0 0
```

```
CUTOFF
70.0
CHARGE
+1

&END

&ATOMS

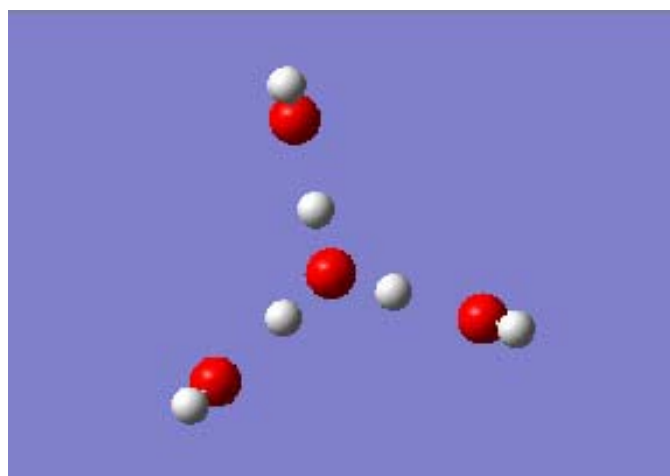
*H_BLYP.PP30 KLEINMAN-BYLANDER
  LMAX=S
  9
  xyz coordinate for nine hydrogen atoms

*O_BLYP_glue KLEINMAN-BYLANDER
  LMAX=P
  4
  xyz coordinate for four oxygen atoms

&END

&DFT
  NEWCODE
  FUNCTIONAL BLYP
  GC-CUTOFF
  1.D-8
&END

&PROP
  POPULATION ANALYSIS MULLIKEN
&END
```



Geometry figure for H_9O_4^+

(Courtesy of Gaussian Inc. Used with permission.)