# 10.675 Assignment #4

due 10/21/04

In this problem set, you will use Car-Parrinello Molecular Dynamics (CPMD) to calculate the adsorption energy of oxygen atom on the Si(100) surface and compare it to the experimental data that you can find.

1. Log on to NCSA from SecureCRT from your own machine by:
   ssh cu.ncsa.uiuc.edu
   usrname:
   password:
   or ssh usrname@cu.ncsa.uiuc.edu
   password

2. Before you submit the jobs, make sure you have the following files in your home directory (Of course you can put them to different folders and then specify the directory of different folder in your job script). You can copy these files from: /u/ac/hairong/public

   Executable cpmd: cpmd.x;
   Potentials for O and Si: O_BLYP_glue and Si_BLYP_glue;
   Input files for atomic oxygen, bare silicon surface, and adsorption of atomic oxygen on si(100): o, si_surf, and o_si_surf ;
   The script to run your job: mpi.ll (you can change the name as what you want).

3. The mpi.ll (listed as file 1 at the end of this document), is the shell script you should use to submit the jobs. The mpi.ll file is self-demonstrative, you need to modify it very easily and get cpmd to run. Here are some useful commands for ncsa operation:
   Submit the job: llsubmit *filename*
   Check status of your job: llq –u *usrname*
   Cancel your job: llcancel *job number*
   To check how many hours you have used: usage –u *usrname*
   (*P_usage* will list how many hours you have used; Remember everybody has 250 hours for the whole semester)
   The above operations are related to queue system. If you just want to do single processor calculation, you can copy the script file *mpi.ll* as any other name such as *script*, use
   *chmod +x script*
   to change it to an executable file, and then use
   *./script &*
   to run it. In this way, you do not have to wait in the queue system, but it has CPU time limit of 30 mins.

4. The files 2-4 attached at the end of this document are the input files for the adsorption calculation. You don't need to modify them. Just run them with the instructions in *mpi.ll* (file 1).
   But you can refer to http://www.cpmd.org/cpmd_on_line_manual.html for the function of each keyword. (Note: Since we are modeling the surface with periodic boundary conditions, we

need some vacuum space, which has been set up for you (in the size for unit cell). Also to simulate the surface, we usually model several layers of the surface and fix a few bottom layers to mimic the bulk crystal. To save on computing time, we just fix all the silicon layers during this exercise.)

5. The last two attached files at the end of this document are the pdb files for the input coordinates for bare silicon surface and adsorption of O on si(100) which we used in cpmd calculation. You can visualize it in cerius2 or GaussView.

Attached file 1: script to run cpmd on ncsa supercomputing center

```
-----------------------------------------------------------------------

#@ shell = /usr/bin/csh
#@ job_name = o
#@ environment = COPY_ALL
#@ notification = complete
#@ account_no = mfj
#@ job_type = parallel
#@ class = batch

#@ wall_clock_limit = 2:00:00       #Specify job CPU limit of 2 hours
#@ resources = ConsumableCpus(1) ConsumableMemory(2 Gb)
#@ output = $(job_name).$(jobid).out
#@ error = $(job_name).$(jobid).err

#@ tasks_per_node = 8         # Specify number of nodes for parallel running
#@ job_type = parallel
#@ queue
############################################################

#set echo                # echo commands before execution; use for debugging

poe /u/ac/hairong/public/cpmd.x /u/ac/hairong/input/o /u/ac/hairong/potential >
/u/ac/hairong/output/o_out ;;

# exectable binary code is /u/ac/hairong/public/cpmd.x;
# pseudo-potential files are at /u/ac/hairong/potential;
# o and o_out are the input and output files
# you can modify the input file and output file path to your own directory
# ncsa is using queue system. (your job will not run immediately after submit)
# but as mentioned in step 3, you can run job immediately on a single processor
```

Attached file 2: input file for atomic oxygen

---

```
&CPMD
  OPTIMIZE WAVEFUNCTION
  oPTIMIZE GEOMETRY
  rESTART WAVEFUNCTION LATEST
  rESTART WAVEFUNCTION COORDINATES LATEST
  LSD
  CONVERGENCE
   0.000001 0.0001
  STORE
   100
  MAXSTEP
   1000
  ODIIS
   5
  GDIIS
   3
&END

&SYSTEM
  ANGSTROM
  SYMMETRY
  8
  CELL
  11.43  0.950 0.475  0  0  0
  CUTOFF
  20.0
  MULTIPLICITY
  3
&END

&ATOMS
*O_BLYP_glue   KLEINMAN-BYLANDER
   LMAX=P
   1
1.00000    1.00000    1.00000
&END

&DFT
  FUNCTIONAL LDA
&END

&PROP
  POPULATION ANALYSIS MULLIKEN
&END
```

Attached file 3: input file for bare silicon surface (3 layers, p(2x2) unit cell with 12 Si atoms in total)

---

```
&CPMD
  oPTIMIZE WAVEFUNCTION
  OPTIMIZE GEOMETRY
  rESTART WAVEFUNCTION LATEST
  rESTART WAVEFUNCTION COORDINATES LATEST
  CONVERGENCE
   0.000001 0.0001
  STORE
   100
  MAXSTEP
   10000
  ODIIS
    5
  GDIIS
   3
&END

&SYSTEM
  ANGSTROM
  SYMMETRY
  8
  CELL
  11.43  0.950 0.475  0  0  0
  CUTOFF
  20.0
&END

&ATOMS

*Si_BLYP_glue   KLEINMAN-BYLANDER
   LMAX=P
   12
0.000   0.000   0.000
1.357   1.357   1.357
0.000   2.715   2.715
1.357   4.073   4.073
2.715   0.000   2.715
2.715   2.715   0.000
0.000   5.430   0.000
1.357   6.787   1.357
0.000   8.145   2.715
1.357   9.503   4.073
2.715   5.430   2.715
2.715   8.145   0.000

&END

&DFT
  FUNCTIONAL LDA
&END

&PROP
```

```
  POPULATION ANALYSIS MULLIKEN
&END
```

Attached file 4: input file for adsorption of atomic oxygen on silicon surface
(Here we use three layers, p(2x2) unit cell with 12 Si atoms totally)

```
-------------------------------------------------------------------------

&CPMD
  oPTIMIZE WAVEFUNCTION
  OPTIMIZE GEOMETRY
  rESTART WAVEFUNCTION LATEST
  rESTART WAVEFUNCTION COORDINATES LATEST
  CONVERGENCE
   0.000001 0.0001
  STORE
   100
  MAXSTEP
   20000
  GDIIS
   5
  GDIIS
   3
&END

&SYSTEM
  ANGSTROM
  SYMMETRY
  8
  CELL
  11.43  0.950 0.475  0  0  0
  CUTOFF
  20.0
&END

&ATOMS

CONSTRAINTS
FIX COORDINATES
  12
1 0 0 0
3 0 0 0
7 0 0 0
9 0 0 0
2 0 0 0
4 0 0 0
8 0 0 0
10 0 0 0
5 0 0 0
6 0 0 0
11 0 0 0
12 0 0 0
END CONSTRAINTS
```

```
*Si_BLYP_glue   KLEINMAN-BYLANDER
   LMAX=P
   12
0.000   0.000   0.000
1.357   1.357   1.357
0.000   2.715   2.715
1.357   4.073   4.073
2.715   0.000   2.715
2.715   2.715   0.000
0.000   5.430   0.000
1.357   6.787   1.357
0.000   8.145   2.715
1.357   9.503   4.073
2.715   5.430   2.715
2.715   8.145   0.000

*O_BLYP_glue   KLEINMAN-BYLANDER
   LMAX=P
   1
4.290   4.134   1.360

&END

&DFT
  FUNCTIONAL LDA
&END

&PROP
  POPULATION ANALYSIS MULLIKEN
&END
```

Attached file 5: pdb file for the bare silicon surface

---

```
REMARK   4 3    COMPLIES WITH FORMAT V. 2.0
CRYST1    5.430   10.860    5.430  90.00  90.00  90.00 P 1
SCALE1       0.18416   0.00000   0.00000        0.00000
SCALE2       0.00000   0.09208   0.00000        0.00000
SCALE3       0.00000   0.00000   0.18416        0.00000
HETATM    1 SI1  UNK A   0       0.000   0.000   0.000  1.00  0.00          SI3-
HETATM    2 SI2  UNK A   0       1.357   1.357   1.357  1.00  0.00          SI
HETATM    3 SI3  UNK A   0       0.000   2.715   2.715  1.00  0.00          SI2-
HETATM    4 SI4  UNK A   0       1.357   4.073   4.073  1.00  0.00          SI3-
HETATM    5 SI5  UNK A   0       2.715   0.000   2.715  1.00  0.00          SI2-
HETATM    6 SI7  UNK A   0       2.715   2.715   0.000  1.00  0.00          SI2-
HETATM    7 SI1  UNK A   0       0.000   5.430   0.000  1.00  0.00          SI3-
HETATM    8 SI2  UNK A   0       1.357   6.787   1.357  1.00  0.00          SI
HETATM    9 SI3  UNK A   0       0.000   8.145   2.715  1.00  0.00          SI2-
HETATM   10 SI4  UNK A   0       1.357   9.503   4.073  1.00  0.00          SI3-
HETATM   11 SI5  UNK A   0       2.715   5.430   2.715  1.00  0.00          SI2-
HETATM   12 SI7  UNK A   0       2.715   8.145   0.000  1.00  0.00          SI2-
TER      13      UNK A   0
END
```

Attached file 6: pdb file for the adsorption of atomic oxygen on silicon surface

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```
REMARK   4 3    COMPLIES WITH FORMAT V. 2.0
CRYST1    5.430   10.860    5.430  90.00  90.00  90.00 P 1
SCALE1       0.18416   0.00000   0.00000        0.00000
SCALE2       0.00000   0.09208   0.00000        0.00000
SCALE3       0.00000   0.00000   0.18416        0.00000
HETATM    1 SI1  UNK A   0       0.000   0.000   0.000  1.00  0.00          SI3-
HETATM    2 SI2  UNK A   0       1.357   1.357   1.357  1.00  0.00          SI
HETATM    3 SI3  UNK A   0       0.000   2.715   2.715  1.00  0.00          SI2-
HETATM    4 SI4  UNK A   0       1.357   4.073   4.073  1.00  0.00          SI3-
HETATM    5 SI5  UNK A   0       2.715   0.000   2.715  1.00  0.00          SI2-
HETATM    6 SI7  UNK A   0       2.715   2.715   0.000  1.00  0.00          SI2-
HETATM    7 SI1  UNK A   0       0.000   5.430   0.000  1.00  0.00          SI3-
HETATM    8 SI2  UNK A   0       1.357   6.787   1.357  1.00  0.00          SI
HETATM    9 SI3  UNK A   0       0.000   8.145   2.715  1.00  0.00          SI2-
HETATM   10 SI4  UNK A   0       1.357   9.503   4.073  1.00  0.00          SI3-
HETATM   11 SI5  UNK A   0       2.715   5.430   2.715  1.00  0.00          SI2-
HETATM   12 SI7  UNK A   0       2.715   8.145   0.000  1.00  0.00          SI2-
TER      13      UNK A   0
HETATM   14  O13 UNK B   1       4.290   4.134   1.360  1.00  0.00           O
TER      15      UNK B   1
END
```