Exercises - Wednesday

March 22, 2006

General note: Please notice that the systems presented in these examples *do not necessarily correspond to converged systems e. g.* with respect to the size of the super-cell. In order to keep the computational time reasonable we often had to reduce the size of the cell. This, as well as other parametres such as the cut-off energy should either be tested or, after long experience using the same pseudo potentials etc, obtained from "intuition"!!!

Topics: CP-MD, BO-MD, harmonic vibrations, Kohn-Sham orbitals

Start

- In the shell execute:

```
cd <your-working-directory>
mkdir H2-cpmd
cd H2-cpmd
cp ~/Job_sub.cmd .
cp ~/H2.inp input
```

- Output comes now in file '`output`'

New keywords

- MOLECULAR DYNAMICS CP
- MOLECULAR DYNAMICS BO
- VIBRATIONAL ANALYSIS
- KOHN-SHAM ENERGIES
- TIMESTEP
- EMASS
- CONVERGENCE
- TEMPERATURE
- EMASS
- MAXSTEP
- MAXCPUTIME
- STORE
- TRAJECTORY
- FUNCTIONAL
- ISOTOPE
- LBFGS

1 H_2 — vibrations

Learn

- Car-Parrinello molecular dynamics
- Born-Oppenheimer molecular dynamics

```
&CPMD
  optimise geometry
  lbfgs
  convergence
    1.0E-7 5.0E-5
  vibrational analysis
  restart wavefunction coordinates latest
  convergence
    1.0E-7 5.0E-5
  molecular dynamics cp
  restart wavefunction coordinates latest
  temperature ions
    600
  timestep
     5
  emass
    2000
  maxstep
    1000
  store
    300
  trajectory sample xyz
     5
  real space wfn keep
  maxcputime
    1800
  MOLECULAR DYNAMICS BO
  RESTART WAVEFUNCTION COORDINATES LATEST
  RESTART VELOCITIES ACCUMULATORS
  NOSE IONS
    600 4400
  TIMESTEP
     5
  MAXSTEP
     100
  STORE
     50
  TRAJECTORY SAMPLE XYZ
     2
  REAL SPACE WFN KEEP
  MAXCPUTIME
    1800
  MIRROR
&END
&DFT
  FUNCTIONAL PBE
  GC-CUTOFF
    1.0E-7
&END
&SYSTEM
  ANGSTROM
  SYMMETRY
    0
```

```
  CELL
    6.0000 1.0 1.0 0 0 0
  CUTOFF
    70.0
  POISSON SOLVER TUCKERMAN
&END
&ATOMS
*H_MT_PBE.psp
  LMAX=S
    2
  -0.40 0 0
   0.40 0 0
  isotope
    2
&END
```

1.1 Vibrational analysis

1. Optimise geometry
2. Perform 'VIBRATIONAL ANALYSIS'
3. Perform 'VIBRATIONAL ANALYSIS', but with deuterium

To notice:

- We converge the wave functions and geometry accurately

1.2 Car-Parrinello molecular dynamics

1. Optimise geometry (if you don't have it already in 'RESTART')
2. Perform molecular dynamics using 'RESTART ...'
3. Analyse
   - Period/frequency of oscillation; 33 ps $\approx$ 1 cm^{-1}
   - Look at 'TRAJEC.xyz'
   - Look at 'ENERGIES'
   - What is the average temperature? Is that related to the initial temperature?

To notice:

- The time step and mass of the fictitious electrons has to be set accurately
- Use initial temperature; alternatively do not relax
- Use two restart files to be more safe
- Limit the length either by constraining the CPU time or number of steps

1.3 Born-Oppenheimer molecular dynamics

1. Optimise geometry
2. Run Born-Oppenheimer molecular dynamics

To notice:

- Minimally you only have to set the time step (only for ions, thus $\Delta t \approx$ factor 6-10 smaller than the period of the highest vibration; secondly, you probably want to set explicitly the convergence criterion
- You can try thermostats, velocity scaling, ...

2 CO — molecular frontier orbitals

Change job

- In the shell execute:

```
mkdir ../CO-orbitals
cd ../CO-orbitals
cp ~/Job_sub.cmd .
cp ~/CO.inp input
```

2.1 (Virtual) Kohn-Sham orbitals

1. Optimise geometry
2. Perform '`VIBRATIONAL ANALYSIS`'; GIY for the literature value (or *e. g.* `http://webbook.nist.gov/chemistry/`
3. Calculate '`KOHN-SHAM ENERGIES`' and orbitals
4. Obtain '`CUBEFILE ORBITALS`'
5. Visualise them; what is the symmetry of the HOMO, LUMO and LUMO+1?
6. Calculate the expected number of plane waves for the wave functions and density; how does it agree with the present value?
7. If you have time? Optimise quickly the electronic structure at different cell sizes and cut-off energies; how does the length of FFT's depend on them? How does the computational time change? What do you expect, if you would insert an extra oxygen atom to form CO_2 but keep the rest of the parametres fixed, how would the number of plane waves and length of FFT's change?

To notice:

- The lattice constant and cut-off energy are set to too small values, just in order to speed up to calculation
- To calculate the virtual orbitals one has to use `KOHN-SHAM ENERGIES` in `CPMD`