Exercises - Thursday

March 22, 2006

Topics: Spin, TDDFT

Start

- In the shell execute:

```
cd <your-work-directory>
mkdir O2-spin
cd O2-spin
cp ~/Job_sub.cmd .
cp ~/O2.inp input
```

- Output comes in file 'output'

New keywords

- LSD
- MULTIPLICITY

- ELECTRONIC SPECTRA

1 O$_2$ — multiplicity

Learn

- How to control the spin state of the system

1.1 Multiplicity, or spin state

1. Optimise geometry in the singlet state

2. Optimise geometry in the triplet state

3. Optimise geometry in the quintett state

4. Which charge state is the most stable one?

5. Do two calculations in the singlet state with and without `LSD` always necessarily give the same answer?

1.2 Eigenvalues

1. Calculate the eigenvalues in the stable state; which levels are degenerate?

   To notice:

- If you want to calculate `CUBEFILE`s for the virtual states you first have to do the `KOHN-SHAM ENERGIES` and RESTART with the number of `STATES` including also the number of calculated virtual orbitals

2 Formaldimine — excited states

Learn

- how to calculate excitation energies

- relax structures in the excited state

Change job

- In the shell execute:

```
mkdir ../H2NCH-exc
cd ../H2NCH-exc
cp ~/Job_sub.cmd .
cp ~/H2NCH.inp input
```

```
&CPMD
  optimise geometry
  lbfgs

  electronic spectra
  restart wavefunction coordinates

  OPTIMISE GEOMETRY
  TDDFT
  RESTART WAVEFUNCTION COORDINATES LINRES
  CONVERGENCE ORBITALS
    1.0E-7

  MIRROR
  STRUCTURE ANGLES
&END
&TDDFT
  STATES SINGLETS
    3
  TAMM-DANCOFF
  FORCE STATE
    1
&END
&DFT
  FUNCTIONAL PBE
  GC-CUTOFF
    1.0E-7
&END
&SYSTEM
  SYMMETRY
    0
  CELL
    12.0000 1.0 1.0 0 0 0
  CUTOFF
    70.0
  POISSON SOLVER TUCKERMAN
&END

&ATOMS

*C_MT_PBE.psp KLEINMAN-BYLANDER
  LMAX=D
    1
  1.50 0 0
*N_MT_PBE.psp KLEINMAN-BYLANDER
  LMAX=D
    1
  0.00 0 0
*H_MT_PBE.psp KLEINMAN-BYLANDER
  LMAX=S
    3
 -1.00  1 0
  2.50  1 0
  2.50 -1 0
&END
```

2.1   Excitation energies and geometries in the excited state

1. Optimise geometry

2. Perform 'ELECTRONIC SPECTRA'; this will necessitate the &TDDFT section

3. You can calculate and visualise the different frontier orbitals, if you want to know how they look like. What are the active orbitals taking part in the excitation?

4. Shift the two hydrogen atoms of the –NH group out of the molecular plane and optimise the geometry in the electronically excited state using TDDFT

To notice:

- When you want to start *e. g.* an geometry optimisation using TDDFT you always need to evaluate the 'ELECTRONIC SPECTRA' first

- When restarting a TDDFT calculation ALWAYS move the previous RESTART file to 'RESTART' and NEVER use the option 'RESTART LATEST'! KOHN-SHAM ENERGIES in CPMD