Exercises - Friday

March 22, 2006

Topics: NMR, van der Waals, Wannier orbitals & centres & ELF

Start

• In the shell execute:

```
cd <your-work-directory>
mkdir H20
cd H20
cp ~/Job_sub.cmd .
cp ~/H20-nmr.inp input
```

• Output comes in file 'output'

1 NMR shield tensor for H_2O

- 1. Get CH4.inp and H2O.inp from the homedirectory
- 2. Optimise geometry of H_2O
- 3. Optimise geometry of CH_4
- 4. Carry out NMR calculations with the LINEAR RESPONSE keyword in the control section and the following section



- 5. compare your results to Literature values (GIY)
- 6. what happens to the shift if you change the hybridization state of the oxygen (tip: protonate the water molecule to get H_3O^+)? What happens to the shift if you change the bondlength?

2 vdW-correction scheme

Compute the energy of interaction curve for the ethylene dimer using BLYP, the empirical correction, and the atom centered correction.

- copy the file Ethyl.in from home
- optimize the geometry of the ethylene dimer constraining inter molecular distance (z) of the carbons, thus moving only the hydrogen atoms along all x,y,z axes (view structure with vmd to check it first)
- keep intramolecular structure fixed and vary only the intermolecular distance for values between 2.8 and 4.3 Å. Is your cell size big enough for that? For which cell size exhibits your dimer converged energies of interaction? Why is there no BSSE-error in CPMD?
- Now, include the following section into your calculations:

&VDW VDW CORRECTION 1 C6 1 2 -92.99225 4.4425 1 &END

• Next replace your carbon pseudopotentials by a file which contains the following:



rerun the same energy of interaction curve

• plot the 3 curves, how do they compare to literature?

3 Wannier centres and orbitals

Learn

• calculate the Wannier centres and orbitals

Please select your favourite molecule, and copy from the home directory the input file for it. First run a geometry optimisation, then perform the following run (the rest of the input remains the same; please move your restart file RESTART.1 to RESTART):

```
&CPMD

RESTART WAVEFUNCTION COORDINATES

MOLECULAR DYNAMICS

MAXSTEP

DIPOLE DYNAMICS WANNIER

WANNIER WFNOUT ALL

PRINT WANNIER

1

wannier reference

-7.5 -7.5 -7.5

&END
```

Now you can plot the ionic geometry with the Wannier centres using VMD; the file is called 'IONS+CENTERS.xyz'. Next you can look at your Wannier orbitals, however for that you need to transform the files given by CPMD into cube files. For that perform the command

/home/cpmd/CPMD/tools/cpmd2cube/cpmd2cube.x WANNIER_1.1

Now you can transfer the cube file given by 'cpmd2cube' to your PC and visualise it using VMD. If you have chosen e.g. water or methane, you can try to plot all the four orbitals at the same time. How do the orbitals look like, is it familiar to you?

The keyword WANNIER REFERENCE can be used to shift the centre of the box to a wanted position. Now it is commented out (*i. e.* written with lower-case letters)