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Tutorial on van der Waals Density Functionals

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Outline
Exercise 1. Interplanar interaction in Graphite
Exercise 2. Interaction of water with benzene

Download the exercise

```
scp  student@172.30.11.211:Tutorials/Exercise_8_vdW/exercise_8_vdW.tar.gz .
```

Or via web from http://172.30.11.211/tutorials/

Unpack it using

```
tar -zxvf   exercise_8_vdW.tar.gz
cd Exercise_8_wdW
```

Verify that you can execute pw.x from the shell. If not, set the PATH variable according to your installation directory, for example

PATH=$PATH:$HOME/ChemUtils/Espresso/espresso-5.0.1/bin/
or
PATH=$PATH:$HOME/ChemUtils/Espresso/espresso-4.3.2/bin/

Search if you have the file vdW_kernel_table in the Quantum ESPRESSO distribution

find ~/ -iname 'vdW_kernel_table'

The file should be in the directory espresso-4.3.2/pseudo/ or espresso-5.0.1/pseudo/, or in the directory specified by pseudo_dir in the input files (see the exercise 1), and at runtime, in the director specified by pseudo_dir= ….

If ithere is no file in the distribution there is a packed version at the directory Exercise_8_wdW. Run the command

bunzip2 vdW_kernel_table.bz2

You can generate the table using the program generate_vdW_kernel_table.x, then copy vdW_kernel_table to the file.

Exercise 1. Interplanar interaction energy of graphite.

Go to directory ex1-graphite

cd ex1-graphite

Edit the shell script run.sh and fix the lines

PATH=$PATH:$HOME/ChemUtils/Espresso/espresso-5.0.1/bin/

pseudo_dir = '/home/emenendez/ChemUtils/Espresso/espresso-5.0.1/pseudo',
(modify according to your instalation and the version you are using)

Verify that the directory set by pseudo_dir exists and contains the files C.pz-rrkjus.UPF, C.pbe-rrkjus.UPF, and vdW_kernel_table

missing pseudoptential files can be downloaded from http://www.quantum-espresso.org

C.pz-rrkjus.UPF, is for LDA calculations
C.pbe-rrkjus.UPF, is for GGA/PBE calculations.
C.pbe-rrkjus.UPF, together with vdW_kernel_table are for vdW calculations.

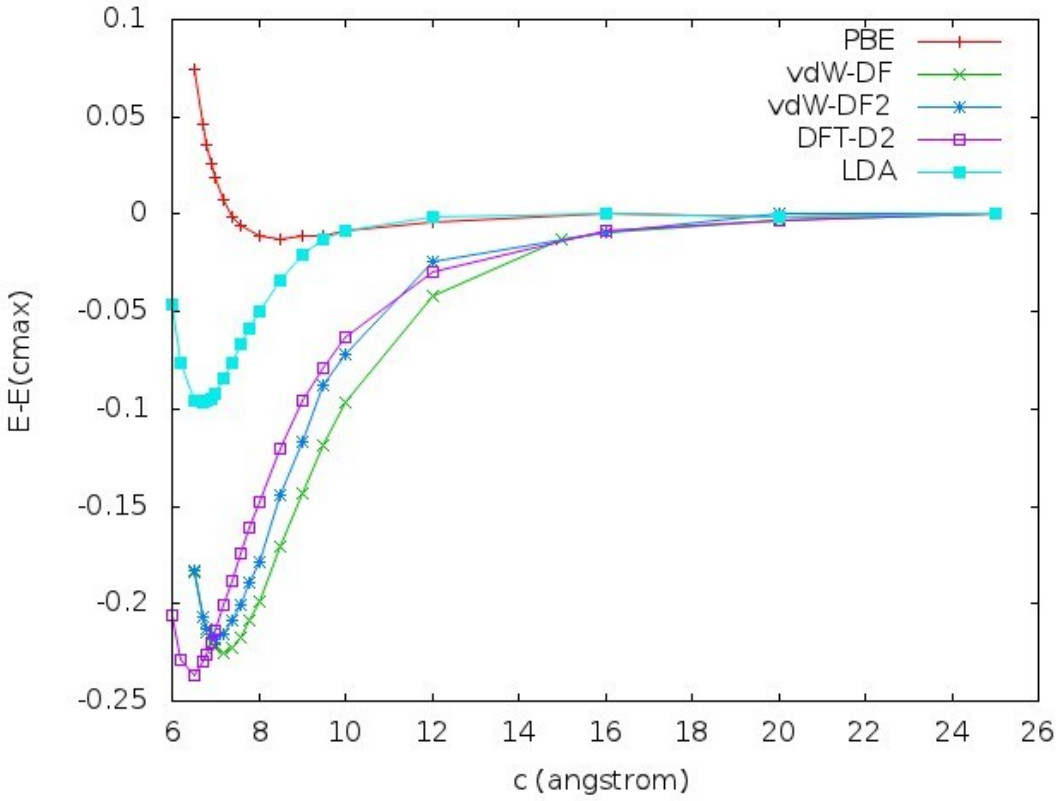
Run the script

./run.sh

it will take some time to run. In other window view the file run.sh and understand what it is being done.
The first run is done with the PBE functional (because it uses C.pbe-rrkjus.UPF). You may verify it at the output files.

When the script ends,
plot the file e_vs_c.dat

you should see the PBE function of the following plot.



To obtain the other data we must modify the script run.sh to set the different functionals.

Now, to obtain the results for the vdW-DF functional, edit run.sh and uncomment the line (i.e., delete the symbol !)

```
!    input_dft              = 'vdW-DF'
```

and run again the script run.sh

now, for the vdW-DF2, comment the above line and uncomment

```
!    input_dft              = 'vdW-DF2'
```

and run the script. Plot all results.

Note that in all the plots the energies are shifted for setting to zero the energy of the configuration with c=25 angstroms.

If you have already finished the calcultions with PBE, vdW-DF and vfW-DF2, you can plot the results with the gnuplot command

```
plot "./e_vs_c.dat" i 0 u 1:($2+620.179) w lp t "PBE", "./e_vs_c.dat" i 1 u 1:($2+624.089) w lp t "vdW-DF", "./e_vs_c.dat" i 2 u 1:($2+625.585) w lp t "vdW-DF2"
```

The above plots was obtained using the gnuplot file Figs/plot.gp and using the data Dats/e_vs_c.dat. If there is no time to run all the simulations, copy e_vs_c.dat to the directory Figs and within gnuplot, load "plot.gp" . If there is time, so the following

More fun:
Test the empirical London corrections (DFT-D2) with the option
london=.true. and input_dft = 'PBE'. Comment all the lines ! input_dft = 'vdW-DF....

Test with LDA.

Note that LDA predicts a nice lattice constant, close to experimental 6.7 A.
However, the long range tail is incorrect.

Exercise 2. Interaction of benzene and water

Here we calculate the interaction energy bewteen a benzene and a water molecule.
This system has several local minima and saddle points, and it is not
definitely solevd yet. We shall test only one or two orientations. See PRB 76, 125112 (2007)

Go to directory ex2-benzene

a) **Water molecule upon the benzene.** O atom over the center of benzene and
H atoms poiting symmetrically towards the benzene ring.

Use xcrysden to visualize benzene_water.scf.in

do one calculation to check that all the keywords are correct,
pw.x < benzene_water.scf.in
and fix the errors in the input file.

You may or may not have the pseudopotentials for H and O in the pseudo directory. Copy them from the present directory, or download them from http://www.quantum-espresso.org

Now we obtain the energy as function of the Z coordinate of the oxygen, relaxing the postions of the other atoms. The coordinates of carbon atoms are also constrained. Think why ?
We can do it manually changing the Z coordinates of the water atoms, but it is better to adapt the script run.sh of the example of graphite to automate this task. This script is found at the directory Scripts. Copy it to the present directory

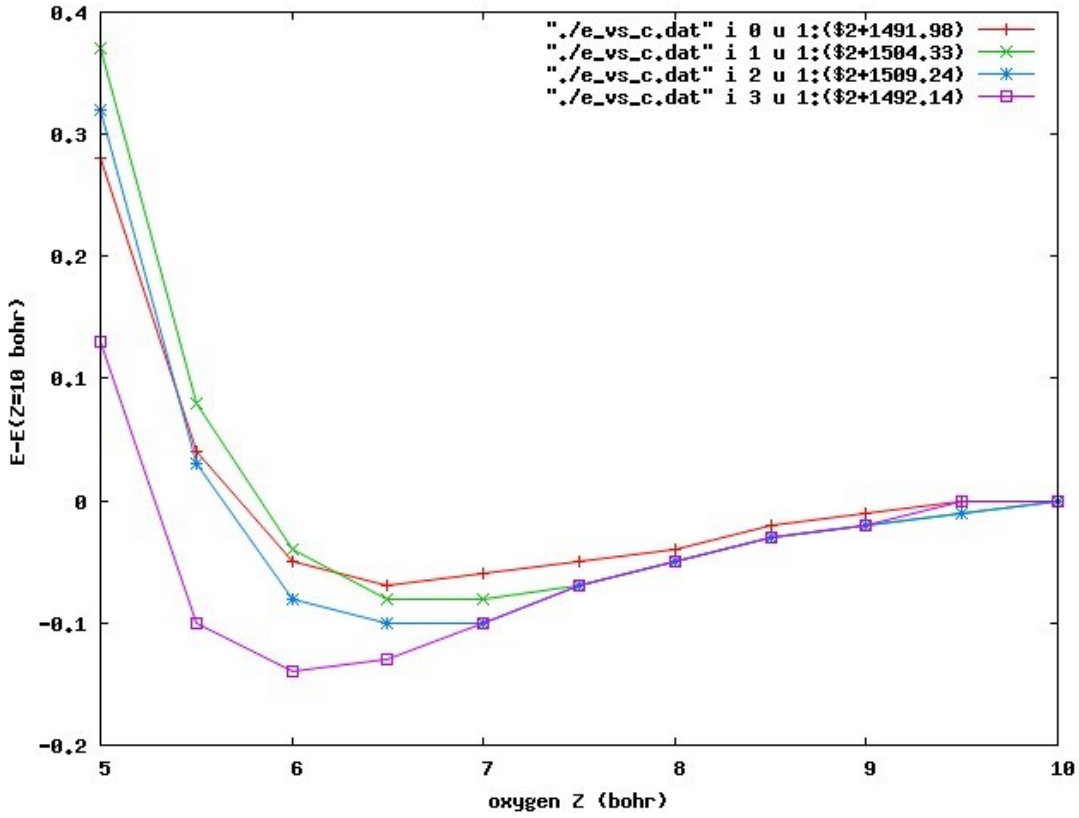
```
cp Scripts/run.sh .
```

Run the script (you may need to fix some parameter as previously with the input file benzene_water.scf.in

```
./run.sh
```

Note, this calculation is long. As you have two processors, you can let the the script running and go to the part b) explained below.

Examine and plot the file e_vs_c.dat . The plot should be one of the ones in the following figure



To obtain the other data we need to chanche the functional in the script run.sh . In the input file generated by the script, the important keywords: input_dft, london

Question: What functional was used in the previous calculation? Examine one output file, e.g., benzene_water.scf.out.PBE.c5.0 to obtain the answer. Do not trust in the name of the output file! Say if it includes any correction for van der Waals forces.

Now edit run.sh and modify the following lines it as follows

```
XCLIST="PBE vdW-DF vdW-DF2"
#XCLIST="PBE"
#postfix="-D"

!    london = .true.,
    input_dft = '${xc}'
```

the above changes will deactivate the Grimme's (london=.true.) DFT-D2 correction and will

launch the calculations with functionals PBE, vdW-DF, and vdW-DF2. At the end you should obtain a file like (but not equal) Results/e_vs_c.dat

b) Now let us obtain the relaxed configuration starting with a different position and orientation of water. Visualize the file benzene_water-pos2.scf.in
Do the relaxations using PBE, vdW-DF, and PBE with london correction. Compare the minized energies with the minimal energies in the other configuration. For every functinal determine the configuration of minimal energy.

You can use and adapt the script Scripts/run-pos2.sh . Copy it to the working directory and modify as needed. The procedure is similar to the case (a).