Joint ICTP-TWAS Caribbean School on Electronic Structure Fundamentals and Methodologies

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Tutorial on Metadynamics

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Outline
Exercise 1. Free energy in the reaction SN2
Exercise 2. Free energy of H_2

Download the exercise
scp r student@172.30.11.211:Tutorials/exercise_11_M.tar.gz .

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

Unpack it using

tar -zxvf   exercise_11_M.tar.gz
cd Exercise_11_metadyn

The name of this file is exercises_metadynamics.pdf

Exercise 0.

The last QE version that works with PLUMED is 4.3.2. Be sure that you have set the PATH variable for this distribution.

Let us install plumed

Change to the QE directory and compile plumed. For example, do

cd /home/student/Tutorials/Installation/espresso-4.3.2
make plumed

The above command downloads the PLUMED files from the web server. If it fails due to problems with internet,
we have to copy manually the PLUMED tarfile in the directory archive of the QE distribution (correct the command if you have a different directory structure)

cp /home/student/Tutorials/Exercise_11_metadyn/PLUMED-latest.tar.gz
/home/student/Tutorials/Installation/espresso-4.3.2/archive/
cd /home/student/Tutorials/Installation/espresso-4.3.2
make plumed

Now change to the directory of the first exercise

cd /home/student/Tutorials/Exercise_11_metadyn/ex1-SN2

open the file ../Refs/plumed_quick_ref.pdf
and read page 6, Section 3 First worked example: SN2 reaction

The input files pw.in and plumed.dat are in the directory.
The pw.in has some differences with the listing on the PLUMED guide. Guess way!
The plumed.dat has no difference with the listing on the guide. Guess why!

The plumed.dat must be in the outdir. Hence, create the outdir (see the name in pw.in) and copy there the plumed.dat
Now you can run a short dynamics with nstep=20 (verify it at pw.in)

pw.x -plumed < pw.in > pw.out

This run should last less than 2 minutes.

Verify that you have the following files has been created

COLVAR HILLS PLUMED.OUT

and delete them

rm COLVAR HILLS PLUMED.OUT

Find the simulation time in the output file

```
grep WALL pw.out
```

The last line should like this

```
    PWSCF        : 2m 19.74s CPU    2m 25.87s WALL
```

Write down the running time.

Now let us test how long it takes with an optimized binary. Download it

```
scp student@172.30.11.211:Eduardo_Menendez/pw.x .
```

and run it (do not forget ./)

```
./pw.x -plumed < pw.in > pw.out2
```

Again verify that exist the files COLVAR HILLS PLUMED.OUT

find the WALL time in pw.out2 and compare it with the previous time.

Exercise 1. Free energy in the reaction SN2.

Now you choose the binary that runs faster and run the full simulation with 2000 steps. Edit the file pw.in and modify

```
    nstep = 2000,
```

And run again

```
./pw.x -plumed < pw.in > pw.out
or
pw.x -plumed < pw.in > pw.out
```

While it runs, open other terminal and look at the input file pw.in.
The following options allow a control of the temperature. Read the file
INPUT_PW.txt (find it!) to understand the meaning.

```
ion_temperature = 'berendsen',
tempw = 300.d0
nraise = 20
```

In my PC (i7-2600 CPU @ 3.40GHz) it took 43 minutes running with 4 four MPI processes.
So, you may go for a snap or a snack, or you can read some paper in the Refs.

Indecent proposal: Try to hack the computer of your system manager's computer and install PLUMED.

After you did it, if the simulation is still running go to directory Outs and follow the instructions.

At the end, you should have the files PLUMED.OUT , HILLS, and COLVAR. PLUMED.OUT gives a report of the simulation. See the Quick Guide in page 10 to see a normal output.

In COLVAR you have as function of time, the values of collective variables (cv1 and cv2), which were defined in plumed.dat

```
# the distance between C-Cl' and C-Cl
DISTANCE LIST 1 3 SIGMA 0.15
DISTANCE LIST 2 3 SIGMA 0.15
```

Plot the cv1 and cv2, and the bias potential. This gnuplot command is usefull
```
plot "./COLVAR" u 1:2 t "distance(1-3)" ,"./COLVAR" u 1:3 t "distance(2-3)","./COLVAR" u 1:4 axes x1y2 w l t "V_{bias}"
```

To see how good was the sampling of the reduced phase space (cv1,cv2) use

```
plot "COLVAR" u 2:3
```

Do you think the sampling is good?

The file HILLS contains a list of Gaussians deposited during the simulations. Column1 1 is the deposition time, columns 2 and are cv1 and cv2, cols 4,5 are the gaussian widths, column 6 have the height, and col 7 is meaningless in this example. See the relation with the line of plumed.dat

```
HILLS HEIGHT 0.001 W_STRIDE 2
```

Free energy reconstructions

Using the information stored in HILLS we can reconstruc the Free energy Surface, which is the sum of the gaussians centered at the pairs (cv1(t),cv2(t)). This is done with the program sum_hills.x. sum_hills.x may need to be compiled. Change to the directory where it is located and compile as follows

```
cd path-of-espresso-4.3.2/PLUMED/utilities/sum_hills/
gfortran -O3 -o sum_hills.x serial.f90 sum_hills.f90
cd -
```

with the last command you should have returned to the working directory. Then run sum_hills.x

```
path-of-espresso-4.3.2/PLUMED/utilities/sum_hills/sum_hills.x -file HILLS -out fes.dat -ndim 2 -ngrid 100 100
```

after running sum_hills.x, you must have a file named fes.dat

with gnuplot, do

```
set pm3d
sp "fes.dat" w pm3d
```

Exercise 2. Free energy of H_2.

Go to the directory ex2-HH/

Here we do well-tempered metadynamics (WTMD). In WTMD. the Gaussian height W of the hills is automagically rescaled during the simulations.
Read page 14 of the QuickGuide.

Create yourself the input file for pw.x with the H_2 molecule. The bond length is aproximately 1.4 bohr. A fast way is to copy the input of the previous exercise and adapt it. Pay attention to set zero total charge.

Run the simulation like in the previous exercise. Note that in this case we have only one collective variable, the H-H distance.

path-to-espresso-4.3.2/PLUMED/utilities/sum_hills/sum_hills.x -file HILLS -out fes.dat -ndim 1 -ndw 1 -ngrid 100 100

Check of the convergence of the free energy. We can obtain an estimate of the FES as function of the simulation time using the -stride option.

path-to-espresso-4.3.2/PLUMED/utilities/sum_hills/sum_hills.x -file HILLS -out fes.dat -ndim 1 -ndw 1 -ngrid 100 100 -stride 150