# Performing DFTB calculation with deMonNano

## 1 DFTB basics

Remember the DFTB energy expression :

$$E^{DFTB} = \sum_{A,B} E^{rep}_{AB} + \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu} + \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B \gamma_{AB}$$

We call

$$E_{band} = \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu}$$

$$E_{coul} = \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B$$

$$E_{electronic} = E_{band} + E_{coul}$$

## 2 Starting the tutorial

get the tutorial documents typing :
wget http ://demon-nano.ups-tlse.fr/TP_GDR.tar.gz
tar -xzvf TP_GDR.tar.gz
source TPvars.sh
cd run

deMon is called by typing deMon

Important files are : deMon.inp
deMon.out : the main output file
deMon.mol type → molden deMon.mol to visualize the geometries

The deMon.inp file :
MAINKEYWORD SUBKEY1 SUBKEY2 ...
MAINKEYWORD' SUBKEY'1 SUBKEY'2 ...
The Geometry should be given at the end
Visit http ://demon-nano.ups-tlse.fr/ for list of keywords

Each line starting with # is not readen by deMon.
Arrows → indicate line to be included in the input file

# 3 Electronic structure of water Molecule

## 3.1 A

Run a simple DFTB calculation
→ DFTB
Specify the path to Slater Koster parameters
→ PARAM PTYPE=NSC
→ ∼/basis
→ GEOMETRY
Enter a very simple geometry (non optimized) for water molecule with appropriate axis in XYZ coordinates :
→ H 1.0 0.0 0.0
...

Explore the deMon.out file. (cat or vi deMon.out)

## 3.2 B

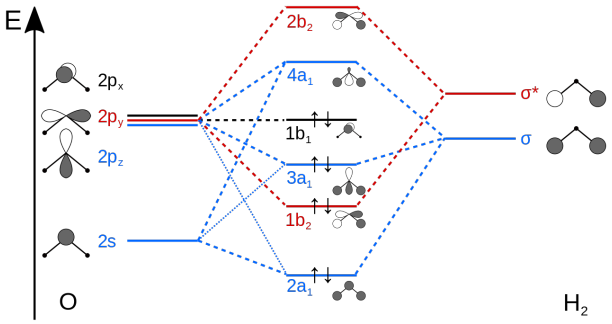
Add debug option to write many information.
→ PRINT DEBUG
Visualize the deMon.out file, search for DFTB matrices F, S, C

## 3.3 C

Add an optimization scheme
→ OPTIMIZATION

Visualize the optimization movie typing molden deMon.mol (movie + Geom. Conv button)

Try to understand the MO coefficients (the appropriate choice of the axis used to write the water molecule in the input file can be very helpfull)



### 3.4 D

Perform a single point SCC calculation on the optimized water molecule.
→ DFTB SCC
→ PARAMETER PTYPE=BIO
with debug option you can follow the different steps in deMon.out
Try changing BIO by MAT
We will keep the MAT parameter in the following.

## 4 Molecular dynamics of Coronene

### 4.1 A

Get the geometry of coronene. (cat data/coronene.xyz » deMon.inp )
Perform a molecular dynamics simulation with initial velocities set to zero
→ MDYNAMICS ZERO

### 4.2 B

Specify a timestep of 0.5 fs
→ TIMESTEP 0.5
Specify the number of steps with
→ MDSTEPS MAX=400

### 4.3 C

Change the initial velocity conditions by specifying an equivalent initial temperature :
→ MDYNAMICS RANDOM=300
Visualize the trajectory in deMon.mol with molden, you can change output frequency with OUT= ? ? as subkeyword of MDSTEPS

## 5 Harmonic spectra of Coronene monomer and dimer

### 5.1 A

Keep the geometry of coronene but replace the dynamics by a simple optimization.
Explore the deMon.out file and visualize the deMon.mol trajectory

### 5.2 B

Perform a frequency analysis at the end of the optimization (keep the OPTIMIZATION keyword)
→ FREQUENCY
Visualise the harmonic spectrum with molden (Norm. Mod. button), and the associated modes.
What are the active modes ?

### 5.3 C

Create the geometry of a coronene dimer with two superimposed molecules. Add a dispersion correcion to the DFTB line : → DFTB SCC DISP
Perform an optimization of the dimer.

### 5.4 D

Compute the frequency analysis for the optimized dimer (copy and pas the optimized geometry or perform optimization and frequency analysis in the same calculation).
Visualize the vibrational modes with molden in order to identify the inter- and intra (soft and hard) molecular modes and their position in the spectrum. Are their imaginary frequencies (represented by negative values ? What does it mean ?)

### 5.5 E

Create a dimer in a twisted superimposed form.
Optimize and compute the normal mode analysis.
What can be said from this geometry ?

### 5.6 F (optional)

Create and explore larger clusters.

## 6 Temperature evolution of the electronic spectra of cationic Methylene-Pyrene Isomers

### 6.1 A

Get the geometry of Methylenpyren
Optimize its structure in the cationic state :
→ CHARGE +1

### 6.2 B

Use the optimized geometry as input for a new calculation
Level of theory : DFTB SCC with BIO parameters
Perform a single point calculation and compute the elecronic spectrum (with LRESP subkeyword of DFTB)

### 6.3 C

Perform the same calculation for the second isomer of methylenpyren (again in cationic form).
Compare the spectra for the two isomers.
How it compares with DFT results (see the TDDFT_results.dat file for results of TDDFT-B3LYP-6-31G(d,p)

### 6.4 D

Perform a Molecular Dynamics simulation (about 1000 steps).
Change intial energie (RANDOM keyword)
Compute and sum TDDFTB spectra periodically (FRESP keyword)
→ DFTB SCC LRESP FRESP=10
Repeat for the two isomers and analyse the temperature evolution on the electronic absorption spectra of the two isomers. The spectrum is stored in spectra.out that can be visualized with gnuplot.
gnuplot
p 'spectra.out' w l

## 7 Temperature evolution of the IR spectrum of Coronene.

### 7.1 A

Get the Geometry of the coronene
Use the MAT parameters for SCC DFTB calculation
Optimize the geometry and compute harmonic frequencies
Visualize vibrational modes with molden and identify the frequency of the C-H out of plan mode ($\gamma_{CH}$).

## 8 B

Note : section B and C work together. The require long computational time to be completed BUT the computation of the spectrum (part C) can be done (at lower quality) even if the dynamics is not finished. Don't hesitate

to include results of other groups to improve of your own results!!!

Perform molecular dynamics (don't forget to remove the FREQUENCY keyword) for initial kinetic energies between 200 and 1500 K (temperature equivalent).
→ MDYNAMICS RANDOM=100
Specifiy no thermal bath → MDBATH NONE
No global rotation/translation → CONSERVE ALL
Store the dipole in new file → DIPOLE OUTFILE
Take a timestep of 1.5 fs for 100000 steps
What is the average temperature (deMon.out) , why ? Look at the deMon.dip file

# 9 C

Compute the Fourier transform of the dipole autocorrelation function with external/ftdip.exe.
Visualise the evolution of the $\gamma_{CH}$ mode with the temperature.
You can use gnuplot, type gnuplot
Control x axis : set xrange [800 :870]
plot : p 'sigma.txt'w l
Experimentally [1], the $\gamma_{CH}$ is reported to be redshifted when the temperature increases following a shift of 1.6-2.3 $10^{-2}$ $cm^{-1}$ per Kelvin. Compute this anharmonicity factor from your calculations and compare.

# 10 Optional section : Monte Carlo exploration

## 10.1 A

Get the MOLECULES file and create the following deMon.inp :

```
MONTECARLO MAX=10000
MCTEMP TMC=300 OUT=1
DFTB SCC DISP
PARAM PTYPE=MAT
/usr/local/deMonNano/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
```

1. Joblin et al.. AA. 1995, 299, 835

2 WAT
3 WAT

Try to understand the MOLECULES and deMon.inp files, run the code and visualize the outputs (deMon.out and deMon.mol)

### 10.2 B

Modify the frequency for rescaling the step lenght → MCTEMP TMC=300 OUT=1 **RESCALE=10** Visualize the deMon.mol trajectory file. What does it change ?

### 10.3 C

Add a confinment wall
MONTECARLO MAX=10000 **WALL=6**
Visualize trajectory, What does it change ?

### 10.4 D

Add a debug option
MONTECARLO MAX=10000 WALL=6 **NDBG=ON**
What can you say about the acceptance rate, step lenght ?

### 10.5 E

Remove the NDBG option and perform a parallel tempering Monte Carlo exploration with 10 trajectories following a geometric evolution for the temperature distribution. Exchanges are tested each 20 steps
→ MCTEMP **GEOM NTEMP=10 TEMPMIN=40 SMOD=20 TEMPMAX=300** RESCALE=10

Visualize the different trajectories
→ molden deMon.04.mol ...
→ molden deMon.10.mol ...
Put **SDBG=0N** as a subkeyword of MCTEMP , it creates a debug_swap file that you can visualize for instance with gnuplot : p 'debug_swap.dat' u 1 :2 w l ; rep " u 1 :3 w l ; rep " u 1 :4 w l ;

### 10.6 F

The goal is to find the most stable geometry for a cluster of two water molecules and one benzene, starting from a geometry where the two water molecules are on different sides of the benzene.

DFTB **MEMOSCC DISP EPSMUL**
PARAM PTYPE=MAT

/usr/local/deMonNano/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 1.0 0.0 3.0 1.0 0.0 0.0 0.0
3 1.0 0.0 6.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 BZZ
3 WAT

The DFTB line contains slight modifications of the DFTB energy (dispersion correction, weighted Mulliken charges, not detailed here) Find the appropriate Parallel Tempering conditions to get the correct optimized geometry (two water molecules on the same side).

When done, perform the same calculation removing inter-trajectory exhanges (put SMOD=1000000). Conclusion ?