Performing DFTB calculation with deMonNano

Mathias Rapacioli
Laboratoire de Chimie et Physique Quantiques
Toulouse , France

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/handson_deMonNano2025.tar.gz
tar -xzvf handson_deMonNano2025.tar.gz
vi TPvars.sh
change the correct paths to deMon and FT
source TPvars.sh
cd run

All the calculations are expected to be run in non-parallel : type : EXPORT OMP_NUM_THREADS=1

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

Modify deMon.inp to give the correct path to basis directory deMon is called by typing deMon

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

Perform a single point SCC calculation on the water molecule.
→ DFTB SCC
→ PARAMETER PTYPE=MAT
Try changing MAT by BIO
We will keep the BIO parameter in the following.

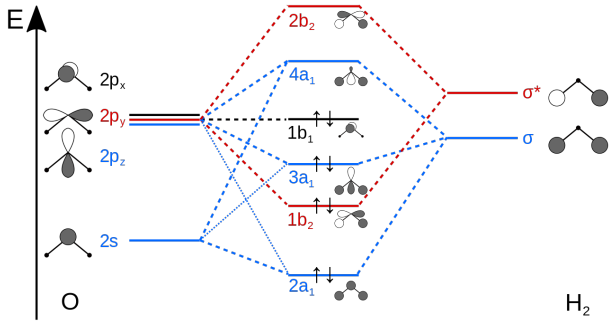
3.3 C

Add an optimization scheme
→ OPTIMIZATION

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

3.4 D

Perform a single point SCC calculation on the optimized water molecule. Add debug option to write many information.
→ PRINT DEBUG
Visualize the deMon.out and deMon.coef file, search for DFTB matrices F, S, C



4 Molecular dynamics of Coronene

Remove the DEBUG option

4.1 A

Get the geometry of coronene. (cat data/coronene.xyz » deMon.inp)
Potential is DFTB SCC with MAT parameters 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=100
Visualize the trajectory in deMon.mol with molden (geom. conv. button)

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. OUT=1 prints all steps.

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 on the last geometry (copy-past from deMon.mol and remove OPTIMIZATION KEYWORD)
→ FREQUENCY
Visualise the harmonic spectrum with molden (Norm. Mod. button), and the associated modes.
What are the active/inactive modes and why ?

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 (without FREQUENCY analysis).

5.4 D

Compute the frequency analysis for the optimized dimer (copy and pas the optimized geometry).
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 the first isomer of Methylenpyren
Level of theory : DFTB SCC with BIO parameters
cat data/methylpyren_iso1.xyz » deMon.inp
Optimize its structure in the cationic state :
→ CHARGE +1

6.2 B

Use the optimized geometry as input for a new calculation
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) (OPTIMIZATION followed by TDDFTB calculation).
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 spectrum_final.out that can be visualized with gnuplot.

gnuplot
p 'spectrum_final.out' w l

7 Monte Carlo exploration

7.1 A

Get the MOLECULES file and create the following deMon.inp :
MONTECARLO MAX=10000 WALL=6
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
2 WAT
3 WAT

Try to understand the MOLECULES and deMon.inp files, run the code and visualize the outputs (deMon.out and deMon.01.mol).

7.2 B

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**

Visualize the different trajectories
→ molden deMon.04.mol ...
→ molden deMon.10.mol ...
Put **SDBG** 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 ;

7.3 C

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 ?