

## 1. Computational Details

In this work we saw output files given to us, first of all is easy to know that the main computational program used for the propouse of the study was the program deMon-Nano [1] which is a software package for Density Functional Theory based Tight Binding (DFTTB) calculations. It is part of the deMon (density of Montréal) program suite [2]. Those codes are available on the web pages: deMonNano and deMon2k.

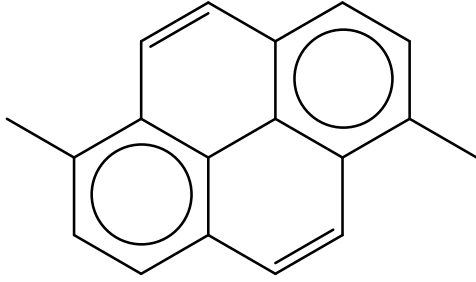


Figure 1: Dimethylenepyrene molecule.

Since the output files write down how many time was required for the calculation we can presume that the number of processors was four, its because the **TOTAL TIME** is four times the **REAL TIME**, the processors used. About the memory, the maximum destined to allocate is 8000.000 MBYTES and DFTB requieres 0.580 MBYTES of allocatable memory.

The starting guess point geometry to optimize was probably taken from literature or was done with help of some visual representation builder as Avogadro [3] or GAUSSVIEW [4]. In this report we use GNU PLOT [5] for visual representations of plots.

## 2. Step 1

Firstly is necessary optimize the molecule geometry at the theory level that was used. For that propouse on the input file the next keywords was used:

- **DFTB**: theory level is Density Functional based Tight Binding. And **SCC** to self-consistent charge variant of DFTB.
- **OPTIMIZATION MAX=500**: set the Maximum number of SCC cycles. That just to expand the default maximum, which is 100.

Few words about DFTB, the main point starts taking the density as a sum of some reference density, adding a small fluctuation:  $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})$ , and expanding the energy (as a function of  $\rho$ ) into a Taylor series up to a given order.

$$E[\rho_0 + \delta\rho] = E_0[\rho_0] + E_1[\rho_0, \delta\rho] + E_2[\rho_0, (\delta\rho)^2] + E_3[\rho_0, (\delta\rho)^3] + \dots$$

Consequently, consider only terms with up to the second order of density fluctuations, the energy can be expressed as:

$$E = \sum_{i=1}^N n_i \langle \phi_i | \hat{H}_0 | \phi_i \rangle - \frac{1}{2} \iint \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho_0] - \int \rho_0(\mathbf{r})V_{xc}[\rho_0(\mathbf{r})]d\mathbf{r} + E_{nn} + \dots$$

$$+ \frac{1}{2} \iint \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\partial^2 E_{xc}}{\partial \rho \partial \rho'} \right|_{\rho=\rho_0} \right) \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

The geometry is written down on the same input file, it was not consider any extra charge for the molecule, *i. e.*, **CHARGE 0**. The basis are in `~/basis/` at the computer where the calculations was carried out, where was gotten `~/basis/skf/bio-scc/cc.spl`, `~/basis/skf/bio-scc/ch.spl`, `~/basis/skf/bio-scc/hc.spl` and `~/basis/skf/bio-scc/hh.spl`

With that input file, the output file was gotten after 12.747 s of computing. Really fast, we know that DFTB is roughly three orders of magnitude faster than DFT which is already faster than wavefunction methods.

### 3. Step 2

With the previous calculation, the geometry optimized was taken to compute the next step, with the next keyword at the input file **LRESP** to perform a TDDFTB calculation Linear Response.

Where the Linear Response TD-DFT(B) only takes into account components of a desntity fluctuation  $\delta\rho(\mathbf{r},\omega)$  that depend linearly on the external perturbation, *i.e.*:

$$\delta\rho(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega)\delta V_{ext}(\mathbf{r}',\omega)d\mathbf{r}'$$

with:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta \rightarrow 0^+} \sum_{k=1}^N \sum_{l=1}^N (f_k - f_l) \frac{\phi_l(\mathbf{r})\phi_k(\mathbf{r})\phi_l(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\varepsilon_l - \varepsilon_k) + i\eta}$$

and,  $\delta V_{ext}(\mathbf{r}',\omega)$  is the linearized time-dependent KS potential, from:

$$\hat{V}_{eff}[\rho(\mathbf{r})] = \hat{V}_{ne}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \hat{V}_{XC}[\rho(\mathbf{r})]$$

At this point is possible sumarize the next, reading the output file of these step:

Table 1: Summary Table of Energy,  $E_h$  unit

Summary Table	
Description	Energy
DFTB Electronic	-36.64694927
DFTB Band	-36.65447764
DFTB Repulsive	1.16712873
DFTB Coulomb	0.00752837
DFTB Total	-35.47982055
DFTB HOMO-LUMO gap	0.0553812
DFTB (HOMO)-(HOMO-1) gap	0.0431804

Also, at this step we can know about the spectrum, particularly about the transitions. About its energy, oscillation strength, that for singlets and triplets, as we shown in the Table 2. Where we can see the allowed excitations (Osz. strength different than zero).

Table 2: Transitions for diMethylenePyrene

w [eV]	Osz. strength	Transition	Weight	E_sp [eV]	Sym.
2.389	0.3985879	42 -> 43	0.602	1.507	S
2.771	0.0000000	41 -> 43	0.691	2.682	S
3.188	0.0000000	39 -> 43	0.568	3.141	S
3.225	0.0173636	40 -> 43	0.796	3.083	S
3.483	0.0000000	42 -> 46	0.428	3.657	S
3.717	0.0000000	38 -> 43	1.000	3.717	S
3.849	0.0402239	42 -> 45	0.645	3.563	S
3.917	0.0089270	37 -> 43	0.761	3.802	S
3.933	0.0000000	36 -> 43	1.000	3.933	S
4.264	0.0000000	42 -> 46	0.455	3.657	S
1.319	0.0000000	42 -> 43	1.139	1.507	T
2.542	0.0000000	41 -> 43	0.918	2.682	T
2.849	0.0000000	42 -> 44	0.855	2.918	T
3.01	0.0000000	39 -> 43	0.958	3.141	T
3.047	0.0000000	40 -> 43	1.006	3.083	T
3.528	0.0000000	42 -> 45	1.001	3.563	T
3.573	0.0000000	42 -> 46	0.981	3.657	T
3.689	0.0000000	37 -> 43	0.957	3.802	T
3.717	0.0000000	38 -> 43	1.000	3.717	T
3.933	0.0000000	36 -> 43	1.000	3.933	T

#### 4. Step 3

Now, with the information obtained by the other two steps, was posible to start a compute for the spectrum, with four particular sub-steps, that four substeps changing the next keyword **MDYNAMICS** **RANDOM=** with the values 200, 500, 1000 and 1500.

The first keyword **MDYNAMICS** activates the Born-Oppenheimer molecular dynamic, and the second one **RANDOM=** starts a trajectory using random initial velocites, which have no net momentum or angular momentum and give the requested temperature specified after the equal sign.

That means, that the next substeps will provide the spectra with 200 K, 500 K, 1000 K and 1500 K. Even if the molecule are not physical chemistry avialbe at that temperature, we are not in that analysis.

Finally, the last keyword **TIMESTEP** specifies the time step of the molecular dynamic in femtosecond, for all four cases the **TIMESTEP** was 0.5.

In all cases we have a detailed output for spectra and another one with just the main points to the spectra plots. We are plotting the **spectrum\_final.out** for the 4 substeps in the Figure 2. Spectrums that we will analyze.

Is possible to see the more themperature the more interference. Not having resolution with 5000 K or more, and being not readable with 1000 K, where would be impossible to know which molecule we would have (even with experimental data).

Looking at the spectra with the lowest temperature and since we know the molecule (diMethylenePyrene cation) we can elucidate how the signals are in. For the H atoms at the methyl the spectra has a signal that integrate 4. We guess that is the signal around 2 ppm.

Another signal would appear because the two H atoms at 2 and 7 molecule position. That signal would appear close to 3 ppm. Finally the  $H^1$ -NMR would have had a signal for all the others H atoms, inegrating for 6 with a really closer signals for all of these H atoms, since theirs chemical shift are basically the same around 4 ppm.

That correspond, more or less with what we see. Knowing now that we sorted out the H atoms in three ways. All four spectra “has” that. However, just at 200 and maybe at 500 K is possible to elucidate the integral values, but not the best.

Exeperimentally we know that the  $H^1$ -NMR are done with temperatures upper, but closer to liquid  $N_2$ , 80K. Now we know, with 200 K we are at approximation that spend really few computing time.

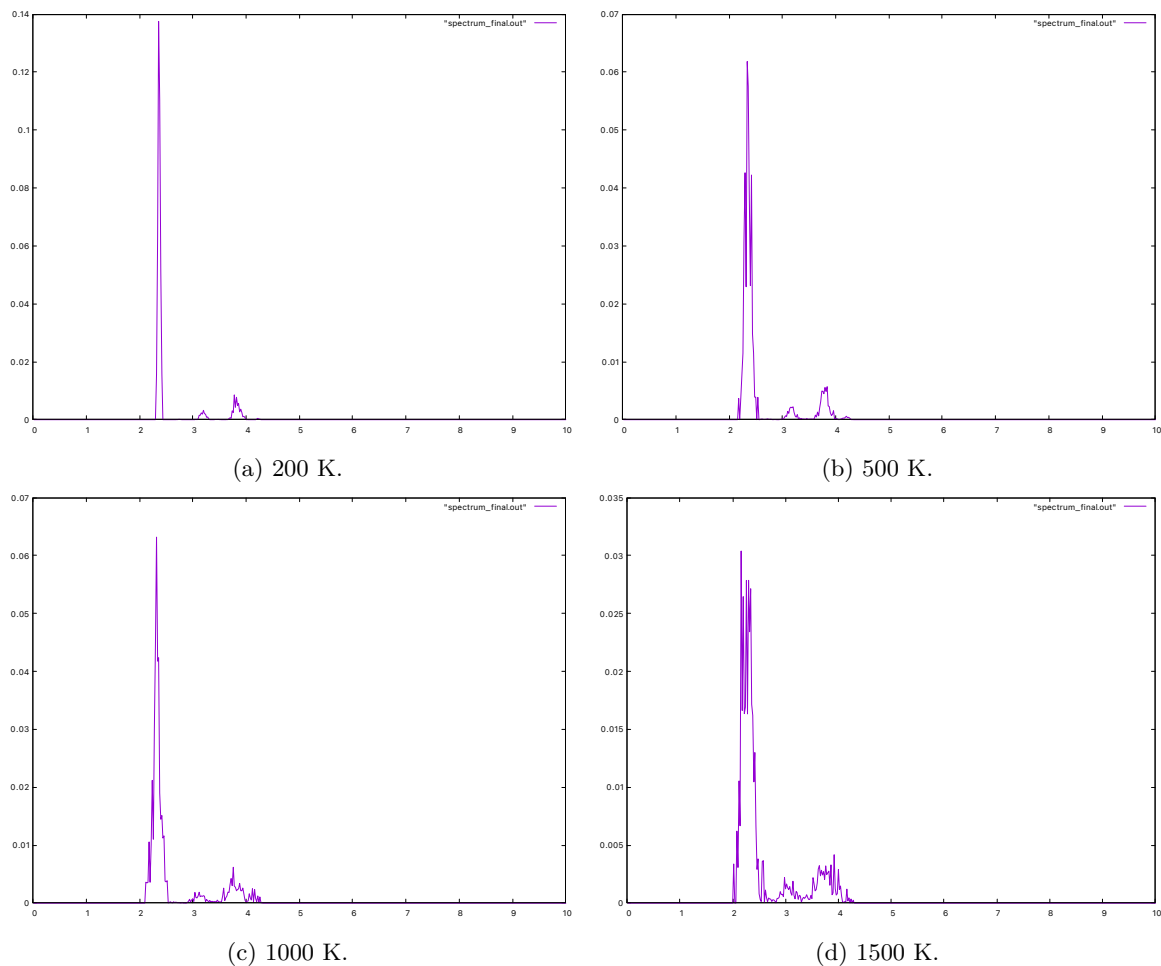


Figure 2: Substeps a, b, c & d

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