Title: Excited States Dynamics of Diacenaphtho Thiophene with Libra

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Introduction

I used Libra[1] package to look into the excited states of Diacenaphtho Thiophene (DAT) molecular crystals. DAT and its derivatives are potential hole transport layer material for Perovskite solar cells (PSCs) materials in due to the presence of hydrophobic elements, and pi stacked packing. PSCs are solar cells that includes a perovskite-structured compound as the light-harvesting active layer. They have high potential as in little over a decade, PSCs have increased efficiencies from about 3% to over 25%[2]. One of the challenging part of PSCs is the Hole Transport Layer (HTL) as they need to have high intrinsic hole mobility (> 10-2 cm2/Vs), should perform well without doping, should have proper band edge alignments with perovskites and the anode, should be Inexpensive and easy to form films, and they should be hydrophobic, high chemical, thermal, and photostable[3]. Thus, I am looking into various properties of DAT to evaluate its potential.

Methods

The calculations were performed with four steps as explained in the Libra Tutorial for NBRA (neglect of back-reaction approximation) dynamics workflow[4]. The crystal structure of DAT was obtained from Cambridge Crystallographic Data Centre (CCDC) shown in figure 1. DAT is Monoclinic, and in the P21/m space group. In the first step, classical molecular dynamics was performed using CP2K for around 2300 steps in 300k temperature. In the second step, molecular overlaps and time overlaps were calculated using Time-Dependent Density Functional Theory (TD-DFT) for the steps 1200 to 1399. In the third step, non-adiabatic couplings were calculated in between the excited states for both single particle basis and many-body basis. Finally, the nonadiabatic dynamics were performed in Fewest Switches Surface Hopping (FSSH), Modified Simple Decay of Mixing (mSDM), Instantaneous Decoherence at the Attempted Hops (IDA), and Decoherence Induced Surface Hopping (DISH) method.

Results

From the MD trajectory, as shown in Figure 2, it is evident that the system is thermalized. With the TD-DFT calculation, 10 excited states (LUMO+10) were selected. The excitation energies of the states are shown in figure 3. It is evident from the figure that the excited states are coupled and highly convoluted, which is characteristic for solid state materials. Figure 4 shows the density of states for each element for different types of orbitals. Among C, H, and S, the density from C atoms contribute highest to the total density. Figure 5 shows the Nonadiabatic Coupling Distribution for both the Single Particle (SP), and Many Body (MB) basis. Figure 6 shows the influence spectrum for all the states from the ground state up to 10^{th} state. Figure 7 shows the adiabatic population of the excited states calculated with the DISH method, and Figure 8 shows the map for average decoherence times for the states.

Figures

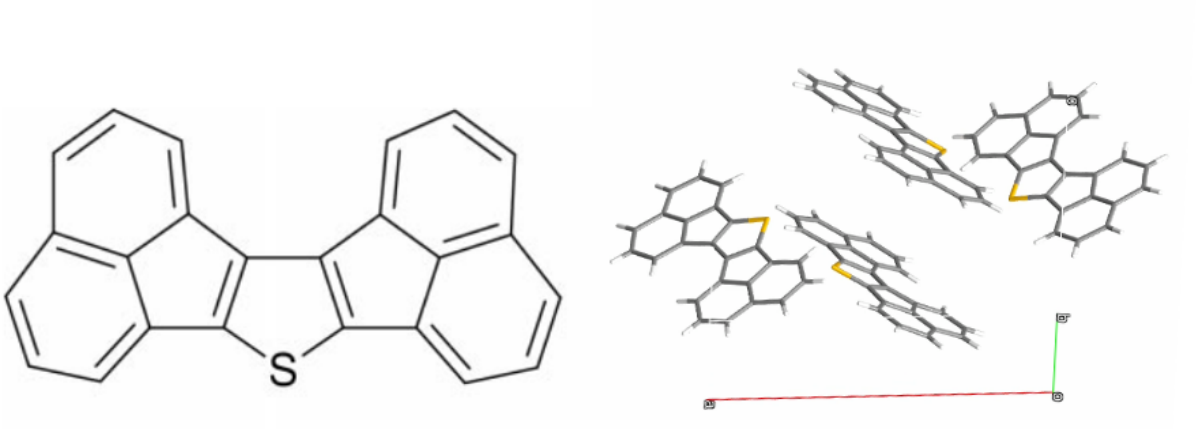

Figure 1: Structure of Diacenaphtho thiophene (DAT) (left), Molecular Crystal of DAT (right)

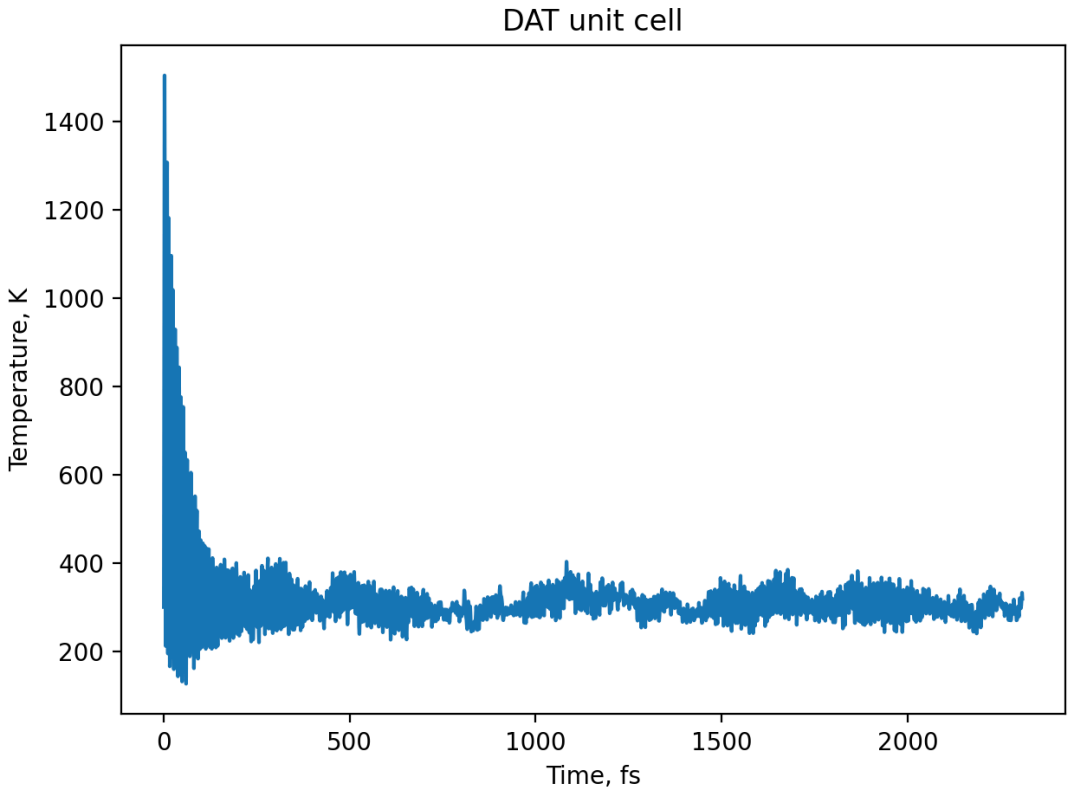

Figure 2: Time vs Temperature of MD trajectory

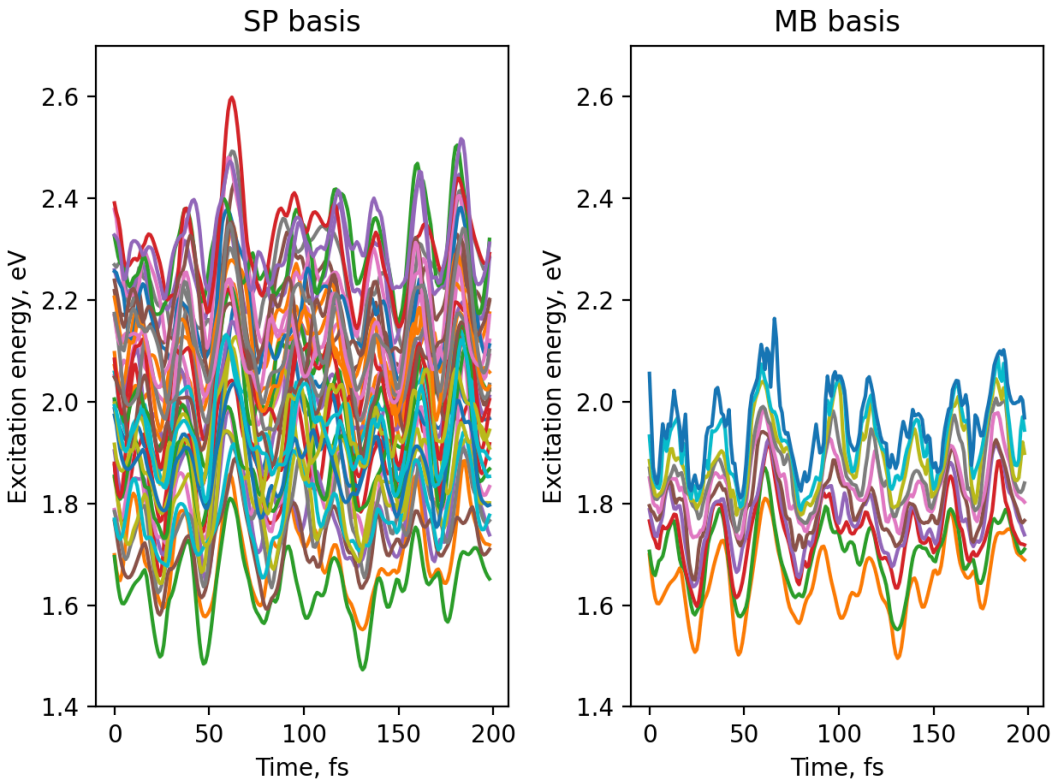

Figure 3: Excitation Energies vs Time

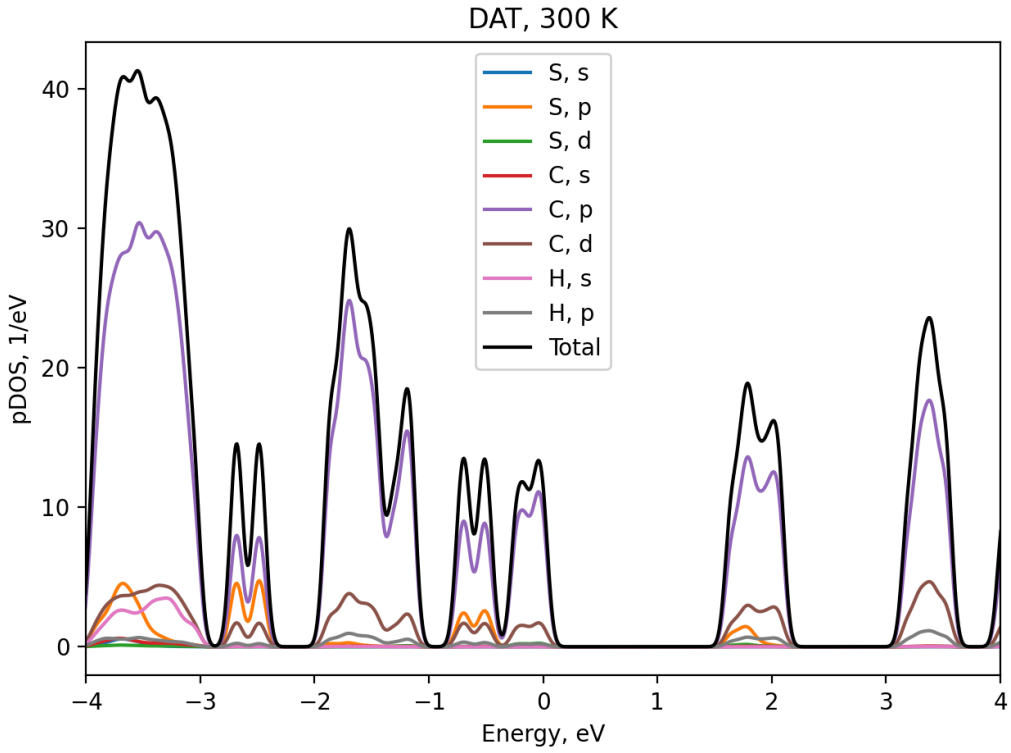

Figure 4: Density of States

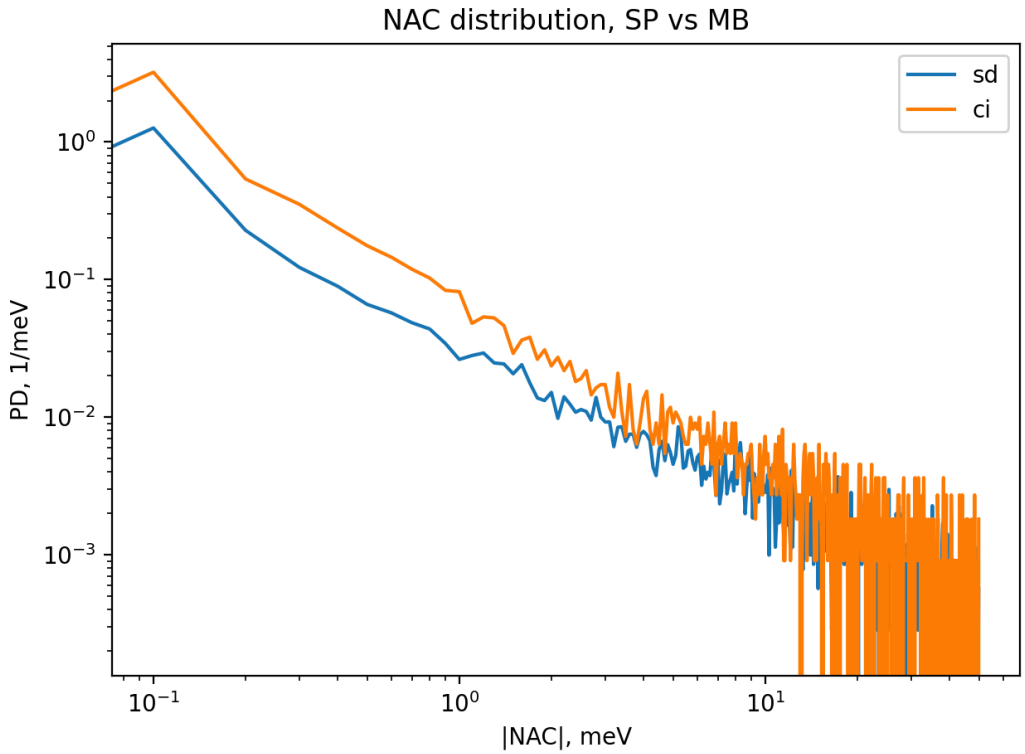

Figure 5: NAC distribution

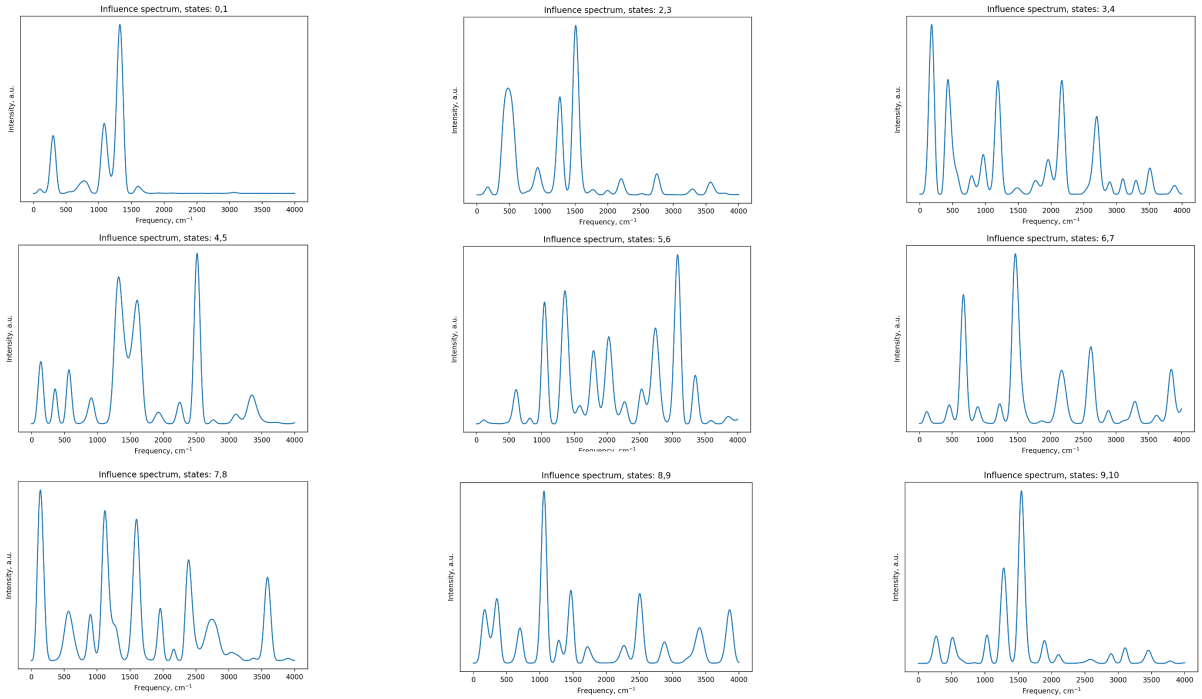

Figure 6: Influence spectrum between states

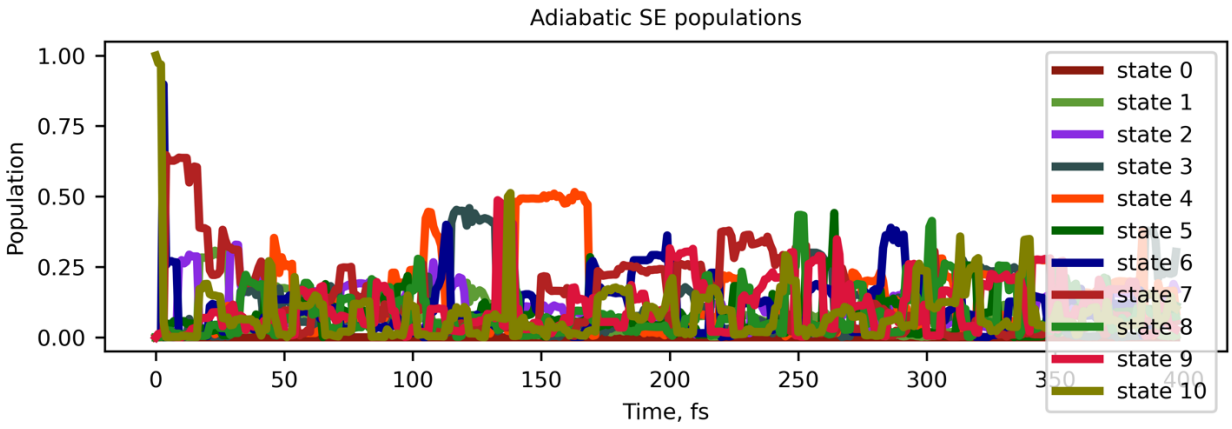

Figure 7: DISH adiabatic populations

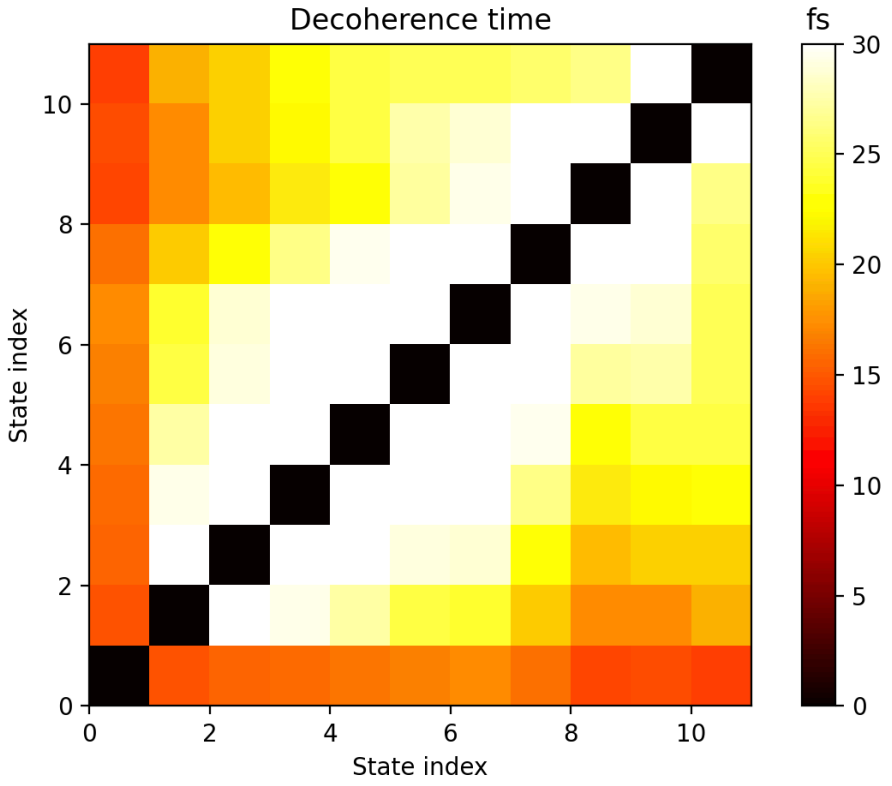

Figure 8: Average decoherence times map

References

(1) Shakiba, M.; Smith, B.; Li, W.; Dutra, M.; Jain, A.; Sun, X.; Garashchuk, S.; Akimov, A. Libra: A Modular Software Library for Quantum Nonadiabatic Dynamics. *Softw. Impacts* **2022**, *14*, 100445. https://doi.org/10.1016/j.simpa.2022.100445.

(2) Zhao, X.; Wang, M. Organic Hole-Transporting Materials for Efficient Perovskite Solar Cells. *Mater. Today Energy* **2018**, *7*, 208–220. https://doi.org/10.1016/j.mtener.2017.09.011.

(3) Ke, Q. B.; Wu, J.-R.; Lin, C.-C.; Chang, S. H. Understanding the PEDOT:PSS, PTAA and P3CT-X Hole-Transport-Layer-Based Inverted Perovskite Solar Cells. *Polymers* **2022**, *14* (4), 823. https://doi.org/10.3390/polym14040823.

(4) *compchem-cybertraining/Tutorials_Libra: Tutorials showcasing various capabilities of Libra*. https://github.com/compchem-cybertraining/Tutorials_Libra (accessed 2023-06-30).