

Excited State Dynamics using Libra and SHARC packages
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Introduction

My project uses both Libra¹ and SHARC² packages to calculate the excited state dynamics of various molecules. For this study I chose to explore lithium aluminum hydride (LiAlH₄), and 2-thiouracil. LiAlH₄ is an important reducing agent in organic chemistry, generally dissolved in diethyl ether, it is commonly used to convert ketones and esters into alcohols.³ Due to its utility and widespread use, it makes an interesting species to develop a deep understanding of. 2-Thiouracil is in a class of molecules which are modified nucleobases. It is the uracil molecule with one of the oxygens swapped out for a sulfur group, in this case the oxygen between the two nitrogen atoms. Studies suggest that modified nucleobases may have utility in gene editing and modification, as fluorescent markers, anti-inflammatory drugs, and cytotoxic agents; thus, it is useful to study the excited state dynamics of these molecules.⁴⁻⁷

Methods

To study the dynamics of LiAlH₄, the CP2K methods in the Libra quantum chemistry package were used.¹ Following the NBRA (neglect of back-reaction approximation) dynamics workflow, there are 4 steps to calculating the dynamics. The first step consists of running a classical adiabatic MD. Step 2 the time-overlaps and non-adiabatic couplings (NAC) are calculated, this can be done in the many body or single particle basis. In the third step you apply a phase correction to the time-overlaps and make use of state tracking, which allows you to go from Kohn–Sham (KS) orbital basis to an excited slater determinant basis. In the final step you compute the dynamics of the system, there are various methods that Libra allows you to use.

Data for the crystal structure was found via “The Materials Project”, LiAlH₄ is in the P12₁/c1 space group and has a monoclinic structure with 24 sites at a band gap of 4.34 eV.⁸ The time overlaps were calculated using Time-Dependent Density Functional Theory (TD-DFT) starting at step 1200 to 1999, split into 20 jobs. The NACs in step 3 were computed in two ways, using the Hamess-Shiffer-Tully (HST)⁹ method and the Meek-Levine NPI¹⁰ approach. The many body and single particle MO's that were used in subsequent steps were calculated with the HST method. Finally, the nonadiabatic dynamics were ran in four ways, the fewest switches surface hopping (FSSH), both forms of the modified simple decay of mixing (mSDM), and instantaneous decoherence at the attempted hops (IDA).^{11,12} For the mSDM method, energy gap matrices were calculated using the vibronic Hamiltonian in the slater determinant basis, dephasing rates were calculated with the vibronic Hamiltonian in the MB basis.

The study of 2-Thiouracil and was both done with the SHARC package² using the Linear Vibronic Coupling (LVC) Model. First an optimization and frequency calculation are done at the TD-DFT level using the ORCA package.¹³ Then the LVC template is created using the SHARC-

ORCA interface. 2-Thiouracil was calculated with a def2-svp basis and the b3lyp functional. There was 3 singlets and 2 triplet states declared for the calculations. A total of 400 trajectories with a 700-femtosecond simulation time were calculated. Of the 400 trajectories, 353 passed the diagnostics and were used in the final excited state calculations. Both classical and quantum populations were determined, as well as spectra, and two crossings were calculated for 2-thiouracil. Transitions between excited states were determined and the difference matrix was used in the fitting procedure.

Results

The distribution of the NACs, in the many body (MB) and single particle (SP) basis, for both the NPI and HST methods can be seen in figure 1. In the SP case, the general shape of the distribution follows closely between the two algorithms. Figure 2 shows the NACs in the MB and SP basis calculated from each method. It can be seen in both methods the SP basis is much more scattered and less connected, where the MB basis is uniform and well connected. Figure 3 shows the excited state energy vs time in the MB and SP basis. For HST method in the MB basis, all states are consistently in the 5-6 eV range, whereas the SP basis there is a split between 0-2 eV and 6-7 eV. The NPI method is also split but has a wider distribution of energies, either in the 0-4 eV range or 6-10 eV range. The spectrum was also calculated and can be seen in figure 4.

The MO's and time overlaps calculated via the HST method were used in computing the dynamics of the system. Figure 5 shows the decoherences between states, the FSSH and IDA is much smoother and has a longer coherences than the mSDM method, with most states in the 10-15 fs range. The mSDM method is scattered with the highest coherence being around 12 fs. Figure 6 shows the fits to the populations for each of the methods. All the fits generally agree, $\tau = 474.5 \pm 40.7$ (FSSH), $\tau = 420.3 \pm 57.4$ (IDA), $\tau = 421.7 \pm 29.2$ (mSDM), and $\tau = 462.9 \pm 45.2$ (mSDM2).

Figure 7 shows the classical and quantum populations for 2-thiouracil, both of which look very similar. Based on the difference matrix (Table 1), the molecule is excited to the S2 and S1 states, which then depopulate to the S1, T1 and T2 states. A fitting procedure was performed which found the transition rates between states to be, $S2 \rightarrow S1 = 10.6 \pm 1.1$ fs, $S1 \rightarrow T1 = 843.4 \pm 77.8$ fs, $S1 \rightarrow T2 = 2716.7 \pm 259.3$ fs, and $T1 \rightarrow T2 = 1220.2 \pm 536.8$ fs. Comparing these results to a study done by Mai et al, the overall population graphs agree in shape, however the rates are not as comparable, with reported rates of $S2 \rightarrow S1 = 59 \pm 12$ and $S1 \rightarrow T1 = 540 \pm 100$.⁴ Figure 8 is a spectrum of the molecule, which gives a correct peak centered around 275 nm, but misses a peak that should occur centered around 200nm.^{5,14}

Figures

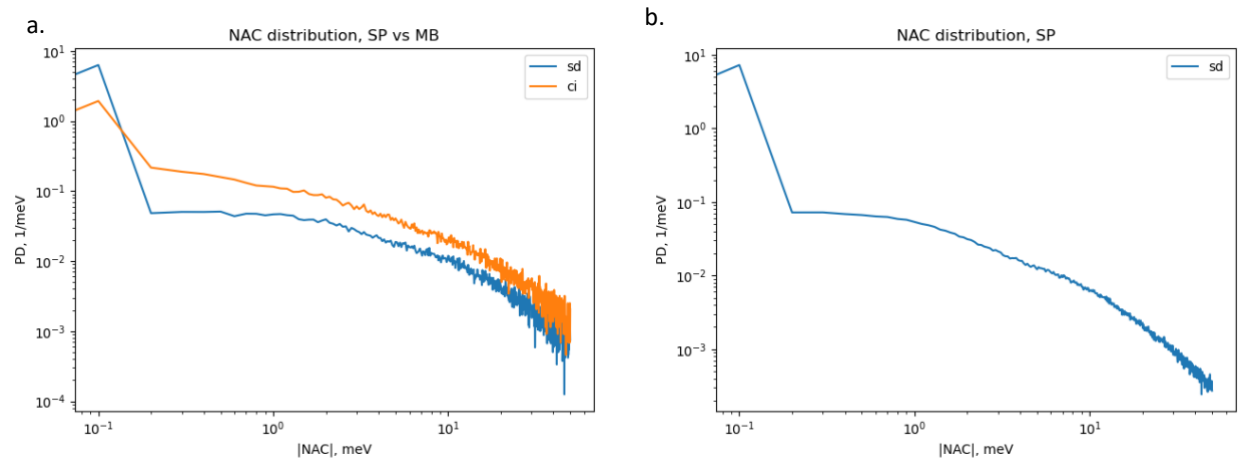


Figure 1. NAC distributions using a) HST and b) NPI methods

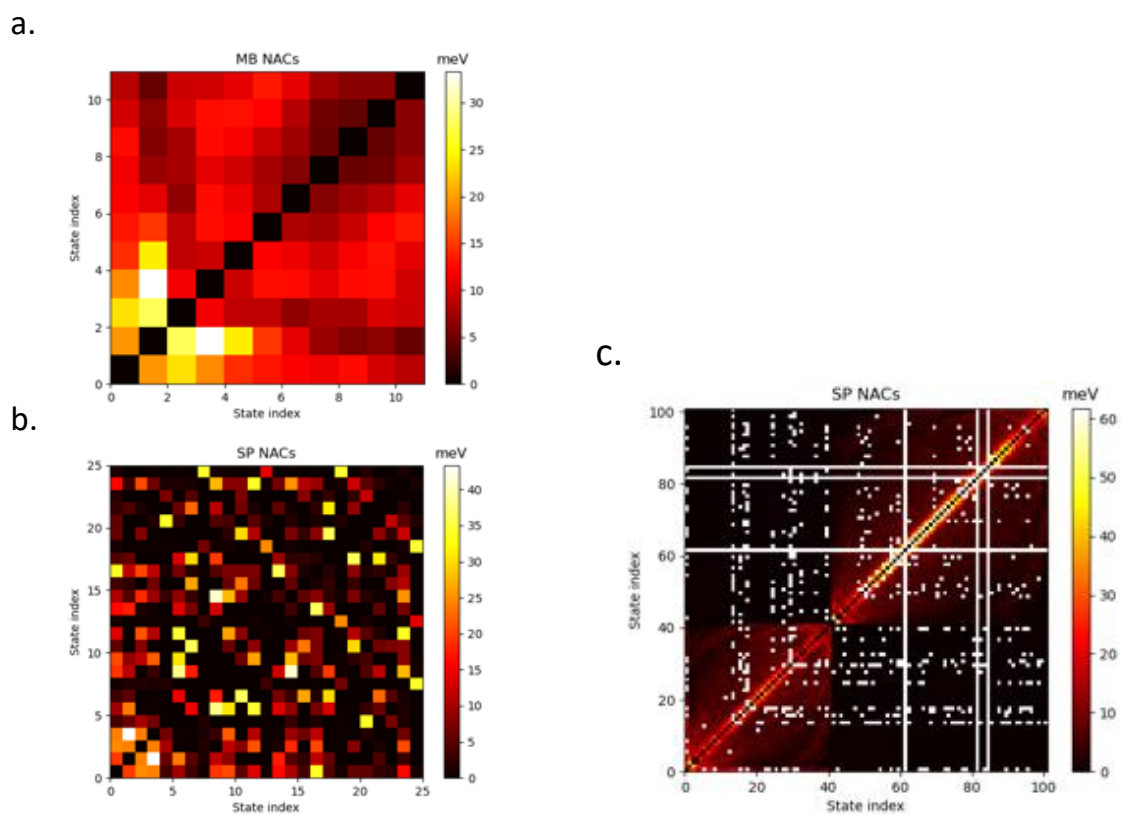


Figure 2. MB and SP NAC matrices using HST method (a,b), and SP NACs using NPI method (c).

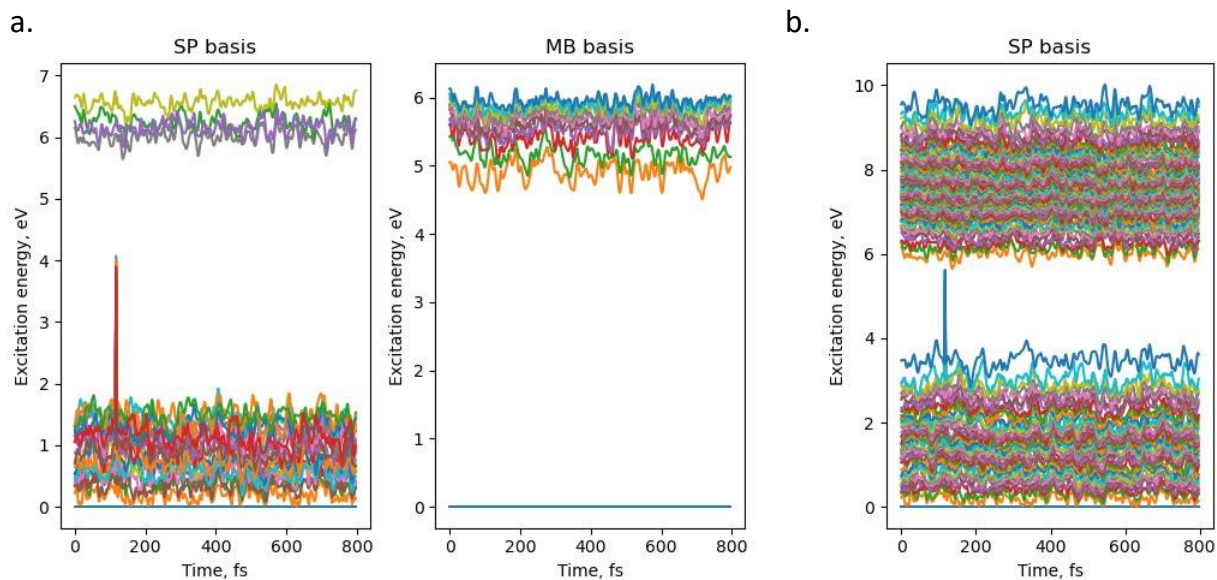


Figure 3. State energies vs time for the HST method (a) and the NPI method (b)

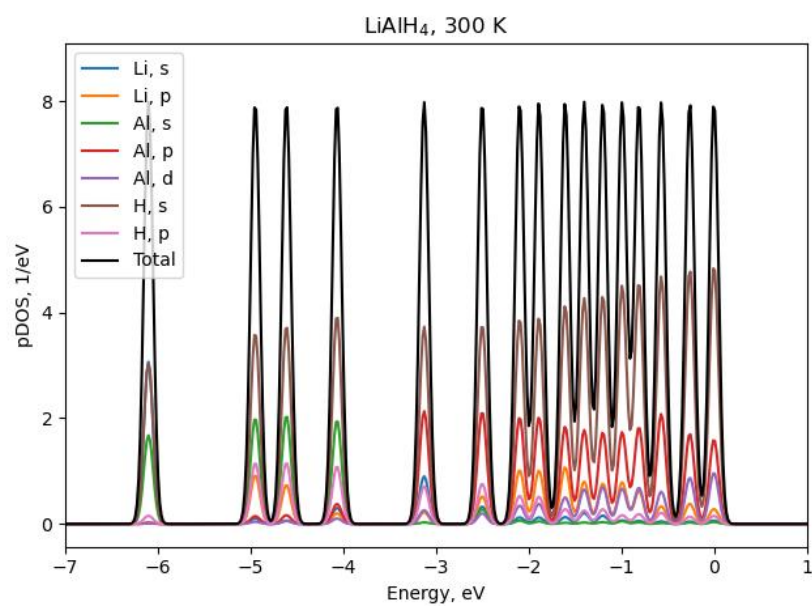


Figure 4. LiAlH_4 spectrum including angular momenta

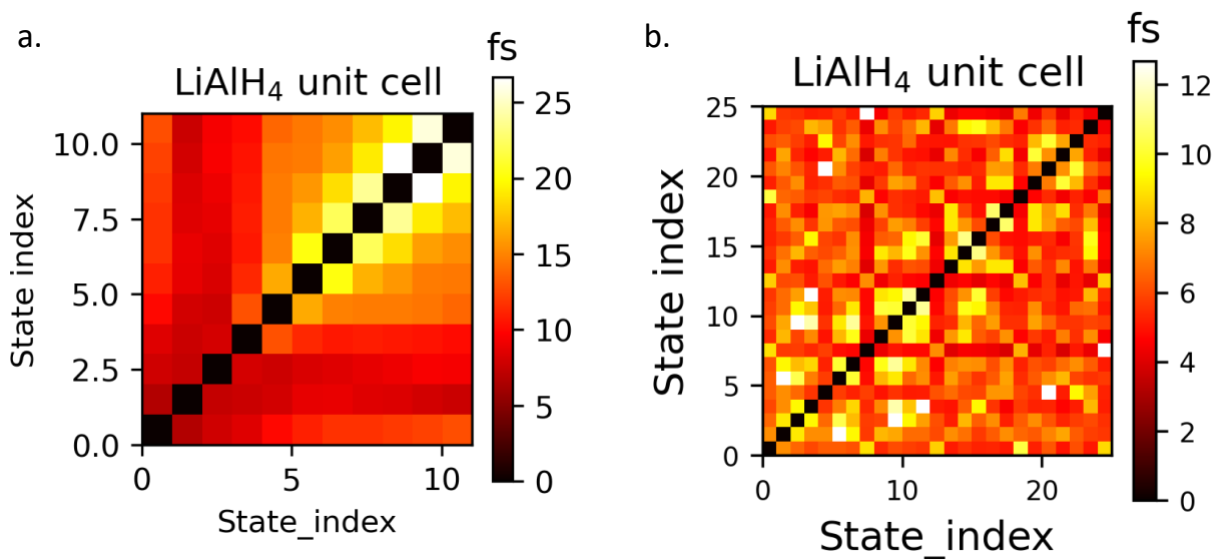


Figure 5. Decoherences calculated for FSSH/IDA (a) and mSDM (b)

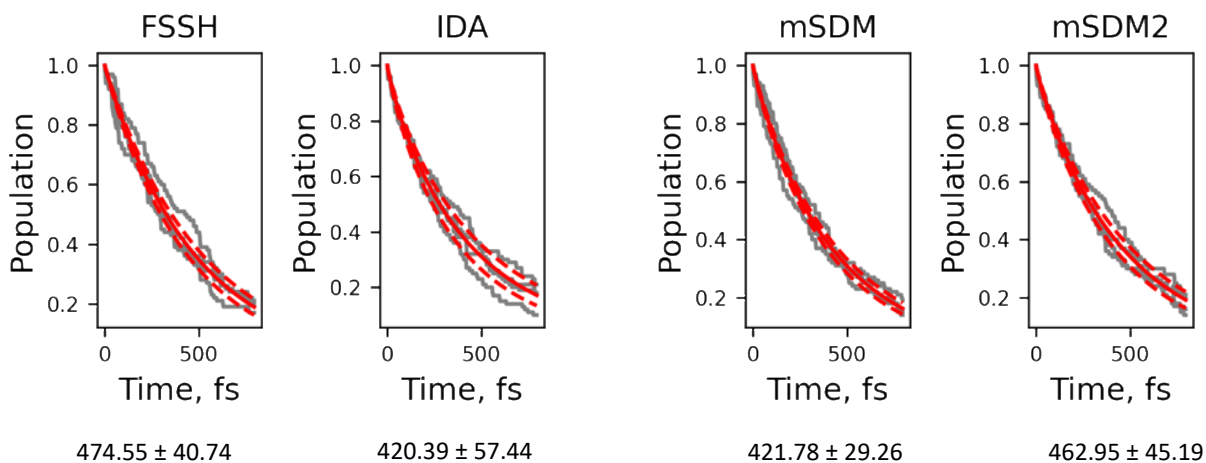


Figure 6. Fittings for each method

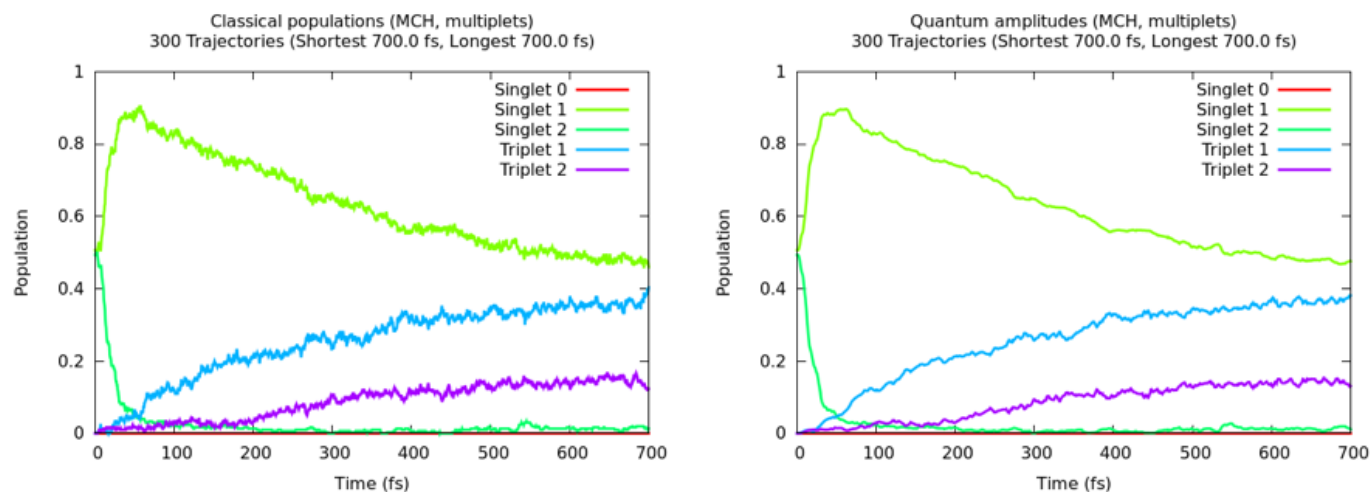


Figure 7. Classical and Quantum populations from 300 trajectories agree well over the 700 fs timeframe.

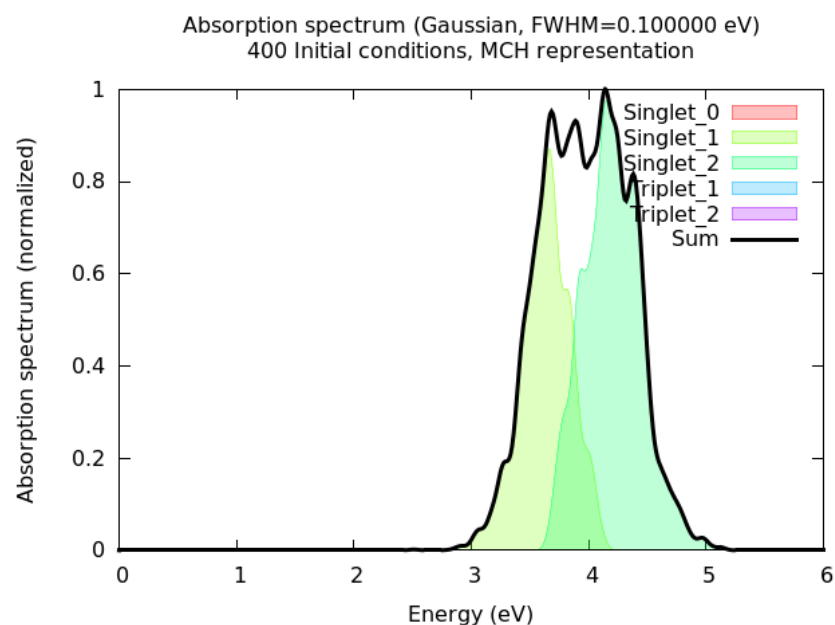


Figure 8. Calculated spectrum of 2-thiouracil

Table 1. Difference Matrix of 2-Thiouracil

	S0	S1	S2	T1	T2
S0	0	0	0	0	0
S1	0	0	142	-131	-25
S2	0	-142	0	0	-2
T1	0	131	0	0	-10
T2	0	25	2	10	0

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