

Excited State Dynamics using Libra and SHARC packages

Nathan Jansen

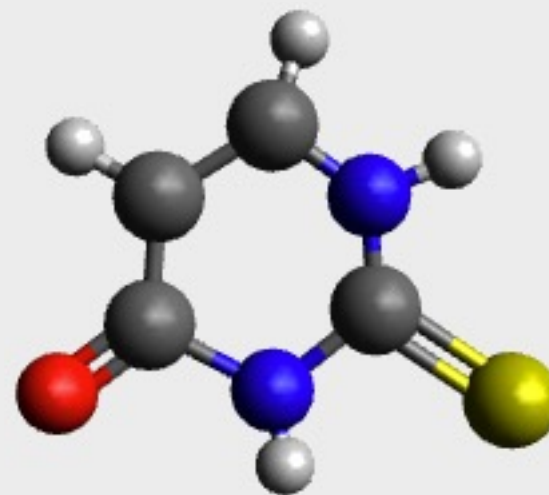
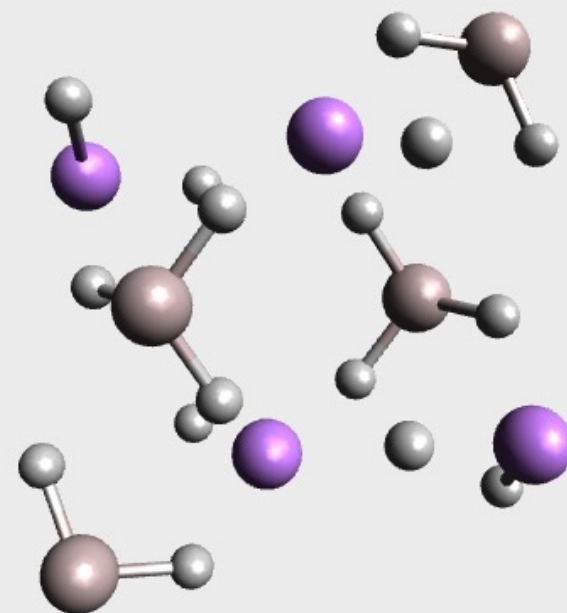
07/22/2022

Cyber Training Workshop 2022



Motivation

- LiAlH_4
 - Common reducing reagent in organic synthesis
 - Converts ketones and esters into alcohols
- 2-Thiouracil
 - Modified nucleobase¹
 - Gene editing and modification
 - Fluorescent marker
 - Anti-inflammatory drugs
 - Cytotoxic agents



Methods

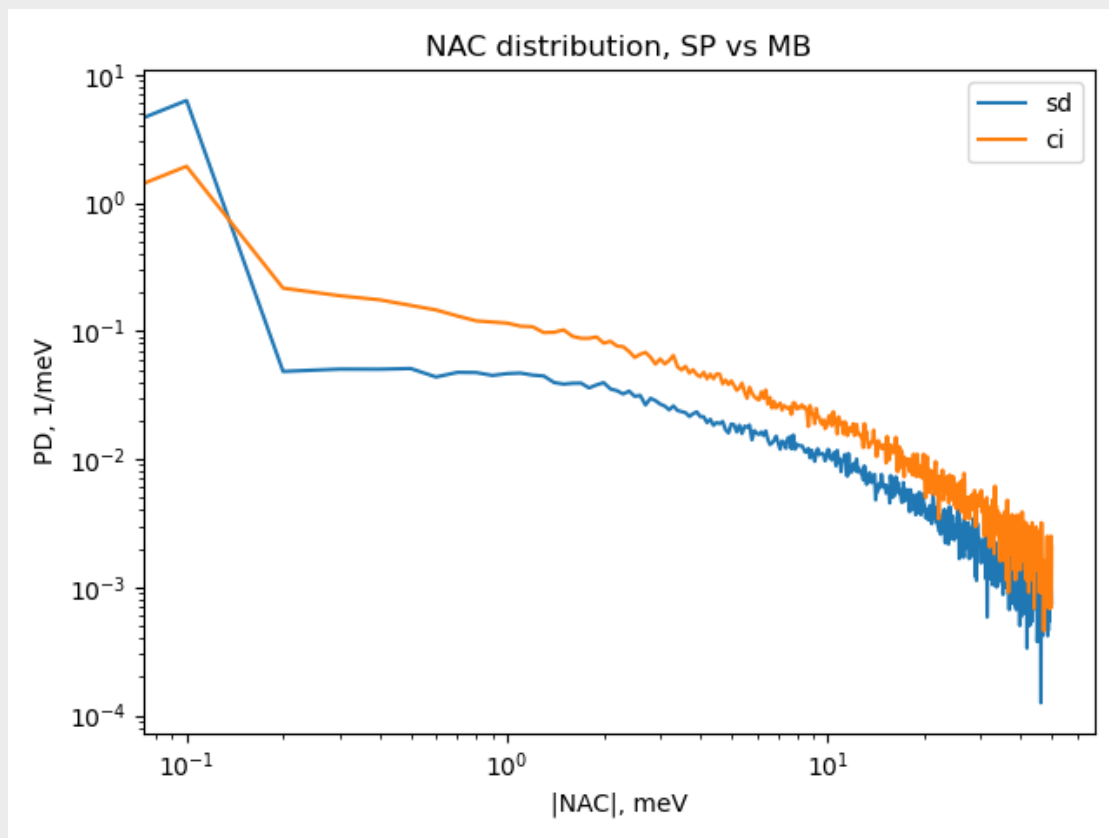
- Libra Package²
 - TD-DFT
 - DZVP-MOLOPT-SR-GTH basis
 - PBE Functional
 - NBRA workflow
 - HST and NPI
 - FSSH, IDA, mSDM
- SHARC Package³
 - TD-DFT (ORCA)⁴
 - def2-svp basis
 - b3lyp functional
 - LVC
 - 400 trajectories @ 700 fs
 - 3 Singlets 2 Triplets



LiAlH_4 NAC Distribution

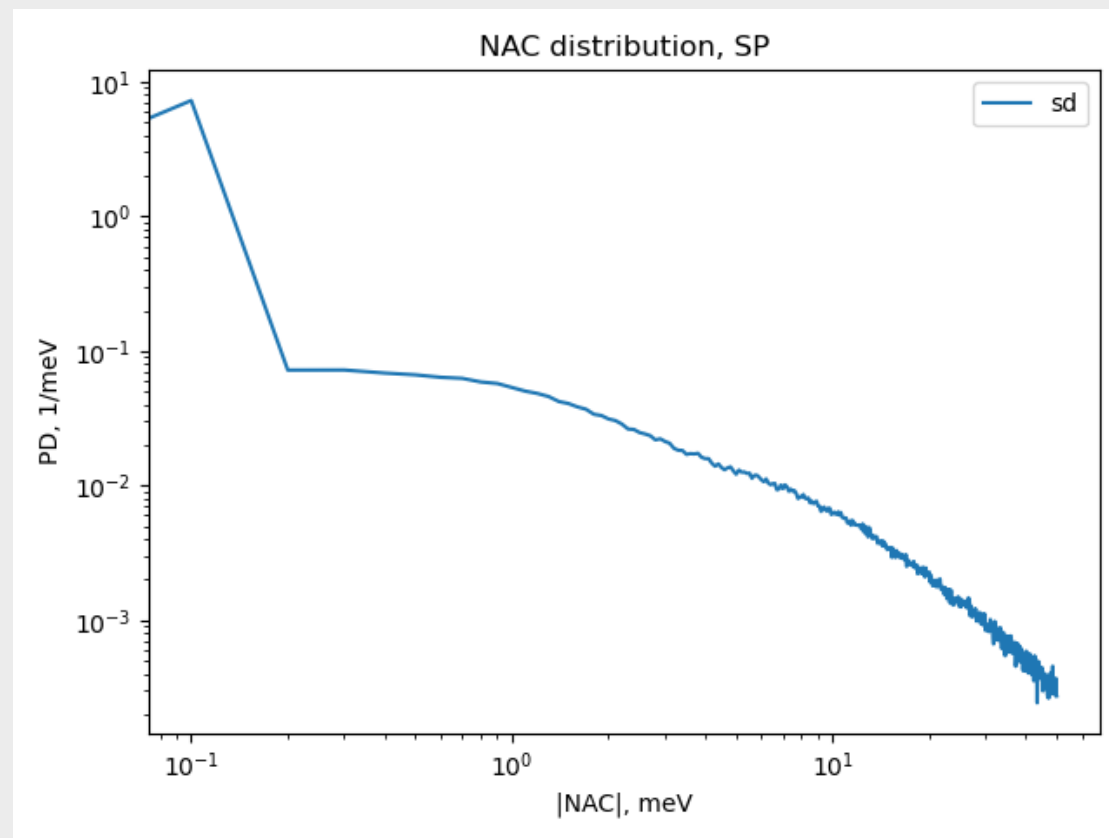
HST

a.



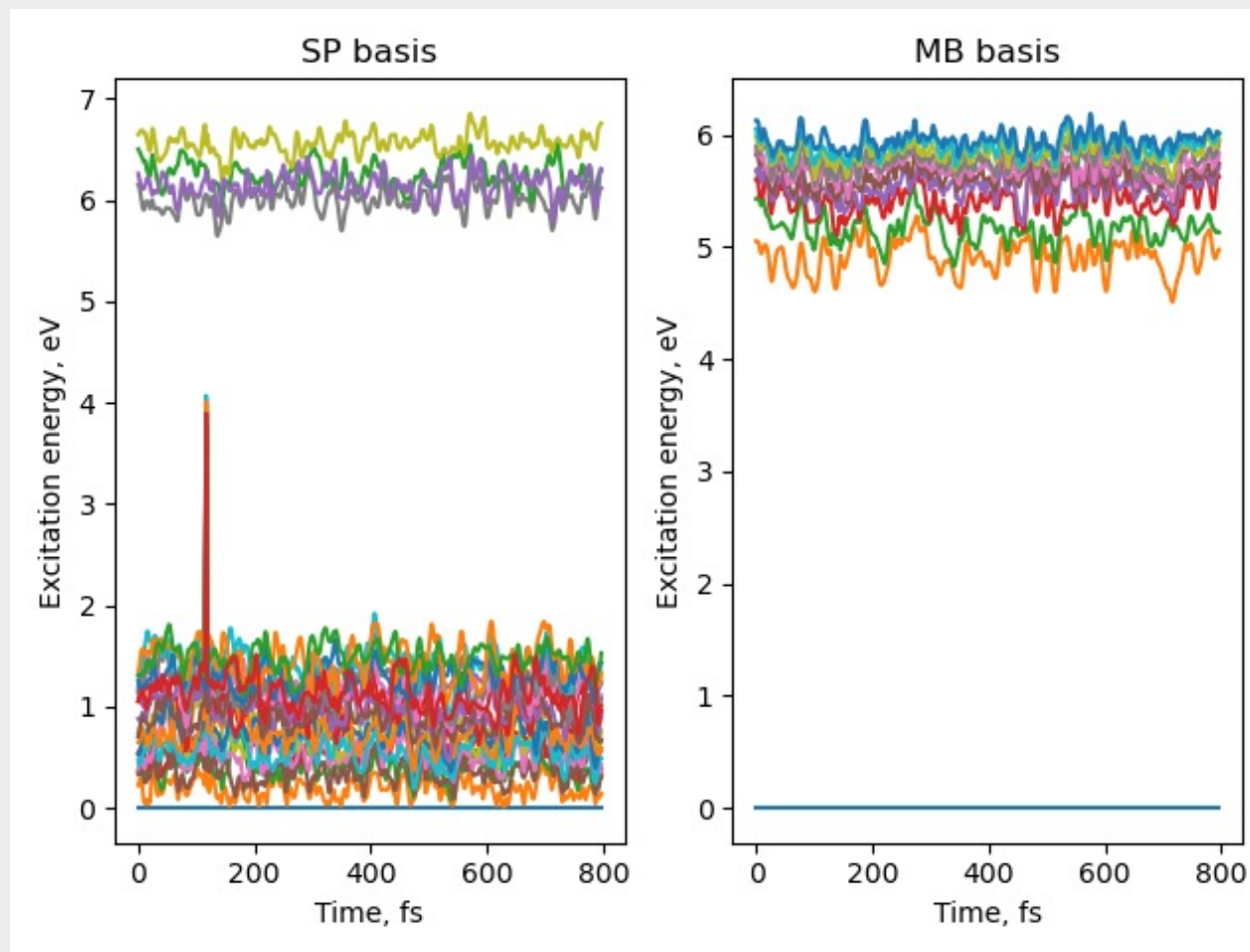
NPI

b.

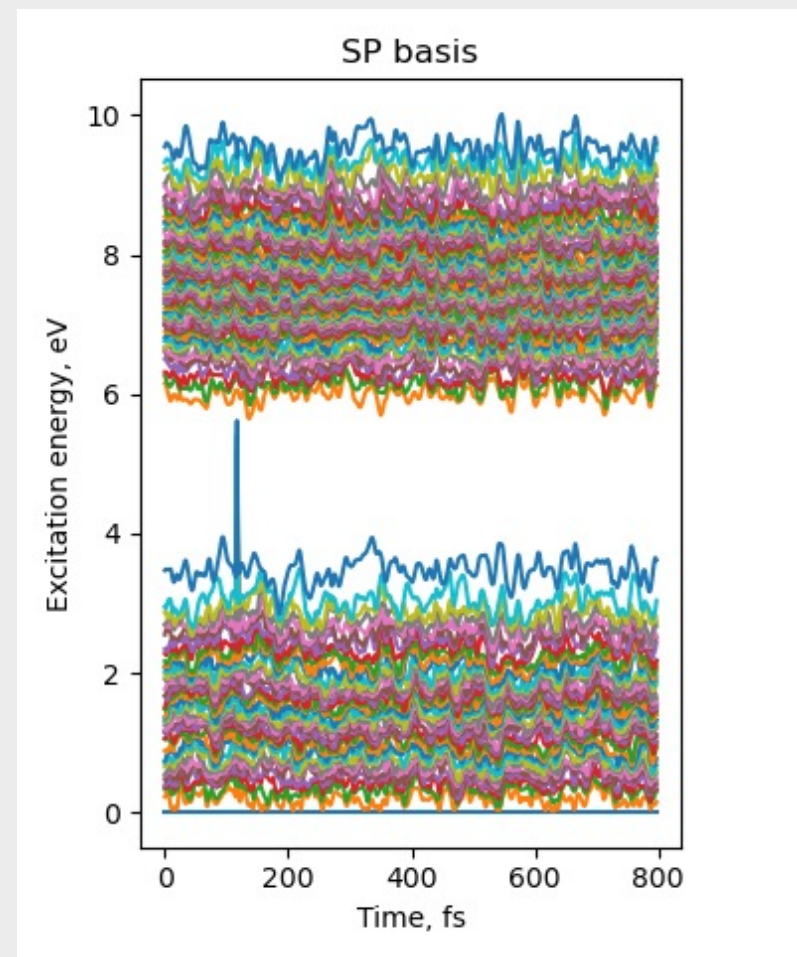


LiAlH₄ Excited State Energy vs Time

a. HST

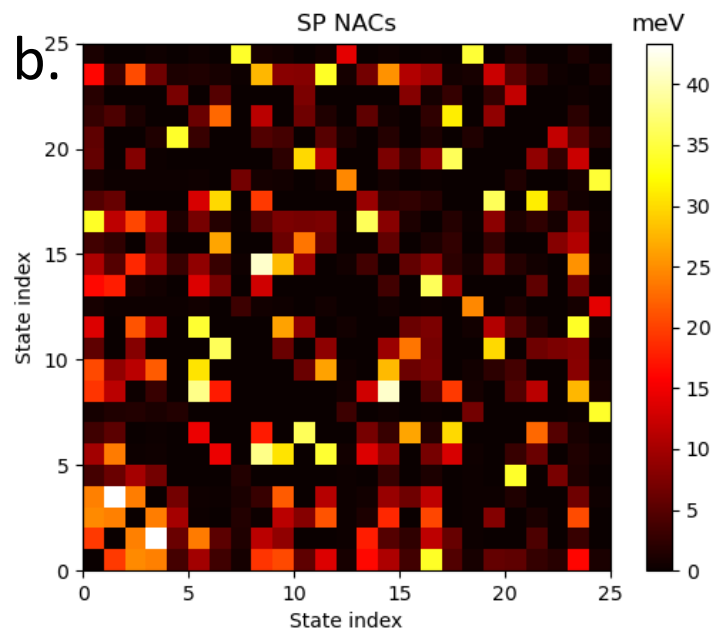
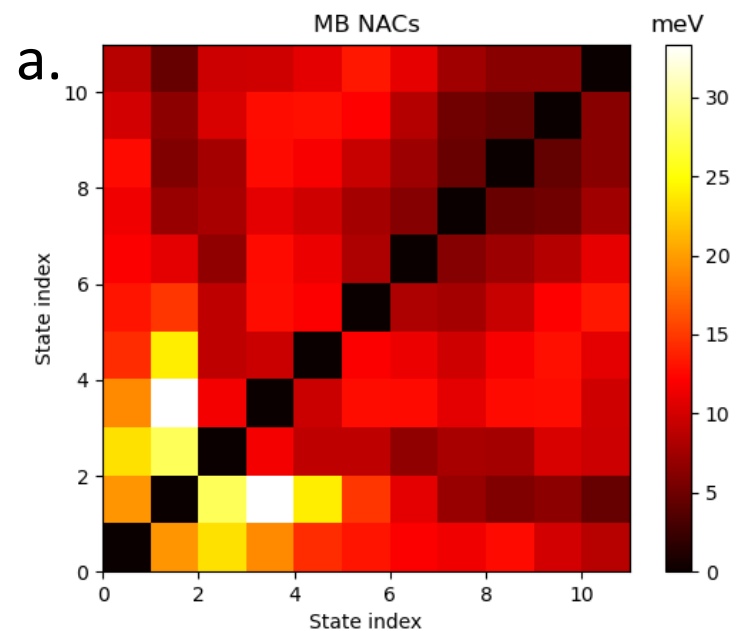


b. NPI

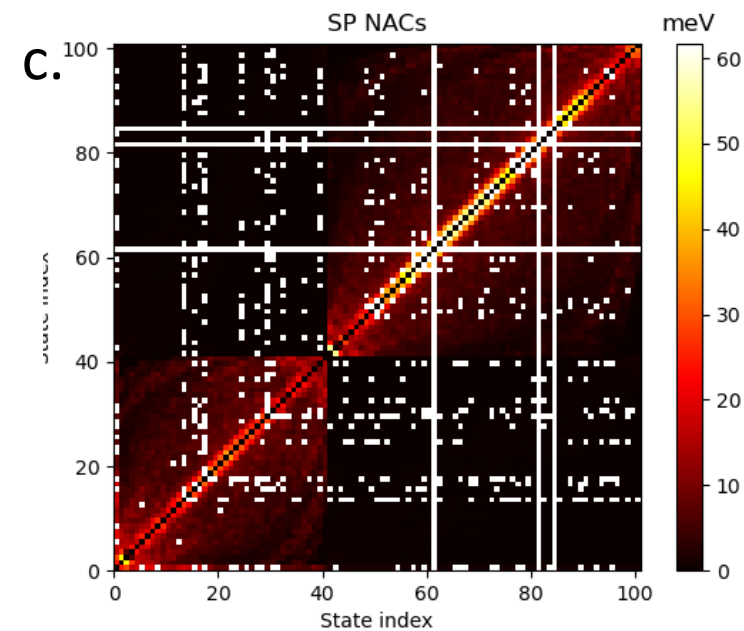


LiAlH₄ NACs

HST

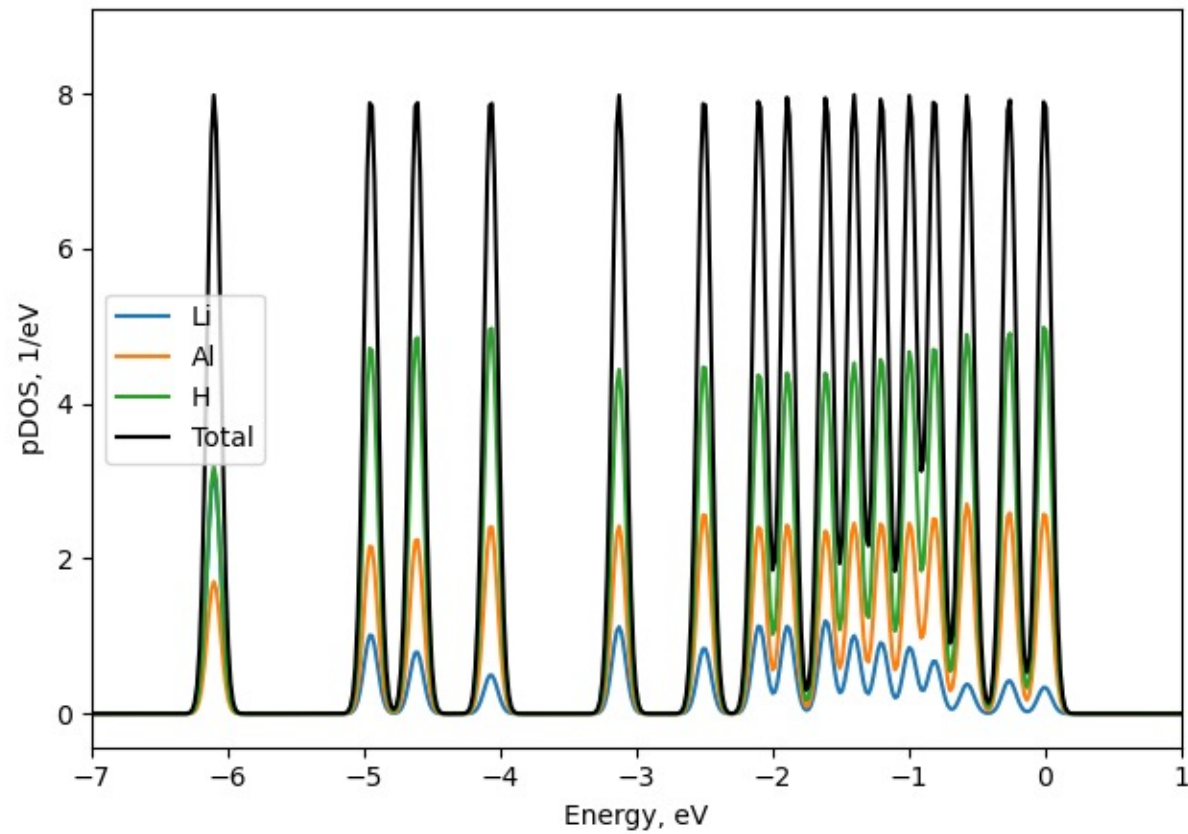


NPI

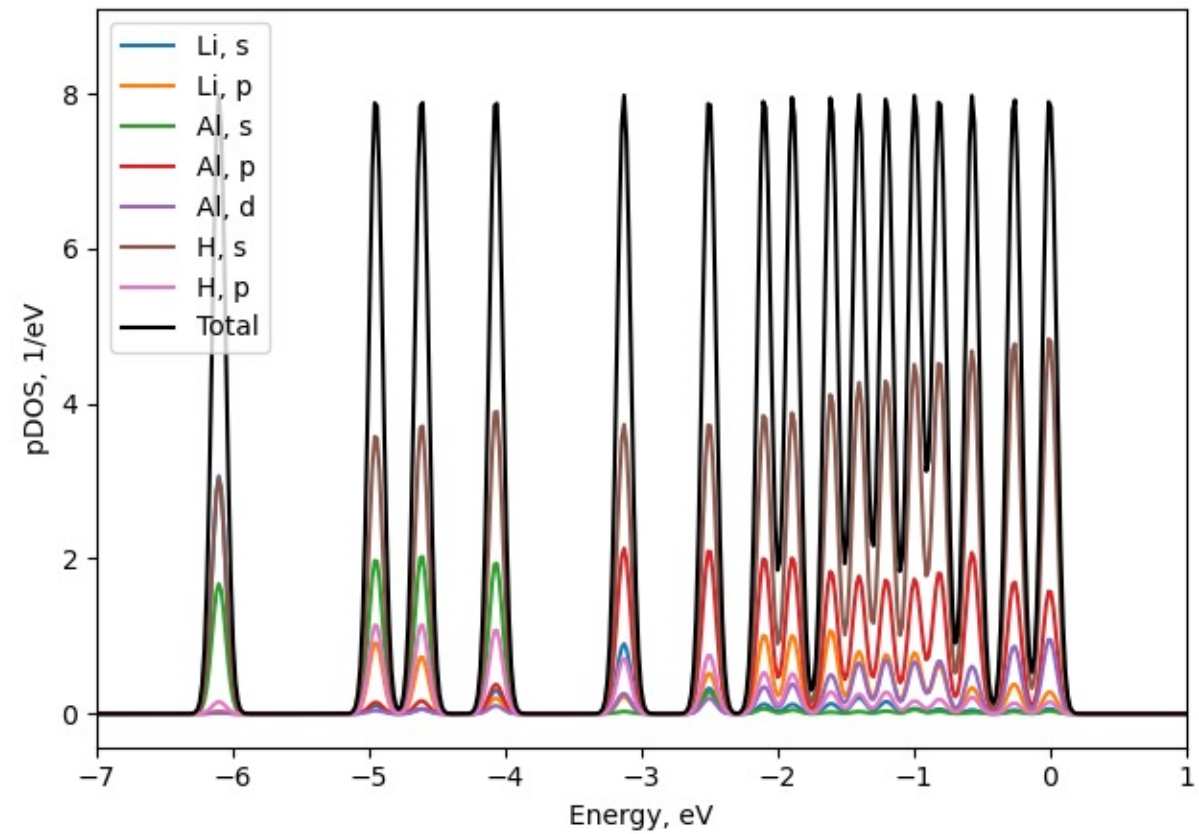


LiAlH₄ Spectrum

LiAlH₄, 300 K

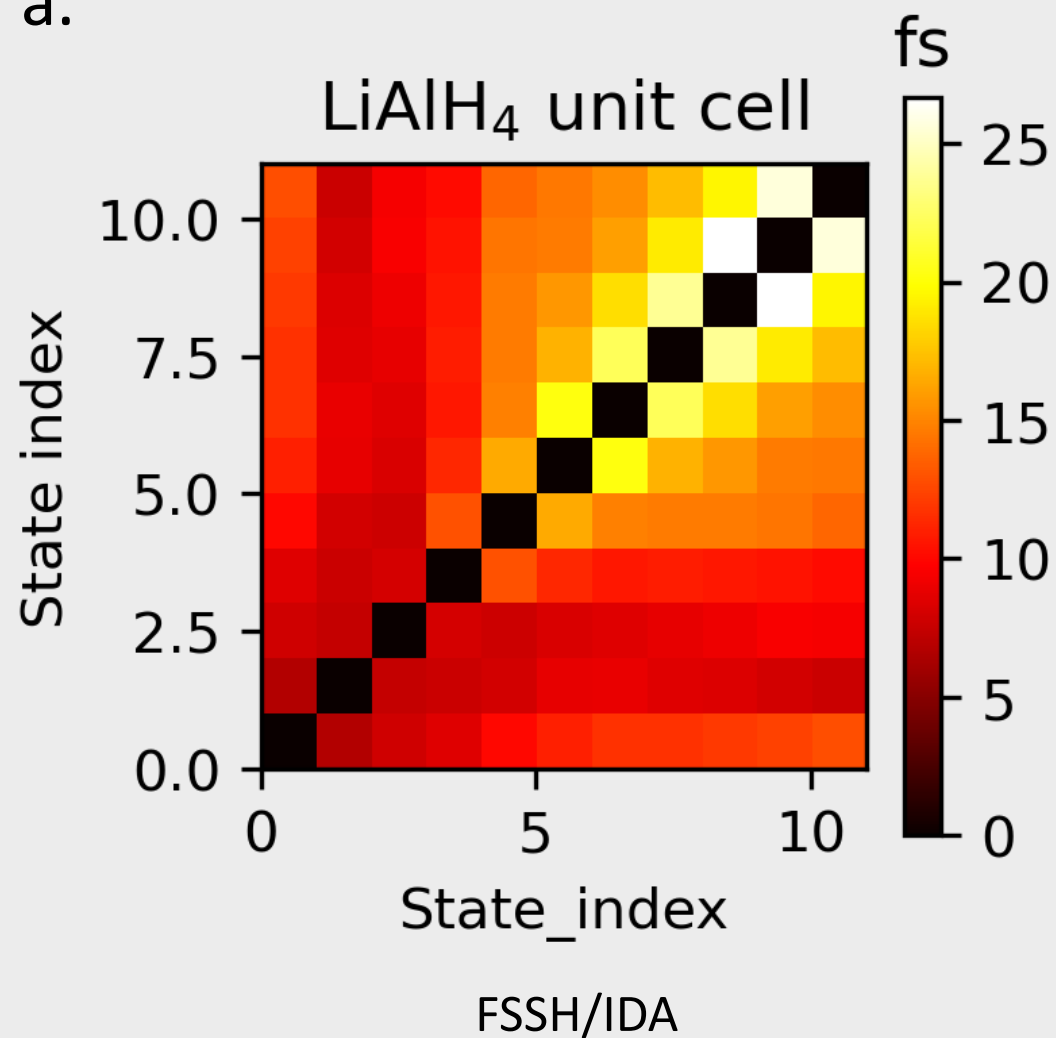


LiAlH₄, 300 K

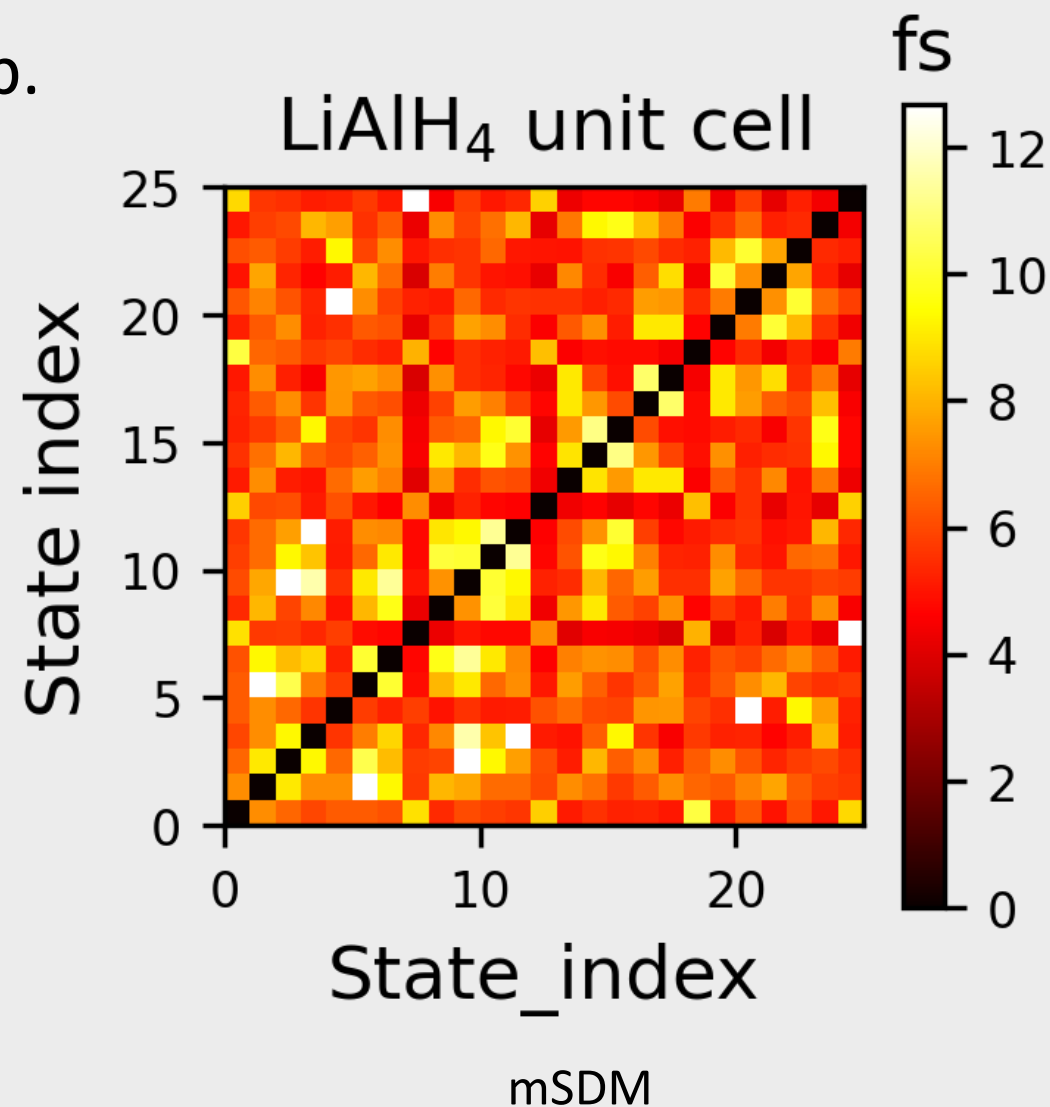


LiAlH₄ Decoherence

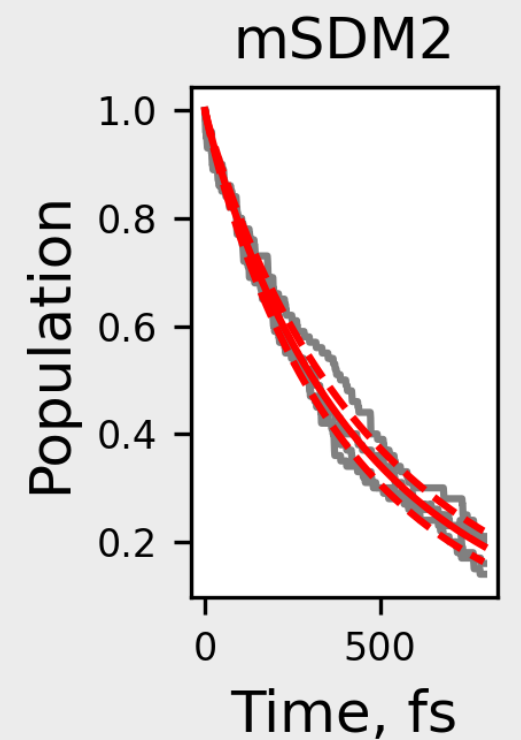
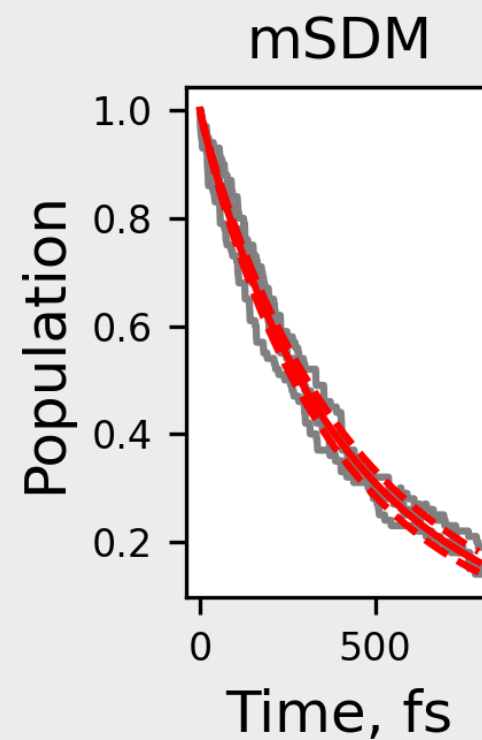
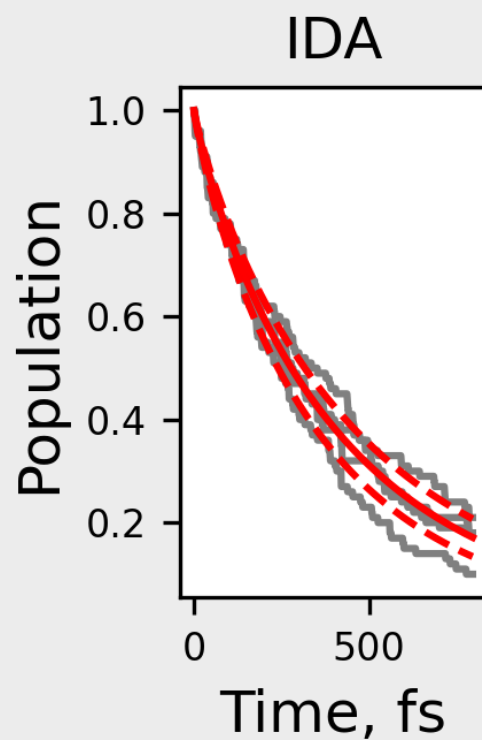
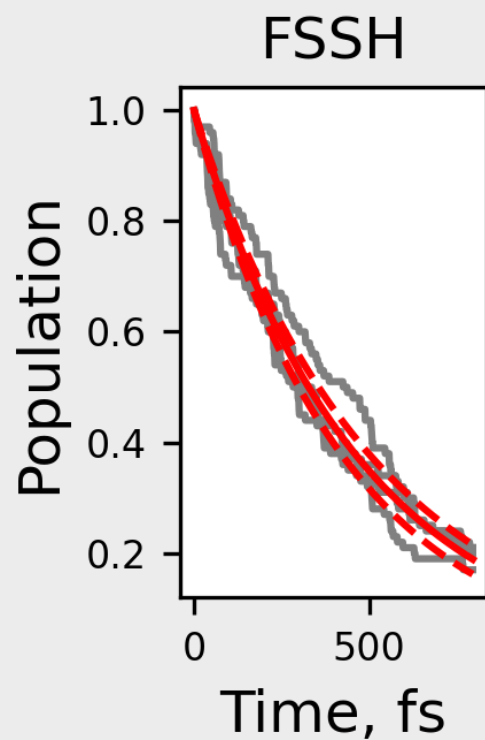
a.



b.

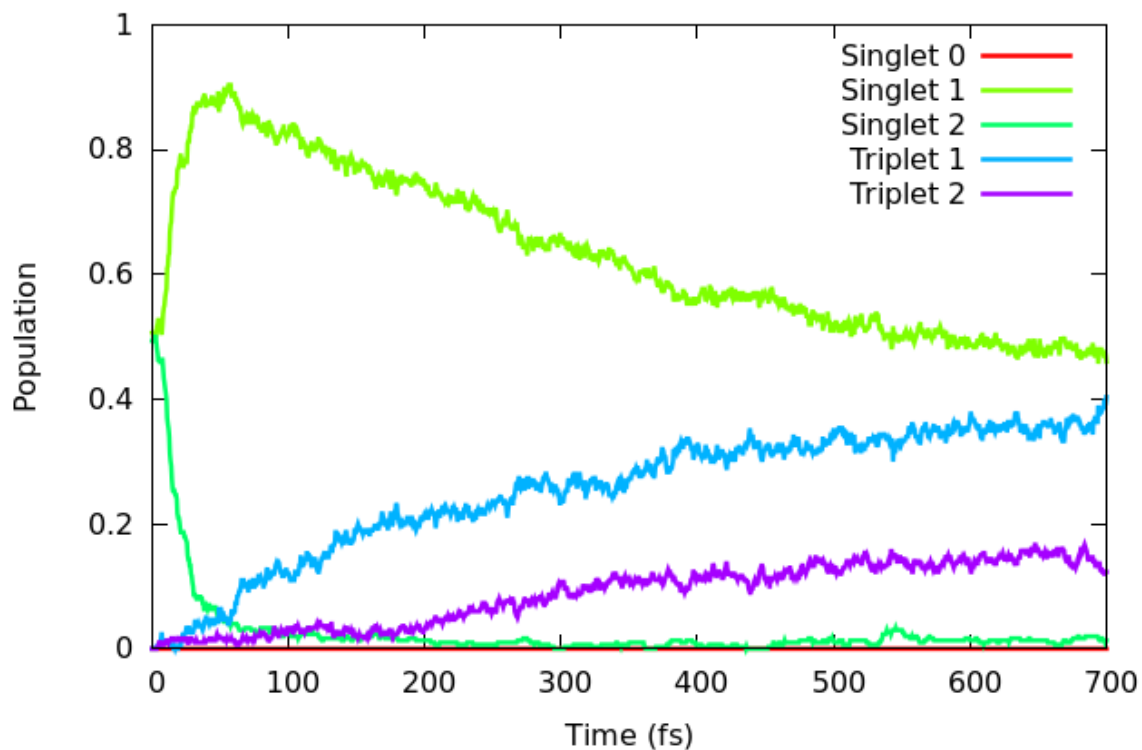


LiAlH₄ Dynamics Fits

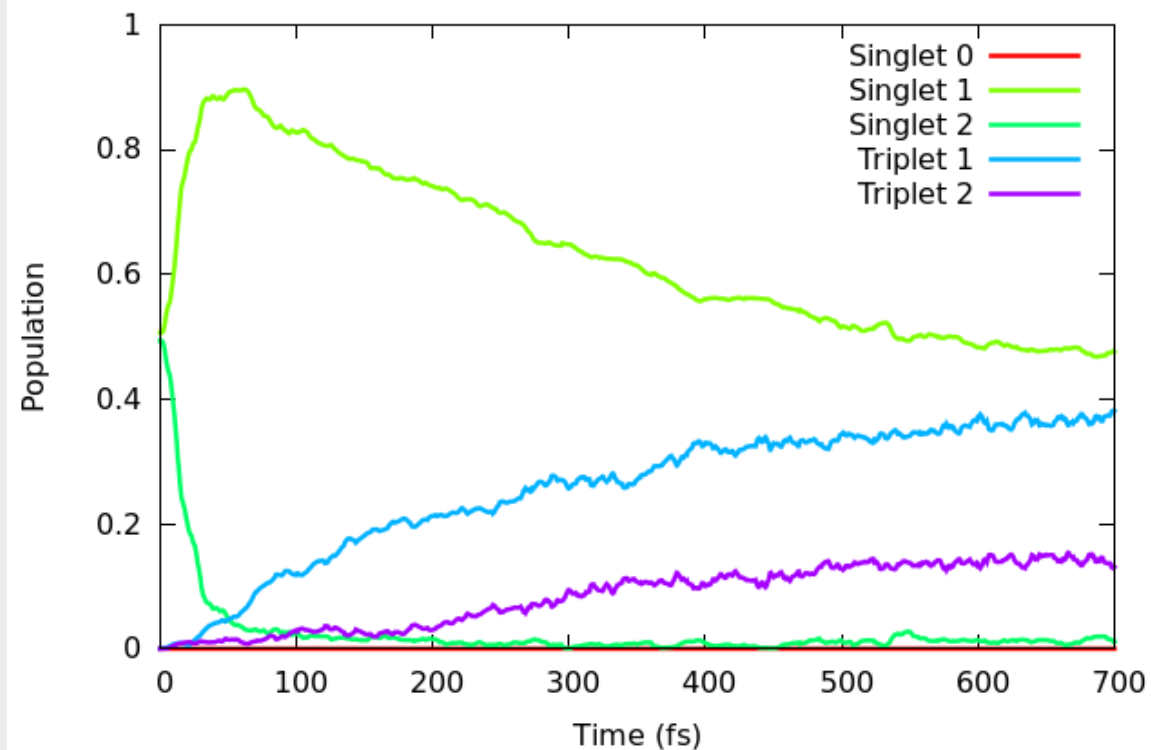


2-Thiouracil Populations

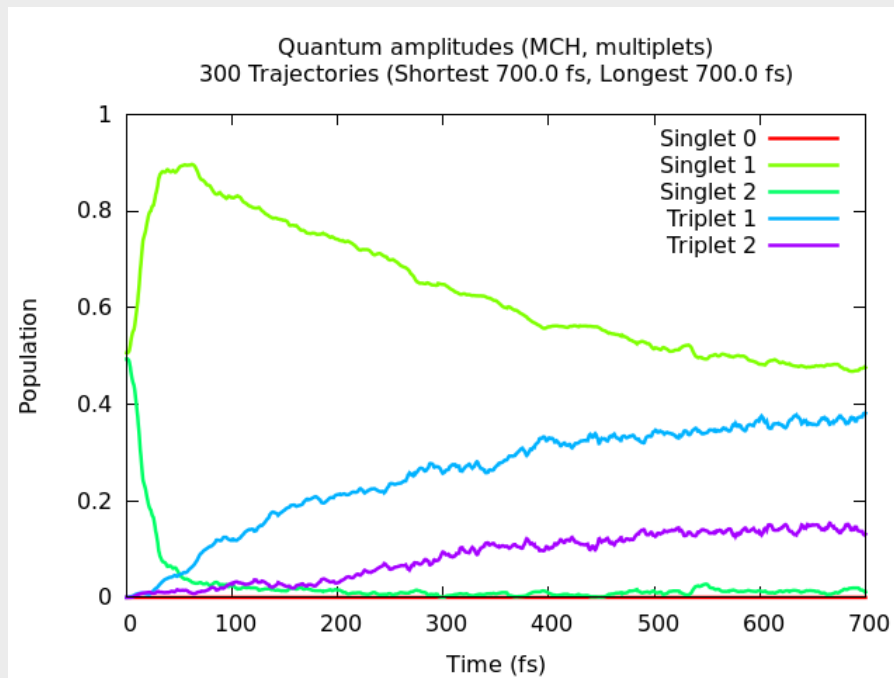
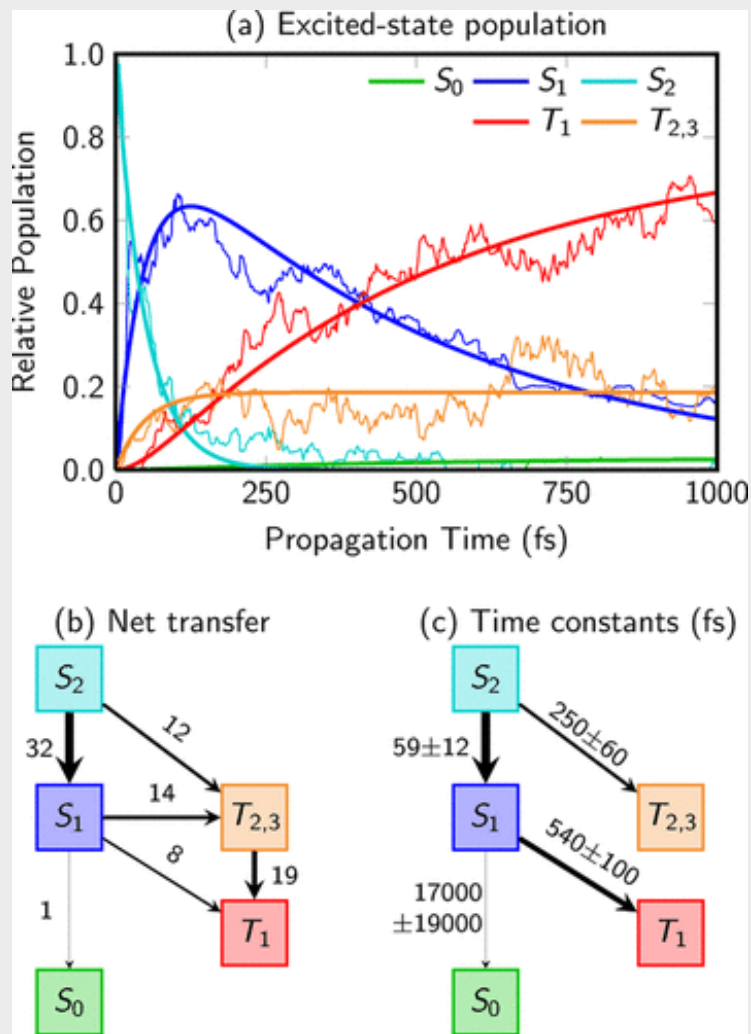
Classical populations (MCH, multiplets)
300 Trajectories (Shortest 700.0 fs, Longest 700.0 fs)



Quantum amplitudes (MCH, multiplets)
300 Trajectories (Shortest 700.0 fs, Longest 700.0 fs)



Comparison to Literature



	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

$$S2 \rightarrow S1 = 10.6 \pm 1.1 \text{ fs}$$

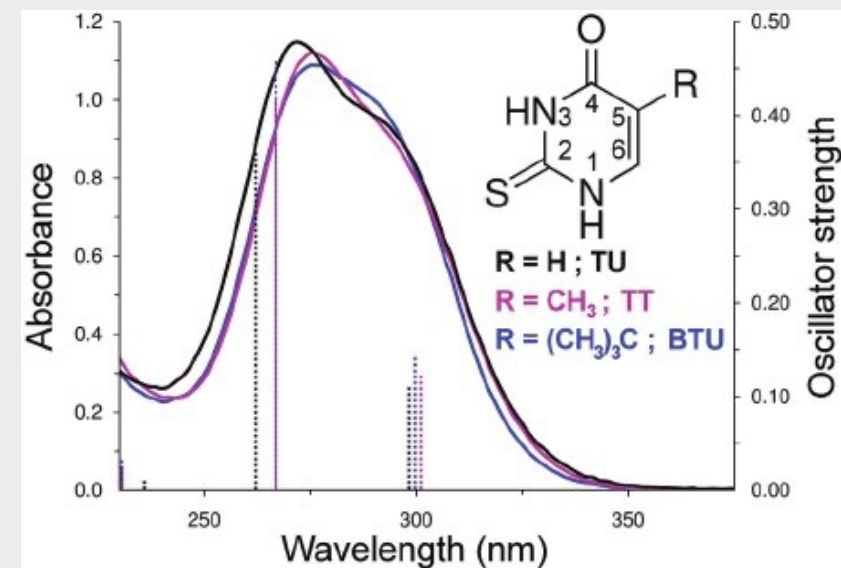
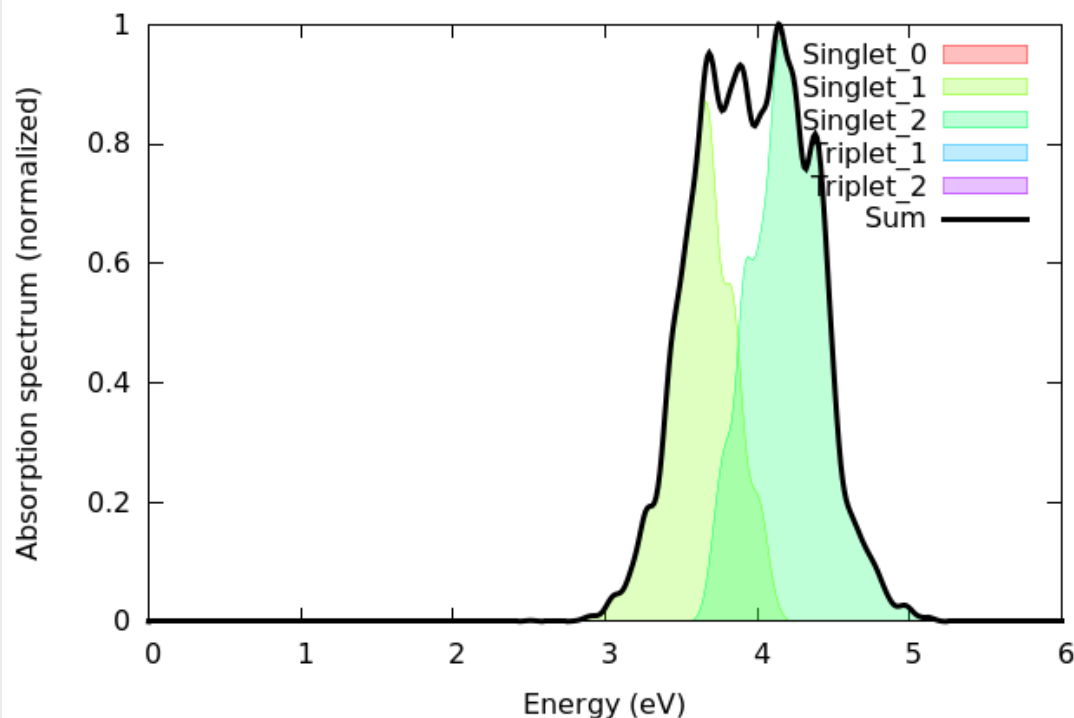
$$S1 \rightarrow T1 = 927.5 \pm 74.7 \text{ fs}$$

$$S1 \rightarrow T2 = 2716.7 \pm 259.3 \text{ fs}$$

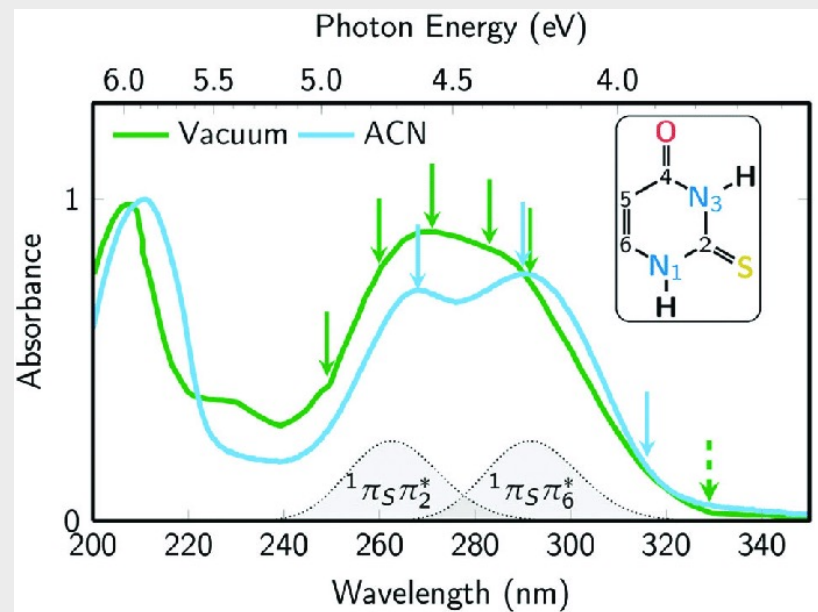
$$T1 \rightarrow T2 = 1220.2 \pm 536.8 \text{ fs}$$

2-Thiouracil Spectrum

Absorption spectrum (Gaussian, FWHM=0.100000 eV)
400 Initial conditions, MCH representation

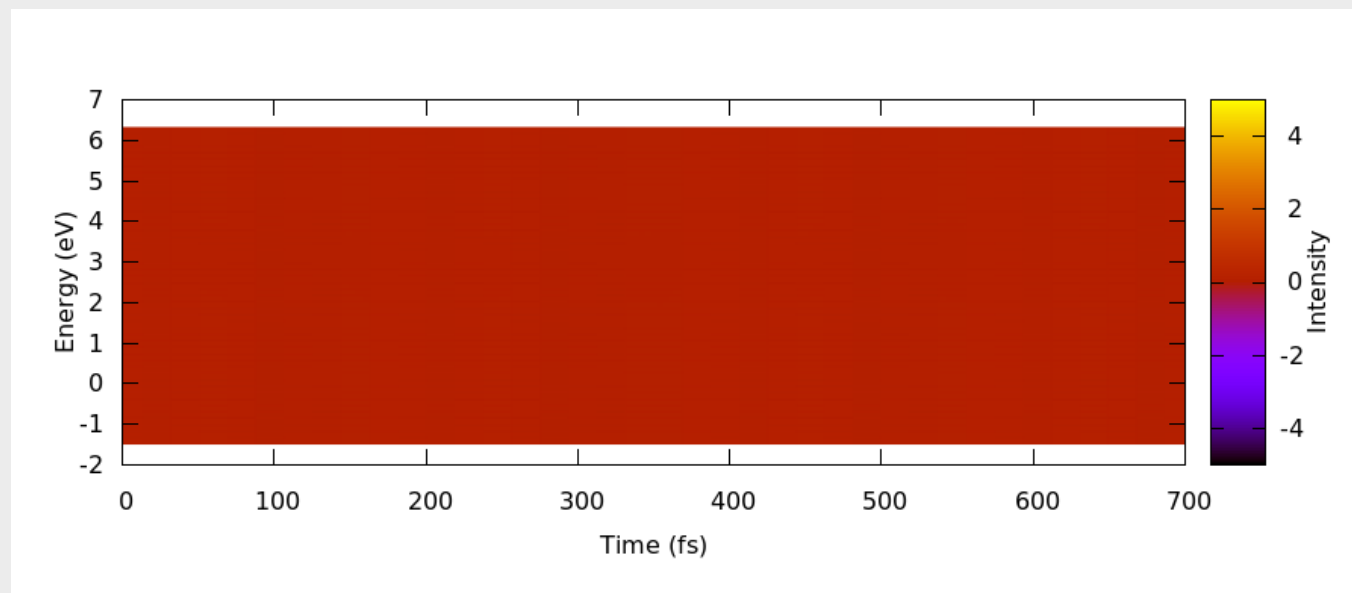
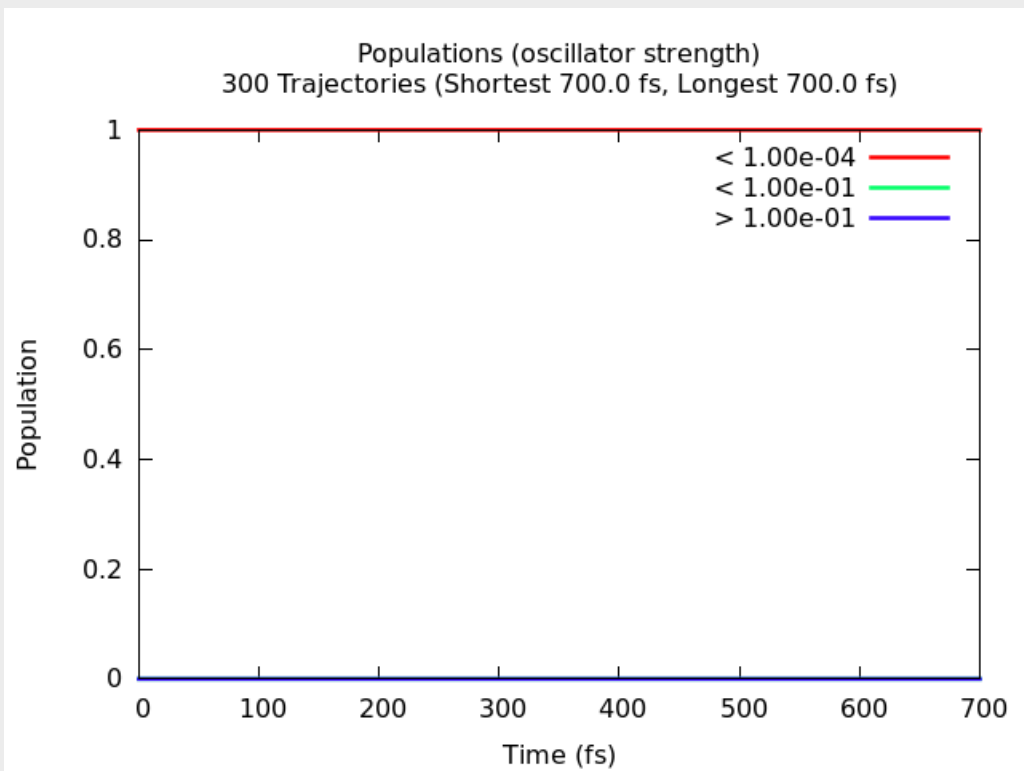


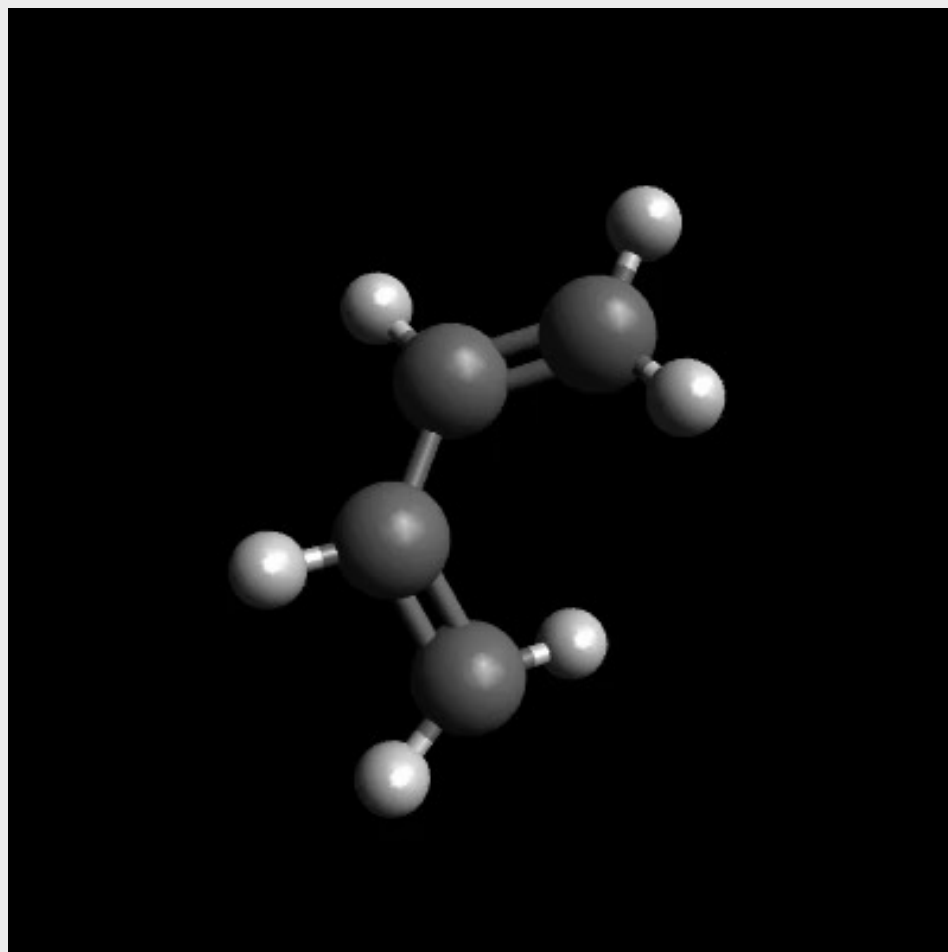
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J. A. Sánchez-Rodríguez et al. Phys. Chem. Chem. Phys., 2017

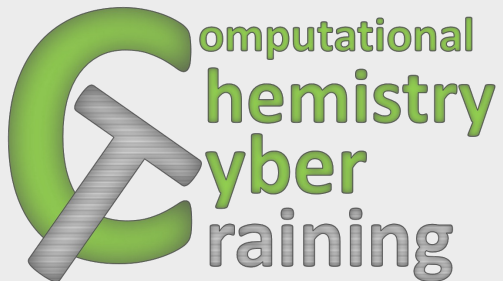
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References

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