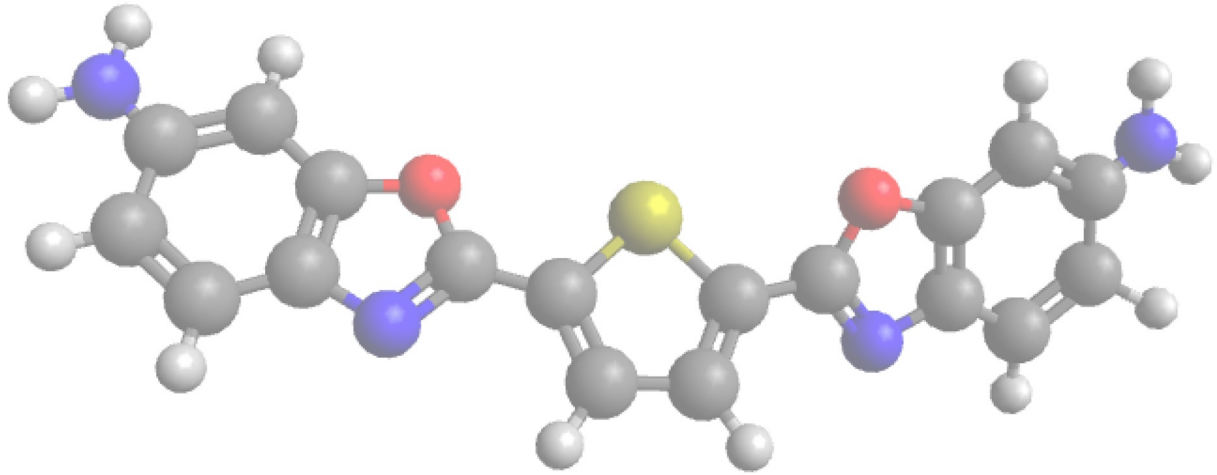
Investigation of nonadiabatic dynamics in BBTA



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Excited States and Nonadiabatic Dynamics
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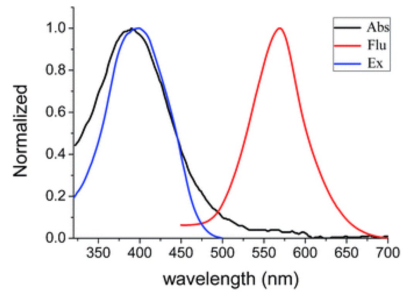
Background

First synthesis of BBTA:
(2,5-bis(6-amine-benzoxazol-2-yl)thiophene)

Gao, Z.; Hao, Y.; Zheng, M.; Chen, Y., A fluorescent dye with large Stokes shift and high stability: synthesis and application to live cell imaging. *RSC Advances* **2017,** *7* (13), 7604-7609.

- strong fluorescence at 568 nm: BBTA was clearly expressed in mitochondria with high contrast
- exhibits very large Stoke's shift (186 nm) in buffer solution : large Stoke's shift is important to minimize cross-talk between the excitation source and fluorescent emission.
- high photostability: it is important for bioimaging, especially for long-term cellular imaging, to investigate biological processes.
- low cytotoxicity

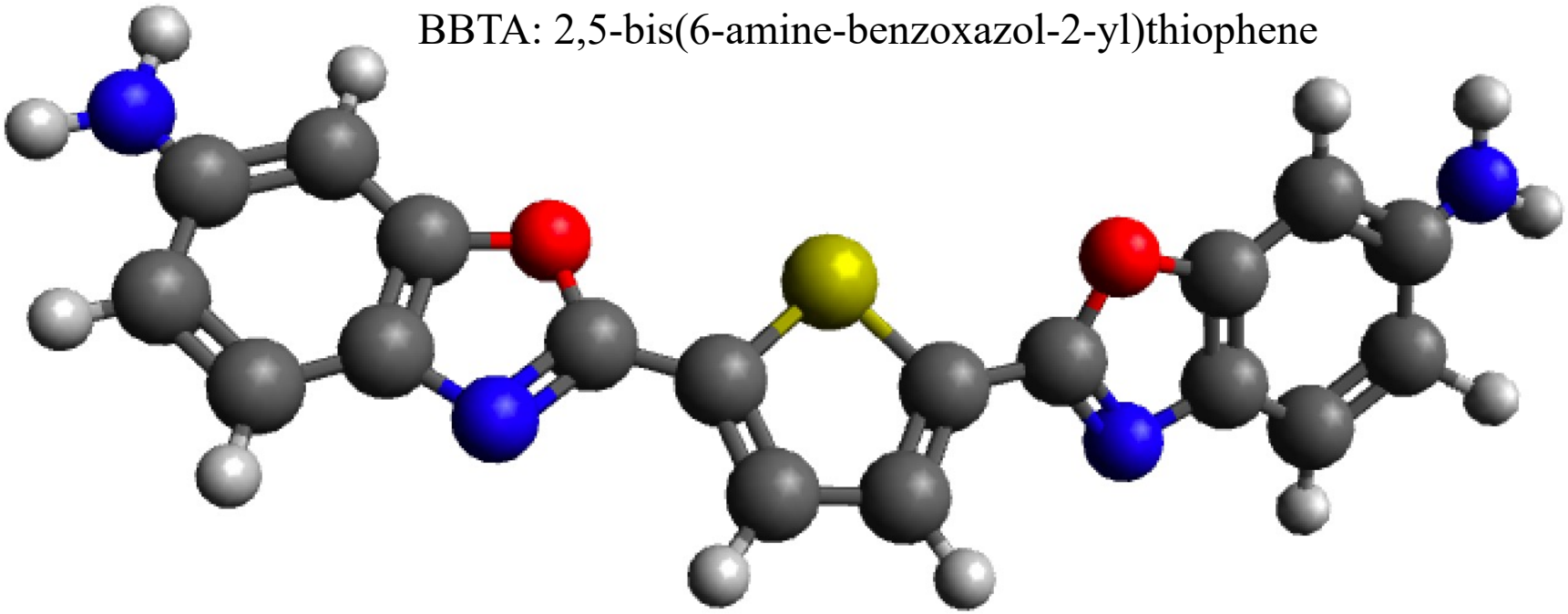


Absorption, excitation, and fluorescence spectra of BBTA

Goal of project: to understand the strong emission in BBTA

Computational details

BBTA: 2,5-bis(6-amine-benzoxazol-2-yl)thiophene



Geometry optimization (gas phase) and frequency calculation (no imaginary frequencies):
Gaussain: PBEPBE/6-31G(d) (Discovery cluster at Northeastern University)

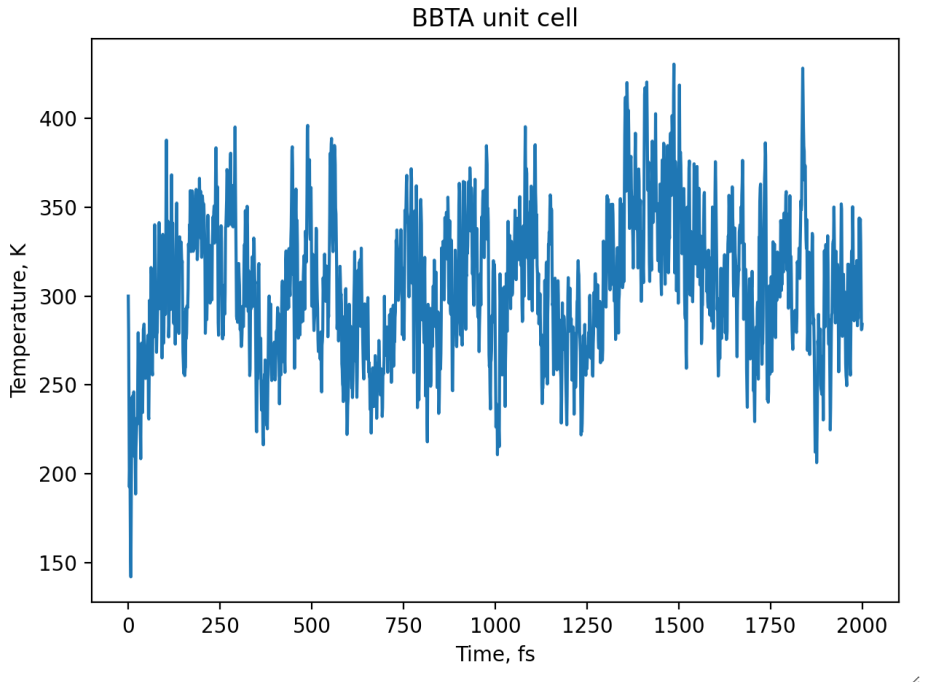
Nonadiabatic calculations are performed using:
Libra/CP2K (Center for Computational Research (CCR) at University at Buffalo)

Test with Libra/CP2K

Step 1: Molecular dynamics

params['A_cell_vector'] = [21.0416393280, 0.0000000000, 0.0000000000]
params['B_cell_vector'] = [0.0000000000, 21.0416393280, 0.0000000000]
params['C_cell_vector'] = [0.0000000000, 0.0000000000, 21.0416393280]

BASIS_SET: DZVP-MOLOPT-GTH
POTENTIAL: GTH-PBE



- Trajectory should be thermalized, but is not!
- Need to do MD for longer time, decrease the time step (now it is 1 fs)

Test with Libra/CP2K

Step 2:

initial step of the trajectory ‘istep’ = 1200
final step of the trajectory ‘fstep’ = 1225
Number of jobs ‘njobs’ = 5
Lowest_orbital=90-10
Highest orbital=90+11

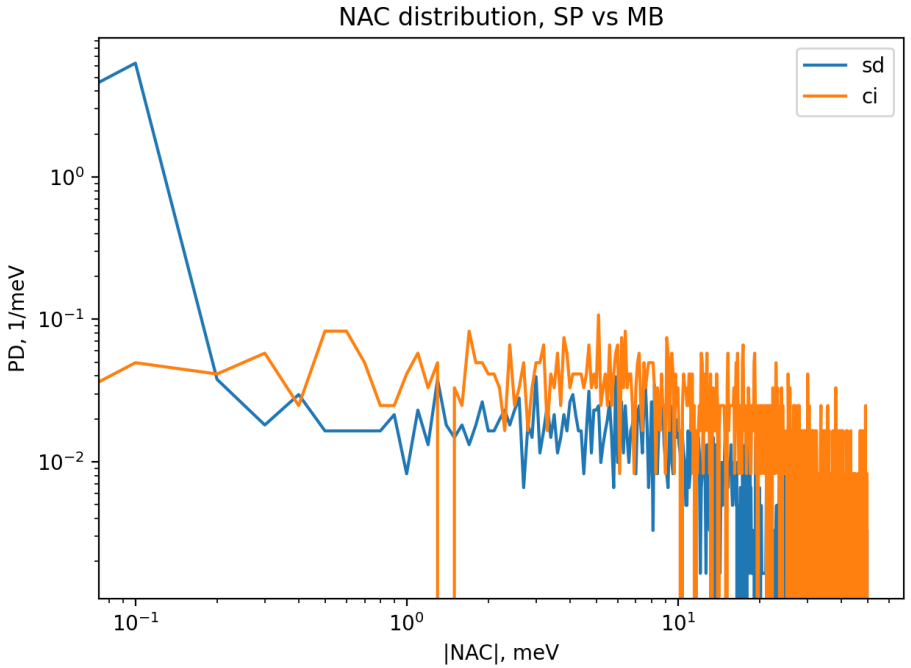
After this step finishes, in res file:
S_ks_1210.npz: overlap for same geometry
St_ks_1210.npz: overlap for two consecutive geometry

Test with Libra/CP2K

Step 3:

- Nonadiabatic coupling are computed after phase correction and state reordering
- Nonadiabatic coupling obtained with nac_algo of 0 (Hammes-Schiffer)
- 100 excited states due to excitation from 10 occupied to 10 unoccupied orbitals

'num_occ_states': 10, 'num_unocc_states': 10: nonadiabatic coupling is computed between 10 occupied and 10 unoccupied states

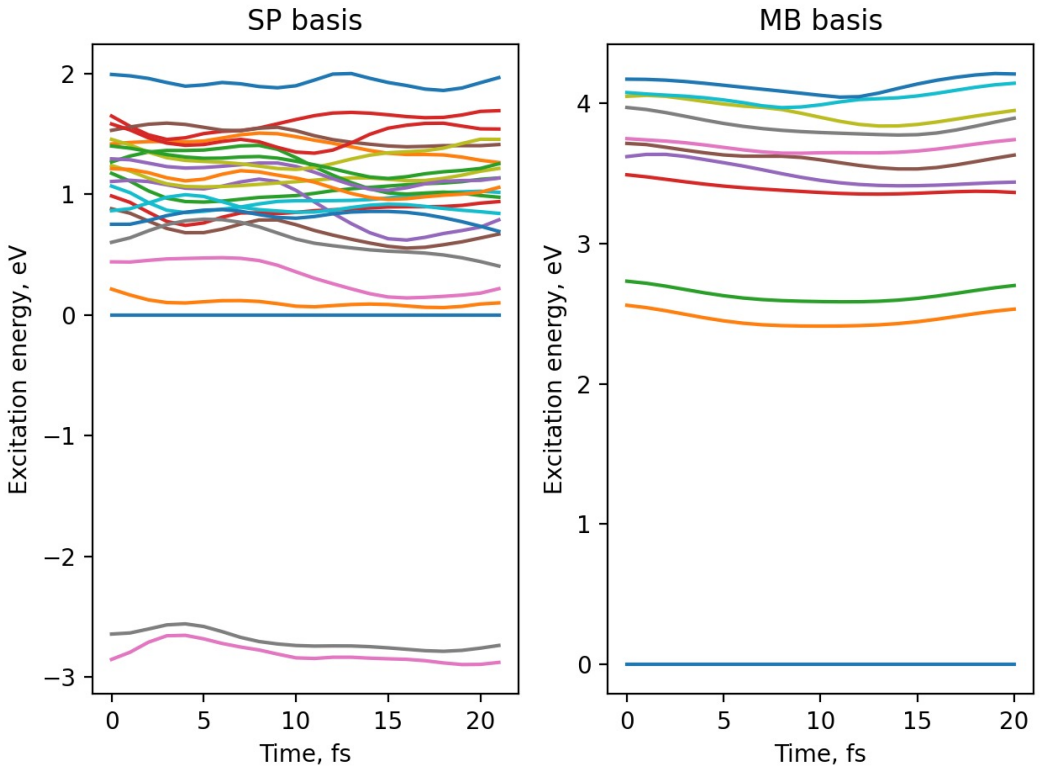


From figure:
For ci there is less probability of finding small NAC compared to sd

Probability distribution of nonadiabatic coupling: Slater determinant and ci basis

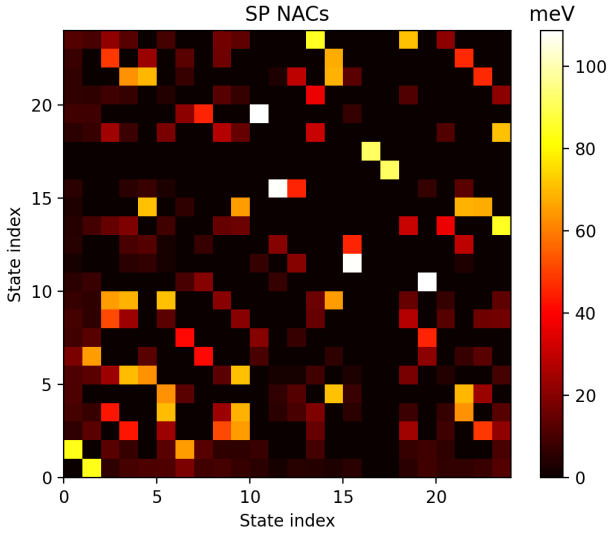
Test with Libra/CP2K

Step 3 contd..:

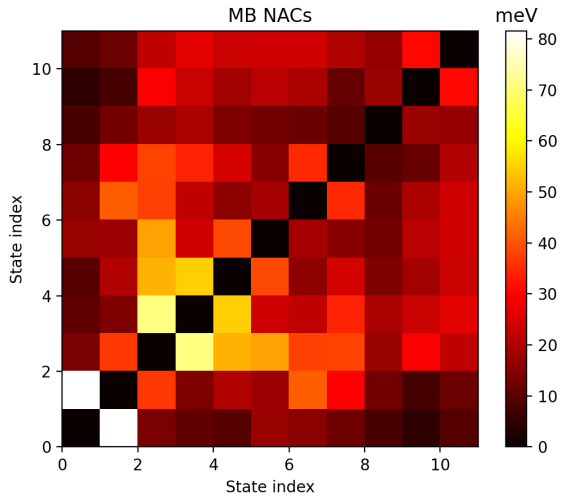


Excited states energy vs time

average NAC matrix for single particle excitations



average NAC matrix for ci excitations



Test with Libra/CP2K

Step 4: Fewest Switches Surface Hopping

init_states = [10]
batches = list(range(4)) # for each initial state, calculation is run four times. It is important because it is stochastic algorithm.

rates = None   #dephasing time
gaps = None   # energy gap
Not needed for FSSH and IDA

rep_ham=1 # adiabatic representation of Hamiltonian
"momenta_rescaling_algo":0   #momentum not rescaled #NBRA

"ntraj":25. # number of surface hopping trajectories

Test with Libra/CP2K

Step 4 cont’d..:

- namd_regular/_start_s10_FSSH_batch1/ SH_pop.txt shows the population is initialized at 10th state
- Even in 20 steps, the population gets transferred to other lower states

0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	1.00000e+00
0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	1.00000e+00
0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	8.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	0.00000e+00	4.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.80000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	4.00000e-02	8.00000e-02	0.00000e+00	0.00000e+00	0.00000e+00	8.00000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	4.00000e-02	8.00000e-02	4.00000e-02	0.00000e+00	0.00000e+00	7.60000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	8.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	8.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	8.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	8.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01
0.00000e+00	0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	8.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01
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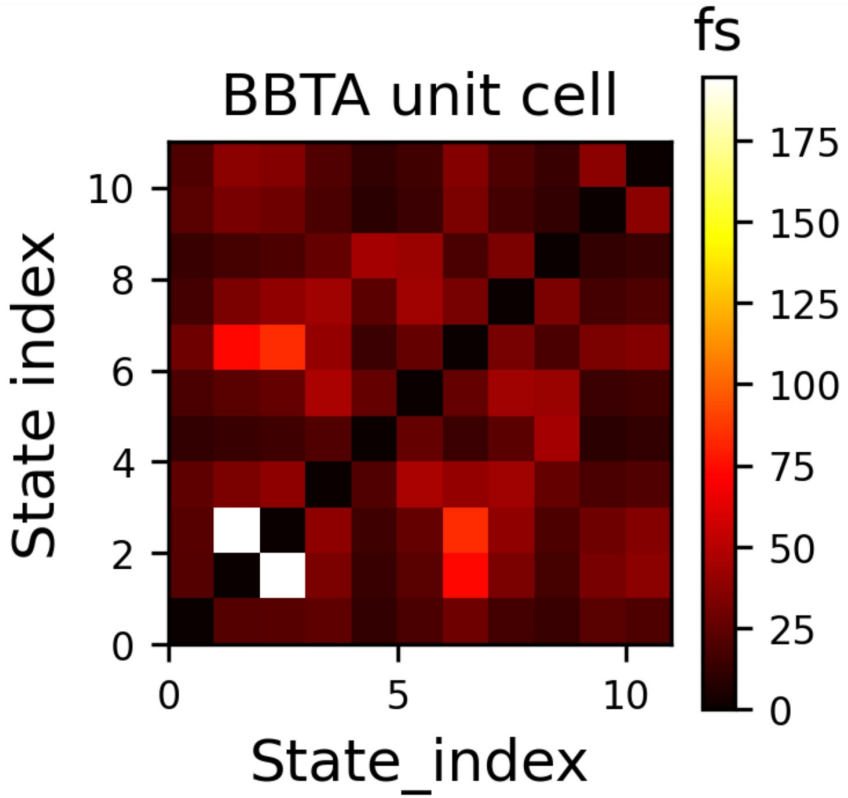
0.00000e+00	0.00000e+00	4.00000e-02	4.00000e-02	4.00000e-02	4.00000e-02	1.20000e-01	0.00000e+00	0.00000e+00	0.00000e+00	7.20000e-01

Test with Libra/CP2K

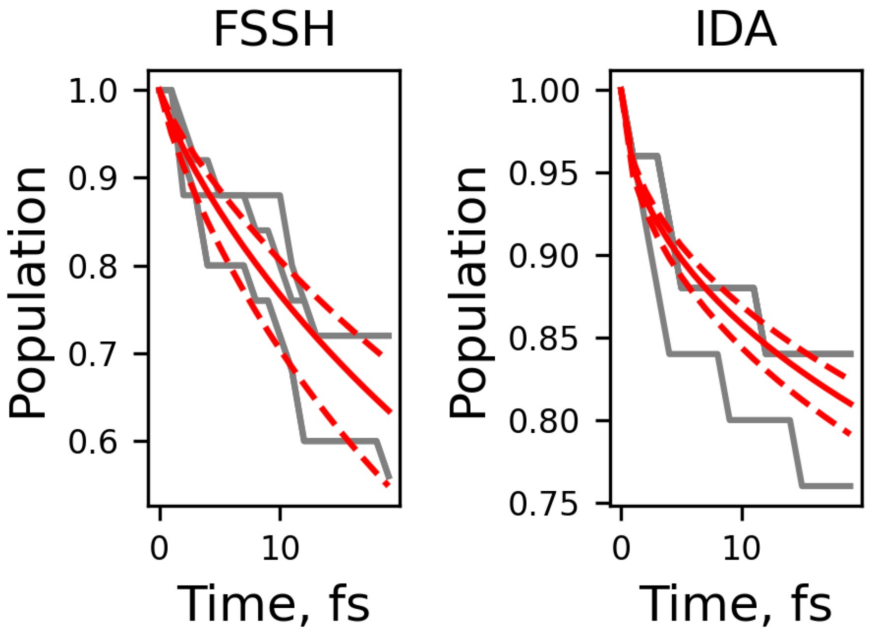
average decoherence times between pairs of states



Population fitting to $P(t; E_0) = \exp(-(\frac{t}{\tau})^{\beta})$

Average time scale is computed for the fits that has an R^2 value more than 0.01

decay dynamics of the 10th state



Test with SHARC

Opt+Freq:
6-31G**, Cholesky decomposition, 10 electrons on 8 orbitals, 3 singlet states
Calculation did not finish for ~8 days

Also, Wigner distribution sampling is good for the reasonably rigid systems

Next steps

To get reasonable result:

- Equilibrate the system
- Use larger active space i.e. use more orbitals for the dynamics calculation using params[‘lowest orbital’] and params[‘highest orbital’]
- Do nonadiabatic coupling calculation for longer duration using istep and fstep
- More surface hopping trajectories

Inteesting future tests:

- How dynamics differ with nac_algo of 0 (Hammes-Schiffer) and 1 (Norm-preserving interpolation) method
- How dynamics differ with taking initial conditions from Wigner distribution anf from MD

Acknowledgements

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