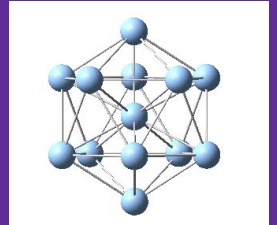


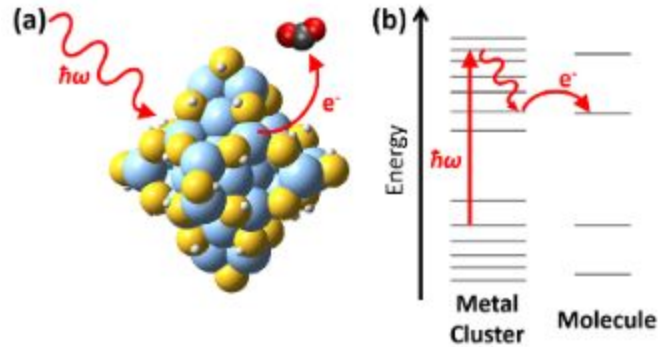
Non-Adiabatic Molecular Dynamics of Ag Nanoclusters using Semiempirical Methods

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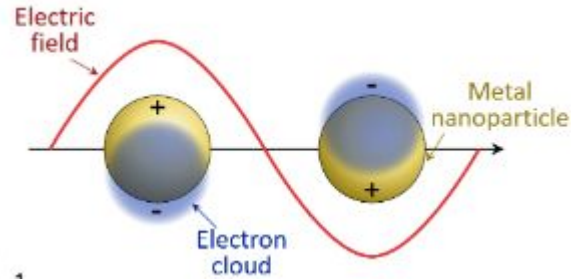
Background

- Conversion of solar energy into usable forms is important
- Noble metal nanoclusters have promise in solar photocatalysis, largely due to their ability to support plasmon-like excited states



Plasmons

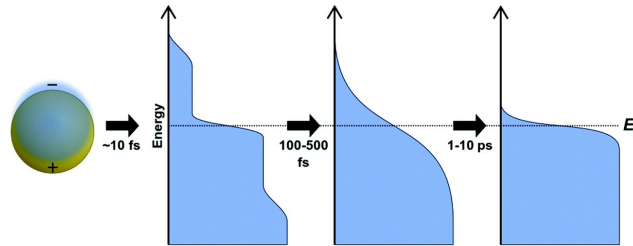
- Coherent, collective oscillation of the conduction band electrons



- In other words: a collective excitation involving many different electronic transitions with nearly the same energy
- Plasmons strongly absorb light at a specific wavelength
 - Wavelength is tunable by changing size/shape of the nanocluster

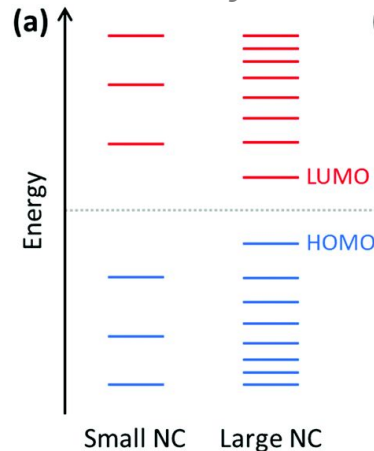
Plasmon Decay

- Plasmon decay occurs very quickly (within tens of fs)
 - Difficult to harness the resulting hot electrons due to fast decay
- Decay timescales are a property of interest
- Finding nanoclusters with longer decay times could help increase the efficiency of plasmonic photocatalysts



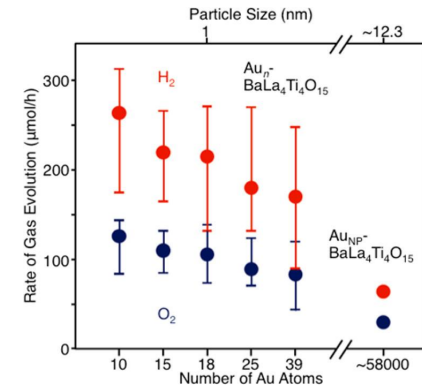
Size dependence of Plasmonic Nanoclusters

- Plasmons are well-defined in large nanoclusters with ~100 atoms
- As size decreases, orbitals change from a continuum to discrete MOs
- Definition of plasmon starts to break down, excited states become excitonic in character
- Larger energy gaps between states delays decay and recombination



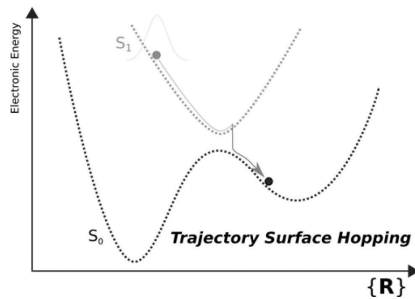
Size dependence of Plasmonic Nanoclusters

- Small nanoclusters been shown to have higher photocatalytic activity than larger nanoparticles
- Transition from plasmonic character to excitonic character as nanocluster size decreases has important impacts on dynamics
- Investigation using quantum mechanical methods has the potential to elucidate the structure-property relationship between nanoclusters and plasmonic states



Non adiabatic molecular dynamics

- Non-adiabatic molecular dynamics (NAMD) is a quantum chemical modeling method that can simulate excited state dynamics
 - Trajectory surface hopping (TSH) - propagates a swarm of independent trajectories along an excited state PES, with some probability of hopping to lower excited states that increases in regions of strong non-adiabaticity
- NAMD is very computationally expensive, especially for larger systems



Semiempirical Methods

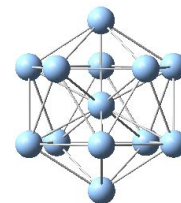
- Hartree-Fock based methods that reduce the number of integrals in the wavefunction
- Only valence electrons are considered explicitly
 - Minimal basis set used
- Zero differential overlap (ZDO) approximation: $\mu_A \nu_B = 0$
 - Overlap matrix \mathbf{S} is reduced to a unit matrix
 - One-electron integrals with three centers are set to zero
 - Neglect three and four center two-electron integrals
- Specific semiempirical methods make additional approximations
 - Differences are mostly in the treatment of two-center integrals
- Parameters based on experimental data are introduced to “replace” neglected integrals
- Computational cost scales with the number of basis functions

Intermediate Neglect of Differential Overlap (INDO)

- Neglects two-center, two-electron integrals not of the Coulomb type
- INDO/S method has been parameterized for Ag nanocluster excited states
 - 2-3 orders of magnitude faster than DFT for spectroscopic calculations
- Because INDO/S is HF based and gives a wavefunction, we can use it to calculate the overlap matrices and NACs
- Calculating the NACs using INDO/S can greatly reduce the time it takes to run NAMD calculations

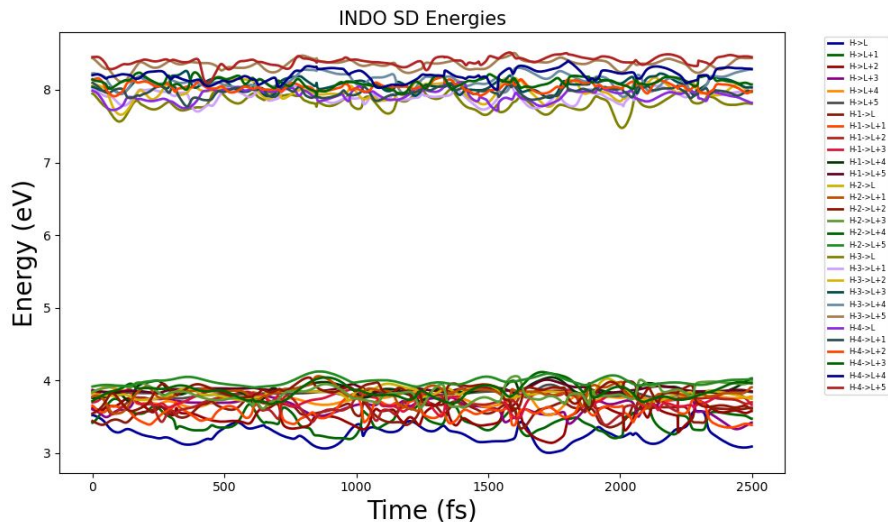
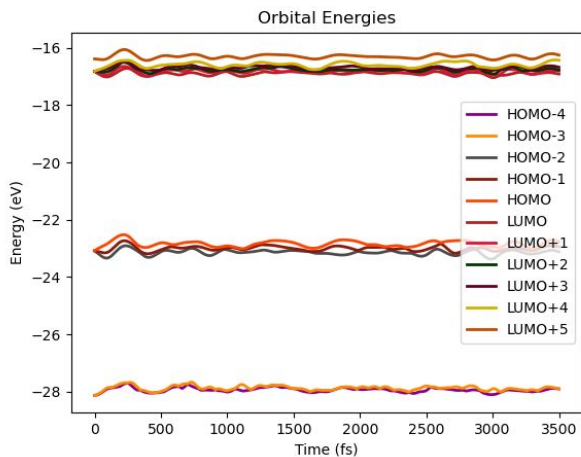
Methods

- Modeling the excited states of icosahedral Ag_{13}^{5+} nanocluster
- We interfaced MOPAC (implementation of the INDO/S hamiltonian) with Libra
 - MOPAC calculates the orbital energies and NACs
 - Libra runs TSH dynamics
- Using NBRA workflow in Libra
- Initial trajectory was run for 2500 timesteps using DFT with a plane wave basis set
- FSSH algorithm used, 30 initial conditions for 1000 steps each



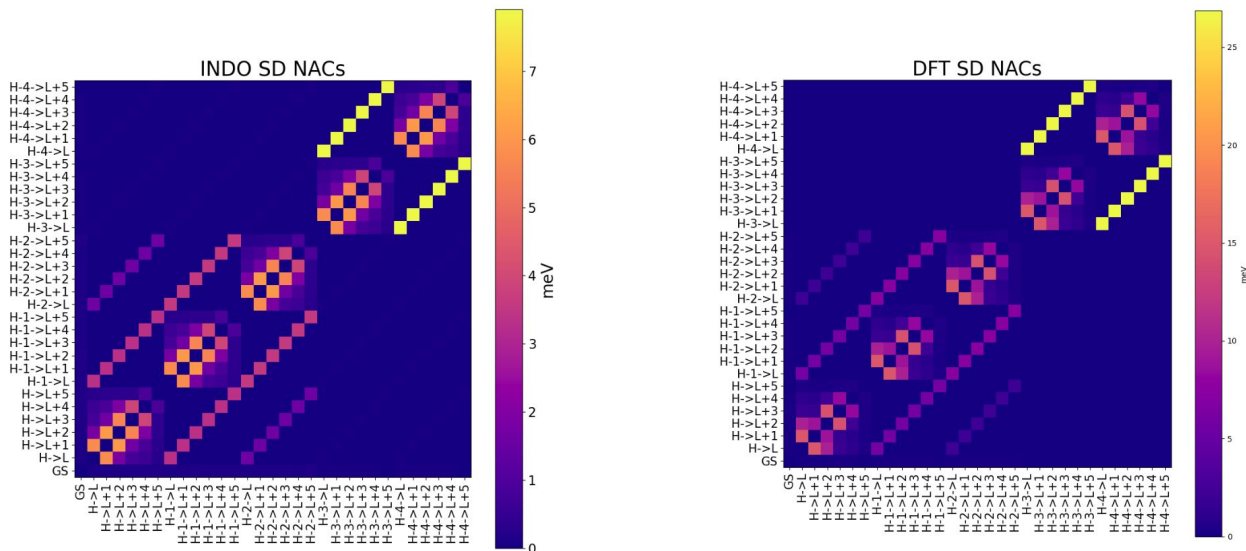
Results

- 3x degenerate HOMO and 5x degenerate LUMO
- Slater determinant energies for transitions ranging from HOMO-4 to LUMO+5 were calculated

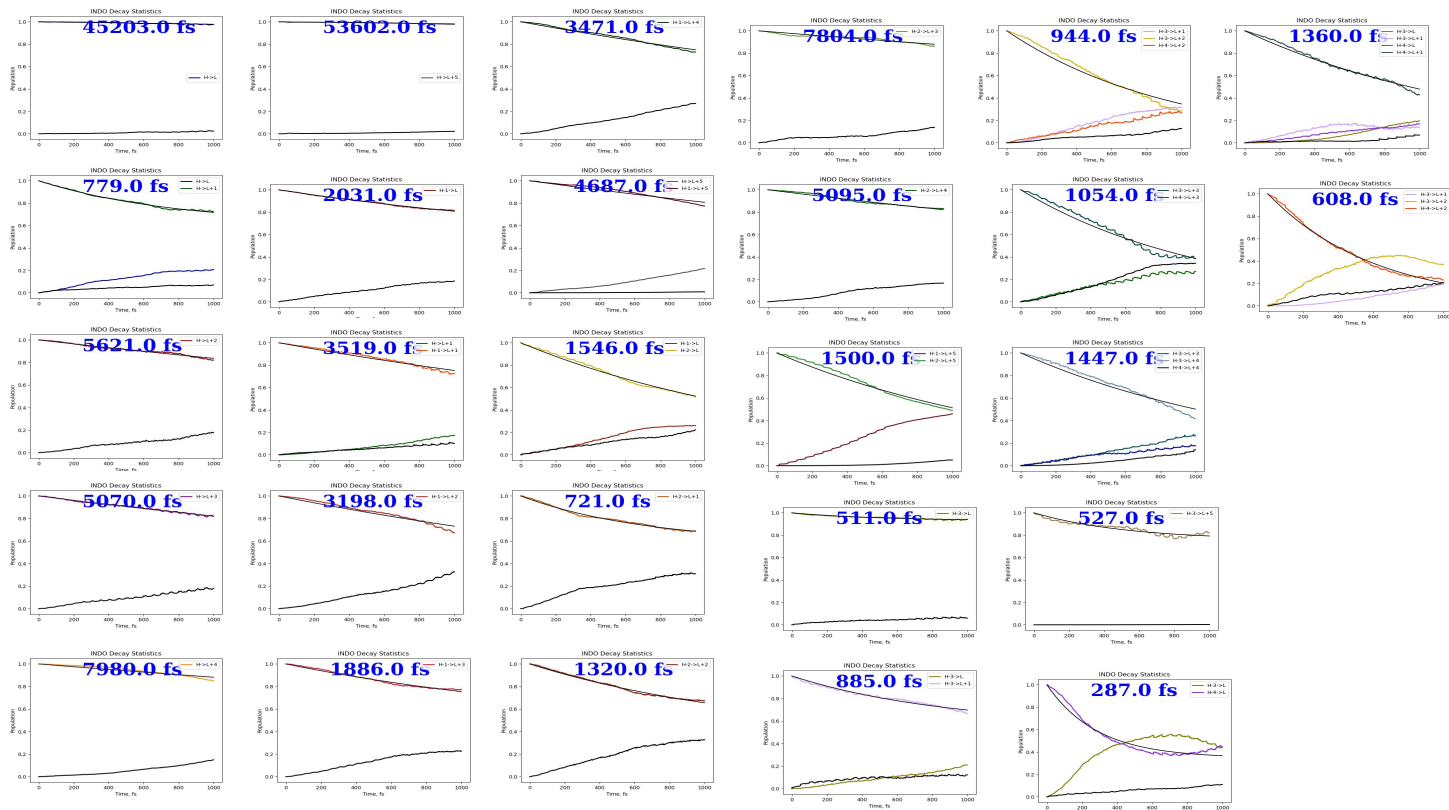


Non-adiabatic couplings

- Calculated NACs using both INDO and DFT to compare results
- Computation time is ~ 100 - 1000 x faster with INDO than with DFT
- INDO NACs are ~ 4 x smaller than DFT NACs but qualitatively agree

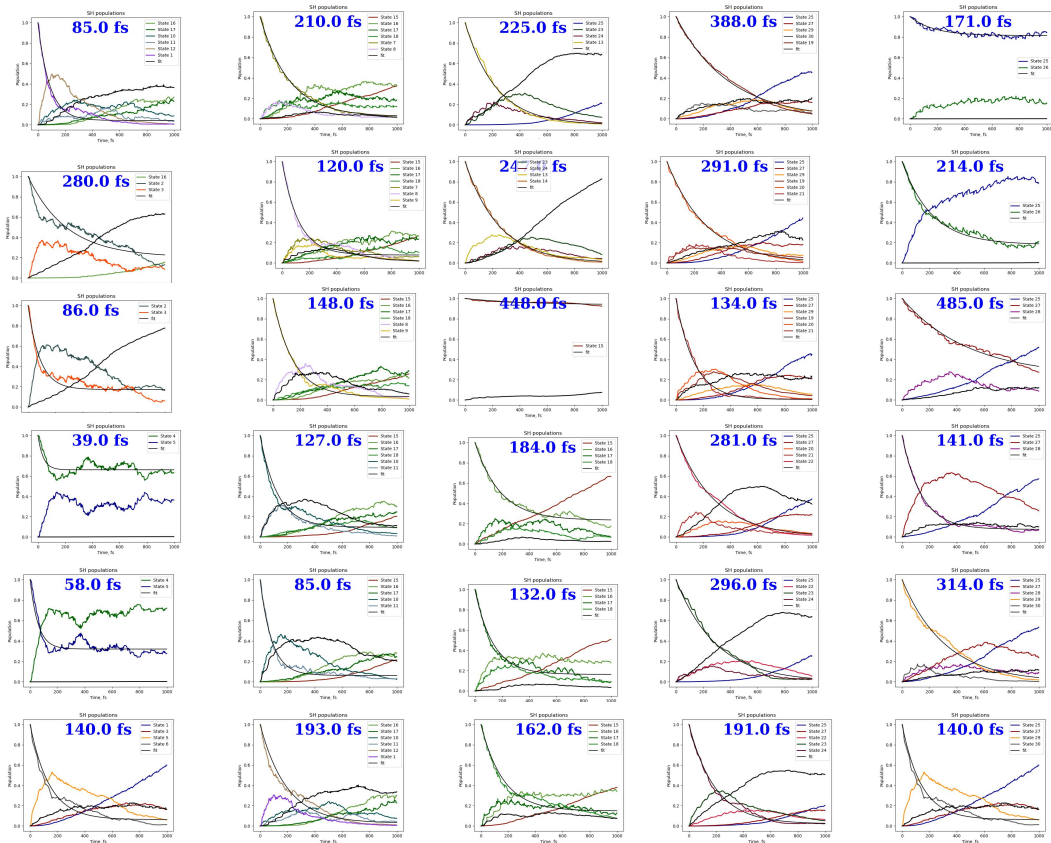


Decay from excited states in the SD basis - INDO



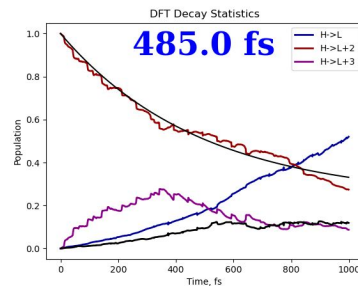
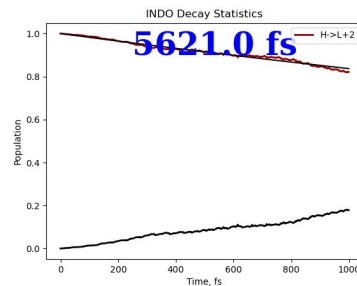
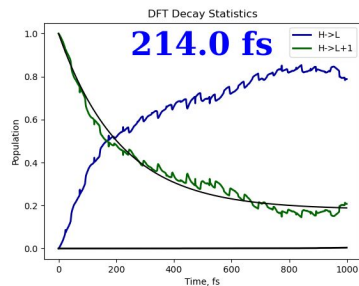
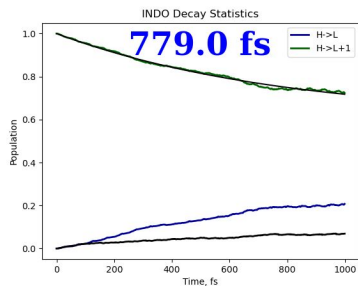
Decay from excited states in the SD basis - DFT

Results



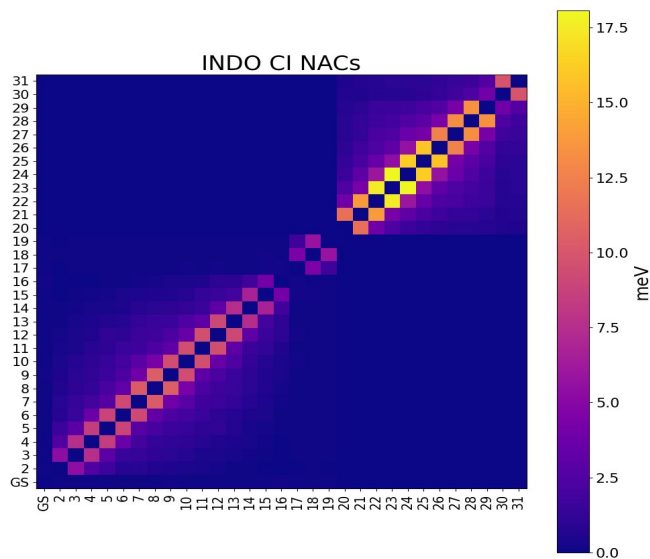
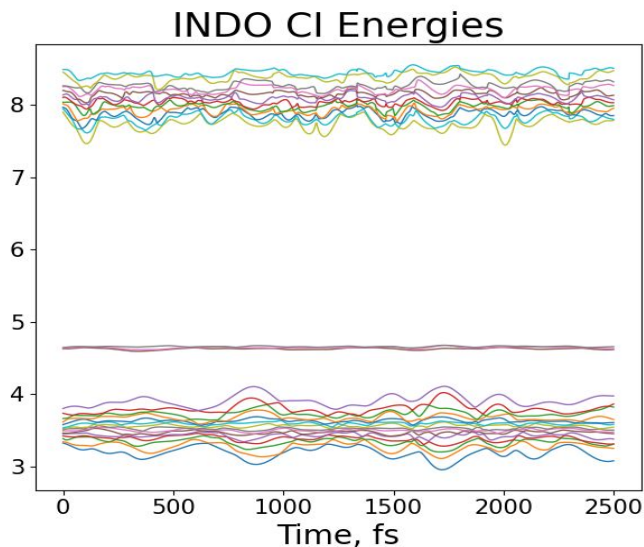
Decay from excited states in the SD basis

- INDO decay is significantly slower than DFT decay in the SD basis
 - Off by an order of magnitude in almost all cases
 - Lower NACs leads to fewer hops and slower decay

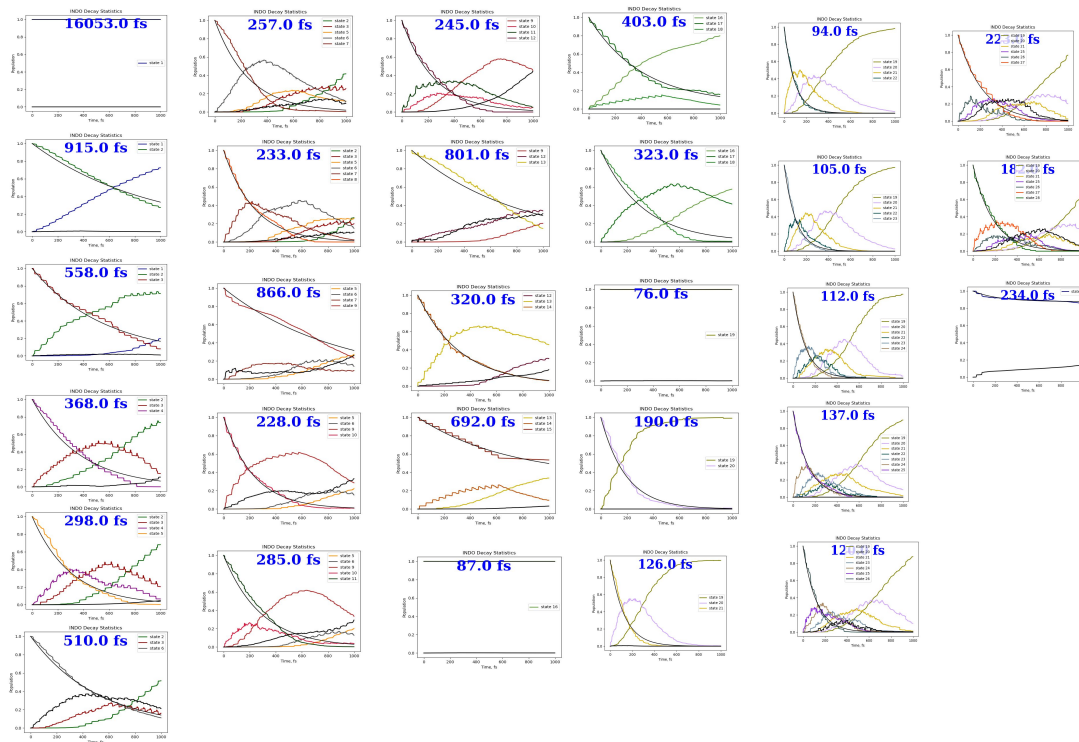


The Configuration Interaction (CI) basis

- CI basis uses a combination of slater determinants to create an excited state
- More accurate than single SD, especially in highly degenerate systems

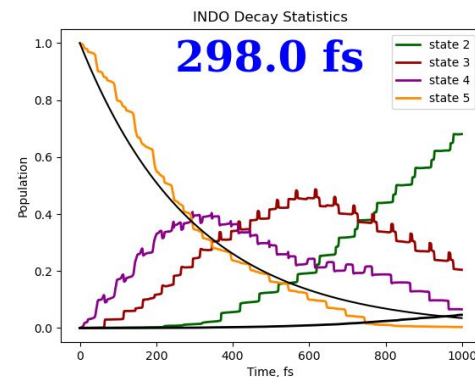
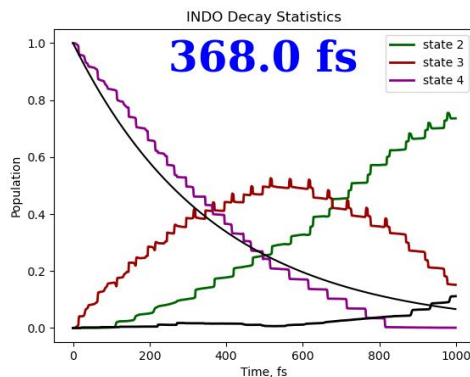
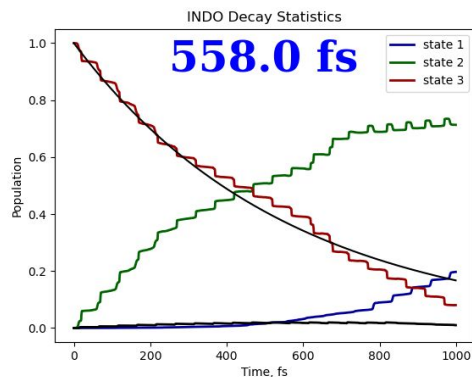


Decay from CI excited states



Decay from CI excited states

- Decay from first 30 excited states computed
- No DFT comparison data
- Decay timescales in CI basis are more in line with expectations
- Average time for decay from the initial state is 339 fs



Future Directions

- Investigation of poor accuracy of SD NACs and decay times
 - Potentially caused by overestimation of d orbital energy by INDO or underestimation of decay times by DFT
- Analysis of CI data
 - Examining contributions to excited states
- Improving accuracy of NAMD with different surface hopping algorithms
- Application to larger systems
- Moving beyond NBRA

Acknowledgements

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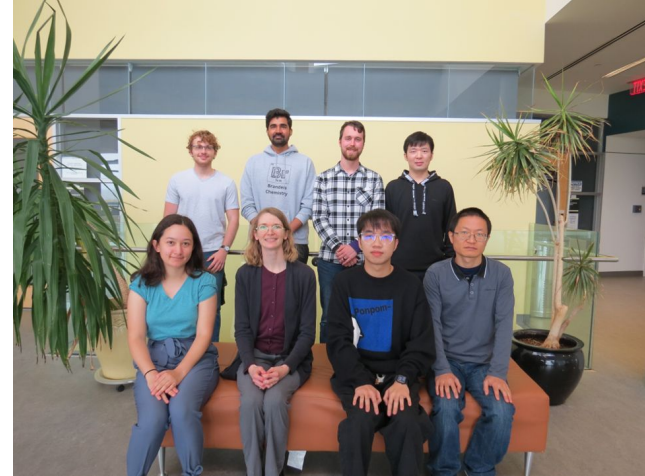
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