# NEXMD with Sander's QM/MM
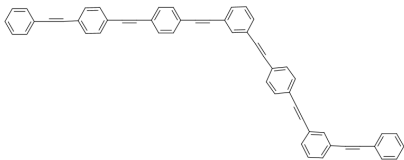## NonAdiabatic Dynamics Using AMBER

Dustin Tracy

University of Florida

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# Conjugate Organic Molecules



- They tend to be very good at energy transfer.
- $2 \to 3 \to 4$
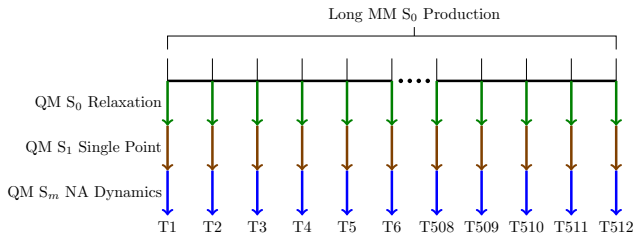- Excited state dynamics can speed or slow this transition.

**Question**

How can we simulate this?

## Possible Solutions

- Run Classical Ground State Dynamics then perform Excited State Energy Calculations on the snapshots.
  - ▶ Excited State dynamics could be different.
  - ▶ In the molecules I studied for example, the excited state had a much more planer dynamics than ground state.
- Run dynamics using the average forces of all the relevant excited states (Ehrenfest).
  - ▶ Often the average force of two states is not a very good approximation of either.
- Run a swarm of trajectories that are allowed to switch between different states (FSSH).
  - ▶ The proportion of the population that are on a certain state represent the probability of the state.
  - ▶ This process can be very computationally expensive.

# General Outline of Dynamics



Long MM $S_0$ Production

QM $S_0$ Relaxation

QM $S_1$ Single Point

QM $S_m$ NA Dynamics

T1  T2  T3  T4  T5  T6  T508 T509 T510 T511 T512

## Example Times

- Perform a long MM trajectory.
- Take snapshot every 1 PS, run QM Ground State for relaxation.
- Excite the System.
- Allow each of these trajectories relax independently.
  - Sum the population in each state to get state probabilities over time.
  - Analyze absorption and emission properties by looking at frequencies and oscillator strengths.

# Long MM Trajectory

## Sampling

The goal of our analysis is to derive the probability of states of a solute in solution. There are many possible conformations for a molecule. If you then include a solvent, the number of snapshots needed to accurately sample the phase space increased even more. A long run is necessary for decent sampling.

## Guidelines

- 1 ps time spacing between MM snapshots at 300K
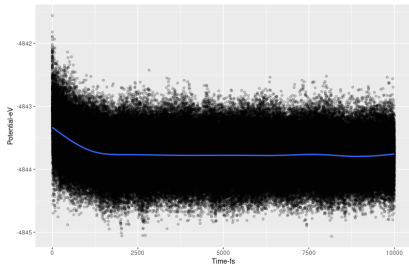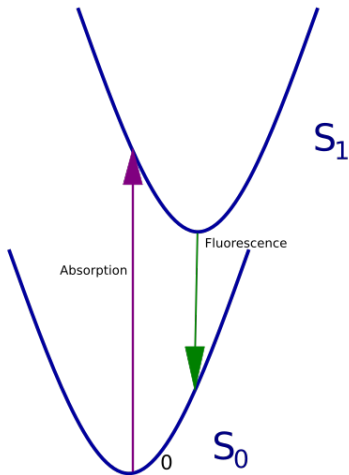- 500 samples for 50 atoms in vacuum

# Ground State Calculations



Figure: QM $S_0$ relaxation of PPV3-$NO_2$ in methanol.

- The algorithm used to decide whether to jump is very sensitive to energies.
- QM/MM energies are not going to be the same as MM and some time is needed to properly relax.

# Excite The System



- We use laser excitations with a wave shape similar to that done in experiments.
- Due to quantum uncertainty these states are also chosen based on the Franck-Condon principle.
- Energy is not conserved. (We're shooting a laser at it.)
- Velocities and coordinates are maintained in this step

# Let the System Relax
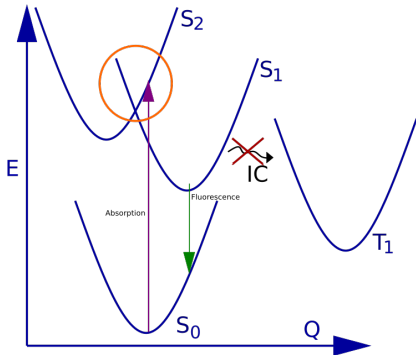


- The molecule will start at a very high excited state.
- When near a crossing of the energies, we have a very strong coupling, the molecule can then hop between the states.
- When there's a switch the velocities of the atoms are adjusted to conserve energy.
- Phosphorescence is not allowed.

# Analyze The Results

## Population Decay

We can plot the proportion of trajectories in each states as a proxy to quantum probabilities of the states. This provides a detailed view of state decay rates.

## Evolution of the Electronic Wave Function

The transition density matrix, needed for the calculation of the hopping probabilities can be repurposed to follow the physical movement of the excited electron density during decay.

## Excited State Energy Relaxation

The molecule is suddenly placed outside of equilibrium. Modeling the excited state relaxation provides some insight into how this energy is dissipated to the thermostat, solvent, both.

## Change in Vibrational Modes

Certain vibrational mode will be heavily coupled to adiabatic state transitions. Some of these could be very fast (Bonds) and others slower (Torsional).

# Why add QM/MM?

NEXMD can perform the above calculations already

## However

- The choice to switch states is sensitive to energies.
- (Solvatochromic) Shifts in emission and absorption energies are known to occur in solvents.
- Applications such as sensors, fluorescent tags, L.E.D's, etc, will include solvent.
- NEXMD uses SQM as a backend, which is part of AMBERTOOLS.
  ▸ This should make NEXMD trivial to use a library in AMBER
  ▸ Unfortunately it didn't.

# How We Did It
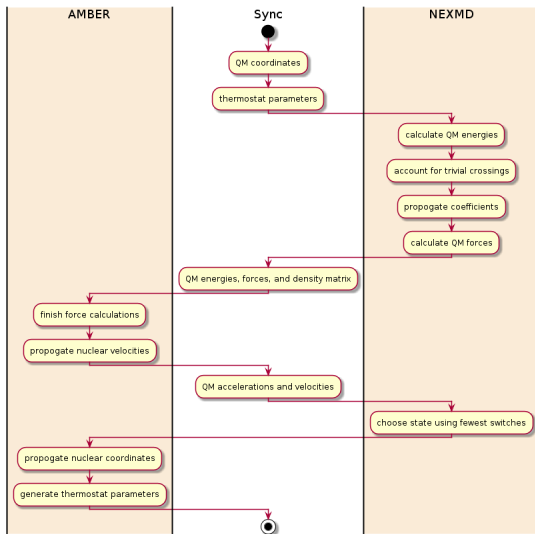
# The Test Systems
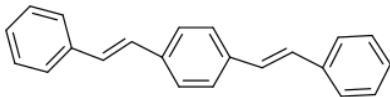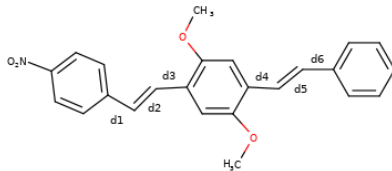
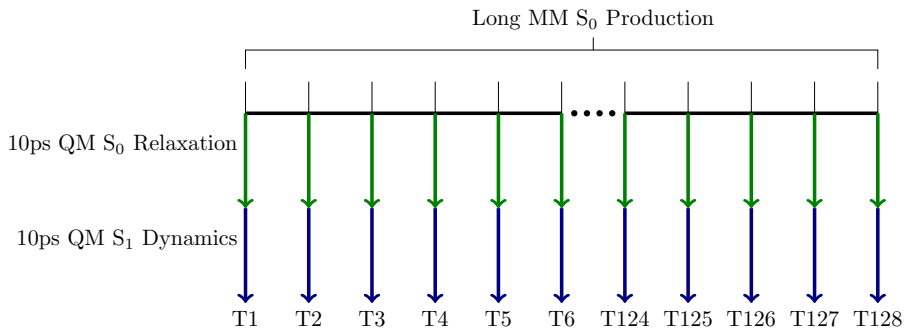polyphenylene vinylene oligimors



Figure: PPV3



Figure: PPV3-NO$_2$

- These systems are small.
- These systems are well studied.
- The Hamiltonian is known to provide reasonable results.

# PPV3-NO$_2$ Solvatochromic Shift

Long MM S$_0$ Production

10ps QM S$_0$ Relaxation

10ps QM S$_1$ Dynamics

T1  T2  T3  T4  T5  T6  T124  T125  T126  T127  T128

| Solvent | Dielectric (debye) |
|---------|--------------------|
| CCL$_4$ | 2.24 |
| CH$_3$OH | 32.7 |
| CHCl$_3$ | 4.81 |

Temperature: 300K
Langevin Constant: 2ps$^{-1}$

# PPV3-NO$_2$ Solvatochromic Shift
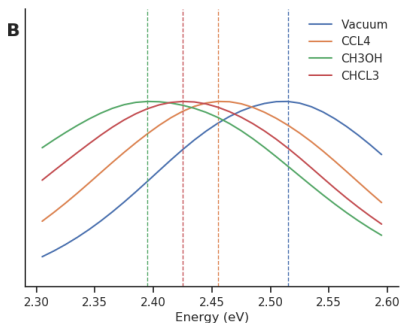


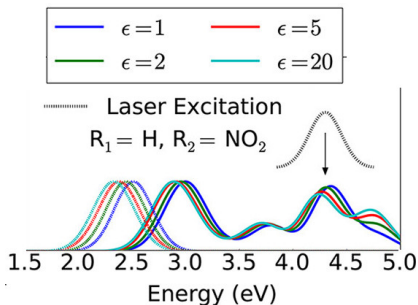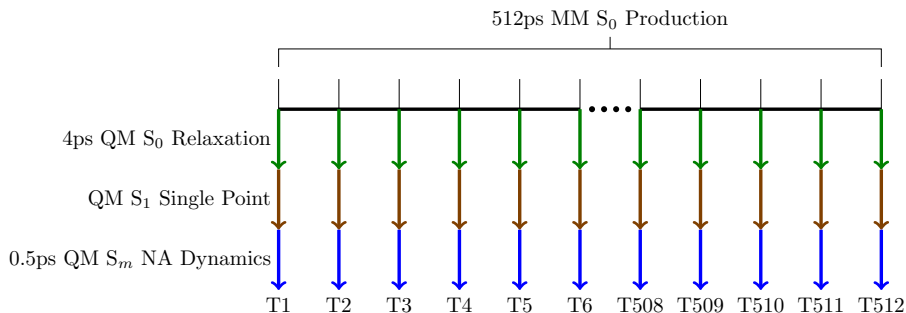Figure: Emission shift found using explicit solvent.



Figure: Emission shift found using implicit solvent. Dotted lines are the emission spectra. [1]

[1] Andrew E Sifain et al. "Photoexcited nonadiabatic dynamics of solvated push–pull $\pi$-conjugated oligomers with the NEXMD software". In: *Journal of chemical theory and computation* 14.8 (2018), pp. 3955–3966.
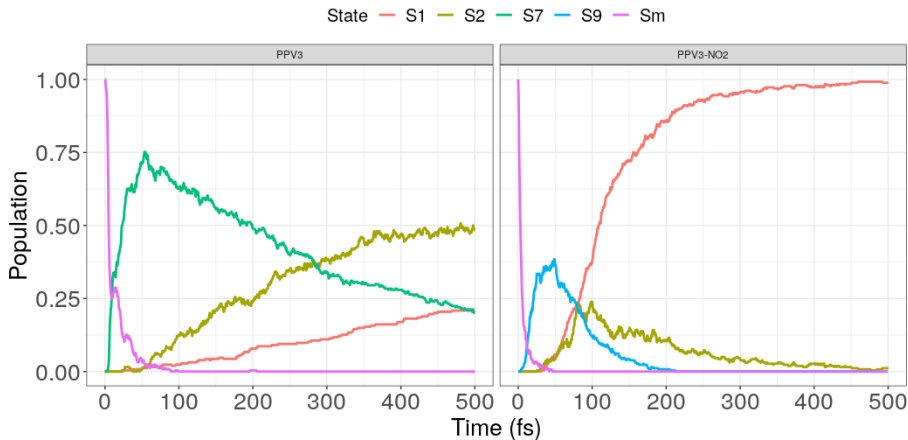
# NonAdiabatic Calculation



512ps MM $S_0$ Production

4ps QM $S_0$ Relaxation

QM $S_1$ Single Point

0.5ps QM $S_m$ NA Dynamics

T1  T2  T3  T4  T5  T6  T508 T509 T510 T511 T512

Temperature: 300K
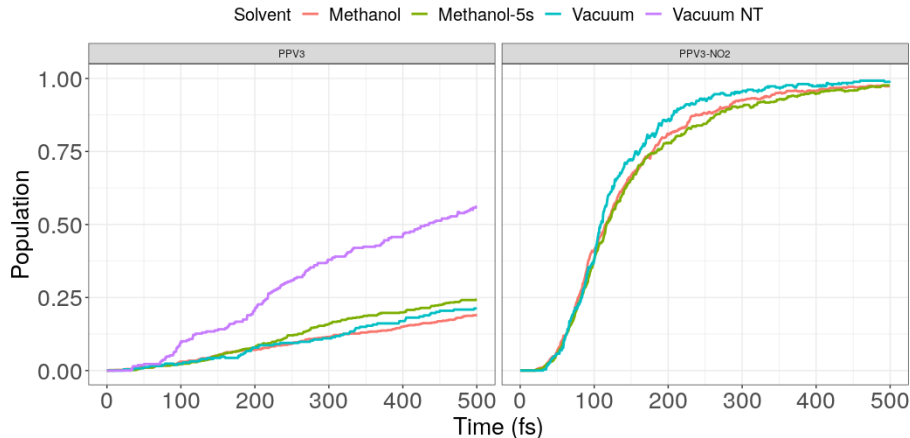Langevin Constant: $2\text{ps}^{-1}$

# NonAdiabatic Calculation



Populations for the excited states with extended lifespans for $PPV_3$ and PPV3-$NO_2$. $S_m$ represents the initial state.

The addition of the $CH_3$ groups and $NO_2$ dramatically accelerates decay.
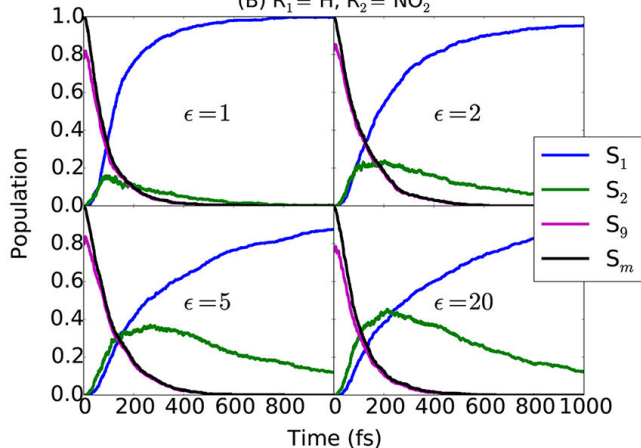
# NonAdiabatic Calculation



Population of the first excited state ($S_1$) of PPV3 and PPV3-NO$_2$ in various solvents obtained from the fraction of trajectories in each state. NT represents the simulation that did not account for trivial crossings.

# NonAdiabatic Calculation



(B) $R_1 = H$, $R_2 = NO_2$

Closest thing to compare the previous results to. An important difference is the initial excited state and the langevin constant. What concerns me is the significant solvent related $S_2 \rightarrow S_1$ decay rate. Currently testing to this.

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[2]Sifain et al., "Photoexcited nonadiabatic dynamics of solvated push–pull

# Thank You!



**Congratulations Yinuo!**

Sifain, Andrew E et al. "Photoexcited nonadiabatic dynamics of solvated push–pull $\pi$-conjugated oligomers with the NEXMD software". In: *Journal of chemical theory and computation* 14.8 (2018), pp. 3955–3966.