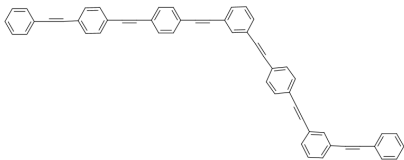# NEXMD with Sander's QM/MM

NonAdiabatic Dynamics Using AMBER

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Conjugate Organic Molecules

- They tend to be very good at energy transfer
- $2 \rightarrow 3 \rightarrow 4$
- 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 Sated Energy Calculations on 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 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.
  - Can be very computationally expensive

General Outline of Dynamics
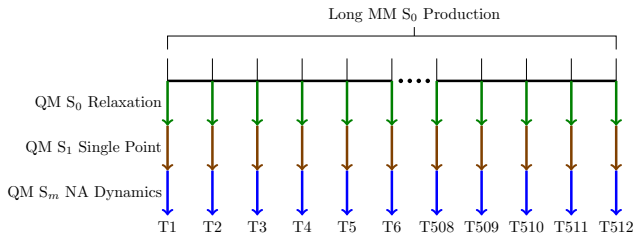
Example Times

- 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. Their are of 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
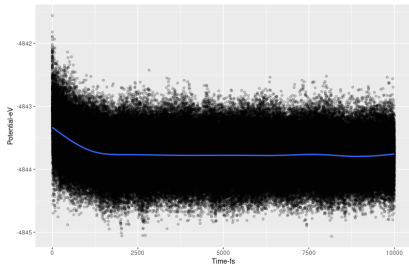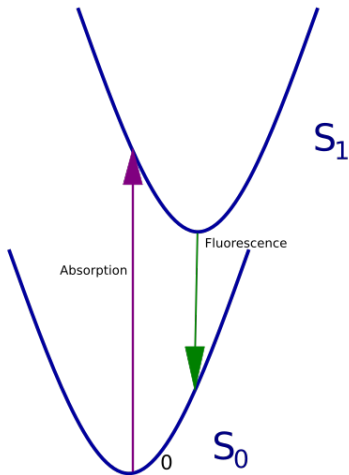
Ground State Calculations

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
- Some time is needed to properly relax

Excite The System

- We use laser excitations with a wave shape similar to that done in experiment
- 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
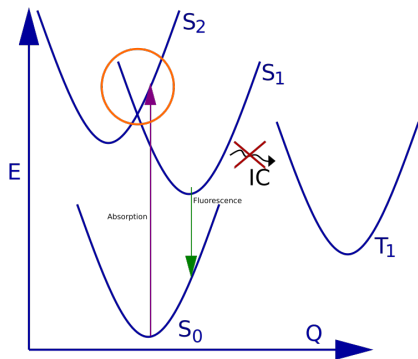
- The molecule will start at a very high excited state
- When near a crossing of the energies, we have a very strong coupling, the state can shift
- When there's a switch the velocities of the atoms are adjusted to conserve energy
- Phosphorescence is not allowed

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.

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.

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.

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
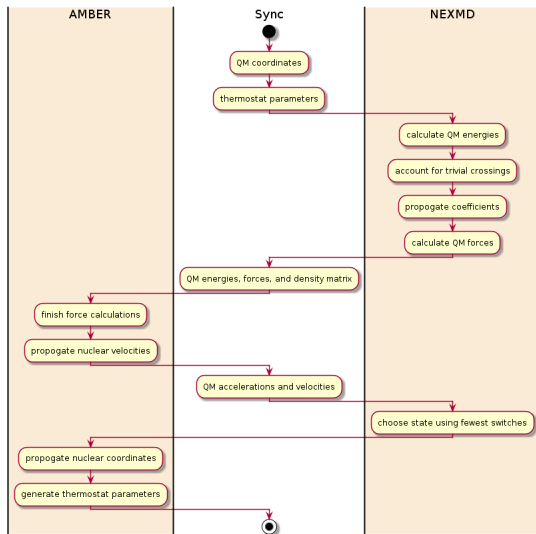
The Test Systems
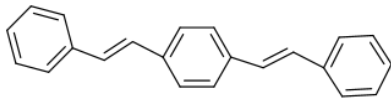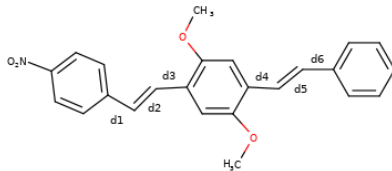
polyphenylene vinylene oligimors

Figure: PPV3

Figure: PPV3-NO$_2$

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