

Methodology and Results

This work closely followed the methodology described in Ref. [1]. First notice that this work utilized NEXMD with the AM1/CIS level of electronic structure theory. To begin, a geometry optimization was performed on the polyphenylene ethynylene (PPE) dendrimer coordinates that were obtained from Ref. [1]. These optimized coordinates were used to perform a ground-state *ab initio* molecular dynamics (MD) simulation for 1300 fs with a time step of 1 fs. These dynamics were run in vacuum under the Langevin thermostat at 300 K and a friction coefficient of 20 ps⁻¹. Then 650 nuclear coordinate and velocity snapshots were sampled from the last 650 fs of this simulation and used to compute a single-point calculation in both vacuum and solvent. In the presence of solvent, the linear response (LR) solvation model was employed in conjunction with the COSMO potential and a dielectric constant of 30 to mimic the effects of a polar solvent. These calculations were employed to compute the average optical spectrum of PPE using a Gaussian spectral broadening with the full width at half-maximum set to 0.36 eV, as specified in Ref. [1]. The computed spectra (Figure 1) demonstrated that S₁ and S₂ exhibit strong absorption. Targeting these two states, I simulated nonadiabatic dynamics for 130 trajectories, initializing all excitations to state S₂. The three lowest energy excited states were propagated with 1000 classical steps and 3000 quantum steps (3 quantum steps for each classical step), and adiabatic state population dynamics were plotted (Figure 2).

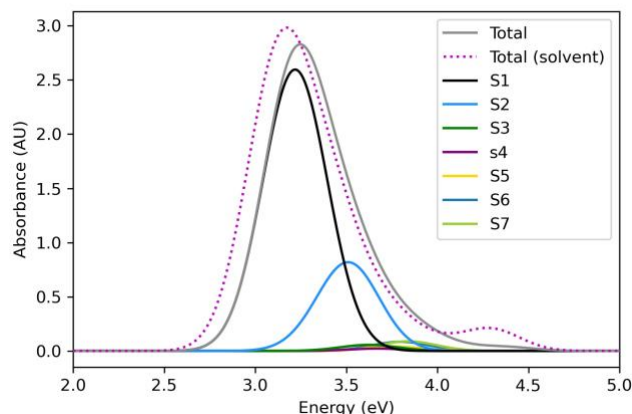


Figure 1: Optical spectrum of PPE from single-point calculations with Gaussian broadening and FWHM = 0.36 eV. The dashed line represents the total spectrum of PPE in solvent ($\epsilon = 30$).

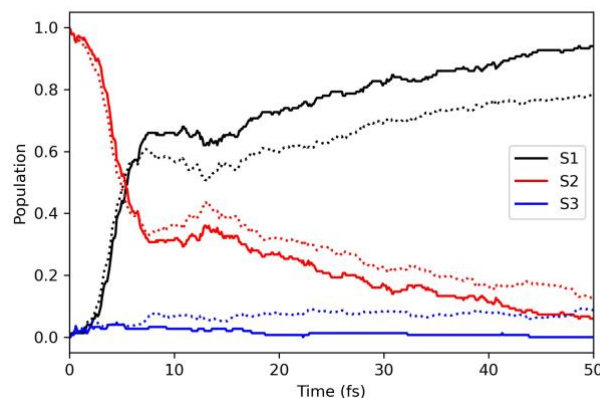


Figure 2: Adiabatic state population dynamics during the nonadiabatic dynamics simulation in vacuum.

Discussion

Figure 1 is in qualitative and quantitative agreement with its respective plot in Ref. [1]. We see that excited states S₁ and S₂ absorb strongly around 3.3 eV and 3.5 eV, respectively. Excited states S₄, S₅, S₆, and S₇ were not observed to absorb as strongly and thus were not included in the nonadiabatic dynamics simulation. Excited state S₃ was included because it shows weak absorption around 3.7 eV (Fig. 1). It is clear from the energies corresponding to the maximum absorption of each excited state that S₁ is the lowest energy state, S₂ is the second lowest energetically, and S₃ is the highest energy of the three. In the NAMD simulation, setup, the initial excitations were initialized to state S₂ to observe the population dynamics leading to its localization on state S₁.

Fig. 2 is in qualitative agreement with its respective plot in Ref. [1], but these plots do not agree quantitatively. One possible improvement would be to simulate nonadiabatic dynamics for 300-400 more trajectories. In Fig. 2, the solid lines represent the classical calculations of the

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populations proportion occupying a given excited state, $N_i(t)/M$; the dotted lines represent the quantum calculations of the population dynamics $\langle |c_i(t)|^2 \rangle$. Figure 2 shows at the initial time that all of the excitations were initialized to state S_2 and immediately transition to the lower energy S_1 state. After 8 fs the rapid decay stops and appears to even increase and, after about 15 fs, the excitation populations on state S_2 decreases as most of these excitations are moving to the lower energy S_1 state. Lastly, notice that these states are weakly coupled to state S_3 as Fig. 2 shows small fluctuations in its populations during the simulation.

Summary

In this workshop, I aimed to gain the skills necessary to perform a Born-Oppenheimer molecular dynamics (MD) simulation of the chlorophyll *a* (Chl*a*) and violaxanthin (Vio) complex using the capabilities of the NEXMD package. To work towards this goal, I closely followed Ref. [1] and was able to acquire the coordinates of the polyphenylene ethynylene (PPE) dendrimer and perform a geometry optimization as well as a ground state *ab initio* molecular dynamics simulation. From these data, I computed single-point calculations in both vacuum and solvent to reproduce the optical spectrum found in Fig. 2c of Ref. [1], which gave the necessary insights to perform a nonadiabatic dynamics simulation of PPE in vacuum and reproduce the data found in Fig. 3a. After completion of the workshop, I plan to continue exploring PPE with NEXMD by performing a nonadiabatic dynamics simulation in solvent as well as transition density analysis. With these skills, I will target the Chl*a*-Vio complex towards understanding the excitation dynamics that lead to the chlorophyll-to-carotenoid dissipation mechanisms that have been previously characterized in Ref. [2].

References

- [1] J. Chem. Theory Comput. 16, 5771 (2020)
- [2] Nat Commun. 11, 1295 (2020)