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Atomistic absorption spectra and non-adiabatic dynamics of the LH2 complex with a GPU-accelerated *ab initio* exciton model
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Recently, we outlined an efficient multi-tiered parallel excitonic framework that utilizes time dependent density functional theory (TDDFT) to calculate ground/excited state energies and gradients of large supramolecular complexes in atomistic detail. In this paper, we apply our *ab initio* exciton framework to the 27 coupled bacteriochlorophyll-a chromophores which make up the LH2 complex, using it to compute linear absorption spectra and short-time, on-the-fly nonadiabatic surface-hopping (SH) dynamics of electronically excited LH2. Our *ab initio* exciton model includes two key parameters whose values are determined by fitting to experiment: d , which is added to the diagonal elements, corrects for the error in TDDFT vertical excitation energies on a single chromophore; and e , which occurs on the off-diagonal matrix elements, describes the average dielectric screening of the inter-chromophore transition-dipole coupling. Using snapshots obtained from equilibrium molecular dynamics simulations (MD) of LH2, best-fit values of both d and e were obtained by fitting to the thermally broadened experimental absorption spectrum within the Frank-Condon approximation, providing a linear absorption spectrum that agrees reasonably well with the experimental observations. We follow the nonadiabatic dynamics using surface hopping to construct time-resolved visualizations of the EET dynamics in the sub-picosecond regime following photoexcitation. This provides some qualitative insight into the excitonic energy transfer (EET) that results from atomically resolved vibrational fluctuations of the chromophores. The dynamical picture that emerges is one of rapidly fluctuating eigenstates that are delocalized over multiple chromophores and undergo frequent crossing on a femtosecond timescale as a result of the underlying chromophore vibrational dynamics. The eigenstate fluctuations arise from disorder in both the diagonal chromophore site energies and the off-diagonal inter-chromophore couplings. The scalability of our excitonic computational framework across massively parallel architectures opens up the possibility of addressing a wide range of questions, including how specific dynamical motions impact both the pathways and efficiency of electronic energy-transfer within large supramolecular systems.