

Modular Path Integral Methodology for Simulating Exciton-Vibration Dynamics

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Real-time path integral methods offer unique capabilities and in some situations allow numerically exact, quadrature-based evaluation of quantum dynamical properties. We have developed a modular decomposition of the path integral (MPI) which provides an efficient, fully quantum mechanical framework for simulating the dynamics of systems characterized by a quasi-one-dimensional topology and mostly local interactions, such as spin chains or molecular aggregates with Frenkel exciton interactions and any number of molecular vibrations. The MPI decomposition proceeds through sequential linking of the quantum paths of adjacent monomers, achieving linear scaling with system size.

The flow of energy in molecular aggregates poses intriguing questions and has been the subject of intense theoretical and experimental work. We have used the MPI methodology to present all-mode, fully quantum mechanical simulations of exciton-vibration dynamics in linear or ring-shaped bacteriochlorophyll complexes, which contain up to 18 molecular units, each with the two relevant electronic states and 50 normal mode vibrations whose parameters are obtained from spectroscopically determined Huang-Rhys factors, over a range of temperatures. The simulations quantify the decohering role of intramolecular vibrations on the dynamics of energy flow in photosynthetic systems.

Further, we have applied the MPI methodology to investigate the excitation energy transfer dynamics of perylene bisimide (PBI) J-aggregates containing two, three, five, or 25 PBI-1 molecular units at zero and room temperature, where 28 intramolecular vibrations in each molecule were treated explicitly. We found that the vibrational modes introduce significant changes to the dynamics, smearing electronic recurrence peaks and introducing a substantial temperature dependence to the time evolution of the electronic populations. We also identified a high-frequency vibronic mode which is primarily responsible for small-amplitude oscillatory features that exhibit variable temperature sensitivity dependent on aggregate length. These results provide a quantitative picture and useful insights into the complex interplay of exciton-vibration interactions in the excitation energy transfer dynamics of molecular aggregates.