Path Integral Disentanglement and Modular Decomposition for Simulating the Quantum Dynamics of Large Systems

Nancy Makri

Departments of Chemistry and Physics
University of Illinois at Urbana-Champaign

The time evolution of the reduced density matrix (RDM) of a system interacting with a dissipative harmonic bath involves influence functional couplings among the path integral variables at all time points. The iterative quasi-adiabatic propagator path integral (i-QuAPI) decomposition exploits the finite length of influence functional memory to decouple the variables beyond the bath-induced memory interval, leading to linear scaling with propagation time, but requires the construction of a tensor whose size increases exponentially with memory length. It has been shown that the path integral can be completely disentangled by recursively spreading the influence functional interactions over longer path segments, while decreasing their contribution. Eventually, the entangled term becomes sufficiently small and may be neglected, leading to iterative propagation of the RDM through simple matrix manipulations with size is equal to that of the bare system. It is found that the temporal entanglement length is practically equal to the memory length. The small matrix decomposition of the path integral (SMatPI) is stable and extremely efficient, extending the applicability of numerically exact real-time path integral methods to multi-state systems.

Beyond system-bath models, real-time path integral methods offer unique capabilities in situations where a suitable decomposition allows numerically exact, quadrature-based evaluation. The modular path integral (MPI) methodology 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 corresponding to adjacent monomers, achieving linear scaling with system size. The MPI methodology has been used to perform all-mode, fully quantum mechanical simulations of exciton-vibration dynamics in linear or ring-shaped bacteriochlorophyll complexes that contain up to 16 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 shed light on the intricate interplay among electronic coherence, linear vs. circular topology, Hilbert space size, and decoherence induced by chlorophyll vibrations and thermal fluctuations.