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Modular Path Integral Methodology for Exciton-Vibration Dynamics of Extended Systems

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This award has supported the development of the modular path integral (MPI) methodology, a fully quantum mechanical approach to electron-vibration and spin-phonon dynamics in extended systems composed of one-dimensional segments. The distinguishing advantage of MPI is the combination of (i) linear scaling with system size and (ii) the ability to account exactly for any number of intramolecular vibrations at zero or finite temperature. Several advances led to a highly efficient algorithm for numerically exact, quantum mechanical simulations of spin- and exciton-vibration dynamics in large molecular aggregates. The MPI methodology has been used to investigate the complex interplay between coherent exciton dynamics and the damping effects of intramolecular vibrations in aggregates of pelynene bisimide containing

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FINAL REPORT

This award has supported the development of the modular path integral (MPI) methodology, a fully quantum mechanical approach to of spin- and electron-vibration dynamics in extended systems composed of one-dimensional segments (see Figure 1). The simplest structure is a one-dimensional lattice A-B-C-D-…, where the units A, B,… may be spins, covalently bonded molecular segments forming a long molecule or polymer, or molecules with important magnetic or electronic properties. The units need not be identical, and the structure may be more complex; for example the chain may have branches or may form a closed ring. Also, each unit may include coupled intramolecular degrees of freedom. The distinguishing advantage of MPI is the combination of (i) linear scaling with system size and (ii) the ability to account exactly, fully quantum mechanically, for any number of intramolecular vibrations at zero or finite temperature. The advances in the MPI methodology and its use to simulate excitation energy transfer and spin-vibration dynamics are described below.

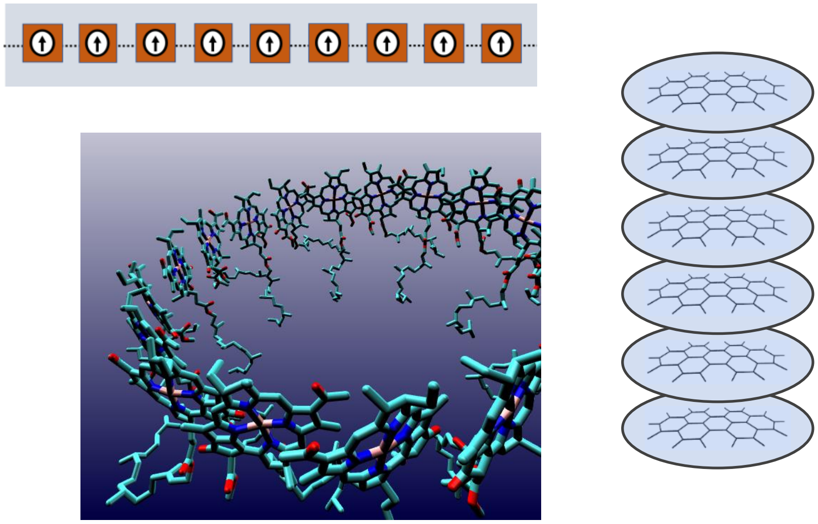

Fig. 1. Examples of systems suitable to the MPI methodology. The linking sequence is illustrated in one of these systems.

1. Overview of MPI

Rather than propagating in time a spatial representation of the many-particle wavefunction or density matrix, the modular path integral (MPI) algorithm proceeds by sequentially linking the paths of adjacent modules, and leads to linear (or, since identical modules are treated just once) sublinear scaling with system size. The MPI algorithm has been developed for systems of a single-file arrangement of units interacting via nearest neighbor couplings, and extended to the calculation of two-particle correlations in arrays that may also contain some long-range interactions, to the treatment of systems with side chains or cyclic structures, to Hamiltonians with off-diagonal couplings between units, and to the modifications required for inclusion the interaction of one or several units of a system with dissipative baths or molecular vibrations.

2. MPI for Hamiltonians with Non-Diagonal Couplings

For many important processes, the intermonomer coupling is not diagonalizable in any single-particle basis. Unfortunately, common choices of the path integral basis lead to path integral representations with twice as many integration variables. Since the cost of path integral calculations grows exponentially with the number of variables, this situation would make simulations feasible for half the propagation length of those possible with local (position-like) interactions.

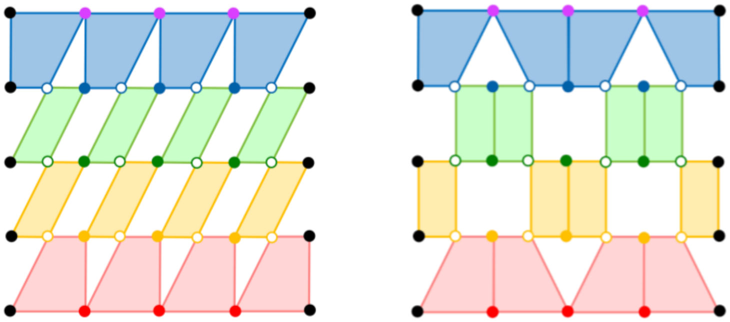

Fig. 2. Schematic illustration of the connections in the exciton MPI expression for a chain of 5 monomers with $N = 4$ using the common short-time propagator (left), as well as alternating propagator sequences (right). Each colored shape corresponds to a two-monomer short-time propagator. Black circles indicate the fixed endpoints. Colored solid and hollow circles represent path and auxiliary variables, respectively.

We have identified an optimal factorization of the time evolution operator, which minimizes the number of path integral variables while ensuring high accuracy and preservation of detailed balance. The idea stems from the diagrammatic representation of the propagator and multi-step path integral, and is illustrated in Figure 2.

3. Efficient MPI Factorization

We have developed and implemented a factorization of the MPI algorithm that leads to a very significant acceleration. This factorization changes the cost scaling from L^2 to $L \log L$, where L is the number of time points on which paths are discretized, leading to dramatic savings that are analogous to those attained by the fast Fourier transform (FFT) algorithm and allowing application of the MPI procedure to systems with larger units and to longer propagation times.

Originally developed for the simpler case of diagonal couplings, the factorization algorithm was subsequently generalized so that it can be applied to Frenkel-exciton and Heisenberg Hamiltonians (Figure 3).

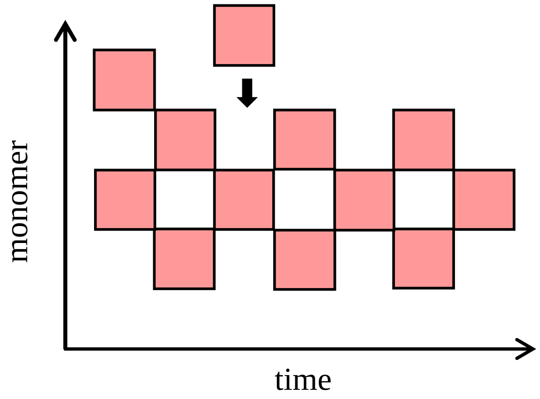

Fig. 3. Illustration of the factorized linking algorithm for nonterminal units in the general case of non-diagonal couplings.

4. Inclusion of intramolecular normal mode vibrations

In addition to spin or electronic states, each unit may include several vibrational degrees of freedom that couple to the electronic manifold. Since the desired observable pertains to the discrete (spin or electronic) degrees of freedom, the vibrations must be included with proper Boltzmann weights and traced over. In most situations it is sufficient to treat intramolecular vibrations at the quadratic level in terms of normal modes. The path integral formulation offers a unique advantage in this regard, allowing contributions from quadratic bath degrees of freedom to be included through influence functional factors at a very small additional effort.

We have derived analytical expressions for the influence functional factors for the general case of nondiagonal coupling operators. This development allows the treatment of intramolecular vibrations or those from a model bath described by a continuous spectral density at minimal cost, regardless of the number of normal modes or the features of the spectral density function.

5. Small matrix decomposition of the Modular Path Integral (SMatMPI)

Until recently, the basic requirement of the MPI approach has been the ability to store the quantum paths of a single unit. While the cost for this storage grows exponentially with propagation time, calculations are often feasible over times that are sufficiently long to capture the dynamics of interest. Nevertheless, there are many situations where important dynamics requires the ability to link the paths over monger time intervals, which requires array storage that exceeds by far the capabilities of even the most advanced computing environments.

To address such situations, the MPI algorithm was recently reformulated taking advantage of the small matrix decomposition of the path integral and its recent generalization to a small matrix representation of quantum paths, developed recently by Makri. The resulting SMatMPI algorithm allows the sequential linking of paths whose length can significantly exceed available array storage and leads to an iterative decomposition in time as well, while preserving the linear scaling with aggregate length.

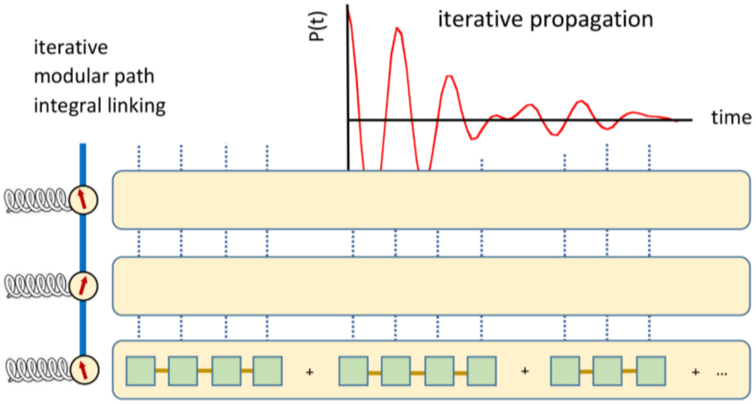

Fig. 4. Schematic illustration of SMatMPI algorithm.

6. Electron-vibration dynamics in J-aggregates

An important goal of our work is the simulation of excitation energy transfer (EET) in molecular aggregates, where the units are connected via Frenkel exciton coupling. Molecular aggregates of perylene bisimide (PBI) based dyes have been of interest to energy research as prospective candidates for artificial light harvesting. Using the MPI methodology we have performed calculations of EET in J-aggregates of PBI containing up to 25 molecular units. Each of these units is represented in terms of two (ground and excited) electronic states, which are coupled to 28 intramolecular normal mode vibrations. The population dynamics of several units are shown in Figure 5, showing the transfer of energy.

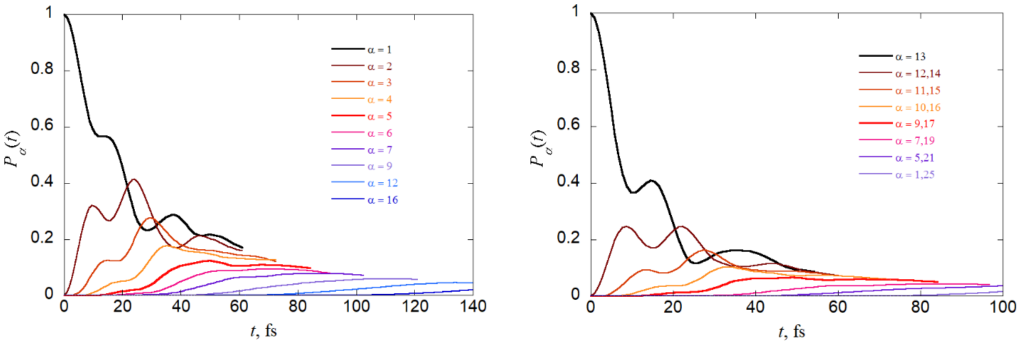

Fig. 5. Exciton-vibration dynamics for $(\text{PBI-1})_{25}$. Electronic populations of several molecular units are shown. The populations of some units are omitted to avoid overcrowding of the figure. Left: edge initial condition. Right: central initial condition.

7. Excitation energy transfer in photosynthetic antenna complexes

The mechanism of excitation energy transfer in photoexcited bacteriochlorophyll (BChl) aggregates continues to pose intriguing questions, which have important implications for the observed efficiency of photosynthesis. We have performed fully quantum mechanical calculations of exciton-vibration dynamics in chains and rings of BChl *a* molecules, with parameters characterizing the B850 ring of the LH2 complex of photosynthetic bacteria.

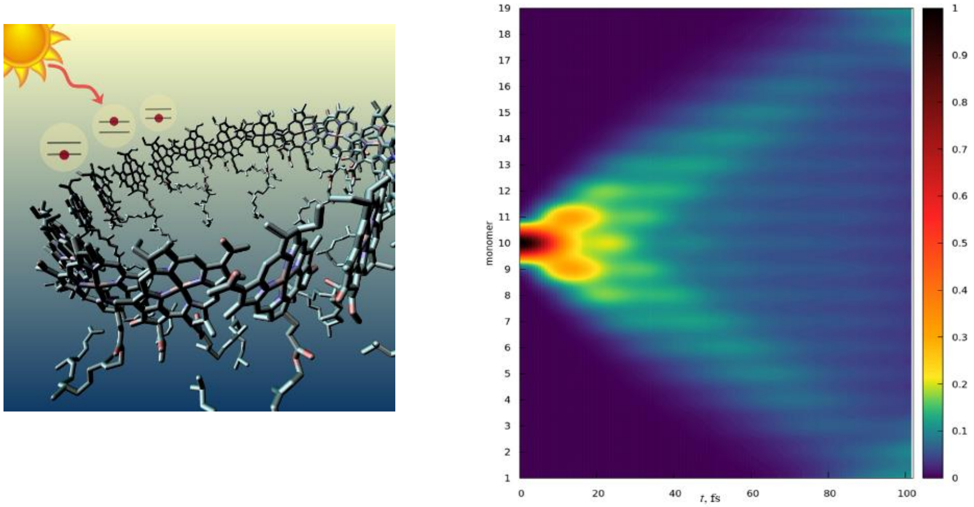

Fig. 6. Excited state populations of the BChl monomers in the LH2 B850 ring as a function of time.

Our calculations treated all 50 coupled intramolecular vibrations on each pigment, with parameters obtained from spectroscopic Huang-Rhys factors. Our results (Figure 6) suggest that the interplay between electronic and vibrational timescales leads to the rapid suppression but not the overdamping of electronic coherence, which facilitates the spreading of excitation energy throughout the aggregate.

Recent work focused on embedding the bacteriochlorophyll complex in its protein scaffold, in order to account for the additional dissipative effects induced by the biological environment. Because of some technical difficulties, more work is required before we can simulate the combined LH2-protein dynamics.

8. Quantum dynamics of spin chains

Chains composed of spin-½ units are of interest to condensed matter physics, material properties and quantum information theory. Depending on the type of coupling between adjacent spins, the spin chain is known as the quantum Ising model in a transverse field or the more general Heisenberg spin chain. These one-dimensional models are characterized by rich physical behaviors, which include spin entanglement dynamics and a quantum phase transition, and have been the subject of countless studies.

In addition to their thermodynamic properties, there has been much interest in the quantum quench dynamics of these coupled spins following a sudden change of the external field. While some properties in a subset of these models and in the infinite length limit are subject to analytical treatment, a plethora of interesting questions continue to present major challenges. In addition to the pure spin dynamics, the spin degrees of freedom couple to the molecular vibrations of each unit, leading to even more complex behaviors that remain completely unexplored.

We have been investigated the dynamics of finite-length quantum Ising chains where each spin interacts with a local dissipative bath resembling that from molecular vibrations. Our results reveal very rich dynamical behaviors, which depend intimately on spin-spin and spin-vibration coupling strength, the temperature, as well as the location of the particular spin within the chain. The typical transition from coherent to incoherent dynamics is very severely altered in these systems, displaying complex patterns that are not present in the single-spin paradigm of quantum dissipative dynamics.