

Modular Quantum and Rigorous Quantum-Classical Real-Time Path Integral Methods

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The quantum-classical path integral (QCPI) offers a rigorous, yet efficient methodology for combining a quantum mechanical description of a target “system” with a classical trajectory treatment of the system’s environment, which is often composed of thousands of atoms.[1-4] Real-time path integral methods are plagued by the Monte Carlo sign problem, while explicit summation of all the terms is not feasible in most situations, as the number of quantum paths grows exponentially with the number of time steps. Since in QCPI each quantum path specifies a sequence of forces that generate a different classical trajectory (from the same phase space point), the number of trajectories also grows exponentially with propagation time. Overcoming these problems has been possible by exploiting decoherence.

The starting point is the identification of two components in the effects induced on a quantum system by a polyatomic environment. The first, “classical decoherence” mechanism is associated with phonon absorption and induced emission and is dominant at high temperature. Within the QCPI framework, the memory associated with classical decoherence is removable. A second, nonlocal in time, “quantum decoherence” process, which is associated with spontaneous phonon emission, becomes important at low temperatures and is responsible for detailed balance.[5] The QCPI methodology takes advantage of the memory-free nature of system-independent solvent trajectories to account for all classical decoherence effects on the dynamics of the quantum system in an inexpensive fashion. Inclusion of the residual quantum decoherence is accomplished via phase factors in the path integral expression, which is amenable to large time steps and iterative decompositions. The QCPI methodology can be used to perform all-atom simulations of nonadiabatic processes in condensed phase environments with thousands of atoms [6], without the need for any assumptions (beyond the classical trajectory treatment of the environment) or adjustable parameters.

Further, a modular path integral (MPI) methodology has recently been developed [7,8], which provides an efficient, fully quantum mechanical framework for simulating the dynamics of Hamiltonians characterized by a quasi-one-dimensional topology and mostly local interactions. The MPI decomposition proceeds through sequential linking of the quantum paths corresponding to adjacent monomers, achieving linear scaling with system size. An efficient factorization leads to almost linear scaling with the number of monomer paths. The scheme is applicable to systems with considerable chemical complexity.

The MPI approach allows fully quantum mechanical simulation of spin models, as well as Frenkel exciton chains, where any number of harmonic vibrations (with appropriate discrete frequencies and Huang-Rhys factors) as well as lattice phonons representing dissipative interactions, may be included (at zero or finite temperature) without a significant increase in computational cost [9]. In combination with the QCPI algorithm, the MPI approach may be used to simulate energy transfer dynamics of molecular aggregates containing many vibrational degrees of freedom in contact with anharmonic environments with unprecedented accuracy.

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