

Rigorous Quantum-Classical Path Integral Formulation of Real-Time Dynamics

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The path integral formulation of time-dependent quantum mechanics provides the ideal framework for rigorous quantum-classical or quantum-semiclassical treatments, as the spatially localized, trajectory-like nature of the quantum paths circumvents the need for mean-field-type assumptions. However, the number of system paths grows exponentially with the number of propagation steps. In addition, each path of the quantum system generally gives rise to a distinct classical solvent trajectory. This exponential proliferation of trajectories with propagation time is the quantum-classical manifestation of nonlocality.

A rigorous real-time quantum-classical path integral (QCPI) methodology has been developed, which converges to the stationary phase limit of the full path integral with respect to the degrees of freedom comprising the system's environment. 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. 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 result involves no assumptions or adjustable parameters beyond the classical trajectory treatment of the environment.

The methodology can be used to perform an all-atom simulation of nonadiabatic processes in condensed phase environments with unprecedented accuracy. Applications to charge transfer reactions in solution will be discussed.