

Quantum-Classical Path Integral: A Rigorous Methodology for Condensed-Phase Dynamics

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Abstract

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 temporal nonlocality or memory.

A quantum-classical path integral (QCPI) methodology has been developed. 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 dominant at high temperature/low-frequency solvents and/or when the system-environment interaction is weak. Within the QCPI framework, the memory associated with classical decoherence is removable. A parallel, nonlocal in time, “quantum decoherence process” is important at low temperatures, although the contribution of the classical decoherence mechanism continues to play the most prominent role. The classical decoherence is analogous to the treatment of light absorption via an oscillating dipole, while quantum decoherence is primarily associated with a component of spontaneous emission, which requires quantization of the radiation field. 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. Preliminary tests on dissipative two-level systems and atomistic simulations of charge transfer in solution suggest that the QCPI methodology is realistically applicable to many processes of chemical and biological interest.