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LECTURE

**“Modular Quantum and Rigorous Quantum-Classical
Real-Time Path Integral Methods”**

Prof. Nancy Makri

**Department of Chemistry,
University of Illinois at Urbana-Champaign,
Illinois, USA**

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

Nancy Makri

Department of Chemistry, University of Illinois at Urbana-Champaign

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 classical trajectories grows exponentially with the number of propagation steps. This exponential proliferation of trajectories with propagation time is the quantum-classical manifestation of nonlocality.

A rigorous quantum-classical path integral (QCPI) formulation of time-dependent observables has been developed, which combines a quantum mechanical description of a target “system” with a classical trajectory treatment of the system’s environment (which may include thousands of atoms). 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. 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, without the need for any assumptions (beyond the classical trajectory treatment of the environment) or adjustable parameters.

A modular path integral (MPI) methodology has recently been developed, 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 methodology has been used to perform all-mode, fully quantum mechanical simulations of exciton-vibration dynamics in linear and ring-shaped bacteriochlorophyll complexes, which contain up to 18 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.