QUANTUM-CLASSICAL PATH INTEGRAL SIMULATION OF CHARGE TRANSFER REACTIONS

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EXECUTIVE SUMMARY

Quantum mechanical calculations on condensed phase or biological systems are prohibitively expensive. Mixed quantum-classical approximations are highly efficient and attractive. However, conventional quantum-classical methods introduce major assumptions in the treatment of the interaction between quantum and classical degrees of freedom. We have developed a rigorous quantum-classical path integral (QCPI) methodology that is free of assumptions and that treats all interactions in full atomistic detail. Our QCPI simulation on Blue Waters of the ultrafast ferrocene–ferrocenium electron transfer reaction in liquid hexane, a standard in electrochemistry, yielded results of unprecedented accuracy and enabled the first quantitative demonstration of Gaussian behavior for a complex molecular solvent. Additional theoretical and algorithmic advances enabled simulation of reactions that span very different time scales. In particular, simulation of this process in a series of solvents with increasing polarity exemplified the interplay between electronic and molecular time scales and energetics and its effects on the kinetics of charge transfer reactions.

RESEARCH CHALLENGE

Tunneling, quantum dispersion, and phase interference play a subtle but very important role in many chemical and biological processes. Quantum mechanical simulations of dynamical processes in the condensed phase continue to be extremely challenging because quantum mechanics is a nonlocal theory, implying an exponentially growing cost with the number of interacting particles.

For many processes of interest, quantum mechanical effects are essential only in the treatment of a small number of particles (e.g., a proton, or a small number of electronic states associated with a charge transfer reaction). The remaining particles (solvent molecules or biological medium) can be adequately described via classical dynamics. Unfortunately, the traditional Schrödinger formulation of quantum mechanics (which is based on delocalized wave functions) is incompatible with Newtonian trajectories (which are local in space). In the Schrödinger formulation, the interaction between the quantum and classical partitions cannot be treated without resorting to severe approximations.

METHODS & CODES

The focus of our work has been the development of a rigorous quantum-classical formulation based on Feynman path integral formulation of quantum mechanics. The local nature of the Feynman paths leads naturally to quantum-classical treatments that are free of *ad hoc* assumptions. The quantum-classical path integral (QCPI) methodology that we developed is a rigorous quantum-classical formulation. However, the QCPI expression appears impractical, as it contains an astronomical number of terms. Several advances in the understanding of interference and decoherence have recently made the QCPI methodology practical for the simulation of condensed phase reactive processes.

QCPI treats the small system of interest by full quantum mechanics, while the effects of the environment are captured via standard molecular dynamics (MD) procedures. Two widely used MD packages, NAMD and LAMMPS, are used to yield trajectories subject to forces obtained using the coordinates of the charged particle, which are specified by the given path. The dynamics captured along a classical trajectory augments the Hamiltonian of the quantum system through a time-dependent term, which leads to level fluctuations and eventually to decoherence. The exponential proliferation of trajectories with propagation time is avoided through a tensor decomposition that exploits the memory-quenching effects of condensed phase environments. The QCPI algorithm is characterized by classical molecular dynamics scaling and is fully parallelizable.

RESULTS & IMPACT

The QCPI methodology has enabled the simulation of charge transfer reactions in solution with unprecedented accuracy. The dynamics of the prototypical ferrocene–ferrocenium electron transfer pair was studied in a series of organic solvents of increasing polarity. Our first simulation of this electron transfer reaction in liquid hexane employed 1,320 atoms interacting via CHARMM force fields. More recent work has studied the same reaction in a series of solvents of increasing polarity.

The all-atom QCPI simulations shed light on the complex interplay among molecular/solvent time scales, electronic couplings, and reorganization energy, particularly on the way that these effects determine the rate of the reaction, the nature (exponential or nonexponential) of the dynamics, and the validity of Gaussian response. They also demonstrate how the interference among quantum mechanical phases leads to decoherence, and
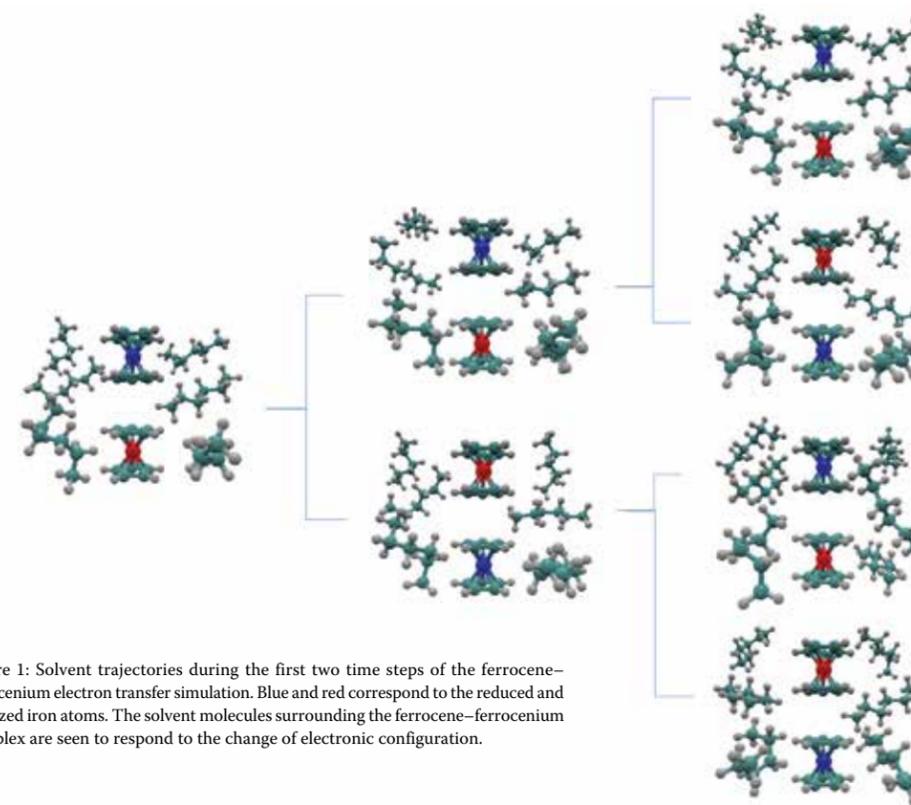

Figure 1: Solvent trajectories during the first two time steps of the ferrocene–ferrocenium electron transfer simulation. Blue and red correspond to the reduced and oxidized iron atoms. The solvent molecules surrounding the ferrocene–ferrocenium complex are seen to respond to the change of electronic configuration.

reveal substantial quantum delocalization of the otherwise classical solvent as a result of its interaction with the quantum electron transfer pair.

WHY BLUE WATERS

The QCPI formulation is well suited to a decomposition based on multi-level parallelism, and Blue Waters provides the ideal platform for its implementation. Specifically, the set of system paths is distributed across nodes; one processor within each node is assigned to the quantum mechanical calculations, while the other performs supporting trajectory computations. Moreover, because the trajectories are independent and generally relatively short, it is possible to assign a single trajectory to each core within a given processor while maintaining computational efficiency. This multi-level approach has the benefit of minimizing communication time while maximizing concurrent processing, since related classical and quantum-mechanical calculations are performed within the same node, where inter-processor communication should be much faster than if the information were more widely distributed.

PUBLICATIONS AND DATA SETS

Makri, N., Blip-summed quantum-classical path integral with cumulative quantum memory. *Reaction Rate Theory: Faraday Discussion*, 195 (2016), DOI: 10.1039/C6FD00142D.

Makri, N., Quantum-Classical Path Integral. *49th Midwest Theoretical Chemistry Conference* (Michigan State University, East Lansing, Mich., June 1–3, 2017).

Bose, A., and N. Makri, Quantum Mechanical Rate Calculations in Condensed Phase Reactions. *49th Midwest Theoretical Chemistry Conference* (Michigan State University, East Lansing, Mich., June 1–3, 2017).

Makri, N., Rigorous Quantum-Classical Path Integral Formulation of Real-Time Dynamics. *Workshop on Understanding Quantum Phenomena with Path Integrals: From Chemical Systems to Quantum Fluids and Solids* (ICTP, Trieste, Italy, July 3–7, 2017).

Makri, N., Interference, Decoherence, and Quantum-Classical Path Integral Simulations with Thousands of Atoms. *American Conference on Theoretical Chemistry* (Boston University, Boston, Mass., July 17–20, 2017).

Walters, P.L., and N. Makri., Quantum-classical path integral calculations of ferrocene-ferrocenium charge transfer in solution. *American Conference on Theoretical Chemistry* (Boston University, Boston, Mass., July 17–20, 2017).