

QUANTUM–CLASSICAL PATH INTEGRAL SIMULATION OF ELECTRONIC TRANSITIONS

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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 of the ultrafast ferrocene–ferrocenium electron transfer reaction in liquid hexane on Blue Waters yielded results of unprecedented accuracy and enabled the first quantitative demonstration of Gaussian behavior for a complex molecular solvent. Simulation of slow processes in sluggish solvents remains challenging however. The present phase of the work focuses on the blip decomposition of the QCPI code, which leads to a dramatic acceleration of the calculation. In addition, current work incorporates an efficient classical trajectory-based method for including zero-point energy effects in the solvent.

RESEARCH CHALLENGE

Classical molecular dynamics methods are inadequate for describing charge transfer and (more generally) electronic transitions. On the other hand, quantum mechanical simulations of dynamical processes in the condensed phase continue to be extremely challenging because quantum mechanics is a nonlocal theory requiring computational cost that scales exponentially 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 degrees of freedom (e.g., the coordinates of a proton or a small number of electronic states). 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

This work focuses on the further development and implementation of a rigorous quantum–classical methodology

based on Feynman’s path integral formulation of quantum mechanics [1]. The quantum–classical path integral (QCPI) methodology [2–6] takes advantage of the local nature of the Feynman paths to treat the interaction of a quantum mechanical subsystem with a classical environment without any *ad hoc* assumptions.

The QCPI expression appears impractical, however, because it contains an astronomical number of terms. Several advances in the understanding of interference and decoherence [7] 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 applied 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.

Current work implements a new acceleration of the code, which is based on the blip decomposition of the path integral [8–10]. This decomposition eliminates the vast majority of terms required, leading to a dramatic reduction of CPU time. Further, the QCPI code is augmented to allow the treatment of zero-point energy in the degrees of freedom treated via classical trajectories. This is important for molecular solvents, which contain high-frequency vibrations, as well as for processes in crystalline solids, in nanoscale structures such as carbon nanotubes, or in quantum fluids. The inclusion of zero-point energy is achieved by quantizing the thermal-phase space distribution using classical trajectories [11] or a new path integral-based approach [12] that does not suffer from a severe “sign problem” and thus converges rapidly.

RESULTS & IMPACT

The QCPI methodology enables the simulation of charge-transfer reactions in solution with unprecedented accuracy [13]. The ability to perform all-atom calculations with potential interactions treated in full detail leads to results of unparalleled

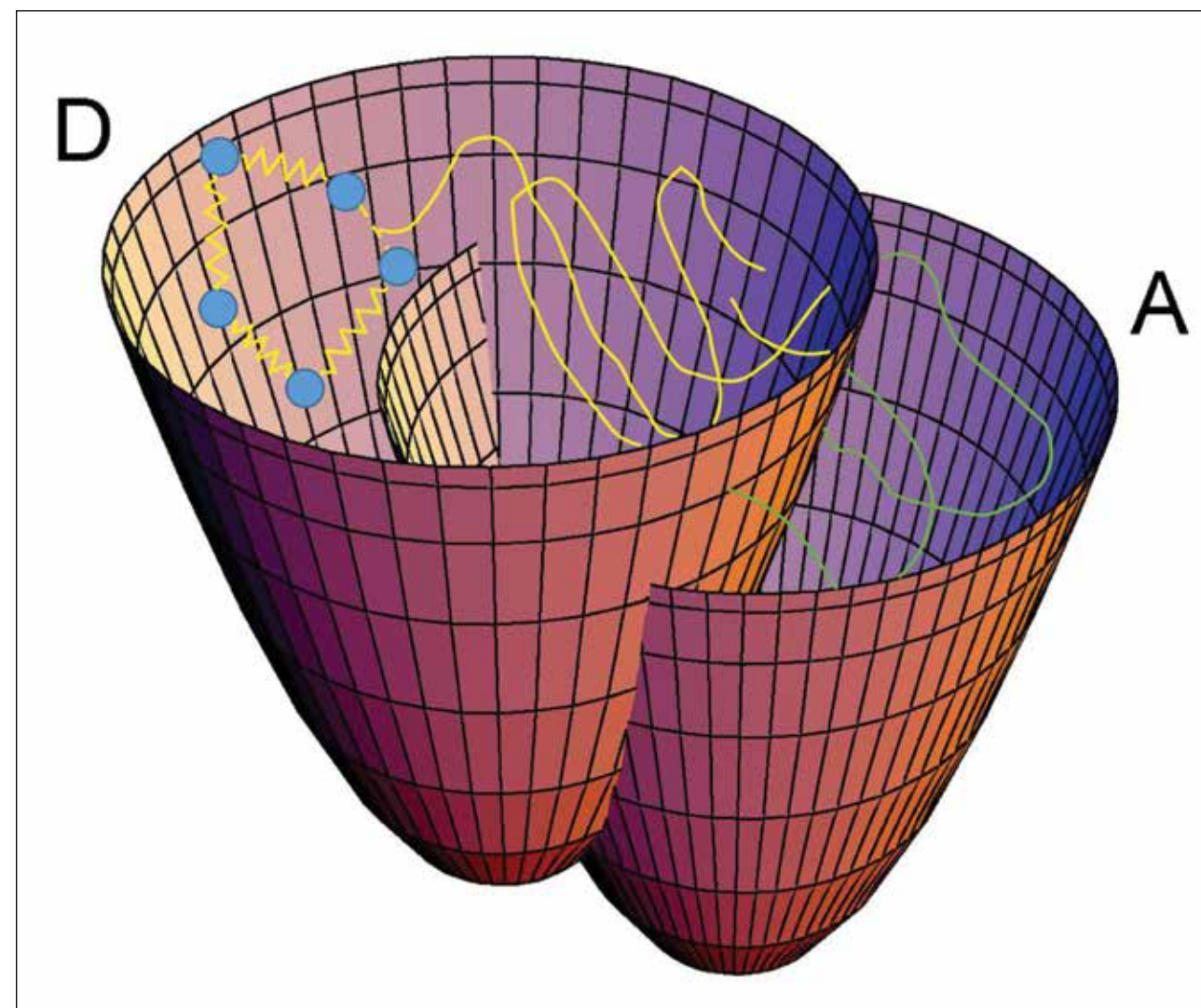


Figure 1: Schematic illustration of a classical trajectory with initial conditions sampled from a path integral-quantized phase space density and hopping between the donor and acceptor potential surfaces corresponding to the two charge states of an electron transfer pair according to instantaneous quantum states.

precision. These calculations shed light on the complex interplay among molecular/solvent timescales, electronic couplings, and reorganization energy [14], 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 the Gaussian response model. They also demonstrate how the interference among quantum mechanical phases leads to decoherence, and reveal substantial quantum delocalization of the otherwise classical solvent as a result of its interaction with the quantum electron transfer pair [13].

WHY BLUE WATERS

The QCPI formulation is well suited to a decomposition based on multilevel 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 relatively short, it is possible to assign a single trajectory to each core within a given processor while maintaining computational efficiency. This multilevel 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 interprocessor communication should be much faster than if the information were more widely distributed.