QUANTUM-CLASSICAL PATH INTEGRAL SIMULATION OF PROTON TRANSFER IN SOLUTION

Allocation: Illinois/60 Knh
PI: Nancy Makri[1]
Co-PI: Thomas C. Allen[1]

[1]University of Illinois at Urbana–Champaign

EXECUTIVE SUMMARY:

Quantum mechanical effects play an essential role in chemical and biological processes. Our group has recently developed a rigorous quantum–classical path integral (QCPI) methodology [1–3] in which one particle is treated by full quantum mechanics while the effects of the environment are captured via classical trajectories. The QCPI approach is free of *ad hoc* assumptions, allowing a faithful description of interference effects and leading to correct product distributions. Its implementation on Blue Waters provides a detailed picture of proton transfer in solution with unprecedented accuracy.

INTRODUCTION

Quantum mechanical effects are prominent in many chemical and biological processes, yet they present a major challenge to simulation. The main difficulty in the development of quantum mechanical simulation algorithms stems from the non-local nature of quantum mechanics, which leads to exponential scaling of computational effort with the number of interacting particles.

For many processes of interest, quantum mechanical effects are vital in the treatment of a small number of degrees of freedom (e.g., those corresponding to a transferring proton), while the remaining particles (solvent molecules or biological medium) could be adequately described via Newtonian dynamics. However, the traditional Schrödinger formulation of quantum mechanics (which is based on delocalized wave functions) does not lend itself to a combination with Newtonian trajectories (which are local in phase space) unless severe approximations are introduced.

METHODS & RESULTS

The Makri group has been pursuing rigorous quantum–classical formulations based on Feynman's path integral formulation of quantum mechanics [4]. The major appeal of this approach stems from the local, trajectory-like nature of the Feynman paths, which leads naturally to combined quantum–classical treatments that are free of approximations. Recent work has described a quantum–classical path integral (QCPI) methodology, which incorporates these ideas as well as several advances in the understanding of decoherence (loss of coherence) processes [5]. QCPI treats a small subsystem by full quantum mechanics, while the effects of the environment are captured via standard molecular dynamics (MD) procedures. Since all quantum interference effects and their quenching by the solvent are accounted for at the most detailed (non-averaged) level, QCPI leads to correct branching ratios and product distributions, allowing simulations of important chemical and biological processes with unprecedented accuracy.

The present project involves the first implementation of QCPI to the simulation of the proton transfer reaction for the phenol-amine complex in methyl chloride [6]. This system is considered a paradigm for proton transfer and has served as a model for many computational investigations using a variety of approximations. Accurate QCPI calculations are being performed at the full atomistic level, as well as within the linear response approximation, in which the solvent is replaced by an effective bath of harmonic oscillators. Thus, the results will also help quantify the validity of linear response on a realistic proton transfer system [7].

LAMMPS, a well-known MD package, has been combined with the QCPI software and adapted to yield trajectories subject to forces obtained with the proton coordinates specified by the given quantum path. The integrated phase along each of these trajectories, averaged with respect to the thermal distribution of the solvent, yields the desired density matrix and any corrections to more economical classical treatments.

We have simulated the dynamics of the transferring particle and obtained the time evolution of the state populations. Extensive tests are currently being performed to verify convergence. The transfer process was dominated by solvent effects, and some high-frequency vibrations of the solvent molecules were strongly coupled to the transferring particle. In addition, strongly coupled sluggish solvent modes affected the proton transfer dynamics via a quantum mechanical decoherence mechanism. The QCPI calculations quantified the significance of these contributions.

Upon completion of the present phase of the work, the QCPI calculations will provide quantitative results for the kinetics of the proton transfer process, along with a detailed understanding of the underlying mechanism(s). This will include the time scale of correlations and decoherence, the distinct roles of fast and sluggish solvent motions and associated quantum effects, as well as the importance of nonlinear solvent effects on the dynamics.

WHY BLUE WATERS?

Implementation of the QCPI methodology requires integration of a large number of classical trajectories from each initial condition sampled from the solvent density. Each of these trajectories interacts with a Feynman path of the quantum subsystem, augmenting the dynamics of the quantum particle via a phase. By exploiting the very mechanism of decoherence, we can circumvent the exponential proliferation of the number of trajectories with propagation time. Still, QCPI calculations on these systems are extremely demanding, and these calculations are not feasible on conventional computational platforms.

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.