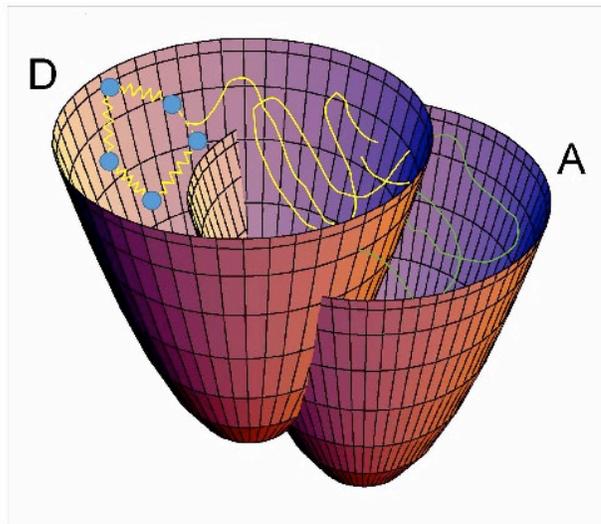




Allocation: Illinois/75 Knh
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Schematic illustration of a classical trajectory with initial conditions sampled from a path integral-quantized phase space density and hopping between the donor and acceptor potential surfaces corresponding to the two charge states of an electron transfer pair according to instantaneous quantum states.

QUANTUM-CLASSICAL PATH INTEGRAL SIMULATION OF ELECTRONIC TRANSITIONS

Research Challenge

Classical molecular dynamics methods are inadequate for describing charge transfer and, more generally, electronic transitions. On the other hand, the cost of quantum mechanical calculations scales exponentially with the number of interacting particles. We have introduced a rigorous quantum–classical path integral (QCPI) formulation, which treats the interaction between quantum and classical degrees of freedom in full atomistic detail without assumptions. However, the QCPI expression involves an astronomical number of terms and thus appears impractical.

Methods & Codes

Several advances in the understanding of interference and decoherence have made the QCPI methodology practical for the simulation of condensed-phase reactive processes. Current work implements a new acceleration of the code, which is based on a decomposition of the path integral that leads to a dramatic reduction of CPU time. Further, the QCPI code is augmented to allow the treatment of zero-point energy in the classical degrees of freedom.

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. 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 multilevel approach has the benefit of minimizing communication time while maximizing concurrent processing.

Results & Impact

The QCPI methodology enables the simulation of charge-transfer reactions in solution with unprecedented accuracy. The ability to perform all-atom calculations with potential interactions treated in full detail leads to results of unparalleled precision. These calculations shed light on the complex interplay among molecular/solvent timescales, electronic couplings, and reorganization energy.