

Path Integral Methods for Nonadiabatic Dynamics: Quantum Transitions from Classical Trajectories

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In the condensed phase, the thermal transfer of a distinguishable electron in either the adiabatic or nonadiabatic regime is well described by path integral methods like Ring Polymer Molecular Dynamics (RPMD) that employ classical molecular dynamics trajectories to capture quantum effects. However, both the simulation of multi-electron, multi-state thermal electron transfer reactions and the simulation of photo-initiated excited state dynamics in complex chemical systems remains a significant challenge.

In this talk, we first introduce a simple extension of RPMD to multi-level systems, an approach that combines the state-space path integral formulation of transition state theory with Mean-Field (MF)-RPMD. Interestingly, although conventional wisdom suggests mean field dynamics are inaccurate in the weak-coupling regime, we achieve quantitative accuracy in rate calculations for a wide range of nonadiabatic electron transfer systems. However, this approach does not include explicit electronic state variables and cannot be used to simulate population dynamics on an excited electronic state manifold.

In the second part of the talk, we introduce a new method, Mapping-Variable (MV)-RPMD, that explicitly incorporates electronic state variables while retaining all the favourable features of RPMD. We numerically demonstrate the accuracy of this method in simulations of photo-initiated excited state dynamics in adiabatic and nonadiabatic model systems and we discuss systematically improving the accuracy of our approximate dynamics.