

Path Integral Methods to Compute Electron Transfer Reaction Rates

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In this work, Marcus theory is extended to include quantum effects in the electron transfer processes. It is well-known that the isomorphism between quantum statistical mechanics of particles and classical statistical mechanics of ring-polymer beads joined together by harmonic springs can be employed to study this quantum effects. Several discretization schemes for the ring-polymer potential is analyzed to study the chemical reaction rates in the deep tunneling regime in the nonadiabatic limit. The instanton describing this rate is composed of a trajectory on reactant surface and another on product surface [1]. This imaginary time orbit has a period of $\beta\hbar$. Previous work [2] has employed discretization scheme where the orbit is divided into N segments, with N_0 beads laying on the reactant surface and N_1 beads on the product surface. In this work, different discretization schemes of the ring-polymer potential is proposed, in which the imaginary time τ of the instanton trajectory is identified as a continuous variable. The rate coefficient is obtained by finding a suitable dividing surface that makes the probability distribution of reaction independent of τ . It is demonstrated that this sort of discretization scheme gives good estimate of rates for both harmonic and linear systems in one-dimension. In fact, as $N \rightarrow \infty$, the rate constant for linear system is found to be exact. The goal is to extend this approach to describe the chemical reaction rates in complex systems where potential energy surfaces cross at multiple points.

[1] P.G. Wolynes, J. Chem. Phys. **87**, 6559 (1987).

[2] J. O. Richardson, J. Chem. Phys. **143**, 134116 (2015).