RPMD: A Software Package for Computing Chemical Reaction Rates Using Ring Polymer Molecular Dynamics

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Ring polymer molecular dynamics (RPMD) has shown considerable promise as a method for including quantum mechanical (zero-point energy and tunneling) effects in calculations of chemical reaction rates [1-3]. RPMD reaction rate theory exploits the isomorphism between the quantum statistical mechanics of a single particle and the classical statistical mechanics of a fictitious ring polymer; it is essentially a classical rate theory in an extended phase space, and is therefore directly applicable to complex chemical reactions in their full dimensionality.

In this work, we present a new general-purpose software package for the computation of chemical reaction rates for arbitrary gas-phase bimolecular reactions using RPMD simulations [4]. The user supplies an input file describing the reactive system and a function for evaluating the external potential of this system. The specification of the transition state dividing surface – which only affects the rate of convergence of the RPMD simulations, not the final computed rate coefficient – has been generalized to work for a wide variety of reaction families. If no external potential is available, the software can generate a suitable potential via on-the-fly *ab initio* calculations using an external quantum chemistry package. The core of the software is written in Fortran 90, making it very efficient; this is wrapped in a Python layer for a more user-friendly, scriptable interface. The RPMD software is demonstrated for a variety of small-molecule hydrogen abstraction reactions, including systems for which quantum reactive scattering calculations are currently infeasible.

References

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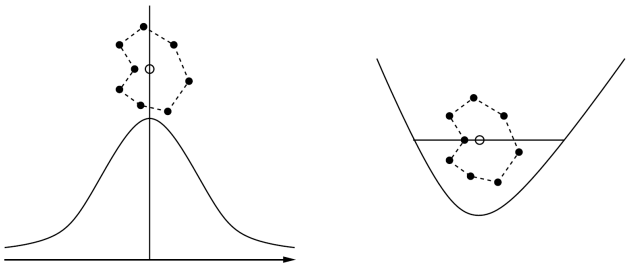

Fig. 1. Ring-polymer molecular dynamics includes the quantum mechanical effects of tunneling and zero-point energy in calculations of chemical reaction rates.