

Chemical Reaction Rates from Ring Polymer Molecular Dynamics

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There is considerable current interest in the inclusion of quantum mechanical (zero point energy and tunneling) effects in the calculation of chemical reaction rates. The importance of these effects is well known: changes in zero point energy between the reactants and the transition state are responsible for the observed kinetic isotope effects in a wide variety of reactions, and tunneling can increase the rate of an activated proton transfer reaction at low temperatures by several orders of magnitude. The exact inclusion of these effects in calculations of chemical reaction rates is still however a very challenging task, because the computational effort that is needed to solve the reactive scattering Schrödinger equation increases exponentially with the number of atoms in the reaction.

A number of approximate methods have been proposed to overcome this problem and to provide a practical way to include these effects in reaction rate calculations. One of the most promising of these is recently developed ring polymer molecular dynamics (RPMD) model [1-3]. This model is based on imaginary time Feynman path integration and exploits the isomorphism between the quantum statistical mechanics of a single particle and the classical statistical mechanics of a fictitious ring polymer. It leads to a reaction rate theory that is essentially a classical rate theory in an extended (n -bead imaginary time path integral) phase space, and it is therefore directly applicable to complex chemical reactions in their full dimensionality.

In this work, we develop an efficient computational procedure for calculating the rates of bimolecular chemical reactions in the gas phase within the RPMD approximation. A key feature of the procedure is that it does not require that one calculate the absolute quantum mechanical partition function of the reactants or the transition state: The rate coefficient only depends on the ratio of these two partition functions which can be obtained from a thermodynamic integration along a suitable reaction coordinate. The procedure is illustrated with applications to several three-dimensional three-atomic reactions and the six-atomic H+CH₄ reaction, for which well-converged quantum reactive scattering results are available for comparison, as well as to several more complex reactions, for which exact reactive scattering calculations are impossible. The ring polymer rate coefficients agree with the exact results at high temperatures and are within a factor of 2-3 of the exact results at temperatures in the deep quantum tunneling regime, where the classical rate coefficients are too small by several orders of magnitude. This is certainly good enough to encourage future applications of RPMD to complex chemical reactions.

References

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