Quantum and Semiclassical Instanton Theories for Chemical Reaction Rates

Christophe L. Vaillant[a], Manish J. Thapa[b], Jeremy O. Richardson[b], and Jiri Vaníček[a]

[a] *École Polytechnique Fédérale de Lausanne,* [b] *ETH Zurich*
christophe.vaillant@epfl.ch

We present a derivation of the quantum and semiclassical instanton expressions for the calculation of reaction rates. Starting from the exact expression for the reaction rate in terms of the flux-flux time correlation function, we use the steepest-descent approximation to obtain the quantum instanton expression, complete with the prescription for finding the optimal dividing surfaces. From the resulting quantum instanton expression, we semiclassically show that two paths contribute to the quantum instanton result, the standard semiclassical periodic orbit and a path which arises from the scattering solutions below the energies of the reactants. If we retain only the periodic orbit, we show that a semiclassical approximation to the quantum instanton results in the well-known semiclassical instanton expression. We show numerically that the quantum instanton prediction for the rate in a 1D asymmetric Eckart barrier potential breaks down severely for large asymmetries due to the contributions of the non-periodic paths. In contrast, the semiclassical instanton result remains accurate below the cross-over temperature. By neglecting the eigenfunctions below the reactant energies, we show that the quantum instanton method improves dramatically in accuracy. The result paves the way for a highly accurate version of the quantum instanton, which will then be a powerful method for calculating reaction rates in severely anharmonic multidimensional systems where the semiclassical instanton may not perform well.