

# Semiclassical reaction rate constant calculations: investigation of anharmonicity and quantum effects

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Semiclassical transition state theory (SCTST) is a relatively simple method for the computation from first principles of reactive rate constants, including quantum effects while accounting for anharmonicity and the coupling between reactive and bound modes.[1-3] In this talk, I will illustrate how we have developed this technique for practical applications[4-7] involving the study of phenomena like kinetic isotope effects, heavy atom tunneling, and elusive conformer lifetimes.[5,6,8]

While many approximate reaction rate theories reduce to the parabolic barrier estimate for the tunneling correction at high temperatures, SCTST, which is based on vibrational perturbation theory (VPT2), gives the exact limit when one considers the leading order term in an expansion of powers of  $\hbar^2$  of the tunneling transmission coefficient.[9-11] Our investigation of molecular reactive systems assesses the importance of the non-linear corrections to the parabolic barrier estimate of the transmission coefficient. When the reaction barrier is significantly anharmonic, it is mandatory to account for non-linear corrections; otherwise, the transmission coefficient overlooks a high-temperature regime which may be dominated by quantum reflection.[12] These results highlight the importance of having a theory such as SCTST that includes the correct high-temperature limit.

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