Computing Tunneling Probabilities based on VPT4-SCTST and Siegert eigenvalues for select model systems

Prateek Goel[1] and John Stanton[1]

[1]University of Florida, Quantum Theory Project, Gainesville, FL 32611-8435

Semi-classical transition state theory (SCTST) in conjunction with second-order vibrational perturbation theory (VPT2) has become a successful tool to compute tunneling probabilities and micro-canonical rate constants for realistic multidimensional systems. Improvements obtained by moving to fourth order vibrational perturbation theory (VPT4) has received less attention in comparison, mostly because of significantly increased computational demand. Though the practical application of VPT4-SCTST remains questionable for realistic systems, an exploration of its properties and usefulness warrants an examination nonetheless. In this work, we study a variety of low-dimensional model systems in order to compute the tunneling probabilities and cumulative reaction probabilities (CRP) based on VPT4-SCTST. Comparison to exact results (analytical when available, numerical otherwise) will be made throughout. In the second part of this work, we also explore the idea of using Siegert eigenvalues associated with the transition state to compute numerically exact as well as semi-classically exact CRP (as originally proposed by Seideman and Miller) for some of these model systems. This method has its own merits and has received little to no attention in the past.