

Nonadiabatic quantum transition-state theory in the golden-rule limit

M. J. Thapa, W. Fang, and J. O. Richardson

*Laboratory of Physical Chemistry, ETH Zürich,
Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland*

In our work, we propose a path-integral method to study non-adiabatic reactions involving two electronic states. Such a reaction cannot be studied using the Born-Oppenheimer approximation. We have recently developed a new quantum transition-state theory to compute reaction rates in multi-dimensional systems in the Fermi's golden-rule regime [1]. Our golden-rule quantum transition-state theory (GR-QTST) is exact in the classical limit for all systems. GR-QTST is related to instanton theory [2], and hence gives excellent estimates of rates in both harmonic and anharmonic model systems even in the deep tunneling regime. Our theory relies on constrained path-integral sampling of dominant energy-conserving paths similar to an instanton. It is applicable to treat chemical reactions in solution, in which the potential energy surfaces exhibit multiple transition states. We show that a related theory known as Wolynes theory [3] can overestimate the reaction rates by multiple orders of magnitude, even for simple one and two-dimensional model systems with two transition states. The rates computed using GR-QTST show excellent agreement with the exact calculations in these systems. Accordingly, our results show that GR-QTST offers a simple approach to accurately calculate electron-transfer rates in complex multi-dimensional molecular systems using a path-integral sampling.

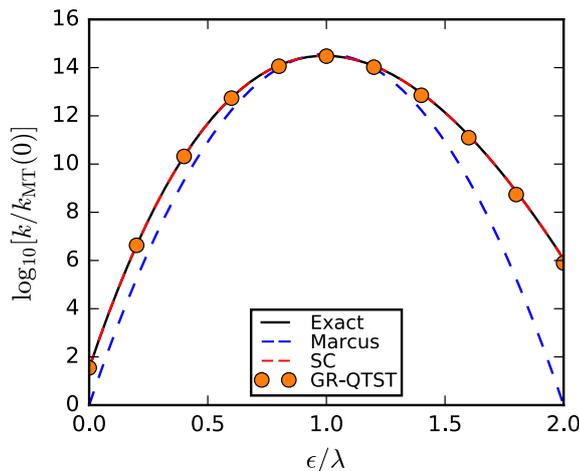


FIG. 1: The plots show the rate constants computed for 8 dimensional system-bath model as a function of bias, ϵ , using various methods. $k_{\text{MT}}(0)$ is the classical Marcus rate at $\epsilon = 0$. 100 ring-polymer beads were used to compute the GR-QTST rates at room temperature. Comparison to rates computed using semi-classical (SC) instanton and exact Fermi's golden-rule methods shows that GR-QTST is very accurate in predicting the electron-transfer rates.

[1] M. J. Thapa, W. Fang and J. O. Richardson. *J. Chem. Phys.* 150, 104107 (2019).

[2] J. O. Richardson, Rainer Bauer and Michael Thoss *J. Chem. Phys.* 143, 134115 (2015).

[3] P. G. Wolynes *J. Chem. Phys.* 87, 6559 (1987).