

Nonadiabatic quantum transition-state theory

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We propose a new quantum transition-state theory (GR-QTST) for calculating Fermi's golden-rule rates in complex multidimensional systems [1]. This method is able to account for the nuclear quantum effects of delocalization, zero-point energy, and tunnelling in an electron-transfer reaction. It is related to instanton theory [2] but can be computed by path-integral sampling and is thus applicable to treat molecular reactions in solution. A constraint functional based on energy conservation is introduced which ensures that the dominant paths contributing to the reaction rate are sampled. We prove that the theory gives exact results for a system of crossed linear potentials and show numerically that it is also accurate for anharmonic systems. It is also seen to perform well for multidimensional spin-boson models, where it even gives good predictions for rates in the Marcus inverted regime.

We demonstrate that for systems exhibiting two or more transition states, rates computed using Wolynes theory [3] can be overestimated by orders of magnitude, whereas the GR-QTST predictions are numerically accurate. This is the case both at low temperature, where nuclear tunnelling makes a considerable contribution, and also in the classical limit, where only GR-QTST rigorously tends to the correct result. Analysis shows that the saddle-point approximation employed by Wolynes theory is not valid in this case and that the method is unphysically dominated by paths located far from the correct transition states. The energy constraint employed by GR-QTST resolves this problem. For a system with strong anharmonicity, where the semiclassical approximations of instanton theory are not valid, the GR-QTST method, which samples configurations around the instanton pathway, is seen to give accurate results. These promising results indicate that the GR-QTST method could be an efficient and accurate approach for simulating electron-transfer reactions in complex molecular systems.

References

1. M. J. Thapa, W. Fang and J. O. Richardson, *J. Chem. Phys.* **150** (2019), 104107.
2. J. O. Richardson, *J. Chem. Phys.* **148** (2018), 200901.
3. P. G. Wolynes, *J. Chem. Phys.* **87** (1987), 6559.