

Microcanonical Instanton Rate Theory Applied to Molecular Reactions

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Instantons describe the tunneling pathways that dominate molecular dynamics at low temperatures [1]. Instantons provide a link between the classical and quantum mechanical descriptions of chemical kinetics in what is called semi-classical transition state theory (SCTST) [2]. This theory is useful because it allows for efficient computation of rate constants in systems where the full quantum description would be too demanding. The new formulation of SCTST gives more accurate dynamics near the cross-over temperature, which was the main failing of the initial model [1]. Our work aims to use this new SCTST model to calculate cumulative reaction probabilities $P(E)$ for molecular systems and to identify thermal rates $k(T)$ that are valid at all temperatures.

We apply this formulation to the collinear $H + H_2$ chemical reaction which has a well-characterized potential energy surface (PES). Quantum mechanical rate constants for this BKMP surface provide exact solutions for which we can compare our results. The new SCTST method gives rate constants that are within an order of magnitude of the quantum results and do not diverge at the cross-over temperature.

Future work will consist of extending this microcanonical instanton method to calculate thermal rates for interesting atmospheric chemical reactions.

[1] J. Richardson, Faraday Discuss. **195**, 49 (2016).

[2] W. H. Miller, J. Chem. Phys. **62**, 1899 (1975).