Perturbatively corrected ring-polymer instanton theory for accurate tunneling splittings

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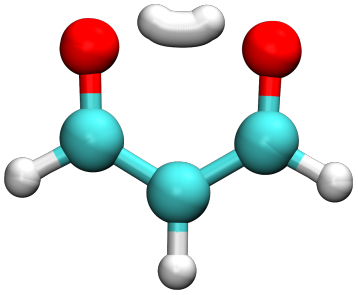
Ring-polymer instanton theory offers a method for effectively computing tunneling splittings. Its mechanism involves computing the leading-order term in the asymptotic expansion of the tunnelling splitting with respect to $\hbar$. We present a method for computing perturbative corrections to this leading-order term (RPI+PC). This technique utilises the knowledge of third- and fourth-order derivatives of the PES along the instanton trajectory to dramatically improve accuracy while preserving computational efficiency. We apply this method to examine the proton and deuterium transfer processes in malonaldehyde and its deuterated isotopomer, respectively. Our perturbative correction demonstrates a reduction in the error from -11% to 2% for proton transfer, with even more favorable results for deuterium. Our accuracy is thus greater than that achieved by diffusion Monte Carlo and path-integral molecular dynamics. Our approach is also simpler to use and computationally more efficient.

This contribution presents the results and methodology outlined in [1] with emphasis on the computational aspect.



[1] Joseph E. Lawrence, Jindřich Dušek, Jeremy O. Richardson; Perturbatively corrected ring-polymer instanton theory for accurate tunneling splittings. J. Chem. Phys. 7 July 2023; 159 (1): 014111. https://doi.org/10.1063/5.0155579