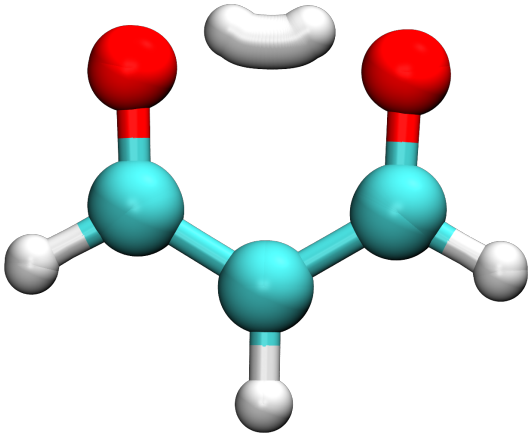
Calculation of accurate tunneling splittings

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We introduce a simple-to-use method for calculating accurate tunneling splittings in molecular systems based on finding the dominant tunneling path (known as the instanton [1]). This can be done straightforwardly using standard optimisation techniques in combination with ab-initio electronic packages [2-3]. In this work we demonstrate how one can go beyond standard instanton theory to include additional anharmonic effects by adding perturbative corrections. This leads to significant improvements both in systems with low barriers and in systems with anharmonic modes. We demonstrate the applicability of our approach to molecular systems by computing the tunneling splitting in full-dimensional malonaldehyde and a deuterated derivative. Comparing to both experiment [4] and recent quantum-mechanical benchmark results [5], we find that our perturbative correction reduces the error from −11% to 2% for hydrogen transfer and performs even better for the deuterated case. This makes our approach more accurate than previous calculations using diffusion Monte Carlo [6] and path-integral molecular dynamics [7-8], while being more computationally efficient and simpler to use by non-experts.



[1] Jeremy O. Richardson, Stuart C. Althorpe, *J. Chem. Phys.,* **2011,** 134, 054109.
[2] Jeremy O. Richardson, *Int. Rev. Phys. Chem.,* **2018,** 37, 171-216.
[3] Adrian N. Beyer, Jeremy O. Richardson, Peter J. Knowles, Judith Rommel, Stuart C. Althorpe, *J. Phys. Chem. Lett.,* **2016,** 7, 4374–4379.
[4] Takeshi Baba, Takehiko Tanaka, Isamu Morino, Koichi M. T. Yamada, Keiichi Tanaka, *J. Chem. Phys.,* **1999,** 110, 4131–4133.
[5] David Lauvergnat, André Nauts, **2023**, 10.26434/chemrxiv-2023-l7npc.
[6] Wataru Mizukami, Scott Habershon, David P. Tew, *J. Chem. Phys.,* **2014,** 141, 144310.
[7] Edit Mátyus, David J. Wales, Stuart C. Althorpe, *J. Chem. Phys.,* **2016,** 144, 114108.
[8] Cristophe L. Vaillant, David J. Wales, Stuart C. Althorpe, *J. Chem. Phys.,* **2018,** 148, 234102.