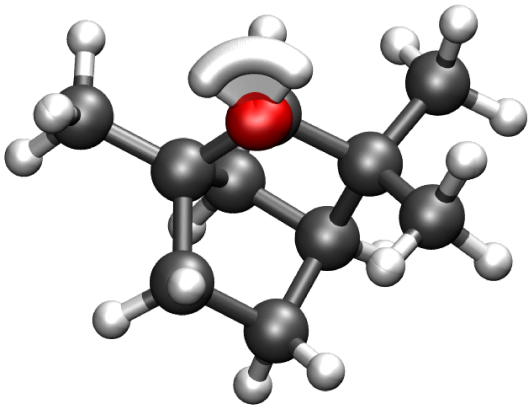
Tunnelling in Complex Molecular Systems: Bridging Theory and Experiment

G. Laude[1], J. O. Richardson[1]*

[1]Department of Chemistry and Applied Biosciences, ETH Zurich

Quantum tunnelling is an ubiquitous phenomenon, relevant to many fields such as astrochemistry and biochemistry. It can for instance, result in larger-than-expected reaction rates, or a splitting of energy levels. However, unfavourable scaling of computational times with respect to system size hamper many attempts at determining tunnelling effects. With instanton theory, [1,2] one will only have to locate an optimal tunnelling pathway (called the instanton) to determine reaction rates and tunnelling splittings. The instanton also provides us greater insight on the tunnelling process by giving us a visual picture, as well as identifying the contribution each atom makes to the tunnelling process. In combination with machine-learning approaches, [3,4] one can choose to employ a higher level of electronic structure theory at a reduced computational cost, thereby increasing the accuracy of the calculations even further. We have now extended instanton theory such that we are able to evaluate tunnelling splittings in asymmetric systems, [5–7] and in vibrationally-excited states. [8] We apply our method to a wide array of complex molecular systems such as malonaldehyde, tropolone, α−fenchol and the vinyl radical, for which our results compare favourably with experiments.



[1] J. O. Richardson, *Int. Rev. Phys. Chem.* **2018**, 37, 171.
[2] J. O. Richardson, *J. Chem. Phys.* **2018**, 148, 200901.
[3] G. Laude, D. Calderini, D. P. Tew and J. O. Richardson, *Faraday Discuss*. **2018**, 212, 237.
[4] G. Laude, D. Calderini, R. Welsch and J. O. Richardson, *Phys. Chem. Chem. Phys.* **2020**, 22, 16843.
[5] E. Jahr*, G. Laude* and J. O. Richardson, *J. Chem. Phys.* **2020**, 153, 094101.
[6] M. Fiechter*, G. Laude* and J. O. Richardson, **2023**, *in preparation*.
[7] A. Nandi, G. Laude, S. S. Khire, N. D. Gurav, C. Qu, R. Conte, Q. Yu, S. Li, P. L. Houston, S. R. Gadre, J. O. Richardson, F. A. Evangelista and J. M. Bowman, *J. Am. Chem. Soc.* **2023**, 145, 9655.
[8] G. Laude and J. O. Richardson, **2023**, *in preparation*.