Instantons and ring polymers

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1. Reaction tunnelling rates

This talk will explain how semi-classical instanton theory can be formulated very simply in terms of ring-polymers[1-4], to yield the dominant 'instanton' tunneling path through a potential barrier. Harmonic fluctuations around this path yield an expression for the instanton tunneling rate, which can be shown[3] to be identical to the instanton rate originally derived by Miller[5] from the exact flux-side time-correlation function. The approach also explains why the simulation technique of Ring Polymer Molecular Dynamics (RPMD)[6] gives realistic predictions of quantum rates in the deep-tunnelling regime.

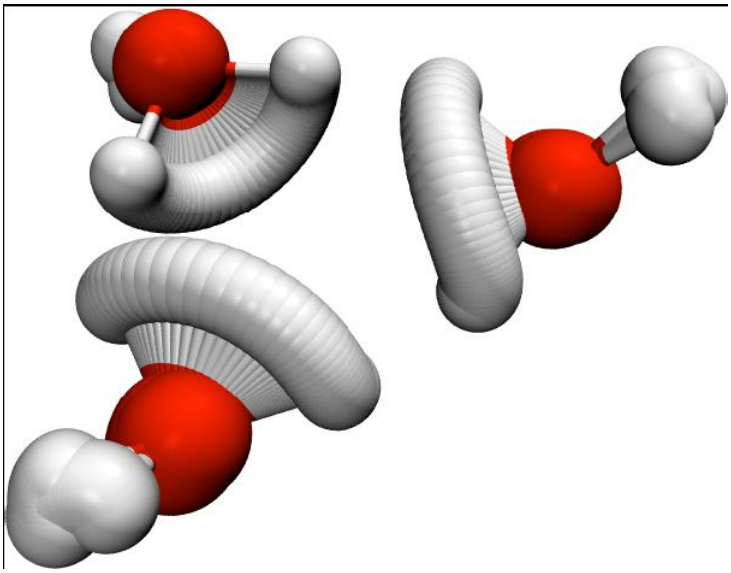

Fig 1 Instanton describing a tunneling pathway in the water trimer.

2. Tunnelling splitting patterns in water clusters

Recently, we have shown that the ring-polymer instanton approach can be extended to calculate tunneling splittings, and that it is a practical method for computing the splitting patterns in water clusters. We describe recent calculations of splitting patterns in clusters ranging from the dimer to the nonamer, and make comparisons

with experimental spectra.

Acknowledgements

This work was funded by the UK Engineering and Physical Sciences Research Council.

References:

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