Quantum dynamics, tunnelling and electron transfer beyond Marcus theory

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The quantum mechanical tunnelling effect can be rigorously studied using a semiclassical approach known as instanton theory [1, 2]. The instanton is defined as the optimal tunnelling pathway through the reaction barrier and can be used to obtain low-temperature rates in polyatomic chemical reactions and provide details on the mechanisms involved.

The ring-polymer instanton method can also be used to calculate tunnelling splittings in molecular clusters [3]. A recent joint experimental and theoretical study of the water hexamer prism [4] has discovered unexpectedly complex tunnelling pathways showing cooperative behaviour of the water molecules. One of these leads to the simultaneous breaking of two hydrogen bonds (Figure 1).

An extension of the instanton method to treating nuclear tunnelling during an electron transfer reaction leads to a quantum generalization of Marcus theory [5]. The new approach however also applies to reactions with anharmonic free-energy surfaces.

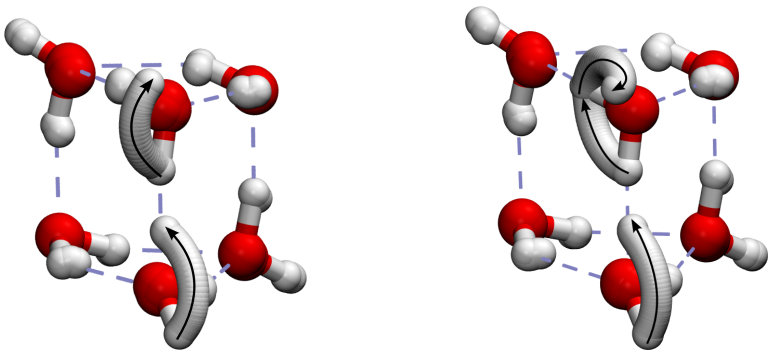

Figure 1: The two feasible tunnelling pathways in the water hexamer prism involving cooperative motion of the water molecules. The first rearrangement breaks only one hydrogen bond whereas the second is able to break two simultaneously.

References

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