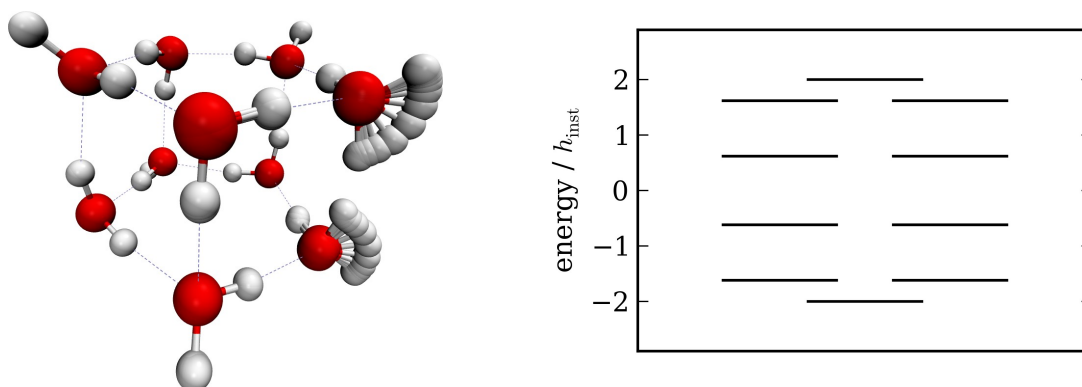


The Hows and Whys of Multidimensional Instantons: Tunnelling effects in gas- and condensed-phase systems

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We describe a simple method for locating semiclassical instantons in multidimensional systems (figure left) [1]. Using steepest-descent integration of a discretized form of Feynman's path integral, these instantons can be used to compute chemical reaction rates in the deep-tunnelling regime and the energy-level splitting pattern (figure right) resulting from tunnelling between degenerate potential wells [2]. Applications are shown for systems in full dimensionality using ab initio potential-energy surfaces including proton-transfers and water cluster rearrangements [3,4].

The discretized instantons are closely related to the method of ring-polymer molecular dynamics [5], which explains why the latter is able to obtain reaction rates so reliably in the deep-tunnelling regime [1]. An extension to simulate nonadiabatic quantum dynamics using the mapping representation [6] in ring-polymer form is discussed.

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