QUANTUM TUNNELLING IN MOLECULES AND CLUSTERS

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Quantum tunnelling leaves fingerprints in the high-resolution spectra of molecules and clusters. This provides a serious challenge for theory to predict and interpret the spectrum. I will discuss recent progress in methods based on path-integral formalism of quantum mechanics, which leads to practical methods for simulating tunnelling even in reasonably large molecules. Instanton theory is based on a semiclassical approximation, from which one obtains a powerful approach requiring no more than a single classical trajectory.[1] The method has been used to elucidate the tunnelling splitting patterns in many molecules including water clusters.[2] More recently, we have developed perturbative corrections to instanton theory which can account for anharmonicity and correct the results in the case of low barriers.[3] For extremely anharmonic systems such as methyl rotations, a nonperturbative solution is required. We have therefore developed a path-integral molecular dynamics approach, which in principle gives identical results to an exact solution of the Schrödinger equation and employs an "Eckart spring" to rigorously project out the ground rotational state. However, our approach does not require wavefunctions and thus avoids the curse of dimensionality of traditional quantum-mechanical approaches, but instead scales linearly with system size.[4]

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