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Barrier compression and tunneling in enzyme catalysed reactions

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Nuclear quantum mechanical tunneling is important in enzyme-catalysed H-transfer reactions. This viewpoint has arisen after a number of experimental studies have described enzymatic reactions with kinetic isotope effects that are significantly larger than the semi-classical limit. Other experimental evidence for tunneling, and the potential role of promoting vibrations that transiently compress the reaction barrier, is more indirect, being derived from the interpretation of e.g. mutational analyses of enzyme systems and temperature perturbation studies of reaction rates/kinetic isotope effects. Computational simulations have, in some cases, determined exalted kinetic isotope effects and tunneling contributions, and identified putative promoting vibrations. In this presentation, we present the available evidence – both experimental and computational – for environmentally-coupled H-tunneling in several enzyme systems, from our recent work on redox enzyme systems. We then consider the relative importance of tunneling contributions to these reactions. We find that the tunneling contribution to these reactions confers a rate enhancement of approx. 1000-fold. Without tunneling, a 1000-fold reduction in activity would seriously impair cellular metabolism. We infer that tunneling is crucial to host organism viability thereby emphasising the general importance of tunneling in biology.