Quantum Tunnelling in Chemical Reactions

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This talk will describe recent theoretical and computational work in our research group on quantum tunnelling in chemical reactions.

Quantum tunnelling can have a major effect on the rate constants for hydrogen atom transfer reactions. The accurate calculation of tunnelling effects and the computation of rate constants remains a major challenge. This talk will describe research from our own group on predicting tunnelling effects in bimolecular and unimolecular reactions.

A method for predicting rate constants will be outlined which brings together quantum dynamical and quantum chemistry techniques in an efficient reduced dimensionality approach. Applications to the hydrogen atom transfer and exchange reactions of hydrocarbons will be described.

Secondly, recent developments in Semiclassical Transition State Theory (SCTST) [1] will be discussed. This will include the development and testing of a SCTST reduced dimensionality procedure with our benchmark quantum dynamical results. Application of SCTST to the unimolecular decay of Criegee intermediates will be described. In addition, an application to the decomposition mechanism of the highly toxic nerve agents sarin and VX will be presented.

The calculations described in the talk were performed by Xiao Shan, Sam Greene and Tim Burd from our research group.

[1] Miller, W. H. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 40.