

Tunnelling in polyatomic chemical reactions

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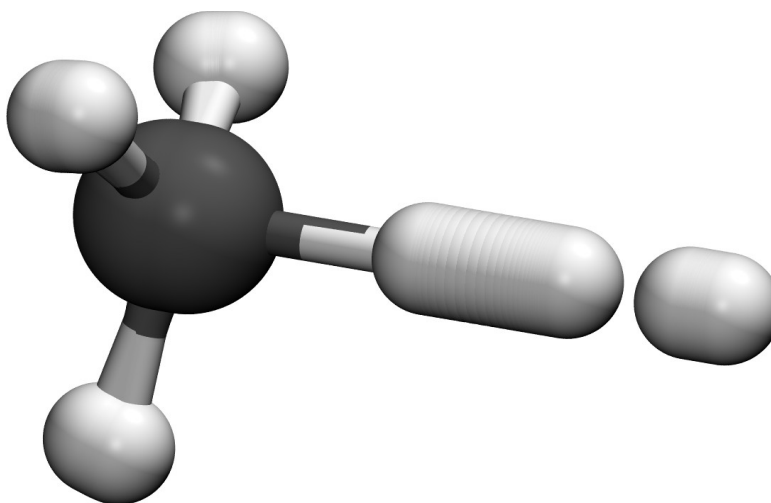
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The quantum mechanical tunnelling effect can be rigorously studied using a semiclassical approach known as instanton theory (1,2). The theory can be used to obtain efficiently low-temperature rates in polyatomic chemical reactions and provide details on the mechanisms involved. Simple arguments will be used to show that the instanton is defined as the optimal tunnelling pathway from reactants to products. The rate predicted by instanton theory is therefore expected to be more accurate than that predicted by tunnelling corrections based on alternative tunnelling pathways.

The numerical application of the method is similar to that of transition-state theory and algorithms for locating transition states can be applied directly to locate instantons. Examples will be given for reactive collisions where the calculations have been coupled to an on-the-fly evaluation of the potential energy surface. In this way, the method has the potential to make a high impact in the study of gas-phase kinetics.

Instanton rate theory is related to other approximate quantum dynamics methods. In particular, it provides an explanation of the success of ring-polymer molecular dynamics at low temperatures (3). There are also applications in molecular spectroscopy for predicting tunnelling splitting patterns as will be described with reference to a recent study of the water hexamer (4).



The figure depicts an instanton describing tunnelling in $H + CH_4$

References

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- (4) Richardson, J.O.; Pérez, C.; Lobsiger, S.; Reid, A.A.; Temelso, B.; Shields, G.C.; Kisiel, Z.; Wales, D.J.; Pate, B.H.; Althorpe, S.C. *Science*, **2016**, 351, 1310.