



PHYSICAL AND THEORETICAL CHEMISTRY

Theoretical Chemical Physics

Professor Michael Collins

The group's main interest is in understanding the mechanisms of chemical reactions. This pursuit involves the development of methods for constructing potential energy surfaces for chemical reactions and the reaction dynamics on these surfaces.

Ab initio quantum chemistry provides accurate information about the energetics of chemical reactions. The potential energy surfaces (PESs) are constructed as an interpolation of this *ab initio* data evaluated at a relatively small number of relevant molecular geometries. Significant progress has now been achieved for moderate sized molecules, so that many different chemical reactions have been investigated. Most of these reactions involve competing mechanisms or reaction pathways and could not be treated using simpler approximate methods. The end result of this work should be a much clearer understanding of the mechanisms of reaction at the molecular level. We are currently pursuing a number of objectives, including further development of the methodology, PES for larger molecular systems, highly accurate PES for quantum reaction dynamics studies of four and five atom systems, many-body expansions for the weak interactions involved in molecular clusters, and coupled surfaces for nonadiabatic reactions.

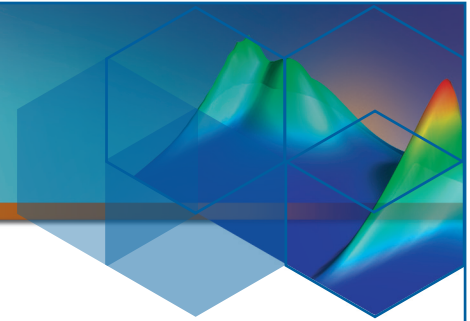
The group's work has been enhanced through collaborations with overseas scientists including the dynamics group of Professor Aoiz and Dr Jesus F. Castillo, Universidad Complutense de Madrid, Associate Professor Dong Hui Zhang at the National University of Singapore, Professor David Yarkony, Johns Hopkins University (nonadiabatic dynamics), Dr Cedric Crespos and Professor Geert-Jan Kroes, University of Leiden (reaction at surfaces), and Professor Mark Gordon, Iowa State University.

Classical Reaction Dynamics for $H+N_2O \leftrightarrow OH+N_2$

We have completed an accurate study of this reaction using classical dynamics on a PES constructed with a high level treatment of electron correlation. The theoretical dynamics confirm the presence of two competing reaction mechanisms and show good agreement with the experimental observations by the Brouard group at Oxford. *(With J Castillo and colleagues [U Complutense de Madrid])*

Hydrogen Abstraction in $H\bullet + CH_4$

The abstraction reactions, $H\bullet + RH \rightarrow H_2 + R\bullet$, have been observed to yield an unusual distribution of rotation–vibration states in the H_2 product. To investigate the mechanism of this class of important combustion reactions, we have continued to pursue accurate PESs for the simplest example, $H\bullet + CH_4$. To facilitate very high dimensional quantum scattering calculations of this reaction, new algorithms for evaluating the PES at billions of molecular configurations have been developed. *(With D H Zhang [National U Singapore])*



Nonadiabatic Chemical Reactions

Many reactions, particularly in combustion and atmospheric chemistry, take place in more than one electronic state. The PES for these electronic states can intersect, and new methods have been developed to describe all the energy surfaces involved and their "interactions".

The code development for this very difficult and important project has been accomplished for the case of two electronic states. Calculations on a model system have verified that it is possible to construct, by interpolation, the potential energy matrix which governs a nonadiabatic reaction. We have now completed the quantum scattering calculations for a simple three atom system to demonstrate the accuracy of the method. (With C Evenhuis, D H Zhang [National U Singapore], D Yarkony [Johns Hopkins U, USA])

Deuterium Exchange

Deuterium takes an active part in interstellar chemistry, leading to an enhancement of the abundances of deuterated molecules. In interstellar clouds, such processes are known as deuterium fractionation. The most relevant of them are thought to be gas phase ion-molecule reactions; specifically the reactions $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$ and $\text{H}_3^+ + \text{D} \rightarrow \text{H}_2\text{D}^+ + \text{H}$. Accurate molecular potential energy surfaces for both systems has now been evaluated, so that accurate theoretical rate coefficients can be evaluated for these reactions and isotopic analogues. (With G Moyano)

Improved PES Construction

The construction of PESs from *ab initio* quantum chemistry calculations is computationally expensive. We have investigated how to improve the efficiency of this procedure through more optimal selection of the data points used in the interpolation procedure. Two new methods have been developed and shown to produce accurate surfaces for a reduced number of *ab initio* calculations. (With G Moyano)

Approximate Ab Initio Quantum Chemistry

Ab initio electronic structure theory provides the practical means to calculate the total electronic energy of moderate-sized molecules. From their data one can calculate thermochemical properties and, in principle, the complete potential energy surface which governs the motion of the atomic nuclei. Hence, chemical reaction dynamics, rate coefficients, and other observables may be evaluated. However, the computational time required to calculate the total electronic energy increases rapidly with the number of electrons in the molecule, and with the level of *ab initio* theory employed. We have developed a systematic series or hierarchy of methods for decomposing a molecule into fragments to obtain a series of approximations to the total electronic energy, at relatively low computational expense. (With V Deev)

<http://rsc.anu.edu.au/research/collins.php>