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 *ab initio* calculations to estimate the molecular energy at any relevant molecular geometry. 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 improved accuracy of 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 collisional energy transfer and molecular clusters, and coupled surfaces for nonadiabatic reactions.

The group's work has been enhanced through collaborations with overseas scientists including Dr Mark Brouard at Oxford University and 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), and Dr C. Crespos and Professor G.-J. Kroes, University of Leiden (reaction at surfaces).

Reaction Dynamics for $H+H_2O \rightarrow OH+H_2$ and $H+D_2O \rightarrow HOD+D$

Recent experiments by Mark Brouard at Oxford have extended the available data on these seminal reactions to high translation energy in the reactants. We are pursuing a combined classical and quantum study of the reaction dynamics. *(with M. Brouard [Oxford U.], J. Castillo [U. Complutense de Madrid], D.H. Zhang [National U. Singapore])*

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

We have completed a preliminary study of this reaction using classical dynamics on a PES constructed with density functional theory. The theoretical dynamics confirm the presence of two competing reaction mechanisms which was inferred from experimental observations by the Brouard group. A more accurate PES, evaluated with high level *ab initio* data, is currently under construction. *(with J. Castillo and colleagues [U. Complutense de Madrid])*

Radical-radical and Combustion Reactions

We have developed *ab initio* PES for the reaction H + HCO (important in hydrocarbon combustion). This reaction is a prototype example of the

competition between direct abstraction and addition–elimination mechanisms. Analogous reactions are currently under investigation. *(with M.H. Smith)*

Hydrogen Abstraction in H + CH_4

The abstraction reactions, H + RH → 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 constructed a very accurate PES for the simplest example, H + CH_4. Further development of this surface to high accuracy is underway in order to provide a basis for very high dimensional quantum scattering calculations. *(with D.H. Zhang [National U. Singapore])*

Interpolation for High Dimensional Surfaces

Quantum scattering calculations for systems of four or more atoms require evaluation of the molecular potential energy over a high dimensional grid comprised of 10^7 to 10^9 or more vertices. A new algorithm has been developed to minimise the computer time involved.

Reactions on Surfaces

The method for constructing PES for gas phase chemical reactions has been extended to evaluate the PES for a chemical reaction on a crystalline surface. Initially, we have demonstrated the accuracy of this approach for a model potential which describes the dissociation of H_2 on a metal surface. *(with C. Crespos, G.-J. Kroes [U. Leiden])*

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 are being developed to describe all the energy surfaces involved and their "interactions". Significant progress on code development for this very difficult and important project has been accomplished this year. *(with C. Evenhuis, and D. Yarkony [Johns Hopkins U., USA])*

http://www.rsc.anu.edu.au/collins.html