



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. Our current work is concentrated in two main areas.

We are developing methods to study chemical reactions which take place in multiple electronic states; such processes are dominant factors in photochemistry, for example. The idea is to use *ab initio* quantum chemistry to supply information on both the energies of the electronic states and the coupling between these states which is caused by the motion of the atoms. This data is then transformed in a potential energy matrix, which can be used to simulate the chemical dynamics.

We are also pursuing a rather new avenue of research into "approximate *ab initio* quantum chemistry". We have devised methods for estimating the energies of quite large molecules from the energies of small molecular fragments (which are very much easier to calculate). In this way, we hope to make the first principles study of chemical reactions feasible for large molecules.

The group's work has been enhanced through collaborations with overseas scientists including the dynamics group of Associate Professor Dong Hui Zhang at the National University of Singapore, Professor David Yarkony, Johns Hopkins University (nonadiabatic dynamics), Professor Geert-Jan Kroes, University of Leiden (reaction at surfaces), Professor Mark Gordon, Iowa State University, and Assistant Professor Ryan Bettens, National University of Singapore.

Hydrogen Abstraction in $\text{H}\bullet + \text{CH}_4$

The abstraction reactions, $\text{H}\bullet + \text{RH} \leftrightarrow \text{H}_2 + \text{R}\bullet$, 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, $\text{H}\bullet + \text{CH}_4$. Quantum scattering calculations of the reaction cross sections and their dependence on the initial state of the reactants can be performed in at most eight dimensions at present. To facilitate high dimensional quantum scattering calculations of this reaction, new algorithms for evaluating the PES in an eight dimensional subspace of the molecular coordinates has been developed and is now being applied. (With D H Zhang [National U Singapore])

Nonadiabatic Chemical Reactions

Many reactions, particularly in photochemistry, 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 methods and computer code to construct two intersecting electronic energy surfaces were completed and applied to the benchmark $H + H_2$ reaction. The quantum scattering on these surfaces revealed the subtle effect of the surface intersection on the differential reaction cross sections.

The code development for the general multi-state case is nearing completion, and is currently being tested on model systems. *(With C Evenhuis, O Godsi, and D H Zhang [National U Singapore], D Yarkony [Johns Hopkins U, USA])*

Hydrogen-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. Gas phase ion-molecule reactions, specifically the reactions involving H and D atoms with HOC^+/DOC^+ play an important role in deuterium fractionation. An accurate molecular potential energy surface for these systems has been evaluated, so that accurate theoretical rate coefficients can be evaluated. *(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 such 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 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. This year has seen the development of a general computer code to implement this approach to evaluate molecular energies and energy gradients (and higher derivatives in some cases) and perform geometry optimisation. Extensive testing of the method is underway. Further development of the methodology has concentrated on the approximation of the relatively weak long-range interactions between well-separated segments of molecules. *(With V Deev)*

Approximate *Ab Initio* Quantum Chemistry of Crystals

The method we have developed to approximate molecular energies might be applied to estimating the energies (and free energies) of crystals. To achieve this, we are producing a new approach which fragments a crystal structure into relatively small components under periodic boundary conditions applicable to crystals. *(With H Netzloff)*

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