Theoretical Quantum Chemistry — Professor Peter Gill

In 1998, Walter Kohn and the late John Pople shared the Nobel Prize for Chemistry for their pioneering contributions to the development of quantum chemistry and density functional theory (DFT) as important tools for chemical scientists. By their actions, the Nobel Committee created a watershed in the history of the field, acknowledging that the classical development of the subjects was drawing to a close and that a new chapter was beginning.

Quantum chemistry is the discipline in which the laws of quantum mechanics are applied to understand and predict molecular behaviour and, as we enter the 21st century, one of the scientific "grand challenges" is to find ways to extend quantum chemistry's realm to the study of large systems, especially those of biological interest, without requiring impracticable amounts of computer time. Broadly speaking, two approaches are available. Either one may try to find shortcuts that will allow existing theoretical models to be applied, or one may invent completely new models that are tailor-made for application to systems with lots of atoms. Our group pursues both courses and, despite the inevitable interruption as we relocated from Nottingham to Canberra, we have recently made useful progress on both fronts.

Wigner and Action Intracules

The Heisenberg Uncertainty Principle informs us that it is not possible to simultaneously measure exactly both the position and momentum of a particle. However, we have introduced the Wigner intracule $W(u,v)$, a function that gives the quasiprobability of finding two electrons whose separation r_{12} in position space is u and whose separation p_{12} in momentum space is v. From this, we can derive the action intracule $A(w)$ which gives the quasiprobability that the separation product $r_{12}p_{12}$ is w. These functions give a more detailed picture of the motion of electron pairs than has been previously available and we have recently calculated the intracules for a variety of atoms and molecules, in both the ground and excited states. (The cover of this year's Report shows the Wigner intracule of the Li_2 molecule as it dissociates.) We have also conjectured that the correlation energy – a component of the total energy that is essential for an accurate understanding of bond formation – is related to the action intracule through the equation

$$E_{\text{corr}} = \int_{0}^{\infty} A(w)\, G(w)\, \mathrm{d}w$$

where G(w) is a universal (but as yet unknown) function. If this is true, and useful approximate G(w) functions can be discovered, it will have a major impact on the field. *(With D P O'Neill, and N A Besley [U Nottingham, UK])*

DFT for harmonic vibrational frequencies
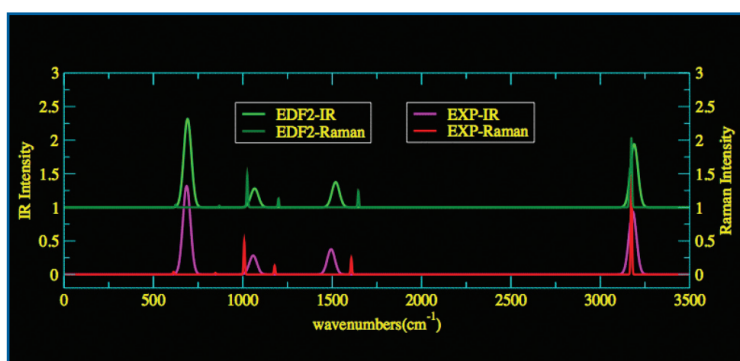
DFT is often used to predict the vibrational (*i.e.* infra-red or Raman) spectra of molecules but the distinction between harmonic and anharmonic modes is not always made: when a calculated harmonic frequency agrees with an experimental anharmonic one, one is obviously getting the right answer for the wrong reason. We have therefore constructed a new density functional (EDF2) that is designed to give accurate harmonic frequencies and this has been incorporated into the Q-CHEM program. The figure compares the experimental harmonic frequencies of the benzene molecule with the EDF2 harmonic values. We are now extending this work to treat anharmonic frequencies. *(With C Y Lin, and M W George [U Nottingham, UK])*

Do Molecules Contain Atoms?

When atoms bond to form molecules, their atomic identity is partly lost. Where, for example, is the boundary between the hydrogen and oxygen atoms in a water molecule? We are interested in the problem of extracting atoms from a molecule's electron density and we have devised a method based on integral equations for achieving this. At this stage, the method is practical only for diatomics but we hope to extend this in the future. If this can be accomplished, it may allow us to perform complicated calculations on large molecules by first using our approach to partition the electron density into well-defined atomic pieces. *(With A T B Gilbert, and S W Taylor [U Auckland, NZ])*

Density Functional Theory Without the Noise

Traditionally, DFT calculations use quadrature (numerical integration) to compute the exchange-correlation energy. Unfortunately, quadrature inevitably introduces numerical errors ("noise") into the calculations and these can cause both technical and chemical problems. Accordingly, we have tried to devise exchange-correlation functionals that can be evaluated without resort to quadrature and recently, using the Hölder inequality, we have constructed the first such functionals. *(With S H Chien)*

Positron Annihilation

Positron annihilation rates in many polyatomic molecular gases are anomalously high. Qualitatively, this can be explained by positron capture in vibrational Feshbach resonances, which can occur for molecules with positive positron affinities. To verify this idea quantitatively, we examined the densities of the vibrational excitation spectra of the *n*-alkanes from propane to nonane and proposed that positron capture is mediated by vibrational doorway states, in which positron binding is accompanied by the excitation of fundamentals. *(With G F Gribakin [Queen's U, Belfast])*

http://rsc.anu.edu.au/research/gill.php