

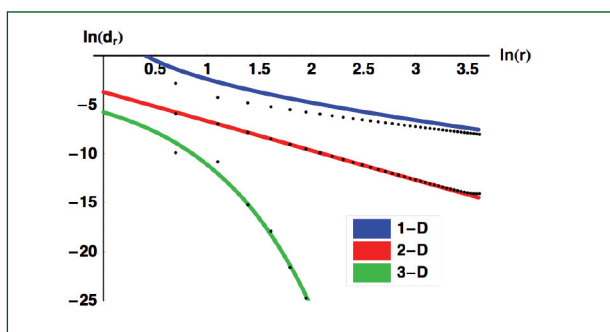


THEORETICAL QUANTUM CHEMISTRY

PROFESSOR PETER GILL

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 using impracticable amounts of computer time. We are contributing to this exhilarating field in several ways.

Decay Behaviour of Least-squares Expansion Coefficients



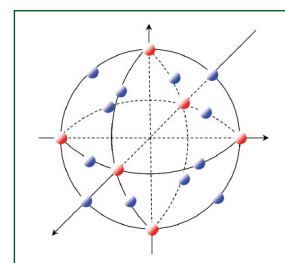
Although it is common to approximate the electron density by a linear combination of expansion functions, little was known about the rate at which the expansion coefficients d_r decay with distance r . We found empirically, and then proved rigorously, that the decay is slow ($1/r$) if the expansion basis is one-dimensional (1D), moderate ($1/r^2$) in the 2D case, but surprisingly fast ($e^{-\alpha r}$) in the 3D case. (With A T Gilbert, and M Head-Gordon [U Berkeley, USA], S Taylor [U Auckland, NZ], G Friesecke [U Warwick, UK])

Electron Correlation in Hookium and Small Molecules

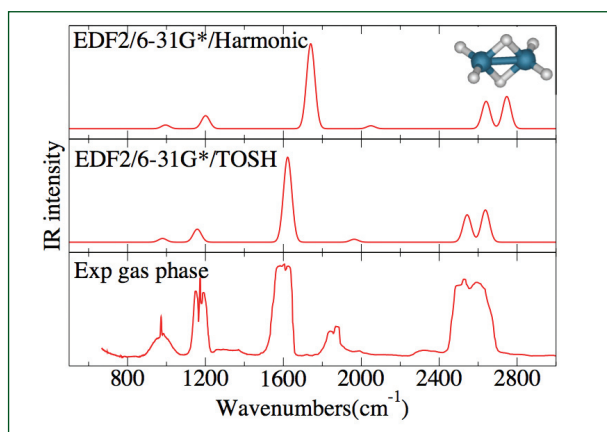
In order to develop better methods for computing molecular energies, it is desirable to have a set of benchmark molecules for which the true correlation energies are known. It was curious, therefore, that such a dataset did not appear to have been tabulated in the literature. However, by judiciously combining high-quality experimental and computational data, we were able to determine the correlation energies of a set of 56 small molecules and a "model atom" called hookium. These results should be useful for the assessment of new quantum chemical methodologies. (With D P O'Neill)

High-speed Density Functional Calculations

Traditional DFT calculations use quadrature (numerical integration) to compute the exchange-correlation energy and the challenge is to design quadrature grids that are as small as possible (to maximise speed) but as accurate as possible (to minimise numerical errors). We have developed a new grid, SG-0, that employs approximately 1500 points around each nucleus and consumes only half as much CPU time as the SG-1 grid. It is less accurate than SG-1 but, on balance, offers an attractive compromise that is particularly suitable for preliminary investigations of moderately large biochemical systems. It is the default grid within the new Q-Chem 3.0 software package. (With S H Chien)



Anharmonic Vibrational Frequencies



We have extended our earlier work on the calculation of accurate harmonic frequencies by testing the performance of a number of anharmonic algorithms and developing a new one called TOSH. This enables us to make more accurate predictions of vibrational (*i.e.* infra-red or Raman) spectra, without recourse to empirical scale factors. In collaboration with various experimental groups, we have computed the spectra of *p*-fluorotoluene, 2-aminopurine, α -tocopherol and diborane. (With C Y Lin, R D Webster, and K L Reid, M W George [U Nottingham, UK])

Multipole-derived Atomic Charges

Atomic charges in molecules are not observable quantities but chemists nonetheless find them valuable for interpretive purposes. Many methods have been proposed for calculating these ill-defined quantities, none is entirely satisfactory. We have developed the necessary theory to compute the charges that reproduce as many of the low-order multipole moments of the system as possible. (With A T B Gilbert, and A C Simmonett [U Nottingham, UK])

Intracules and the Correlation Problem

We have extended our earlier work by introducing the Omega intracule $\Omega(u,v,\omega)$, a function that gives the probability of finding two electrons whose interelectronic position and momentum vectors have magnitudes u and v , respectively, and which subtend an angle ω . This provides a more detailed picture of the motion of pairs of electrons than had been available previously and we have conjectured that the correlation energy is given by

$$E_{\text{corr}} = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u,v,\omega) G(u,v,\omega) d\omega dv du$$

where $G(u,v,\omega)$ is a universal (but as yet unknown) function that we call the correlation kernel. Omega intracules are mathematically troublesome but we can now generate them for small molecules with sp basis sets and we have begun an assessment of their properties. (With D L Crittenden, D P O'Neill, and N A Besley [U Nottingham, UK])

The n-Electrons-in-a-box Problem

Density functional theory (DFT) is based on a hypothetical infinite box containing an infinite number of electrons. In order to improve our understanding of this model (which is usually called jellium), we have performed restricted Hartree-Fock calculations on finite analogues of it, containing up to $n = 174$ electrons. (With S Ghosh [U Nottingham, UK])

