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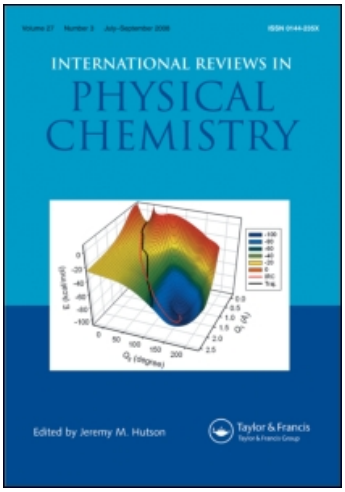

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Quantum chemistry in the University of Cambridge

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To cite this Article Handy, Nicholas C.(1988) 'Quantum chemistry in the University of Cambridge', International Reviews in Physical Chemistry, 7: 4, 351 — 370
To link to this Article: DOI: 10.1080/01442358809353217
URL: http://dx.doi.org/10.1080/01442358809353217

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INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1988, VOL. 7, NO. 4, 351–370

Quantum chemistry in the University of Cambridge†

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Important developments in the theory and application of Quantum Chemistry during the period 1948–88, arising from work of theoretical chemists at the University of Cambridge, are discussed. The outstanding contributions of S.F. Boys are detailed, and the significance that this work of the 1950s had on quantum chemistry is recognized. A description of Boys' later work is also given. An outline of some of the contributions from Cambridge in the last ten years is also described. A list of names or researchers in quantum chemistry for the period is given. The advances which have been made are linked to the history of the development of the computer service, and this is discussed.

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1. Introduction

Quantum chemistry may be defined as that branch of theoretical chemistry whose principal purpose is to determine the potential energy surface $E(\mathbf{R})$. The subject stands firmly on the foundations of quantum mechanics, and needs only the values of the fundamental constants (e, $\hbar$, $4\pi\varepsilon_0$, m_e, atomic numbers). The Born–Oppenheimer approximation is introduced to separate electronic and nuclear motion. The quantum chemist therefore attempts to solve the electronic Schrödinger equation

$$H\Psi(\mathbf{r},\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) \tag{1}$$

$$H = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}} + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}} \tag{2}$$

for the wavefunction $\Psi(\mathbf{r},\mathbf{R})$ and $E(\mathbf{R})$ as accurately as possible (in this review we shall not discuss relativistic contributions to the Hamiltonian H). $\Psi(\mathbf{r},\mathbf{R})$ is constrained by the Pauli principle to be antisymmetric for the interchange of electronic coordinates $\mathbf{r}$, and furthermore the wavefunction must vanish when any electron is at infinity.

In principle, knowledge of all relevant potential energy surfaces allows the complete understanding of all chemical processes. Knowledge of the wavefunction and derivable properties (e.g. dipole moment surfaces, polarizability surfaces) allows the complete understanding of transitions between different molecular states. Whilst we recognize that the theory and understanding of chemical reactions and transition processes are highly complex and there remain outstanding problems, advances in this area are coupled with advances in our ability to obtain more accurate representations of the potential surfaces and property surfaces.

Quantum chemistry is now a recognized branch (or tool) of chemistry. This has happened because quantum-chemical calculations are now of an accuracy to

† Based on a lecture delivered on 13 October 1988 to celebrate the installation, at the University Chemical Laboratory, of a CONVEX C2 mini supercomputer, for the specific use of the research groups of Dr N. C. Handy (Quantum Chemistry) and Dr D. C. Clary (Chemical Reactions). The paper also includes part of a lecture given in December 1987 to celebrate the fiftieth anniversary of the foundation of the Cambridge University Mathematical Laboratory.

contribute to our understanding of chemical processes. This itself has come about because of theoretical advances in the methodology of the subject and also because of the tremendous increase in computer power which is now available to the computational scientist.

In this review we start by examining some of the early methodological advances made in the Cambridge University Theoretical Chemistry Department. There have been only three Professors of Theoretical Chemistry at Cambridge:

Professor Sir John E. Lennard-Jones (1933–53)
Professor H. Christopher Longuet-Higgins (1954–67)
Professor A. David Buckingham (1969–)

and each has contributed very significantly both in their own researches and as leaders of major research groups. Because this review is specifically limited to quantum chemistry, many of the advances in the wider area of theoretical chemistry which have come from Cambridge will not be mentioned.

2. The early period 1948–60

The library of the theoretical chemistry department holds all the Ph.D. theses submitted from the department. The first is that of C. A. Coulson, dated August 1936, entitled 'The Electronic Structure of Molecules'. The pre-war work of the department under J. E. Lennard-Jones is outside the scope of this review and the knowledge of the writer, but important work was undertaken by Lennard-Jones and Coulson on integral evaluation during this period (there is a full chapter in Coulson's thesis on integrals). It may also be of interest to note that the fifth thesis was that of S. F. Boys, entitled 'The Quantum Theory of Optical Rotation', dated October 1937.

Before commencing the general review, reference must also be made to the outstanding work of D. R. Hartree, Professor of Mathematical Physics at the University of Cambridge, on the calculation of wavefunctions for atoms, at the Self-Consistent Field level of accuracy (Hartree 1957). Using a hand calculator, atomic wavefunctions at the so-called Hartree–Fock level of accuracy were achieved by numerical procedures. It is also noted that in 1939, Hartree with his father (W. Hartree) and B. Swirles (now Lady Jeffreys) performed the first multiconfiguration self-consistent field calculation, the chosen system being O^+ (Hartree *et al.* 1939).

The schools of R. S. Mulliken in Chicago and J. E. Lennard-Jones in Cambridge were responsible for the early important work in molecular orbital theory. In particular G. G. Hall (Hall 1951), a student of Lennard-Jones, in a paper entitled 'The molecular orbital theory of chemical valency. VIII. A method of calculating ionization potentials', gave the following equations for the determination of the molecular orbital coefficients a_{ij}:

$$\psi_i = \sum_j a_{ij}\omega_j \tag{3}$$

in the closed-shell case

$$\sum_r a_{ir}\left\{H_{lr} + \sum_{\substack{n \\ j,k}} a_{nj}a_{nk}[2(lj|G|rk) - (lj|G|kr)]\right\} - E_{ii}a_{il} = 0 \tag{4}$$

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where the one- and two-electron integrals are defined through

$$H_{lr} = \int \omega_l H \omega_r \, \mathrm{d}x \tag{5}$$

$$(lj|G|rk) = \int \omega_l(1)\omega_j(2)\frac{1}{r_{12}}\omega_r(1)\omega_k(2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \tag{6}$$

These are, of course, the well known Self-Consistent Field equations. Hall (with Lennard-Jones) knew the importance of these equations, in particular that ionization potentials were approximately equal to the negative of the quantities E_{ii}.

At the same time that this work was going on in Cambridge, C. C. J. Roothaan in Chicago was also developing a rigorous mathematical framework for molecular orbital theory. In his first landmark paper (Roothaan 1951), the SCF equations for the closed-shell ground state were also derived. Roothaan discussed in some detail the nature and properties of the SCF eigenproblem, interpreted the eigenvalues and discussed the effects of molecular symmetry. Today we all recognize the importance of Roothaan's first paper with its insight towards the development of quantum chemistry.

At the same time that Lennard-Jones and Hall were laying foundations for molecular orbital theory, S. F. Boys, who had joined the Theoretical Chemistry Department in 1948, was commencing his great contribution to the subject. Boys' first paper, and probably his masterpiece, was entitled 'Electronic wavefunctions. I. A general method of calculation for the stationary states of any molecular system' (Boys 1950 a). In the Introduction, Boys states the purposes of his work:

> '... to describe a method of successive approximation by which stationary state electronic wavefunctions for any configuration of atoms can be calculated to any desired degree of accuracy by inclusion of sufficient terms.
> ... This method does not depend upon any numerical integration process.
> ... Such a method has not previously been reported.
> ... The new mathematical analysis which makes this possible consists in the evaluation of integrals between Gaussian functions, which are all evaluated explicitly.
> ... It is proposed that the Gaussian functions should be used in the construction of many Slater determinants, and the use of these determinants in the Ritz variation method'.

In this way Boys laid the foundation for modern quantum chemistry. Today we all use gaussians for molecular calculations, and if we wish to go beyond the SCF approximation and include electron correlation effects then, in one way or another, we use a linear combination of determinants.

The second section of this paper held the key, for in two pages Boys derived the formulae for the gaussian molecular integrals in terms of the error function integral. Boys then argued that all integrals involving generalized gaussians $x^p y^q z^s \exp(-ar^2)$ could be obtained from these by differentiation. Boys concluded by observing that 'direct application to complicated cases would involve very heavy computing but may be worthwhile in special cases'. We all know that arguments about the need for computer time for quantum chemists carry on today.

Boys' first reported study of the convergence problem was for the ground state of Be (Boys 1950 b), where his ten-term configuration interaction wavefunction gave an energy 0·04 hartree above the experimental value. In a later paper (Boys 1953 a), using

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14 terms, Boys studied the three lowest states of the Be atom. At the end of this paper he acknowledges a grant for a calculating machine—underlining the fact that these calculations were performed by hand. The next paper (Boys 1953 b) reported similar calculations on boron and carbon.

Boys was very concerned at this time with the complexity of the formulae needed to evaluate the matrix elements of determinants of orthonormal functions (which he called detors), and he published a series of papers on this problem. Probably his greatest contribution here was to recognize that by far the best way to proceed was to make a computer do all the hard work, and with R. C. Sahni (Boys and Sahni 1954) he achieved this on the EDSAC (Electronic Delay Storage Automatic Calculator), the computer which was built in 1948 in the Mathematical Laboratory under Dr M. V. Wilkes. Hence the vector coupling coefficients which were essential for the matrix elements were evaluated automatically, the key being that Boys recognized that they could be generated sequentially.

V. E. Price was the first of Boys' students to use the computer. At that time (1950), EDSAC had 512 storage locations, and the principal purpose for which he used it was the evaluation of atomic integrals. It took 2 h to calculate the 400 integrals required by Price, instead of an estimated 1 month by hand. The machine was also used to solve the eigenproblem, which was thought to be 'very large', with dimensions 32×32, because the matrix could not be stored in the memory. An iterative scheme was used, very similar to the one used by most of us today for substantially larger matrices. Boys and Price (Boys and Price 1954) published wavefunctions for Cl, Cl^-, S and S^-, involving 32-term CI wavefunctions (single and double replacements).

One of Boys' influential articles was published in *Nature* with G. B. Cook, C. M. Reeves and I. Shavitt (Boys *et al.* 1956), entitled 'Automatic fundamental calculations of molecular structure', where he drew to the attention of the wider community that 'the advent of automatic machines has simplified and made practical calculations for the structure and properties of molecules, not only as a means for performing the arithmetical operations but also for the carrying out of much of the mathematical analysis of the most formal type'. In this paper calculations on BH, H_2O and H_3 were presented. Internal coordinate quadratic force constants were presented for H_2O. Linear H_3 was interesting because, as Boys observed, such calculations are not restricted to the determination of stable equilibria, but may also be applied to the activated complex as well. For H_2O, a 96-term CI wavefunction was involved.

A most important landmark meeting in quantum chemistry took place in June 1959 at the University of Colorado, Boulder, the proceedings of which were published in *Rev. mod. Phys.*, Volume **32** (1960). R. G. Parr was Chairman, and the Steering Committee included J. O Hirschfelder, R. S. Mulliken and J. C. Slater. The volume makes stimulating reading. C. A. Coulson, the eminent Oxford theoretical chemist, who had been a student of Lennard-Jones in Cambridge, gave the after-dinner speech, to an audience which must have included C. C. J. Roothaan, W. Kolos, A. D. McClean, A. Weiss, M. Yoshimine, B. J. Ransil, R. K. Nesbet, L. C. Allen, S. F. Boys, P. O. Löwdin, R. McWeeny, A. C. Bratoz, R. Daudel, B. Pullman, A. Pullman, A. Moscowitz, R. S. Berry, M. Karplus, E. U. Condon, K. Ruedenberg and E. B. Wilson. Coulson discusses at length whether the whole group of theoretical chemists was about to split into two, one of which was 'quantum chemistry' with members performing computations on molecules with 20 electrons or less—these were 'the *ab initio*-ists'; the other group, 'the *a posteriori*-ists', preferred to study highly complex issues through quite elementary concepts (why is the HF bond so strong and the FF bond so weak?).

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Coulson also mentioned that it was 'abundantly clear' that until many-centre integrals could be coped with, there would be a hold-up in polyatomic molecule calculations (the significance of Boys' paper had not been realized at this stage). Coulson also observed that a single-configuration wavefunction must inevitably lead to a poor energy. He made wise comments about theoretical chemistry in general, but these are outside the scope of this review.

At this meeting, Roothaan gave his second paper (Roothaan 1960) on SCF theory—the extension to open shell systems; and he presented applications on He, Li and Be. Famous calculations on two-electron atoms were presented by Roothaan and Weiss (Roothaan and Weiss 1960) and Kołos (Kołos and Roothaan 1960) and others presented calculations on the H_2 molecule. B. J. Ransil (Ransil 1960) presented SCF calculations on a number of first-row diatomic molecules, using minimum Slater-type basis sets. L. C. Allen (Allen and Karo 1960) presented a compilation of the *ab initio* calculations reported to 1959; today we would describe them as SCF using minimal STO basis sets.

It was at this meeting that Boys presented some outstanding papers. With J. M. Foster (Foster and Boys 1960 a) he introduced his localized orbitals, defined such that the centroids should be as far as possible apart being consistent with orthonormality. His application to formaldehyde (Foster and Boys 1960 b) showed the centroids to be where one would expect. The result is that the 'Boys localizer' facility is part of most quantum chemistry programs today. These calculations on formaldehyde used a minimal Slater basis, but the difficult three- and four-centre integrals were evaluated by expanding the Slater-type functions with up to nine gaussians! CI calculations were performed, with 51 configurations. Boys' greatest chemical achievement was his calculation on CH_2, which was reported at this meeting (Foster and Boys 1960 c). At this time it was not clear whether the $^1A_1$ or the $^3B_1$ would be the ground state; indeed, it was argued by some that the ground state was a linear triplet. They used eight basis functions, and again performed CI, and varied both bond length and bond angle. They found the $^3B_1$ to be the ground state, with an angle of 129°, and the $^1A_1$ to lie 0·04 (25 kcal mol^{-1}) hartree higher with a bond angle of 90°. Boys adds that 'a detailed assessment of the possible error suggests that this order is true'. In fact, these calculations were quite remarkable, especially when the calculations contrasted with the current evidence. Today we know that the $^3B_1$ is the ground state (by 9 kcal mol^{-1}) with an angle of 134°. The paper on CH_2 with Foster is, according to *Current Contents*, one of the 100 most-cited papers from *Reviews of Modern Physics* for the period 1955–86.

With that paper there ends the major innovative period of Boys' contributions to quantum chemistry. Before closing this period, it is interesting to include a partial list of some of the theoretical chemists who worked in Cambridge during the period 1950–60. In parentheses are included later positions held by these eminent scientists.

B. J. Alder (Research Scientist at Livermore Laboratory, California).
A. D. Buckingham (Professor of Theoretical Chemistry, University of Cambridge).
G. B. Cook (Professor of Computer Science, Hull, U.K.).
J. M. Foster (Research Scientist at Radar Research Establishment, Malvern, U.K.).
J. S. Griffith (died 1970) (Professor of Chemistry, University of Pennsylvania).
G. G. Hall (Professor of Mathematics, University of Nottingham).

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A. C. Hurley (died 1988) (Research Scientist at CSIRO, Melbourne, Australia).
H. F. King (Professor of Theoretical Chemistry, Buffalo, New York).
A. D. McLachlan (Research Scientist at the MRC Laboratory, Cambridge).
I. M. Mills (Professor of Chemistry, University of Reading).
J. N. Murrell (Professor of Theoretical Chemistry, University of Sussex).
R. K. Nesbet (Research Scientist at IBM, Almaden, California).
L. E. Orgel (Research Professor in the Salk Institute, California).
R. G. Parr (Professor of Theoretical Chemistry, University of North Carolina at Chapel Hill).
J. A. Pople (Professor of Theoretical Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania).
V. E. Price (Professor of Computer Science, City University, U.K.)
C. C. J. Roothaan (Professor of Theoretical Chemistry, University of Chicago).
L. Salem (Professor of Theoretical Chemistry, Université de Paris-Sud).
I. Shavitt (Professor of Theoretical Chemistry, Ohio State University, Columbus, Ohio).

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3. The middle period, 1960–72

After 1960, Boys became interested in more novel ways for solving the Schrödinger equation. Perhaps he realized that the complexities and enormity of CI calculations warranted a further look at the form of the wavefunction. Certainly he was aware that the problem of the electron–electron cusp was a principal reason for the slow convergence of the CI wavefunction. He was also driven by the idea that if the expansion functions were well chosen, then the wavefunction would converge very quickly. When the writer commenced research in 1964, Boys was anxious to look at wavefunctions of the form

$$\Psi = \Pi f(\mathbf{r}_i, \mathbf{r}_j, r_{ij})\Phi \equiv C\Phi \tag{7}$$

where Φ is a determinant of orthonormal orbitals. It may be of interest to describe how this research proceeded. As C. A. Coulson (Coulson 1973) notes in his memoir, it was necessary for a student of Boys to follow his ways, do things as he did them, and so fit into his plan of research.

The first application of the wavefunction was to benzene, in the π-electron approximation, thus

$$\Phi = A(\phi_1^2\phi_2^2\phi_3^2) \tag{8}$$

where

$$\phi_i = \sum c_{Ai}\pi_A \tag{9}$$

and π_A are atomic π-orbitals. Equation (9) was substituted into equation (8) to give Φ as a linear combination of determinants D_π of atomic π-orbitals, the coefficients c_π of each of these D_π determinants being fixed by equation (9). Each D_π determinant was then multiplied by a correlating factor

$$f_\pi = \Pi(1 + \tfrac{1}{2}r_{AB}) \tag{10}$$

where A, B run over all the centres of the π orbitals in D_π and r_{AB} is the distance between these carbon atoms. In other words, the correlating factors adjusted the coefficient of the determinant D_π from c_π to $c_\pi f_\pi$. In this way a new wavefunction

$$\Psi = \sum c_\pi f_\pi D_\pi \tag{11}$$

was obtained for benzene, in which electron correlation effects had been introduced through equation (10). It was possible to show that the idea was correct, by evaluating $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$, using the Pariser–Parr–Pople (PPP) scheme for integral evaluation. The result was that the energy obtained in this way was almost the same as that achieved by J. Koutecky (Koutecky *et al.* 1964) through a CI calculation within the PPP scheme. The results were equally good for all the low-lying electronic π-states of benzene.

It was the success of these calculations (the last that Boys performed on the EDSAC 2) that led him to examine further the merits of the wavefunction (7). The great strength of the form was that it was possible to obey the electron–electron cusp condition, by choosing f to include terms of the form

$$1+\tfrac{1}{2}r_{ij} \quad \text{or} \quad \exp(\tfrac{1}{2}r_{ij}/(1+ar_{ij})) \tag{12}$$

However, the principle difficulty of (12) is that they were not pure correlation effects, because r_{ij} itself included orbital effects, and thus if terms like (12) were introduced into f, then it was also necessary to introduce one-electron terms which would compensate for these orbital terms. Thus the form of f which was ultimately favoured was

$$f(\mathbf{r}_i, \mathbf{r}_j, r_{ij}) = \exp(G(\mathbf{r}_i, \mathbf{r}_j, r_{ij}) + g(\mathbf{r}_i) + g(\mathbf{r}_j)) \tag{13}$$

For an atom $g(\mathbf{r}_i)$ was a linear combination of powers of $\bar{r}_i$ $(\equiv(r_i/(1+ar_i))$ and $G(\mathbf{r}_i, \mathbf{r}_j, r_{ij})$ was a linear combination of terms involving $\bar{r}_{ij}$ $(\equiv(r_{ij}/(1+ar_{ij}))$, $\bar{r}_i$ and $\bar{r}_j$.

The determination of the expectation value of H for this wavefunction, $\langle C\Phi|H|C\Phi\rangle/\langle C\Phi|C\Phi\rangle$, was clearly impossible, but Boys saw that it was possible to proceed through

$$HC\Phi \equiv EC\Phi \Rightarrow C^{-1}HC\Phi = E\Phi$$

or

$$E = \langle \Phi C^{-1}HC\Phi\rangle \tag{14}$$

and thus an energy could be determined through the expectation value of the operator $C^{-1}HC$. The beauty of this operator was that the integrals to be evaluated were no worse than those currently met in quantum chemistry; they could be evaluated by numerical quadrature because there was no difficulty at electron–electron coelescence as the electron–electron cusp condition was rigorously obeyed.

To determine the adjustable parameters in C and Φ, the following equations were solved:

$$\langle \delta(C^{-1}\Phi)|H-E|C\Phi\rangle = 0 \tag{15}$$

$C^{-1}HC$ is not a hermitian operator, and so Boys developed his own theory (Boys 1969) on the convergence of this type of secular equations. His result was that the error in E was proportional to $\mu^+\mu$, where μ is a measure of the error of $C\Phi$ and μ^+ is a measure of the error of the best possible combination of $C^{-1}\Phi$ and $\delta(C^{-1}\Phi)$. In this way it can be seen that not only could the value of E be very good if $C\Phi$ was sufficiently accurate, but also that the error crucially depended upon the best combination of the l.h.s. that could

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be achieved. In practice, the whole scheme showed success when the compensating orbital terms $g(\mathbf{r})$ were introduced into f, and it is clear why this was the case.

Calculations were performed (Handy and Boys 1969 a) on Ne and Ne^+. For Ne the energy obtained was $-128{\cdot}962$ hartree compared with the experimental value of $-128{\cdot}929$ hartree. The ionization potential for Ne was calculated to be 0·796 hartree, compared with the experimental value of 0·791 hartree. In these calculations, C contained eight adjustable parameters and there were six basis functions to represent the radial parts of all the orbitals.

A calculation was also presented on LiH (Handy and Boys 1969 b), for which 10 orbital basis functions and 38 correlation expansion functions were used. The energy obtained was $-8{\cdot}063$ hartree to be compared with the experimental value of $-8{\cdot}070$ hartree.

Boys called this method the 'transcorrelated' method. No significant work has been presented on this method since 1973. The reasons are many, the most significant of which is that the method is exceedingly complex. The principal difficulty was the operator $C^{-1}HC$, and at that time (and today) we have sufficient difficulty working with the operator H. Looking at the transcorrelated method from the knowledge we have today (1988), it is probably clear that the method would suffer from the principal deficiency that all quantum chemistry methods suffer—the expansion set problem. A large basis set would be required for the orbitals, and a very large correlation expansion set would be required for C. It is most likely that reliable results would only be obtained if analytic integration schemes were used, and this must mean the use of correlated gaussian functions (Handy 1972). If all this is true, then the complexity of the method means that the approach would not stand up against the best methods in use today, in particular coupled-cluster schemes (Čížek 1966).

In the early 1970s Boys instigated two more highly significant pieces of research. The first was with F. Bernardi (Boys and Bernardi 1970), where he was addressing the problem of the accurate calculation of intermolecular forces, such as the interaction potential of two H_2 molecules. In that paper he suggested that for a bimolecule AB, the separate energies W_A and W_B are calculated with the full set of expansion functions used in the calculation of the energy W_{AB} of the bimolecular system. That is, his *counterpoise* procedure involves the calculation of W_A in the same way that W_{AB} is calculated, but with the number of electrons for A and the nuclear charges on B set equal to zero. This paper was therefore both Boys' recognition and his solution of the basis set superposition error (BSSE) problem. Today there is not known to be any better way of dealing with this problem, in spite of endless papers in the literature.

The second piece of research, commenced by Boys with a research student, M. G. Bucknell, in the last year of his life, was the determination of vibration–rotation wavefunction and energies for any given potential surface, using the variational secular equation method. The research proceeded far enough with Boys for him to know that it would be successful (Bucknell *et al.* 1974). Although this may not be quantum chemistry, this piece of work is included here because it helped establish a new approach for theoretical spectroscopy, based on the variational method, for triatomic and tetraatomic molecules.

However, it is important to place Boys' work of the period 1960–72 in context. It cannot be suggested that this work was significant in the development of today's quantum chemistry (with the one exception of the Boys–Bernardi counterpoise method for the basis set superposition error). As the computer facilities improved, and especially as the algebraical programming languages became available, many quantum

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chemists were making important progress, especially in the United States. It is a difficult task to select leading contributions, and the reader is referred to Schaefer's selection of important papers of the period (Schaefer 1984). Here we shall mention just a few of the names, with a hint of their contributions: E. Clementi (Clementi 1963) (atomic SCF calculations with STO basis sets); S. Huzinaga (Huzinaga 1965) (optimized gaussian basis sets); R. K. Nesbet (Nesbet 1963) (large CI problems); G. Das and A. C. Wahl (Das and Wahl 1966) (multiconfiguration self-consistent field studies); P. E. Cade (Cade *et al.* 1966) (diatomic SCF calculations); C. F. Bender and E. R. Davidson (Bender and Davidson 1966) (natural orbital CI calculations); A. D. McLean and M. Yoshimine (McLean and Yoshimine 1967) (linear molecule wavefunctions); K. Morokuma (Morokuma and Pederson 1968) (hydrogen bonds); W. Kołos and L. Wolniewicz (Kołos and Wolniewicz 1968) (hydrogen molecule); T. H. Dunning (Dunning 1970) and I. Shavitt (Hosteny *et al.* 1970) (contracted gaussian basis sets); J. A. Pople (Newton *et al.* 1970) (the GAUSSIAN-70 system and systematic studies of polyatomic molecules); W. Meyer (1971) (pair natural orbital calculations); and B. Roos (Roos 1972) (large-scale CI calculations).

Even this brief list shows that quantum chemistry was becoming very much a combined effort. Besides the development of new methodology by several groups, important applications were being made (such as further investigations with methylene). By 1972, gaussians were being widely used, as demonstrated by a calculation by E. Clementi (Clementi *et al.* 1971) on the guanine–cytosine base pair using 105 contracted gaussian basis functions. Calculations at the SCF level on small molecules were becoming straightforward, and large-scale CI calculations were contemplated.

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4. The modern period, 1973–88

It is not possible to describe in a review of this nature all that has happened in quantum chemistry in the last 15 years. Therefore, we shall concentrate on the effort in quantum chemistry in Cambridge, and relate it where possible to developments elsewhere.

Any reasonable quantum chemistry group today must have its own set of packages for *ab initio* calculations. Over a period of 10 years, R. D. Amos has been responsible for the development of the 'Cambridge Analytic Derivatives Package', CADPAC (Amos and Rice 1988). This package was developed principally for the modern supercomputer with a CRAY-type architecture. The following is a list of its present capabilities.

SCF calculations (RHF, UHF, GRHF).
One-electron properties, including distributed multipole analysis (DMA).
Gradient of the energy; geometry optimization.
Coupled Hartree–Fock equations.
Polarizabilities (including frequency dependence).
Magnetizabilities.
Dipole, quadrupole and polarizability derivatives.
Infrared and Raman intensities, vibrational circular dichroism.
Second derivatives of the energy, harmonic frequencies.
Møller–Plesset perturbation theory:
  through third order in the energy;
  through second order in one-electron properties;
  dipole moment derivatives and polarizabilities (closed shell);

gradients of the energy (closed shell);
second derivatives of the energy, harmonic frequencies (closed shell).
Projected unrestricted MP2 energies.

The principal limitation of the package is a maximum of 255 basis functions.

CADPAC is now portable, and copies exist on CRAY, IBM, CONVEX, SCS, ALLIANT, and VAX computers. It is supported by an 80-page manual, and it is now available worldwide. It is particularly attractive to those interested in molecular properties as it has features (such as the DMA) not available elsewhere. The MP2 analytic second derivatives are also a unique feature. It is also believed to be the best available general package for supercomputers.

The first such package which was distributed on a worldwide basis was the GAUSSIAN series of programs, in particular GAUSSIAN-76 (Hehre *et al.* 1986) from the school of J. A. Pople at Carnegie-Mellon University. Through 1987, the GAUSSIAN program was available to all at a cost of no more than a handling charge. This policy made good quantum chemistry available to all who had access to a reasonable computer. Today it has been recognized that these enormous packages (of 200 000 lines or more) represent many man-years of effort, and their maintenance and continual updating and improvement cost a lot of money. Therefore, CADPAC is not distributed free, but a charge is made on a sliding scale (university research group—computer centre—industrial company). The income is used to support personnel, to send students to conferences and to pay maintenance and other charges related to computing equipment. We believe that the success of this policy is a recognition of the importance of quantum chemistry, as well as encouraging industry to employ quantum chemists and exploit this science.

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Our research in Cambridge today is largely centred on CADPAC as a core; it is our principal tool for chemical investigations and any new successful developments are linked to it. We are always trying to improve its capabilities, but such capabilities must have wide applicability. Today therefore we are concentrating on the following enhancements:

(i) Analytic third and fourth derivatives at the SCF level. These will permit the *ab initio* evaluation of the important anharmonic spectroscopic constants, including fermi-resonance effects.

(ii) A large scale SCF program. Almlöf (Almlöf *et al.* 1982) introduced the 'direct SCF' procedure, whereby integrals are never stored in an SCF calculation, but are calculated if needed. This opens up the possibility of performing SCF calculations on molecules with 100 atoms needing 1000 basis functions. The value of such calculations to chemistry is unlimited. The way we shall proceed is that the SCF one-electron density yields a multipole distribution (Stone and Alderton 1985) for the molecule. This multipole distribution then governs the electrostatic interaction of this molecule with other molecules, and thus the behaviour of the molecule in a liquid environment may be studied, for example. It may also be possible to optimize partially the geometries of these large molecules, as well as include some correlation effects (Head-Gordon *et al.* 1988, Saebo and Almlöf 1989). It is probable that these very large scale calculations will have great importance in the next 10 years.

(iii) A very fast configuration–interaction based program. Such a program covers a multitude of variants, in particular those versions which are size-consistent (Pople *et al.* 1976). It is now recognized that size consistency

($E(AB) = E(A) + E(B)$, when the molecules A and B are infinitely separated) is more important than using a method which is based on the variational upper-bound principle. The simplest of such schemes is the Coupled Pair Functional (CPF) scheme of Ahlrichs (Ahlrichs *et al.* 1985).

CADPAC is not a package which today is designed for the whole potential surface, but rather it concentrates on that region where bonds are not broken. To study the whole surface, or indeed excited states, a much more general package is required. There seems to be no alternative to the Multi Configuration Self-Consistent Field (MCSCF) approach to this problem. A tremendous effort has been devoted to MCSCF theory in the last 10 years, much of which may be associated with the names of B. Roos, P. E. M. Siegbahn (Roos *et al.* 1980), I. Shavitt (Shavitt 1977) (particularly for matrix element evaluation using the unitary group approach), R. Shepard (Shepard 1987), B. Lengsfield (Lengsfield 1982) and P. Jorgensen (Olsen *et al.* 1982). In particular, P. J. Knowles (of Cambridge) and H.-J. Werner (H.-J. Werner and P. J. Knowles 1985, 1988) have developed an MCSCF package called MOLPRO (Molecular Properties) which has excellent convergence characteristics (although not fully quadratic). Such a package is able to study ground- and excited-state surfaces simultaneously, and thus calculate matrix elements between them. One recent study using MOLPRO has led to a correct interpretation of the photoelectron spectra of CO_2 for the first time (Knowles *et al.* 1988). In summary, there is no question that if high accuracy calculations on small molecules involving the breaking or making of bonds are required, then a program such as MOLPRO must be used, and such programs are now operative (another example is COLUMBUS due to I. Shavitt and R. Shepard (Lischka *et al.* 1981)).

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In principle, programs such as CADPAC and MOLPRO can do most of the quantum chemistry available today. However, we (Colwell *et al.* 1985) have also spent some time developing a smaller version of CADPAC, called MICROMOL, designed for teaching purposes and for those who do not have access to the larger computer. This program, developed by S. M. Colwell primarily for IBM/PC machines, performs closed- and open-shell SCF calculations, together with analytical gradients of these. The program is linked to graphics facilities if required, and it is distributed on floppy disks. It is designed for computers costing about $2000, and for calculations which need less than 100 basis functions. About 250 copies of MICROMOL have been distributed, and the whole project was supported by a grant from IBM and by an award from the Computers in Teaching Initiative, sponsored by the U.K. Computer Board.

The above discussion emphasizes our view that it is important to have good packages with state-of-the-art methodology if good science is to be done. It is also important to have available good computer facilities for both development and production purposes. We discuss this in the next section.

In recent years, the quantum chemists in Cambridge have been actively concerned with the development of new methodology for quantum chemistry. We have benefited greatly from interaction with the research group of H. F. Schaefer at Berkeley and now at Athens, Georgia. We shall now briefly discuss some of these developments.

One of the major successes in quantum chemistry in this period has been the development of gradient theory, following on from the 1969 paper of P. Pulay (Pulay 1969). Pulay showed how it was possible, by analytic means, to calculate the gradient of the SCF energy. That he could do this was principally because he was using gaussian basis functions, for it follows that the differential of an s-type gaussian is a p-type gaussian. This is the other important reason why gaussian basis functions are here to

stay. It was some time before gradient theory really made its impact, principally because of the algebraic complexity involved in the calculation of two-electron integrals with higher angular momentum gaussian functions. This problem was overcome by M. Dupuis, J. Rys and H. F. King (Dupuis *et al.* 1976), who showed that it was simplest to evaluate these integrals using an exact quadrature scheme. Once this was available, then J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley (Pople *et al.* 1979) presented an efficient code for the evaluation of analytical second derivatives at the SCF level for the first time; in the same paper they presented MP2 energy gradients. To obtain these it was necessary to solve the coupled-perturbed Hartree–Fock equations of J. Gerratt and I. M. Mills (Gerratt and Mills 1968). The availability of gradients meant that minima and transition states could be optimized. The availability of second derivatives also yielded harmonic frequencies of vibration.

The period 1978–79 was a very exciting time in Berkeley for quantum chemistry. By that time H. F. Schaefer and W. H. Miller (Schaefer and Miller 1976) had purchased a minicomputer for their research in theoretical chemistry. The advantages were abundantly clear, for they were free of the whims of computer centres whether it concerned charging, downtime, maintenance or plain inefficient management! They had the machine to themselves 24 hours a day, 7 days a week. Their first machine was only a factor of 30 slower than the best available computer of the time, the CDC7600.

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The research in Berkeley was progressing apace, mainly because of (a) the realization that gradient theory had a tremendous role to play and (b) the work of J. Paldus (Paldus 1974) and I. Shavitt (Shavitt 1977) showed how general matrix elements between configuration state functions (a linear combination of determinants which are eigenfunctions of $\hat{S}^2$) could be efficiently evaluated using the so-called Graphical Unitary Group Approach. It was the work of B. R. Brooks (Brooks and Schaefer 1979) which first made large-scale configuration interaction a practical proposition, although today we recognize that the real importance of GUGA is that it displayed the 'shape' and 'similar features' of the CI secular matrix (Siegbahn 1979). J. D. Goddard and the writer (Goddard *et al.* 1979) investigated gradient procedures for MCSCF wavefunctions with an application on the transition state for the $CH+H_2$ reaction. Shortly thereafter several of us (Brooks *et al.* 1980) put our knowledge together to evaluate the energy gradient for CI wavefunctions. A visit by J. A. Pople showed us, as is often the case when exciting things are happening, that he was also on the topic, as demonstrated by a simultaneous publication (Krishnan *et al.* 1980). The situation was therefore that by the end of 1980, good SCF energy, gradient and second derivative codes were available, together with the more sophisticated correlated methods, in particular Møller–Plesset theory at second order, MP2, or configuration interaction, both of which were available with gradients.

In Cambridge, the writer had brought back from the U.S.A. many of the Berkeley ideas, and the nucleus of a quantum chemistry group was being formed. R. D. Amos had started work on his quantum chemistry suite of programs, and W. I. Ferguson (Ferguson and Handy 1980) started to implement GUGA to give a general CI program. It was at this time that the first Full CI program was constructed (Handy 1980) and, although it was inefficient, the possibility of performing very large Full CI calculations was shown, if a basis of Slater determinants was used. It was on a follow-up visit to Berkeley that P. Saxe observed that benchmark calculations could be performed, if the program was run on their CDC7600. Thus with the encouragement of H. F. Schaefer, a Full CI calculation on H_2O with a double-zeta basis set was performed (Saxe *et al.* 1981). Soon afterwards R. J. Harrison performed further Full CI calculations (Harrison

and Handy 1983) on, in particular, stretched H_2O, using the CRAY-1 computer recently installed at Daresbury. It is significant that it was the enhanced memory, and not the vector facility, of the CRAY-1 which was so useful at this stage. These early benchmark calculations on polyatomic molecules using non-minimal basis sets were extremely useful to other workers as calibrations for their methods, and it is recognized today that any new quantum chemistry method for the inclusion of electron correlation is so calibrated.

Full CI took another step forward with P. E. M. Siegbahn's factorization scheme (Siegbahn 1984) for the evaluation of CI matrix elements; P. J. Knowles (Knowles and Handy 1984) very soon recognized how such a factorization made a determinant-based Full CI program completely vectorizable on the CRAY computer. C. Bauschlicher, at NASA Ames Research Center, recognized the importance of this super-efficient code in the context of a CRAY-2 computer. In spite of the fact that we only sent him a listing of the program, Bauschlicher and his co-workers managed to get the program to run on a CRAY-2 (the first significant program to run on this machine). The first of many publications then appeared using this program (Full CI on HF and NH_2 (Bauschlicher *et al.* 1986)), with the result that a large quantity of knowledge has been gained on the accuracy of correlated wavefunction calculations. The principal conclusion of this work is that it appears that if best accuracy is required across the entire potential energy surface, then only MCSCF plus CI is the guaranteed method. It is unfortunately very expensive, and only possible for small systems. That such large calculations are possible was first shown in collaboration with D. Fox, P. Saxe and H. F. Schaefer in Berkeley, when a CI calculation using the GUGA scheme, was performed on C_2H_4 (Fox *et al.* 1982) with in excess of 10^6 CSFs. Today, CI calculations of this magnitude are fairly routine, although it must be added that the enormity and cost of these calculations have given quantum chemistry a bad name in some quarters. However, the fact remains that if chemical accuracy is to be achieved, very large calculations with large basis sets must be performed, and an increasing number of chemists recognize that this is the only way to study the whole of the potential energy surface.

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One of the advantages of the Full CI program which was recognized in Cambridge, was that it was possible to examine the convergence of Møller–Plesset theory (Møller and Plesset 1934). MP theory through fourth order (MP2, MP3, MP4) had been popularized by the school of J. A. Pople in a very extensive set of calculations (Hehre *et al.* 1986), and it had been made generally available with GAUSSIAN 82. It was therefore appropriate to examine the convergence of the MP energy series (for both RHF closed shell and UHF theory). The results were illuminating (Handy *et al.* 1985) demonstrating that for RHF closed shell systems, at distorted geometries, convergence was erratic, and that for UHF wavefunctions convergence was very slow when there was some spin contamination in the UHF wavefunction. The results meant in particular that a greater degree of care needed to be attached to the interpretation of calculations based on the UHF wavefunction, and also that considerable efforts have been made to eliminate spin contamination from these calculations (Schlegel 1986).

It is both remarkable and fortunate for quantum chemistry that second-order perturbation theory with the Møller–Plesset scheme (MP2) is so easy and yet introduces typically 80% of the dynamic electron correlation effects. Whilst on a visit to R. J. Bartlett, R. J. Harrison observed to the writer that it should be possible to evaluate MP2 energy second derivatives analytically. This followed on from some theoretical work with H. F. Schaefer (Handy and Schaefer 1984) on the evaluation of energy derivatives for correlated wavefunctions, with relation to perturbation theory's $(2n+1)$

rule. In Cambridge at that time we were fortunate in having several expert students and post-doctorals (R. D. Amos, J. F. Gaw, J. E. Rice, E. D. Simandiras, T. J. Lee), and so they set about writing the code, in competition with R. J. Bartlett's group (R. J. Harrison, W. D. Laidig and G. B. Fitzgerald). The result was that a good MP2 second-derivative code was developed (Handy *et al.* 1985 b). One of the best quantum chemistry conferences was organized at this time by P. Jørgensen and J. Simons in Denmark, on gradient theory. The leading players were present, and the subsequent NATO publication (NATO 1985) demonstrates how far gradient theory has been developed.

Today (1988) in Cambridge, work is progressing with the extension of J. F. Gaw's original code (Gaw *et al.* 1985) for the evaluation of SCF analytic third and fourth derivatives. Soon the quantum chemist will be able to make valuable contributions to theoretical spectroscopy, especially for anharmonic constants which are responsible for the transfer between vibrational modes of a polyatomic molecule. The second major thrust is the development by C. Murray and R. D. Amos of the highly efficient very large scale SCF program. Quantum chemistry has often been criticized for being a small- or medium-sized molecular tool, and therefore not really of value to the bio-organic chemist. With the development of these programs, contributions in this area become a possibility. The difficulty will be the identification of problems where a significant contribution can be made, and this will demand collaboration with these chemists.

This highly personalized review of quantum chemistry developments in the last 10 years will be completed by a short account of three chemical studies which have been made possible by these advances.

4.1. *A study of* $(C_2H_2)_2$ *and* $(C_2H_2)_3$ (*Alberts* et al. 1988)

These studies were initiated by a seminar from B. J. Howard (Prichard *et al.* 1987), who from a gas-phase infrared spectroscopic study could not determine the structure of the acetylene trimer, although they knew it was planar and had to have either D_{3h} or C_{3h} symmetry. It was not difficult for I. L. Alberts and T. W. Rowlands, using the SCF analytic second derivative package in CADPAC, to ascertain that the C_{3h} structure was the minimum.

A reading of the experimental literature encouraged further study of the dimer, for it was not known whether the 'T'-shaped C_{2v} structure or the 'staggered-parallel' C_{2h} structure was the minimum. Examination at both the SCF and MP2 level showed that the C_{2v} structure was the minimum and that the C_{2h} structure was the transition state between two equivalent but distinct C_{2v} structures. The barrier was calculated to be $70\,cm^{-1}$, and along the 'reaction' pathway, the distance between the C_2H_2 midpoints was approximately constant. It was later verified by several experimental groups (Bryant *et al.* 1988, Fraser *et al.* 1988) that this was the true picture, and the energy level splittings could be interpreted in terms of a tunneling motion between four equivalent minima.

At the request of one of the experimental groups (D. F. Eggers and R. O. Watts), R. Bone is now examining the related problem for the trimer, although this is much more complex because of the great increase in the number of possibilities for minima and transition states. A large amount of computer time is necessary.

This problem is an example of the important contribution that quantum chemistry has made to the study of hydrogen-bonded systems. Not only is it possible to determine optimum hydrogen-bonded structures (for which it is important to include dispersion

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effects, through electron correlation, mostly simply by the use of MP2), but also to determine the important frequency shifts associated with the motion of the H atom in the donor molecule. In the primary journals, there is now a wide range of demonstrations of the interplay of theory and experiment for such complexes. One final comment on these calculations: the basis sets that can be used are often small, and it is essential in such circumstances to use the BSSE correction of S. F. Boys (Boys and Bernardi 1970).

4.2. *The* ab initio *prediction of infrared spectra* (*Senekowitsch* et al. 1989)

Now that it is possible to determine accurately both the energy and the dipole moment vector at a large number of points on a potential energy surface, all the data is available for the prediction of the i.r. spectra. In practice, the data points are fitted by least squares to an appropriate analytical form. Then the ro-vibrational energy levels and wavefunctions are determined by the variational secular equation method for molecular vibrations (after S. F. Boys (Bucknell *et al.* 1974)). The standard formulae may then be used to determine the dipole moment matrix elements between these wavefunctions, and hence the spectra may be produced. The first significant investigation with this procedure, a collaboration principally between P. Rosmus and S. Carter, on H_2S shows excellent agreement for the shape in the region of the fundamental bending vibration between the theoretical spectrum and the observed spectrum of I. M. Mills.

This example is a demonstration of the value of knowledge of a significant portion of the potential energy surface. Such surfaces enable the theory of theoretical chemists who are dynamicists to be much more significant.

4.3. *The accurate prediction of spectroscopic band origins* (*Handy* 1989)

This example demonstrates the value that *ab initio* calculations can contribute to theoretical gas-phase vibrational spectroscopy. There are now a number of calculations from Cambridge which demonstrate that (a) harmonic frequencies are often calculated to an accuracy of better than 2% if the MP2 method is used with a large basis set (typically triple-zeta plus double polarization plus f functions) and (b) anharmonic corrections are often calculated to an accuracy of better than 10% if the SCF method is used with a DZP basis set. The combination of these two means that it is now possible to make reliable predictions for spectroscopic band origins, especially if a little experience is used and accumulated on the reliability of (a) and (b) above. The whole point, of course, is that whereas band origins are direct spectroscopic observables, harmonic frequencies and anharmonic constants are not, and there is often insufficient experimental data to determine them reliably.

Such an example was discovered recently using data from J. F. Gaw and E. D. Simandiras. The four fundamentals for NH_3 lie at 3336 (ν_1), 950 (ν_2) 3444 (ν_3) and 1626 (ν_4) cm^{-1}; they should be compared with the calculated values of 3326, 937, 3441 and 1628 cm^{-1}, respectively. The agreement is as is now expected. On the other hand, the experimental values for the harmonic frequencies, taken from a paper by Benedict and Plyler (Benedict and Plyler 1957), are 3506 (ω_1), 1022 (ω_2), 3577 (ω_3) and 1691 (ω_4) cm^{-1}, to be compared with the theoretical values of 3450, 1035, 3596 and 1675 cm^{-1}, respectively. It is clear that the 'experimental' values of ω_1 must be in error. Support for this analysis has come from a recent re-assignment of the NH_3 spectrum by K. Lehmann (Lehmann and Coy 1988), who suggests that ω_1 should be 3478 cm^{-1}. The reason for the error in the original work of Benedict and Plyler is that there is a

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significant fermi resonance between ν_1 and $2\nu_4$, and there was uncertainty about the associated coupling constant.

This example demonstrates the importance of the realization that if large basis sets are used, reliable predictions can be made for geometries and force constants, and secondly that if analytic third and fourth derivatives are available, then significant predictions for overtone spectroscopy become available.

5. Cambridge quantum chemists

An incomplete list of the Cambridge students and post-doctoral associates who have worked with S. F. Boys and N. C. Handy is as follows:

S. F. Boys:

V. E. Price, C. M. Reeves, R. C. Sahni, M. J. M. Bernal, J. M. Foster, G. B. Cook, R. K. Nesbet, I. Shavitt, I. Demetropoulos, P. Rajagopal, M. W. G. Dharmawardana, N. C. Handy, J. R. F. Hewett, M. Wakefield, F. Bernardi, M. G. Bucknell, D. J. Allison, J. A. F. Carvalho.

N. C. Handy:

M. G. Bucknell, A. H. Pakiari, R. J. Whitehead, S. M. Colwell, D. C. Clary, C. J. Edge, W. I. Ferguson, R. Thuraisingham, G. T. Daborn, G. J. Sexton, R. J. Harrison, J. F. Gaw, P. J. Knowles, R. D. Amos, K. Somasundram, J. E. Rice, T. J. Lee, E. D. Simandiras, I. L. Alberts, R. H. Nobes, A. Willetts, C. Murray.

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6. Computers for quantum chemistry at Cambridge

The advances in quantum chemistry have proceeded hand in hand with the advances in computer technology. The first digital computer was the EDSAC, built under the direction of M. V. Wilkes, which gave the university its first computer service in 1949. We have already seen that it was not long before V. E. Price was using this machine for matrix manipulation, and S. F. Boys was using it to evaluate complex algebraic formulae. EDSAC 2 arrived in 1956 with a greater memory (1024 words each of 40 bits), and this was the machine on which, for example, J. M. Foster and S. F. Boys performed their landmark methylene and formaldehyde calculations. Recall that all these calculations used programs written in machine code, and that paper tape was the storage device for both programs and temporary data, although magnetic tape storage was introduced at a later data. EDSAC 2 had 120 distinct machine instructions; the time for a floating point addition was 120 μs and for multiplication 500 μs.

When the writer commenced research in 1964, one still programmed in machine language, but in January 1965, the TITAN machine was installed, together with AUTOCODE, the algebraic programming language. Instead of running the machine oneself, there were now operators and so a regular service was installed, even though for many years the only means of submitting jobs was by paper tape. Although the United States was wedded to cards, Cambridge managed to avoid that rather tedious medium.

In 1974, the time arrived for another upgrade; the choice lay between an ICL machine or the IBM 360 series. It was time for an important decision, and Cambridge was indeed fortunate that the astronomer Professor M. Ryle spoke out so strongly in favour of IBM. The arrival of the IBM machine meant that Cambridge was now programming in FORTRAN, and was therefore compatible with the United States. The 360 was upgraded to the 3080 series in the 1980s.

However, two exciting developments took place in the 1970s. The first, already mentioned, was that H. F. Schaefer and W. H. Miller purchased their minicomputer for

theoretical chemistry, thus enabling their students to be in total command of the computing facility, and not reliant on external influences. The second was the purchase by the U.K. Science and Engineering Research Council of the prototype CRAY-1 computer for the Daresbury Laboratory. This was the world's first computer with a vector facility. It was also significant that V. R. Saunders and M. F. Guest were the quantum chemists at Daresbury at that time, and Saunders in particular rapidly showed how quantum chemists could make amazing use of the vector facility. The CI program of V. R. Saunders and J. H. van Lenthe (Saunders and van Lenthe 1983) and the version of GAMESS developed by M. F. Guest were demonstrations of the lead that the U.K. developed because of the existence of the CRAY at Daresbury. The United States at this time had not recognized the power of the supercomputer, and were instead concentrating on the departmental minicomputers. Of course, the situation has now changed with the advent of several supercomputer centres in the U.S.A., with either CRAY-XMP or IBM-3090 machines. The most recent computer hardware development is the arrival of the CRAY-2 machines, with up to 128 Mwords of memory. One regrets that at the time of writing the U.K. scientific community has no access to such a machine. In the U.S.A. C. W. Bauschlicher has been able to publish 22 papers in the last two years, all of which used the Knowles-Handy Full-CI code run on the NASA-Ames CRAY-2.

And so we reach the arrival of the CONVEX-C2 computer for the use of the quantum chemists and reaction dynamicists at Cambridge today. The advantages of this machine are enormous;

(a) It is a vector machine which delivers one-fifth of the CPU power of a single processor CRAY-XMP. The Cambridge C2 has 8 Mwords of main memory and 2·2 Gbytes of disk storage. Nowhere else in the U.K. is 8 Mwords available to one user if necessary. This availability is enabling Cambridge quantum chemists to perform very large SCF and MCSCF and CI calculations which could not be contemplated elsewhere.

(b) Most researchers like to work regular daytime hours; in the past, the quantum chemists had to work throughout the night to obtain computer time, but this meant that they did not interact with other chemists. The presence of the C2 means that all the Cambridge group can work whenever they wish, they can develop and run programs, and they know that this facility is available every day, all day. R. D. Amos manages the facility, but it needs very little other than some control over queues and disk allocation. It is not an exaggeration to say that our development facility has improved in efficiency three-fold.

(c) The power of the CPU of the C2 means that reliance on the national facilities is considerably reduced. Those facilities (CRAY-XMP) are now used for regular, but large calculations, using for example the normal features of CADPAC, such as geometry optimizations and force-constant determinations at the correlated level. This means that one is not totally dependent on the success of grant applications for computer time; the writer remains convinced that the best research is that for which it is not possible to write a grant proposal in advance; successful grant proposals usually mean that the research is half-done already!

(d) The CONVEX is directly compatible with the CRAY; all development work can therefore be carried out on the CONVEX for later CRAY work. In particular, this means that the copies of the CADPAC program can be prepared for distribution.

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Acknowledgments

We are grateful for the financial support made available for the purchase of the CONVEX-C2. We therefore acknowledge the Science and Engineering Research Council, the University of Cambridge, the Ministry of Defence, CONVEX Computer Ltd and all purchasers of the CADPAC program.

In this review, the writer has made great use of the Biographical Memoir of Dr S. F. Boys F.R.S., written by Professor C. A. Coulson F.R.S. He also found Professor H. F. Schaefer's list of landmark papers in *ab initio* molecular electronic structure methods very useful. Professor A. D. Buckingham F.R.S. carefully read the manuscript, and made many suggestions and corrections.

References

AHLRICHS, R., SCHARF, P., and EHRHARDT, C., 1985, *J. chem. Phys.*, **82,** 890.
ALBERTS, I. L., ROWLANDS, T. W., and HANDY, N. C., 1988, *J. chem. Phys.*, **88,** 3811.
ALLEN, L. C., and KARO, A. M., 1960, *Rev. mod. Phys.*, **32,** 275.
ALMLÖF, J., FAEGRI, K., and KORSELL, K., 1982, *J. comput. Chem.*, **3,** 385.
AMOS, R. D., and RICE, J. E., 1988, *CADPAC, The Cambridge Analytic Derivatives Package*, Issue 4.0, Cambridge.
BAUSCHLICHER, C. W., LANGHOFF, S. R., TAYLOR, P. R., HANDY, N. C., and KNOWLES, P. J., 1986, *J. chem. Phys.*, **85,** 1469.
BENDER, C. F., and DAVIDSON, E. R., 1966, *J. phys. Chem.*, **70,** 2675.
BENEDICT, W. S., and PLYLER, E. C., 1957, *Can. J. Phys.*, **35,** 1235.
BOYS, S. F., 1950a, *Proc. R. Soc., Lond.* A, **200,** 542.
BOYS, S. F., 1950b, *Proc. R. Soc., Lond.* A, **201,** 125.
BOYS, S. F., 1953a, *Proc. R. Soc., Lond.* A, **217,** 136.
BOYS, S. F., 1953b, *Proc. R. Soc., Lond.* A, **217,** 235.
BOYS, S. F., 1969, *Proc. R. Soc., Lond.* A, **309,** 195.
BOYS, S. F., and PRICE, V. E., 1954, *Phil. Trans. R. Soc., Lond.* A, **246,** 451.
BOYS, S. F., and SAHNI, R. C., 1954, *Phil. Trans. R. Soc., Lond.* A, **246,** 463.
BOYS, S. F., COOK, G. B., REEVES, C. M., and SHAVITT, I., 1956, *Nature, Lond.*, **178,** 207.
BOYS, S. F., and BERNARDI, F., 1970, *Molec. Phys.*, **19,** 553.
BROOKS, B. R., LAIDIG, W. D., SAXE, P., HANDY, N. C., and SCHAEFER, H. F., 1980, *Phys. scripta*, **21,** 312.
BROOKS, B. R., and SCHAEFER, H. F., 1979, *J. chem. Phys.*, **70,** 5092.
BRYANT, G. W., EGGERS, D. F., and WATTS, R. O., 1988, *J. chem. Soc. Faraday Trans. II*, **84,** 1443.
BUCKNELL, M. G., HANDY, N. C., and BOYS, S. F., 1974, *Molec. Phys.*, **28,** 759.
CADE, P. E., SALES, K. D., and WAHL, A. C., 1966, *J. chem. Phys.*, **44,** 1973.
ČÍŽEK, J., 1966, *J. chem. Phys.*, **45,** 4256.
CLEMENTI, E., 1963, *J. chem. Phys.*, **30,** 2248.
CLEMENTI, E., MEHL, J., and NIESSEN, W. VON, 1971, *J. chem. Phys.*, **54,** 508.
COLWELL, S. M., MARSHALL, A. R., AMOS, R. D., and HANDY, N. C., 1985, *Chem. Brit.*, **21,** 655.
COULSON, C. A., 1973, 'S. F. Boys', Biographical Memoirs of Fellows of the Royal Society, Royal Society, London, **19,** 95.
DAS, G., and WAHL, A. C., 1966, *J. chem. Phys.*, **44,** 87.
DUNNING, T. H., 1970, *J. chem. Phys.*, **53,** 2823.
DUPUIS, M., RYS, J., and KING, H. F., 1976, *J. chem. Phys.*, **65,** 111.
FERGUSON, W. I., and HANDY, N. C., 1980, *Chem. Phys. Lett.*, **71,** 95.
FOSTER, J. M., and BOYS, S. F., 1960a, *Rev. mod. Phys.*, **32,** 300.
FOSTER, J. M., and BOYS, S. F., 1960b, *Rev. mod. Phys.*, **32,** 303.
FOSTER, J. M., and BOYS, S. F., 1960c, *Rev. mod. Phys.*, **32,** 305.
FOX, D., SAXE, P., HANDY, N. C., and SCHAEFER, H. F., 1982, *J. chem. Phys.*, **77,** 5584.
FRASER, G. T., SUENRAM, R. D., LOVAS, F. J., PINE, A. S., HOUGEN, J. T., LAFFERTY, W. J., and MUENTER, J. S., 1988, *J. chem. Phys.*, **89,** 6028.
GAW, J. F., YAMAGUCHI, Y., and SCHAEFER, H. F., 1985, *J. chem. Phys.*, **81,** 6395.
GERRATT, J., and MILLS, I. M., 1968, *J. chem. Phys.*, **49,** 1719.
GODDARD, J. D., HANDY, N. C., and SCHAEFER, H. F., 1979, *J. chem. Phys.*, **71,** 1525.

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HALL, G. G., 1951, *Proc. R. Soc., Lond.* A, **205,** 541.
HANDY, N. C., 1972, *Molec. Phys.*, **23,** 1.
HANDY, N. C., 1980, *Chem. Phys. Lett.*, **74,** 280.
HANDY, N. C., 1989, NATO ASI Series, Vol.
HANDY, N. C., and BOYS, S. F., 1969 a, *Proc. R. Soc., Lond.* A, **310,** 63.
HANDY, N. C., and BOYS, S. F., 1969 b, *Proc. R. Soc., Lond.* A, **311,** 309.
HANDY, N. C., and SCHAEFER, H. F., 1984, *J. chem. Phys.*, **81,** 5031.
HANDY, N. C., KNOWLES, P. J., and SOMASUNDRAM, K., 1985 a, *Theor. chim. Acta*, **68,** 87.
HANDY, N. C., AMOS, R. D., GAW, J. F., RICE, J. E., and SIMANDIRAS, E. D., 1985 b, *Chem. Phys. Lett.*, **120,** 151.
HARRISON, R. J., and HANDY, N. C., 1983, *Chem. Phys. Lett.*, **95,** 386.
HARTREE, D. R., 1957, *The Calculation of Atomic Structures* (Chichester: Wiley and London: Chapman and Hall).
HARTREE, D. R., HARTREE, W., and SWIRLES, B., 1939, *Phil. Trans. R. Soc., Lond.* A, **238,** 229.
HEAD-GORDON, M., POPLE, J. A., and FRISCH, M. J., 1988, *Chem. Phys. Lett.*, **153,** 503.
HEHRE, W. J., RADON, L., SCHLEYER, P. V. R., and POPLE, J. A., 1986, *Ab Initio Molecular Orbital Theory* (Chichester: Wiley).
HOSTENY, R. P., GILMAN, R. R., DUNNING, T. H., PIPANO, A., and SHAVITT, I., 1970, *Chem. Phys. Lett.*, **7,** 325.
HUZINAGA, S., 1965, *J. chem. Phys.*, **42,** 1293.
KNOWLES, P. J., and HANDY, N. C., 1984, *Chem. Phys. Lett.*, **111,** 315.
KNOWLES, P. J., ROSMUS, P., and WERNER, H.-J., 1988, *Chem. Phys. Lett.*, **146,** 230.
KOŁOS, W., and ROOTHAAN, C. C. J., 1960, *Rev. mod. Phys.*, **32,** 205.
KOŁOS, W., and WOLNIEWICZ, L., 1968, *J. chem. Phys.*, **49,** 404.
KOUTECKÝ, J., ČÍŽEK, J., DUBSKY, J., and HLAVATY, K., 1964, *Theor. chim. Acta*, **2,** 464.
KRISHNAN, R., SCHLEGEL, H. B., and POPLE, J. A., 1980, *J. chem. Phys.*, **72,** 4654.
LEHMANN, K. K., and COY, S. L., 1988, *J. chem. Soc. Faraday Trans. II*, **84,** 1389.
LENGSFIELD, B. H., 1982, *J. chem. Phys.*, **77,** 4073.
LISCHKA, H., SHEPARD, R., BROWN, F. B., and SHAVITT, I., 1981, *Int. J. Quantum Chem. Symp.*, **15,** 91.
MCLEAN, A. D., and YOSHIMINE, M., 1967, *IBM J. Res. Dev.*, **12,** 206.
MEYER, W., 1971, *Int. J. Quantum Chem. Symp.*, **5,** 341.
MØLLER, C., and PLESSET, M. S., 1934, *Phys. Rev.*, **46,** 618.
MOROKUMA, K., and PEDERSON, L., 1968, *J. chem. Phys.*, **48,** 3275.
NATO, 1985, *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, NATO ASI Series, Vol. 166.
NESBET, R. K., 1963, *Rev. mod. Phys.*, **35,** 552.
NEWTON, M. D., LATHAN, W. A., HEHRE, W. J., and POPLE, J. A., 1970, *J. chem. Phys.*, **52,** 4064.
OLSEN, J., JØRGENSEN, P., and YEAGER, D. L., 1982, *J. chem. Phys.*, **77,** 356.
PALDUS, J., 1974, *J. chem. Phys.*, **61,** 5321.
POPLE, J. A., BINKLEY, J. S., and SEEGER, R., 1976, *Int. J. Quantum Chem. Symp.*, **10,** 1.
POPLE, J. A., KRISHNAN, R., SCHLEGEL, H. B., and BINKLEY, J. S., 1979, *Int. J. Quantum Chem. Symp.*, **13,** 225.
PRICHARD, D. J., MUENTER, J. S., and HOWARD, B. J., 1987, *Chem. Phys. Lett.*, **135,** 9.
PULAY, P., 1969, *Molec. Phys.*, **17,** 197.
RANSIL, B. J., 1960, *Rev. mod. Phys.*, **32,** 239.
ROOS, B. O., 1972, *Chem. Phys. Lett.*, **15,** 153.
ROOS, B. O., TAYLOR, P. R., and SIEGBAHN, P. E. M., 1980, *Chem. Phys.*, **48,** 157.
ROOTHAAN, C. C. J., 1951, *Rev. mod. Phys.*, **23,** 69.
ROOTHAAN, C. C. J., 1960, *Rev. mod. Phys.*, **32,** 179.
ROOTHAAN, C. C. J., and WEISS, A. W., 1960, *Rev. mod. Phys.*, **32,** 194.
SAEBO, S., and ALMLÖF, J., 1989, *Chem. Phys. Lett.*, **154,** 83.
SAUNDERS, V. R., and LENTHE, J. H. VAN, 1983, *Molec. Phys.*, **48,** 923.
SAXE, P., SCHAEFER, H. F., and HANDY, N. C., 1981, *Chem. Phys. Lett.*, **79,** 202.
SENEKOWITSCH, J., CARTER, S., ZILCH, A., WERNER, H.-J., HANDY, N. C., and ROSMUS, P., 1989, *J. chem. Phys.*, **90,** 783.
SCHAEFER, H. F., 1984, *Quantum Chemistry* (Oxford: Oxford University Press).
SCHAEFER, H. F., and MILLER, W. H., 1976, *Comput. Chem.*, **1,** 85.

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SCHLEGEL, H. B., 1986, *J. chem. Phys.*, **84,** 4530.
SHAVITT, I., 1977, *Int. J. Quantum Chem. Symp.*, **11,** 131.
SHEPARD, R., 1987, in *Ab Initio Methods in Quantum Chemistry*, edited by K. P. Lawley, *Adv. chem. Phys.*, **69,** 63.
SIEGBAHN, P. E. M., 1979, *J. chem. Phys.*, **70,** 5391.
SIEGBAHN, P. E. M., 1984, *Chem. Phys. Lett.*, **109,** 417.
STONE, A. J., and ALDERTON, M., 1985, *Molec. Phys.*, **56,** 1047.
WERNER, H.-J., and KNOWLES, P. J., 1985, *J. chem. Phys.*, **82,** 5053.
WERNER, H.-J., and KNOWLES, P. J., 1988, *J. chem. Phys.*, **89,** 5803.

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