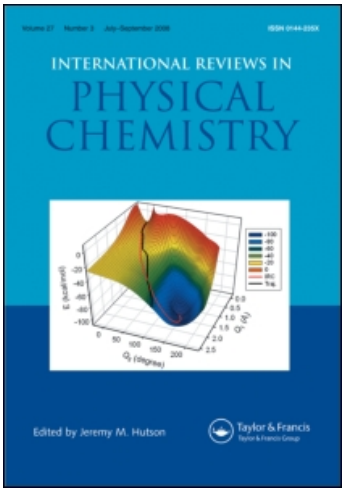

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Book reviews

Advances in Chemical Physics—*Volume 67. Ab Initio Methods in Quantum Chemistry—Part I.* Edited by K. P. LAWLEY. (John Wiley and Sons, 1987.) [Pp. 566.] £65·00. ISBN 0 471 909009.

This is an excellent volume on methodology in Quantum Chemistry, and I am sure it will find a place on many book shelves. There are nine articles occupying 539 pages. The volume demonstrates that the subject has come of age, the reasons being the great advance in both methods and computer hardware. This is not a volume about SCF calculations, but about the successes of the more sophisticated approaches which include electron correlation.

The first article is by P. Bruna and S. Peyerimhoff on excited state potentials, in which the MRDCI method is explained and used to calculate excited-state potential-energy curves for small molecules. I am impressed that for most of the systems there are ten or more states considered. There is a good discussion on the valence orbitals involved, as well as the influence of Rydberg orbitals. This article represents the state of the art on these excited states (173 references).

R. Amos presents an article on molecular property derivatives. He discusses in detail the influence that gradient methods have had on the evaluation of dipole derivatives (for infrared intensities) and polarizability derivatives (for Raman intensities). Attention is given to SCF, MCSCF and MBPT methods. Large basis set SCF calculations are reported for the above properties for H_2O, NH_3, CH_4, C_2H_2, C_2H_4, and there is a good comparison with experiment (as well as 276 references!). A lot of progress has been made in this area.

F. Bernardi and M. Robb have an article on the progress they have made in the computation of transition structures. A judicious use of the MCSCF approach and the idea of diabatic surfaces has enabled these authors to present a good discussion of the various theoretical options to study the problem. They report some studies in detail, including sigmatropic rearrangements and the thermal cycloaddition of two ethylenes (110 references).

H. B. Schlegel reports on the optimization of stationary points on potential surfaces, which is an important topic because of the advances in analytic gradient procedures. There are sections on optimization procedures which use only energies, energy first derivatives and energy first and second derivatives. Methods for location of transition structures and reaction paths are discussed. An important review by an expert in this field (121 references).

K. Balasubramanian and K. Pitzer discuss methods for relativistic quantum chemistry. Necessarily this subject is dominated by the choice of effective relativistic potentials, and recent applications are reported for various diatomics e.g., Pb_2, Sn_2 and BiH. This article updates some earlier reviews (165 references).

The French school is represented by an article on effective hamiltonians by P. Durand and J. P. Malrieu. A distinction is made between 'effective' and 'pseudo' hamiltonians. A cursory glance makes me think that the links made between various approaches (e.g., adiabatic and diabatic) are carefully analysed and that this article is worthy of study (182 references).

R. O. Jones reports on molecular calculations using a density functional formalism, with the uniform gas expression for the exchange-correlation term. Many potential curves with correct features are presented, but I doubt if this approach will be able to compete with more standard quantum chemistry methods, when chemical accuracy is required. Even so, the article is interesting (54 references).

S. Wilson presents a long article on basis sets. This is of course the outstanding problem in this subject, to which I add the comments that not a lot of progress has been made in the last ten years (for polyatomics), and that the largest basis sets possible should be used in every calculation. This article was written in September 1985. Since that time larger full CI calculations have been performed (Bauschlicher *et al.*), and also Almlöf and Taylor have presented an analysis of basis functions for correlated calculations (140 references).

The last article is by R. Ahlrichs and P. Scharf on the Coupled Pair approximation. This is an excellent review on size extensive methods, which leads to their Coupled Pair Functional method

and is a minor change to standard CI algorithms. The CPF scheme, besides showing good results when compared with other calculations of equal cost, has the added advantage that gradient methods are straightforwardly applicable to this functional based approach (103 references).

This short review indicates that this will form a useful reference volume for modern quantum chemistry.

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Theory of Magnetic Resonance. Second edition. By C. P. POOLE and H. A. FARACH (John Wiley & Sons 1987.) [Pp. 359.] £57·50. ISBN 0 471 815306.

This volume covers what might be called the 'classical' aspects of NMR theory. It is mainly concerned with the calculation of line frequencies and intensities in NMR and ESR spectra, including double-resonance experiments. The treatment mostly refers to liquids, but there is some discussion of the special effects seen in solids, especially crystals. The text regards shifts, g factors and couplings as parameters and does not discuss the calculation of these quantities. The subject of magnetic resonance is treated in its widest sense, so that not only NMR and ESR but also Mössbauer resonance, aspects of atomic spectra and crystal field theory, acoustic, muon and optical magnetic resonance, are treated.

The authors have tried to adopt a unified approach to the theory based on a 'direct product matrix expansion of the Hamiltonian'. On the whole this works well, although at times one cannot help feeling that an operator approach would be more conceptionally satisfactory. This is particularly the case when seeking the transformation which diagonalizes a particular Hamiltonian. However, the matrix representations are very suited to machine computation, and the authors quote explicitly many useful representations which will save time when writing programs. The notation adopted is a little unusual, a double over arrow is used for matrices and a single for vectors, which leads to rather fearsome looking equations. In a printed book it would make more sense to use a bold typeface. There is a useful section discussing the properties of matrices; a similar section dealing with tensors is an unfortunate omission.

The first few chapters deal with the magnetic resonance spectra of a two spin system in considerable detail, and then the pace accelerates somewhat through multi-spin $\frac{1}{2}$ and higher spin systems. Considering the time lavished on simple systems it is surprising to find the important and rather difficult concepts of magnetic and chemical equivalence dismissed in a few lines.

The chapter on line shapes utilizes the unfamiliar Anderson approach to the problem, which seems to offer no advantages over what have become the conventional procedures. Powder pattern lineshapes are also discussed.

There are several chapters devoted to double resonance techniques (ENDOR, ELDOR, Overhauser effects, etc). The distinction between double resonance experiments which are described in terms of population changes and those which lead to shifts in resonance positions is carefully noted. The chapters covering ENDOR and ELDOR are excellent and clearly written. Nuclear double-resonance experiments receive a more scant treatment. In particular, the space devoted to the nuclear Overhauser effect does not do justice to a technique that has become of great importance in structural studies.

The closing chapters cover pulsed Fourier transform NMR and two-dimensional NMR in a very cursory manner. They do not really fall into the pattern set by the rest of the text and this is painfully obvious. The reader is unlikely to gain much useful information from these chapters.

In conclusion this volume provides a good exposition of 'classical' NMR theory of line frequencies and intensities together with descriptions of double resonance experiments. The prose style is straightforward and easily readable. The material in the book is timeless and the volume will provide a very useful reference for spectroscopists interest in magnetic resonance phenomena.

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Ab Initio *Methods in Quantum Chemistry, Part II*. Advances in Chemical Physics, Volume LXIX. Edited by K. P. LAWLEY. (Wiley, 1987.) [Pp. 588.] £59·95. ISBN 0471 909017.

This is the second of two excellent volumes devoted to the present status of advanced methods in quantum chemistry. The first (volume LXVII) has recently been reviewed in this journal. Together these volumes introduce most of the modern literature in this field; they contain articles by leading authors, and they will surely find a place on many bookshelves.

In this volume there are two articles on the Multi Configuration Self Consistent Field (MCSCF) method; the first by H.-J. Werner describes the advances he has made in the convergence procedures for this difficult problem, and he discusses some large applications. He also introduces the internally contracted multi configuration reference self consistent electron pair method. This is a most attractive advanced configuration interaction procedure, and when it is fully operational, it could well be recognized as outstanding. The second article on MCSCF is by R. Shepard, who presents a complete picture of the MCSCF problem (132 pages). He starts from first principles, mentioning matrix partitions, spin eigenfunctions and the unitary group approach. He then derives the MCSCF equations, and discusses various approximate second-order convergence procedures. An important section on various forms of MCSCF wavefunction follows, together with the problem of redundant variables. Finally, there is a discussion on the computer implementation of the procedures.

There is an article by J. Oddershede on propagator methods. Although some background material is required before it can be appreciated, it is very useful because it brings up to date the work in this alternative quantum chemistry approach. In particular, there is a compilation of propagator calculations 1977–85.

There is an excellent article by P. Pulay on analytic derivative methods in quantum chemistry. This has (arguably) been the great advance in quantum chemistry of the last ten years, and Professor Pulay describes how derivatives should be evaluated for self consistent field and correlated wavefunctions. He discusses first, second and higher derivatives, and reports on the various programs in existence to evaluate these. I wonder if he is correct in his view that CI second derivatives evaluated analytically may not be superior to finite difference calculations involving CI gradients. (Incidentally, we now have the efficient Møller-Plesset second-order second derivative algorithm requested by Professor Pulay.)

There are two articles which involve density functional theory. The first, by B. I. Dunlap, introduces the theory, and discusses the approximations which lead to the Xα method. Fractional occupation numbers are discussed. The second article is by D. R. Salahub, entitled 'Transition-metal atoms and dimers'. Salabub believes that this approach is the most propitious at the present time for the *ab initio* study of transition-metal chemistry. The local spin density method has been used, and corrections to it are described. There is a good review of calculations on transition-metal dimers, comparing this approach with more conventional CI approaches.

B. O. Roos describes the present status of the complete active space self consistent field method. This most attractive procedure for a correlated wavefunction is described, together with its implementation. Of course, the difficulty is the size of the wavefunction; I do not share the optimism of Professor Roos for its wide use as a starting approximation, but he is the expert, and he demonstrates this by describing calculations on C_2, N_2O_4 and two examples from transition-metal chemistry.

There is a good article by D. L. Cooper, J. Gerratt and M. Raimondi on modern valence bond theory. They are the leading proponents of this approach and their recent calculations have certainly made all of us reconsider our representations for molecular wavefunctions. They introduce the spin-coupled wavefunction expressed in terms of non-orthogonal orbitals, and discuss the evaluation of matrix elements of these functions. They survey their results on CH^+ and CH^{3+}. They also describe their five-term wavefunction for benzene, in terms of localized π functions, and make some challenging remarks on aromaticity. Finally, they argue that the valence bond procedure has much to offer for the study of intermolecular forces; one advantage is that the basis set superposition error can be avoided. Further results from this group using large basis sets will be awaited.

The concluding article is by J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt on weakly bonded systems. They start by introducing the components of the interaction energy, and then discuss supermolecule methods for its evaluation, including SCF, CI and Møller–Plesset approaches, with a mention of size-extensivity problems. The importance of the basis set is underlined. There is a lot of discussion on the BSSE, including the

difficult observation that there are now several well-documented examples where increase in the basis lead to increased BSSE. Weakly bonded systems present a strong challenge to both the experimentalist and the theoretician, and much remains for the quantum chemist before he can be confident of his predictions.

The above should underline the excellence of the articles in this volume.

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Physical Organic Chemistry. By N. ISAACS (Longman, 1987.) [Pp. xviii + 827.] £19·50. ISBN 0582 46366 1.

Physical organic chemistry is concerned with the underlying principles which govern the properties—particularly the reactivity—of organic compounds. It is usually traced back as a separate discipline to the appearance in 1940 of Hammett's book bearing this title. By the time the second edition appeared in 1970 its influence—together with that of Ingold's *Structure and Mechanism in Organic Chemistry* (1953)—had transformed the way we think about organic chemistry. The bigger the subject the more we need to concentrate on underlying principles, and the realization that the myriad reactions of organic compounds belong to just a handful of mechanistic classes provided this essential framework for teaching and thinking about the subject.

Issac's book is the most recent of a dozen in this area. Almost all—this is no exception—follow Hammett's basic format. A discussion of chemical bonding and a resumé of the necessary kinetics and thermodynamics is followed by a treatment of organic reactions by mechanistic class. Isaacs also gives us a useful chapter classifying reagents and mechanisms, and full chapters also on structure—reactivity correlations, solvent and kinetic isotope effects and steric and conformational properties. Pericyclic reactions are treated in some detail, and a chapter on intramolecular reactions includes a section on enzyme catalysis. Substantial chapters on radical reactions and organic photochemistry complete the book.

The coverage is thus remarkably comprehensive: the only topics I can think of which might have been included and are not treated in detail are calculational methods and gas-phase reactions. The writing and exposition are clear, as one expects from an experienced teacher, and the treaments thoughtful, and well-organized. It is also commendably up to date. Marcus theory (in the context of proton transfer reactions) and More O'Ferrall-Jencks diagrams—to take random examples—are discussed and used, and readily accessed by way of a good index. (Electron transfer catalysis is there too, in the logical place, but not indexed.) Tables of experimental data and derived constants abound, making this a useful work for reference as well as learning. It ought to be in any serious library used by organic chemists, and many will want copies for themselves.

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Schrödinger: Centenary Celebration of a Polymath. Edited by C. W. KILMISTER. (Cambridge University Press, 1987.) [Pp. 253.] £30·00. ISBN 0521340179.

This book is the proceedings of a conference held at Imperial College in the spring of 1987 to celebrate the centenary of the birth of Erwin Schrödinger. The 19 papers include three biographical essays. The Introduction by Kilmister gives a brief outline of Schrödinger's biography; Flamm traces the influence on him of Boltzmann. McCrea describes the origin of the Dublin Institute and the parts played by de Valera and Schrödinger in an interesting account based largely on personal recollections and comments by contemporaries.

Five papers analyse aspects of Schrödinger's work. The reader might be surprised that there is no comment on the significance of his basic papers on wave mechanics, but this is sensible since every physicist must be familiar with these papers and their impact. Pauling writes about the early days of the application of wave mechanics to chemistry. McConnell describes Schrödinger's

attempts to develop the Born–Infeld non-linear equations of electrodynamics, and his work on unified field theory is described by Hittmair. Perutz gives a very interesting analysis of 'What is Life?' and concludes 'sadly' that 'what was true... was not original, and most of what was original was known not to be true even when the book was written'. But he stresses the merit of the book in arousing interest in the subject, and drawing attention to the work of Timoféeff–Ressovsky, Zimmer and Delbrück.

Yang describes how Schrödinger had to come to terms with the appearance in the wave equation of complex quantities, and the significance of this fact in further developments.

Lewis reports on the as yet unanswered question of the condensation of interacting bosons, in which Schrödinger had an interest.

One knows that Schrödinger was not happy with the probability interpretation of wave mechanics. Dorling attempts to argue that the interpretation of the wave function as a physical object could be maintained but this seems no more than wishful thinking. Bell has a specific scheme which might avoid the 'collapse of the wave packet' in observations. This is not the place to explain why I regard this as unworkable.

Three essays review the development of quantum chemistry since Schrödinger. Buckingham's review is general, that of Karplus aims at the large molecules of biological importance, and Fukui is concerned with chemical reactions.

The rest of the papers deal with the state of the art in various aspects of quantum mechanics, with no specific relation to Schrödinger. Thirring presents rigorous theorems about the wave equation in atoms. Seaton talks about astronomy. Hawking presents an intriguing, if speculative, idea about quantum effects on cosmology, and Salam gives a lively account of particle physics (given elsewhere on two previous occasions).

According to the preface the volume contains 'most of the invited contributions'. We are not told what has not been included.

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Specialist Periodical Reports. Electron Spin Resonance. Vol. 10B. Senior Reporter M. C. R. Symons. (Royal Society of Chemistry, London, 1987). [Pp. xv + 253.] £75·00/$128. ISBN 0 85186 851 7.

Specialist Periodical Reports were introduced by the Chemical Society in 1967 to supplement and complement the literature coverage provided by Annual Reports. There can be few research-active chemists who have not applauded their value for information-retrieval but nonetheless the publications have had a chequered history. The Society's line, which is promulgated on the dust-jacket of this volume and whereby it seeks to justify the annihilation of some titles in the series, is that it has kept pace with changes in degrees of activity in the various fields of chemistry. An alternative view, which I share, is that the ideal of providing things of value to the scientific community, which is the fundamental reason for the existence of Learned Societies, has sometimes been sacrificed to ruthless analysis of financial profit and loss. Fortunately for those of us who work in electron magnetic resonance the Series on Electron Spin Resonance, whose first Volume appeared in 1973, has survived the Thatcherite onslaught.

That this is so is largely due to the efforts of the Senior Reporter, Professor Martyn Symons. One of his innovations has been to gear the production of Volumes to the highly successful annual international meetings of the Electron Spin Resonance Group. The pattern of these meetings is that they alternate between consideration of organic and of inorganic paramagnets. The 1987 meeting, held in York in March, covered the latter and this volume, which was on sale at the meeting, does likewise. It thus completes Volume 10 of the Series, the first part, which dealt with organic-based systems, having appeared in the Spring of 1986. The literature is covered up to mid-1986, with the time-origin varying somewhat between the individual contributions.

Four of the six chapters in this book are essentially straightforward literature reviews. There is comprehensive literature coverage and there are comments on particularly interesting results. These Chapters deal with, 'Transition Metal Ions' (Gibson), 'Metalloproteins' (Hanson and Pilbrow), 'Spin Trapping Free Radical Metabolites of Inorganic Chemicals' (Mason and Motley), and 'Inorganic and Organometallic Radicals' (Symons). These Chapters are really

aimed at people already in the field, for whom they provide a convenient way into the primary literature. Indeed, one could say that they provide the discriminating man's guide to the literature.

In contrast, the other two chapters are in themselves essentially primary literature. They each take a specific area, and, in addition to reviewing work which has been done, they provide background theoretical and practical information. They could thus be recommended reading for someone seeking to learn about the area, such as a research student, a new postdoctoral worker, or an established worker whose expertise in electron spin resonance had been gained in a different part of the subject. Thus, if I warmly applaud the four chapters mentioned in the previous paragraph, I give these two a standing ovation. They are, 'Spin–Spin Interactions in Weakly Interacting Dimers' (Keijzers) and 'ENDOR Methodology' (Schweiger). Both are excellent: both authors are formidable scientists and they expound their material very well indeed.

To conclude, I must do two things. First, I enthusiastically congratulate the Senior Reporter and all his team on once again having produced an invaluable volume. Second, I urge that all who are working in electron spin resonance make sure that they have a copy available for immediate and repeated consultation.

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Water and Aqueous Solutions. Edited by G. W. NEILSON and J. E. ENDERBY. Proceedings of the 37th Symposium of the Colston Research Society, University of Bristol, April 1985. (Adam Hilger, 1986.) [Pp. 349 + xiii.] £35·00. ISBN 085274 576 1.

The meetings of the Colston Society have been held annually since 1948 and cover topics as diverse as Cosmic Radiation, Universities and the Theater, Metaphor and Symbol, Marine Archeology, the Eruption and Occlusion of Teeth, Utopias, and the Laws of Tort. It is a measure of the current interest in water that it finds itself in this company of subjects.

There are 26 papers grouped into the four headings, 'Water' (9 papers), 'Ionic Solutions' (9 papers), 'Water in Biological Systems' (4 papers), and 'Water in the Environment' (3 papers). The volume is rounded off by the Colston Lecture, by D. H. Everett, which bears the provocative title, 'How Much Do We Really Know about Water?'. It is a significant indication of the fashion of the day that at least one paper in each group (excepting the one concerned with ionic solutions) is concerned with computer simulations. The volume includes a transcript of lively discussions of the papers by the participants in the conference.

The coverage of the subject in a book containing only 342 pages of text could hardly be expected to be complete. A few of the papers attempt, on the whole very successfully, to give a broad survey of some aspect of the subject, but most papers report recent results of work in the laboratories of the authors. The book is, however, intriguing; one can get interesting and challenging insights, not to mention new information, from many of the papers.

Three of the four papers in the section on 'Water in Biological Systems' are by J. L. Finney and co-workers, All of these happened to be particularly interesting to me, and I feel that all physical chemists interested in proteins ought to be aware of them. I was especially interested in Finney's critical discussion of hydrophobic effects, which raises a number of pertinent questions.

This is an excellent book for browsing, and although hardly a 'must' for one's reference shelf, it can be strongly recommended for leisure time reading by all who have any interest in water and aqueous solutions.

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