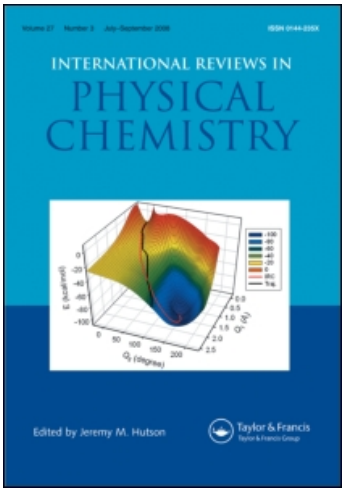

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Book reviews

Physics of Amorphous Materials. By S. R. ELLIOTT. (Longman, 1984.) [Pp. 432.] £25·00. ISBN 0582 44636 8.

Interest in the physics and chemistry of amorphous materials, particularly glassy metals and semiconductors has grown enormously in the past few years. A statistic given by Dr. Elliott in this introductory textbook relates to the number of publications on amorphous materials. During the period 1967–1981 the number has grown steadily from just over 3000 to 10 000. The reason for this growth of interest arises from both the technological importance of disordered materials on the one hand and from the desire to gain a fundamental theoretical understanding of systems which do not possess long-range order. However, in spite of the large volume of work carried out on amorphous systems, there are still important and significant gaps in our understanding and Dr. Elliott has attempted to highlight those areas of controversy which have not yet been resolved. In doing so he has tried to avoid giving too narrow a view of the subject and, where several conflicting points of view exist, has given due weight to each of them. The inevitable disadvantage of this approach is that on many occasions the reader has to be content with a general statement that more work is needed before a consensus view is possible. This is not meant to imply a criticism of the book since I believe that Dr. Elliott has provided a valuable guide to the subject as it was in 1983.

The first three chapters deal with the preparation and structural characterization of amorphous materials and the nature of the glass transition itself. All of these subjects are treated in a clear and cogent manner, due emphasis being given to modern experimental and theoretical methods. A feature of these and later chapters is the collection of interesting problems, some of which are quite demanding.

Chapters 4 and 5 deal with vibrational and electronic properties. It is here that the difficulty in writing a book on a subject which continues to develop at a rapid pace is most apparent. For example, one discussion of the electrical properties of amorphous materials is in terms of the concept of the minimum metallic conductivity first introduced by Sir Nevill Mott. Unfortunately, modern scaling theories seem to rule out this approach on rather general grounds. The real puzzle, not really resolved by Dr. Elliott is why, if scaling theory is to be believed, a substantial body of experimental data appears to support the original model.

The next chapter is concerned with defects which, in the context of disordered systems, refer to departures from an idealized model of the amorphous structure, for example, the continuous random net-work. I would have liked to have seen a rather fuller discussion of the meaning of the Hubbard U which is so central to what follows. Recent calculations indicate that even the sign of U is uncertain, since it involves the cancellation of large terms. Nevertheless, the diligent student prepared to follow up the references and original papers quoted in the book will have gained several useful insights into this important topic.

The final chapter on metallic glasses was included for completeness and provides a brief glimpse of what has become a major field of experimental and theoretical research. To do full justice to this subject requires a volume all to itself.

The aim of the book was to give new postgraduate students a sound introduction to the subject of amorphous materials and to emphasize those topics which remain controversial. I consider that this aim has been achieved and that Dr. Elliott is to be congratulated on bringing together a wealth of physical and chemical techniques, references to theory and a collection of useful experimental data. If read alongside the recent book by Zallen, *The Physics of Amorphous Solids*, which emphasizes the more formal aspects, the student should feel confident to tackle the extensive and growing primary literature of the subject.

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Specialist Periodical Reports—Electron Spin Resonance, Vol. 8. Edited by P. B. AYSCOUGH. (London: The Royal Society of Chemistry, 1984.) [Pp. 509.] £59·00. ISBN 0 85186 821 5.

This eighth volume of a series is the first to have been reproduced directly from camera-ready copy. This would be expected to speed up publication and to reduce cost, not least to the

consumer. It is consequently disappointing to discover that 16 months elapsed between the closing date of the material surveyed and publication, at least seven being after the manuscript left the Editor. This dilatoriness detracts from the scientific usefulness of the book. As regards cost, the volume appears priced so as to optimize income rather than to provide a service to chemistry. The publication costs no longer include typesetting ones, a reduction not carried on to the reader. This despite the print varying greatly in depth from page to page to an extent that some text is uncomfortably light to read. Although all practising E.S.R. spectroscopists would benefit from having these volumes on their bookshelves, the price finds them only where authors or reviewers receive their free copies, or in libraries.

The volume contains reports, rather than reviews (save for one instance), of work published between June 1981 and November 1982. It is reasonable to ask whether it provides anything that a computer search would not. At best the reports do: a good informed and critical one gives the feeling of being led through a major library, allowed to browse and to discover fascinating facts and ideas peripheral to one's own interests. It also establishes the context of each piece of work reported. At worst those few reports which provide merely a list of what has been done offer little. Indeed they have inherent dangers in repeating possibly erroneous conclusions uncritically: unestablished or incorrect ideas may be accepted by the uninformed reader.

The subject coverage is remarkably wide, being concerned with laser magnetic resonance spectroscopy, theory, triplets and biradicals, ENDOR and ELDOR, transition-metal ions, inorganic and organometallic radicals, organic radicals in solids and in liquids, polymers, spin labels, metalloproteins and medical applications. Professor Ayscough is to be commended as Editor on his continual introduction of new topics and for his willingness to commission introductory reviews on them when necessary. However the chapter headings are to some extent determined historically, which may cause exciting new developments, and their potential impact in new besides old fields, to be undervalued. Examples might include optically detected magnetic resonance (O.D.M.R.), electron spin-echo methods and fast transient techniques in general.

This series is uniquely valuable to practitioners and, although the Royal Society of Chemistry's attitude to it appears ambivalent, it is very much to be hoped that it will continue.

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Molecular Diffusion and Spectra. By W. T. Coffey, M. W. Evans and P. Grigolini. (New York: Wiley, 1984) [Pp. xiii + 378.] £66·50. ISBN 0471 87539 2.

This book contains a miscellany of topics and it is difficult to decide for whom it is written. A newcomer to either liquid-state spectroscopy, or the theories of molecular motion in fluids, would not be helped by this book. An established research worker would also find it confusing and unhelpful. To write a successful book, it is necessary to have a clear idea about what one is trying to do and whom one is writing for. The reader needs to be able both to follow the argument in detail and to perceive the overall theme. These authors have not succeeded in writing a coherent or useful book and one is left with the feeling that it is a self-indulgent exercise in describing the authors' recent research.

Although the exposition is confusing and the theme unclear, there are some useful parts. The first couple of chapters describe computer simulations of two specific organic liquids, namely CH_2Cl_2 and CH_3CN. There is a particular emphasis on the effects of large applied fields, the behaviour of correlation functions in different frames of reference and cross terms between translation and rotation. These are interesting topics, but it is misleading to base all the discussion on simulation of so few systems without any indication of the limitation of the particular intermolecular potential used, or of the errors in the computation of the various correlation functions. This work is published elsewhere and does not gain much by repetition.

The second and larger part of the book is devoted to aspects of the theory of reorientation and of brownian motion. A good deal of space is devoted to Langevin equations for molecules in electrical fields, and methods of finding approximate solutions for them, but the most interesting material is the discussion of non-linear effects and stochastic models of chemical reaction. It is typical of this book that this material is contained in a chapter entitled "Examples of the joint use of the AEP and CFP", which gives no physical insight and only means something to those already familiar with the abbreviations used by these authors.

Altogether I found this to be an unsatisfactory book, which is a pity, as the authors are knowledgeable and the topics are interesting. Unfortunately, the lack of synthesis of ideas, the lack of physical insight, and the lack of consideration of the reader make me unable to recommend it.

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Specialist Periodical Reports—Electrochemistry, Vol. 9. Edited by D. PLETCHER. (London: The Royal Society of Chemistry, 1984.) [Pp. xi + 290.] £64·00. ISBN 0 85186 077 X.

This is the second volume of this series to be edited by Dr. Pletcher and it contains six chapters, three of which are sequels of reviews in the preceding volume. Two of these comprise the sort of comprehensive survey of a region of chemistry typical of the Chemical Society's Annual Reports. C. J. Pickett covers 298 publications from the end of 1981 to the beginning of 1983 on the 'Electrochemistry of transition metal complexes' and J. Grimshaw a similar period on 'Organic electrochemistry—Synthetic aspects' with 140 references. Such chapters provide essential material for those working in the field.

The first chapter is this volume, by N. A. Hampson and A. J. S. McNeil, is a continuation of a review on 'The electrochemistry of porous electrodes' dealing here with 'Flow through and three-phase electrodes'. This review covers a longer period of time than the two already mentioned, and has, as a principal feature, an extensive coverage of Soviet work of the past 15 years, notably that of Yu. G. Chirkov. This work makes up nearly two-thirds of the 329 references quoted and there is no doubt that the reviewers have done a useful service in bringing this work to the notice of Western scientists. The field is of great practical importance and at the same time full of challenge to the theorist. It is remarkable that the reviewers have succeeded in presenting a subject of mathematical complexity without the use of any mathematics at all. There are times when this reviewer felt that this was, in fact, not an aid to clarity.

The other three chapters cover subjects new to this series and perhaps because of this the authors adopt a more expository style as well as attempting with much success to assess the present state of their subject.

Chapter 2 on 'Semiconductor electrochemistry' is a lucid presentation characteristic of its author L. M. Peter. It would provide an excellent introduction to a newcomer knowing some background in electrochemistry and semiconductor physics. Essentially the review covers the problem of the efficiency of the conversion of light energy into useful energy using semiconductor electrodes. The inadequacy of the classical approach based on purely energetic considerations is pointed out and the present kinetic models are discussed critically. This timely review will be valuable also for all those attempting to convert solar energy with semiconductor electrodes. The 323 references show how many are interested in this problem.

The review on 'Spectroelectrochemistry' by J. Robinson covers the whole of this relatively new subject in 60 well-organized pages giving 359 references. Each method is clearly presented with a balanced discussion of its capabilities and often an indication of the best sources of further information on practical aspects and interpretation. There is no doubt that this is the best available introduction to this important and growing field of electrochemistry; it is essential reading not only for the beginner but also for the experienced practitioner who will be able to put his own work in better perspective after studying this article. A rare feature is the author's bold attempt to suggest future trends.

The final chapter on 'Solid-state gas sensors and monitors' by D. E. Williams and P. McGeehin deals with a subject not often considered to be a part of electrochemistry despite its evident electrochemical nature. Devices depending on galvanic cells with valid electrolytes and those depending on change in conductivity of a solid electrolyte or semiconductor are the principal subjects here. They are of practical importance in the monitoring of combustion processes, among others. Despite substantial efforts, illustrated by the 143 references, these sensors seem to be dogged by practical problems, particularly stability in the aggressive environments where they are needed. Thus there seems much scope for research, and this article should bring this to the attention of more electrochemists.

The editor deserves our thanks for assembling this excellent volume and cannot be blamed for the extraordinary price ensuring that it is virtually inaccessible to the individual owner.

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Photoelectron Spectroscopy (second edition). By J. H. D. ELAND. (Butterworths, 1983.) [Pp. 271.] £25·00. ISBN 4 08710 57 8.

The techniques of photoelectron spectroscopy and the scope of its applications have expanded greatly since the first edition of Eland's admirable monograph was written in 1972. The purpose and structure of the book remains the same as in that first edition, but most of the chapters have undergone major revision in the light of new developments, and the opportunity has been taken to introduce a number of new topics.

Much of the pioneering work in photoelectron spectroscopy was devoted to the determination of ionization potentials, and to the elucidation of the electronic orbital structure of molecules using Koopmans' theorem. It has now become a mature branch of chemical physics and of chemical structure determination; with rather more emphasis on its relationship to other branches of ion physics and molecular spectroscopy, and even with applications to the physical chemistry of molecular ion reaction rates. All these developments are reflected in the revised text.

The book is written at an introductory level, although it does assume some familiarity with quantum ideas. It gently leads the reader through the basic principles towards the frontiers of the subject. It is full of practical tips for the newcomer to the field, and warns of pitfalls for the unwary. For example, molecular orbital calculations are often used as an aid to spectral assignment. Much care is needed to take account of the nature of each orbital as well as its orbital energy, since the ordering of the computed energies is not necessarily identical to that of the corresponding ionic states. A paper is described in which an excellent correlation was obtained between the successive peaks in a photoelectron spectrum and a set of *ordered* randon numbers!

There are eight chapters and two appendices. Chapters 1 (Principles of photoelectron spectroscopy) and 2 (Experimental methods) introduce the basic photoelectron technique, including the most recent uses of synchrotron radiation to give an intense wavelength tunable light source as an alternative to atomic lamps, and describe simple rules for the interpretation of the electronic structure of photoelectron spectra. Chapter 3 (Ionization) describes the various mechanisms which lead to molecular ionization, outlines the importance of the measurement of angular distributions of photoelectrons, and describes related techniques which give comparable or complementary information, such as electron energy-loss spectroscopy. Chapter 4 (Electronic energies of ionic states) gives a comprehensive but qualitative description of the various theoretical models which have been used as an aid to spectral assignment. Chapters 5 and 6 (Photoelectron band structure – I; and – II, Degenerate ionic states) describe the vibrational and spin–orbit fine structure of photoelectron spectra, and show how these can be used to make detailed deductions concerning changes in molecular structure on ionization and orbital bonding characteristics. Some of the most clearcut examples of the Jahn–Teller distortion of highly symmetrical molecules are included here. Chapter 7 (Reactions of positive ions) points out the differences in the energy level spectra and interatomic forces between molecular ions and neutral molecules, and the consequences for vibrational and electronic energy flow and unimolecular decompositions. Chapter 8 (Applications in chemistry) summarizes a wide range of topical exploitations of photoelectron spectroscopy.

No attempt has been made to provide an exhaustive survey of the literature of photoelectron spectroscopy. However, the book is copiously illustrated with spectra, duly acknowledged when not specially recorded for this purpose, and each chapter has a substantial set of literature references. The book is well produced, and the assiduous reader will not pause long over the few minor errors which have slipped through the proof-reading.

This book can be recommended as a good introduction both to photo-electron spectroscopy in general and to the current frontiers of knowledge in this field. Experienced researchers will also profit from its hints and accumulated wisdom.

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Molecular Potential Energy Functions. By J. N. MURRELL, S. CARTER, S. C. FARANTOS, P. HUXLEY and A. J. C. VARANDAS. (Chichester: John Wiley and Sons, 1984.) [Pp. 197.] £19·95. ISBN 0 471 90540 2.

This book is a research monograph on the analytical representation of potential energy surfaces, with especial consideration of diatomic, triatomic and tetra-atomic molecules. This is a topic which Professor Murrell and his theoretical chemistry group at the University of Sussex have made almost their own in the last ten years, and the book gathers together the results of their many publications, for both single-valued and many-valued surfaces. The book has fourteen chapters and appears remarkably free from typographical errors.

The book is very readable (as we must expect of Professor Murrell) and except for detailed discussion of the best forms for potential energy surfaces, it does not enter into the formal mathematics of the surrounding theory. Each chapter has an up-to-date list of references. Many chapters have contours of the potential energy surfaces determined by this research group, and the potential energy functions themselves are given in tables.

The opening chapter discusses the best analytical forms for diatomic curves; the authors favour the extended Rydberg form. Chapter 2 introduces the important features of potential surfaces and discusses surface crossings and conical intersections. Chapter 3 discusses LEPS functions and surfaces derived from the DIM method. The potential form favoured by Murrell *et al.*, the many-body expansion, is introduced here, represented as a sum of two-body (diatomic), three-body (triatomic) and so on, terms. Those who are critical of this approach will wish to read this chapter carefully, because the case for the convergence of the series is argued here. The analytical form of the n-body terms ($n>2$) is also discussed. This chapter also discusses the important role that *ab initio* calculations have to play, but it is a pity that an unnecessary definition of a Gaussian basis function is incorrect. On the same page the authors are too optimistic in hoping the 'black box' programs for accurate *ab initio* calculations of general potential surfaces will shortly be available. In chapter 4 coordinate systems appropriate to triatomic molecules are introduced. Chapter 5 concentrates on potential forms for Van der Waals molecules; for example the Hutson–Howard potential for ArHCl is given in detail. Chapter 6 discusses the derivation of H_2F and LiFH potentials from *ab initio* data by the least-squares method, and also gives LEPS potentials for Li_3 and Na_3. Chapter 7 describes how spectroscopic data may also be fitted to these analytic potentials. The variational method is used to obtain the vibrational energy levels of the surfaces. Parameters may then be adjusted so that these give agreement with experimental frequencies (examples HO_2, SO_2, C_3, HCN). Chapter 8 is devoted to H_3. Chapter 9 outlines one of the achievements of the Murrell approach—the derivation of two-valued analytic surfaces from the eigenvalues of a 2×2 matrix, each element being expanded in many-body form. Conical intersections arise naturally from this representation. H_2O is the example and there are 15 figures in this chapter. Surfaces with many minima, such as that for O_3, are discussed in chapter 10 and ions are discussed in chapter 11.

In chapter 12, the much more difficult problem of tetra-atomics is discussed. H_2CO is the principal example, where it is argued that the two- and three-body terms give a good balance to the surface as well as correct dissociation properties. Forms for the full four-body terms for H_2CO and C_2H_2 are given. The final chapter summarizes the present position and argues the case for a potential surface data base.

The need for accurate analytical representations for the potential energy surfaces of small molecules is unquestionable: the whole of chemistry is based on potential surfaces. It may in the end turn out to be impossible to generate the whole surface in this way with sufficient accuracy, but this writer believes that the attempt has to be made, and the approach made by the Murrell team has much to offer. It is a unique approach to the problem, and this well written book is a valuable contribution to the subject.

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Quantum Chemistry. By R. DAUDEL, G. LEROY, D. PEETERS and M. SANA. (Chichester: Wiley, 1983.) [Pp. 558.] £48·50. ISBN 0471 90135 0.

This ambitious text, by four distinguished French authors, gathers together many of the recent methodological developments in Quantum Chemistry. It may be considered as a

modernization of the first book with this title by Daudel, Lefebvre and Moser, and although expensive for individuals, it will find a place in most chemistry libraries.

The book is split into three Parts: 'General Quantum Chemistry', 'Methods and Applications of Quantum Chemistry' and 'Going Further into the Nuclear Motions'. Each of the eight chapters has a list of references at the end, and the principal references of the subject are included. There is a preponderance of references to works by French authors, but this is not cause for criticism. However, it is a great pity that there are so many spelling and other errors in the reference lists, because elsewhere the text seems to be of a high standard (although there are a few unfortunates, such as the discussion of modes instead of nodes on p. 9).

The opening chapter on basic ideas and methods discusses one- and two-electron systems, and introduces Daudel's idea of the loge partition of space surrounding a molecule. It is a novelty to see the connection between loge theory and information theory stressed in this chapter. (This reviewer does not like the **M** notation for an electron's coordinates instead of the usual ***r***). The second chapter, 'Calculating Wave Functions', examines the Born–Oppenheimer approximation, the Self-Consistent Field method and Configuration Interaction, and has extended discussion on semi-empirical methods. The third chapter concentrates on the electron density, and is particularly interesting because of its detailed discussion of density differences and Bader partitioning of a molecules' space into fragments.

In Part II, the fourth chapter enters more deeply into the calculation of wavefunctions. The various SCF methods are discussed, as are the methods for the calculation of one and two-electron molecular properties. Chapter 5, entitled 'The Practice of Quantum Chemistry Calculations', is long and detailed. Much of it is involved with the evaluation of Gaussian basis function integrals, but one wonders how much of this is necessary because, as the authors recognize, these are now best evaluated by the Rys quadrature scheme. The SCF method is discussed in further detail, and some very detailed numerical examples of the application of the SCF and CI methods are given. Chapter 6 describes applications of quantum chemistry. It discusses the searching problems for minima and transition states, and applications of loge theory and localization theory for the description of electronic structure. The theoretical calculation of thermochemical data is a section title, and also transition-state theory is discussed. There is a long section on hydrogen abstraction reactions. This is an important chapter which shows the great advances made in *ab initio* computation of molecular structure and molecule reaction properties in recent years, and is a good review of the current situation.

Part III considers in much greater detail the problem of nuclear motion, starting with another discussion of the Born–Oppenheimer approximation. There are detailed discussions on stationary points and the definition of reaction pathways. The latest theory for the evaluation of analytic first and second derivatives in *ab initio* SCF calculations is presented—but this makes the later discussion on numerical derivatives redundant. The standard classical treatment of the rotating-vibrating molecule is presented in all its complexity. Quantum mechanical treatments are also presented, using H_2 as an example. The last chapter, entitled 'The Collision Chemical Process', discusses initially analytic representations of potential surfaces, and their forms near the reaction pathway. The theory for the reaction path Hamiltonian is presented in great detail. Finally, there are three sections devoted to the calculation of reaction rate constants.

From this outline, therefore, the book contains a lot of valuable material for the *ab initio* theoretical chemist. There is a wealth of material on the methodology, as well as applications to the calculation of molecular structures, potential energy surfaces and reaction pathways. This reviewer believes that some of the detail presented in the text was best left in the original papers, especially when its usefulness is not justified. But the authors have made a valiant attempt to present a lot of theory (and many applications) of modern quantum chemistry in one text, and therefore the book should be present in chemistry libraries.

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