Book Reviews [*]

Advanced Series in Physical Chemistry, Volume 2: Modern Electronic Structure Theory, Parts I and II. Edited by David R. Yarkony (Johns Hopkins University). World Scientific: London, 1995. Part I: xiii + 721 pp. $89.00. ISBN 981-02-2987-9. Part II: xiii + 741 pp. $89.00. ISBN 981-02-2988-7.

This treatise is a pedogogically oriented collection of 22 chapters chosen to comprehensively present the quantum mechanics of electronic phenomena in molecules. It is an excellent effort to match increases in the physical understanding of chemistry with the astonishing advances in digital computer power and accessibility. Other and on-going attempts include *Ab Initio Methods in Quantum Chemistry* (K. P. Lawley, Ed.; Wiley: New York, 1987), *Methods in Computational Chemistry* (Stephen Wilson, Ed.; Plenum: New York, 1987 to the present, 6 volumes), *Reviews in Computational Chemistry* (Lipkowitz and Boyd, Eds.; VCH: New York, 8 volumes up to this past summer), and four articles in the 100th Anniversary issue of *J. Phys. Chem.* (August 1996).

The chapters in the volumes under review can be usefully subdivided into six categories.

Formulation of the Many-Electron Problem for Bound Molecular Systems (four chapters). K. Anderson and B. O. Roos develop multiconfiguration second-order perturbation theory. A. D. Becke explains density functional theory (DFT) in the clearest and most conceptually useful brief introduction to this important subject currently available. It is the reviewers opinion that the Kohn−Sham formulation of DFT will rather quickly dominate electronic structure theory and be the principle *ab initio* method in the 21st century. R. J. Bartlett gives a masterful treatment of coupled-cluster theory of which he is one of the principle orginators. Quasidegenerate (multireference) perturbation theory is addressed by M. R. Hoffmann.

Implementation Requirements. Along with the development of many-electron formulations there are numerous additional methodologies required for treating electronic structure problems, and eight chapters describe most of these. First, the all important question of basis sets and the necessary one- and two-electron potential energy integrals over them are fully discussed by T. Helgaker and P. R. Taylor. Jan Almlöf is well-known for his exploitation of the much higher speed of computer CPUs compared to their I/O facilities leading to his “direct” method of re-evaluating all molecular integrals for each iteration in SCF calculations, and his recent death makes his easy-to-follow and comprehensive chapter of special significance. Analytic energy derivatives are necessary ingredients for practical exploration of potential energy surfaces, and the two chapters by R. Shepard and P. Pulay are definitive treatments. Similarily, any chemist desiring to investigate a chemical reaction surface or an optimized molecular geometry needs to become acquainted with Bernie Schlegel’s thorough and graphically elegant chapter. T. J. Martinez and E. A. Carter apply the pseudospectral method to Møller−Plesset perturbation theory. The pseudospectral approach uses a numerical space grid integration scheme that provides a superior method for calculating the bottleneck problem of two-electron integrals, and the *Annu. Rev. Phys. Chem.* (**1991**, *42*, 341) article by Richard Friesner, principle developer of this scheme for quantum chemistry, is the best reference. B. A. Hess, C. M. Marian, and Sigrid Peyerimhoff provide the necessary implementation and examples for determining spin−orbit coupling in molecules, and J. Olsen and P. Jørgensen develop the time-dependent response theory required for evaluating molecular excitations in an external field.

Test of Methods. In two separate chapters H. F. Schaefer *et al.* and K. Raghavachari and L. A. Curtiss expertly survey the results of calculations using the correlated many-electron methods noted above to evaluate equilibrium geometries, dipole moments, harmonic vibrational fequencies, infrared intensities, and bond energies.

Electron−Molecule Scattering. Two chapters by C. Winstead and V. McKoy and T. N. Rescigno, B. H. Lengsfield, and C. W. McCurdy, respectively, study collision theory. It may be noted here that although there are no chapters on solid state chemistry—an important and rapidly growing area—it was probably a correct decision given the size and density of the two present volumes.

Special Topics. D. R. Yarkony gives an interesting and informative account of his research on the omnipresent, but generally avoided, problem of electronically nonadiabatic processes. His Johns Hopkins colleague, H. J. Silverstone, provides a complete mathematical analysis of the famous Schrödinger problem of the hydrogen atom in a uniform electric field.

Applications (four chapters). Approximately 100 molecular species (2−13 atoms, mostly 2−5) have been observed in the interstellar medium, and K. P. Kirby gives a historical account of how standard methods in quantum chemistry have been used to identify and/or characterize several of the unusual molecular aggregates found in outer space. More than 2500 articles have been written on fullerenes, and G. S. Scuseria has carried out *ab initio* SCF calculations on M@C_{28} clusters with M = Mg, Al, Si, S, Ca, Sc, Ti, Ge, Zr, and Sn as well as SCF and DFT calculations on many fullerenes, including C_{60}. Two of the application chapters are especially significant for their attempts to better understand chemical trends and patterns in chemical bonding. C. W. Bauschlicher, S. R. Langhoff, and H. Partridge review their many years of effort on transition-metal-containing molecules and molecular ions using high-level correlated wave functions of the type presented in this treatise. Species studied include the largely electrostatically bound ions with rare gases, H_2, N_2, benzene, OH_2, NH_3, CO, methyl, acetylene, ethylene, and methylene as ligands and the largely covalently bound neutral metal oxides, superoxides, carbonyls, and metal−metal diatomics. The authors give a valuable overview of transition-metal bonding by quantifying the known differential contraction of d orbitals relative to s, left-to-right across the periodic table, and its less pronounced nature for the second compared to the first row. They also quantify the small energy differences between d^ns^2 and $d^{n+1}s$ configurations in neutrals and d^ns and d^{n+1} in ions and the tendency toward promotion to d^{n+1} in ions. $s \pm d\sigma$ hybridization is also illustrated as well as the ability of ± rehybridization to reduce metal−ligand repulsion. Analysis of binding energy trends has enabled them to sometimes differentiate between conflicting experimental values. And their enormous stock of wave function data has certainly helped experimentalists to resolve questions on specific cases and to systematically determine spectroscopic parameters (r_e, D_e, ω_e) for many ions. At the present time, however, the level of interpretation is largely in terms of the mathematical and physics quantities that are the direct result of the quantum mechanical calculations on each species. The chemical concepts, models, and trends in terms of which experimentalists (or non-physics-oriented chemistry graduate students) do their thinking have not yet been created. M. S. Gordon, in his chapter on main group organometallics (C, Si, Ge, Sn, N, P, O, S), has, of course, a much less difficult interpretation problem, and he has been aided by the landmark chemical concepts paper of W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. Gordon has also been clever in abstracting chemically meaningful quantities, e.g., π-bond energies, from *ab initio* calculations on double bond breaking rotational barriers and thermodynamic cycles. His use of the three-center two-electron bond model to understand axial bonds in trigonal bipyramidal species has helped elucidate bond lengths and substitution effects in SiH_3XY^-, and $H_3N-SF_4-NH_3$, and to rationalize the experimental properties of the strained cagelike “atranes” which his Iowa State colleague, J. G. Verkade, has recently synthesized. On the other hand, his quantum mechanically adroit scheme of assessing bending in π-bonded molecules from their diradical character as measured by the natural orbital occupation numbers in MCSCF wave functions needs to be translated into more familiar concepts for most practicing chemists.

Each of the 22 chapters have their own references, each of which are up to date. The index is designed for ease of use with acronyms spelled out and cross-referenced. While the publisher suggests that “the book is aimed at first year graduate or college seniors considering graduate study in computational chemistry...”, this suggestion is more than a bit ambitious. The two-volume set is a necessary addition to chemistry libraries or research group holdings.

The forty-five years of the digital computer revolution has proved that a second path to chemical truth, parallel to the traditional one of physical measurement and experimentation, is available, and the Yarkony-edited treatise demonstrates that two generations of quantum chemists have been very successful in exploiting this opportunity. But most of the advances have been more nearly applied physics than chemical concepts, and this problem has been addressed in a famous article “More Is Different”, by Phillip W. Anderson (*Science* **1972**, *177*, 393). The notion that every field of science has its own uniquely appropriate models, concepts, and laws is currently much discussed, and Roald Hoffmann has an essay on this topic, “Fighting Reductionism”, in his recent book, *The Same and Not the Same* (Columbia

---

[*] Unsigned book reviews are by the Book Review Editor.

University Press: Irvington-on-Hudson, NY, 1995). Theoretical chemists need to give increased attention to creating concepts of greater relevance to experimental chemists.

Leland C. Allen, *Princeton University*

JA9655754

S0002-7863(96)05575-8

Inductively Coupled and Microwave Induced Plasma Sources for Mass Spectrometry. By E. Hywel Evans (University of Plymouth, U.K.) and Jeffrey J. Giglio, Theresa M. Castillano, and Joseph A. Caruso (University of Cincinnati). The Royal Society of Chemistry: Cambridge. 1995. viii + 107 pp. £32.50. ISBN 0-85404-560-0.

This monograph examines various ICP and MIP sources for plasma mass spectrometry. Although the authors state in the preface that this work should be viewed as "...an overview of the technique without being a comprehensive review of the literature; and to provide a tutorial review of the art of interfacing ICP and MIP plasma sources, formed in a variety of gases, with mass spectrometry", it appears that the authors were being somewhat modest. The four chapters in the text contain a wealth of information written in a very readable style. In fact, the authors are to be commended for the stylistic integrity they maintained throughout the text. This text has very few of the abrupt stylistic changes that one generally sees in works with a large number of contributors. The references to literature are numerous and recent, however, not encyclopedic, but are sufficient to give the reader a firm background. The only minor fault is that some of the terminology and acronyms common in the plasma literature are not always fully explained. Despite that minor flaw the monograph is extremely well written and very enjoyable to read. It should be beneficial to anyone in the chemical community desiring information on the state of plasma sources for mass spectrometry.

Harry B. Fannin, *Murray State University*

JA9655101

S0002-7863(96)05510-2

Circular Dichroism and the Conformational Analysis of Biomolecules. Edited by Gerald D. Fasman (Brandeis University). Plenum Press: New York. 1996. x + 738 pp. $125.00. ISBN 0-306-45142-5.

The text is a very clear exposition of the place that circular dichroism (CD) methods take in the study of the macrostructures of large biomolecules in solutions. The choices of the 24 authors, who address their particular specialties in the area of CD, would be very difficult to improve upon. Although written by such a diverse group of individuals, the chapters flow seamlessly into one another. The editor apparently had proposed a uniform approach for the development of each chapter and successfully arranged the order of the chapters to parallel the natural evolution of CD from its beginnings, when it was applied to simple molecular species, to the immensely complicated systems of the biological macromolecules.

Ever since my introduction to the history of chemistry as an undergraduate, I have been amused and entertained by back-stage personal anecdotes that seem to accompany evey scientific development. The opening (posthumous) chapter by Jen Tsi Yang, however, is one of the more poignant pieces that I have ever had the pleasure to read, and sets a perfect stage for the rush of the necessary old and the refreshing new information that is contained in the next 700 pages.

The titled biomolecules are peptides and proteins, nucleic acids (DNA and RNA), and carbohydrates. For the most part these are treated separately, with the major emphasis (eleven of nineteen chapters) devoted to peptides and proteins. Two chapters are specific to nucleic acids, and one is exclusive to carbohydrates. Contributions from the earliest workers in the field of CD of macromolecules are well represented and given due recognition in every case by the use of extensive bibliographies. The authors are also to be congratulated for going so far as to include so many recent citations, some as recent as 1996! If there is anything lacking, it would be the need for more thorough descriptions of mixed biopolymer systems, e.g., glycoproteins and lipoproteins, and the mutual effects of site binding interactions with ligand molecules. In one exception, Chapter 13, written by Professor Donald Gray on the subject of CD spectra of protein−nucleic acid interactions, was especially interesting to me and is presented in a very tidy package by carefully separating the interactions of nucleic acids with specific and nonspecific binding proteins. Structural differences between proteins (where the induced CD activity is a result of the interaction of a typically loose helical structure with a single chromophore, the peptide bond) and nucleic acids (which are typically rigid helical structures in association with multiple chromophores) are applied to the interpretation of the differences in the CD spectral data.

The emphases of most all of the experimental chapters are directed at deriving solution conformations for large soluble and/or globular forms of the bimolecules, and the kinetics and mechanisms that lie behind their interconversions (helix−coil and α-helix−β-sheet transitions). How CD spectra for membrane proteins differ from those of soluble proteins is addressed by Fasman in Chapter 10.

Instrumentation necessary for quality CD detection is described in five separate chapters. Although still wanting in many respects, the progress that has been made in the experimental side of the science of CD is still very far ahead of theoretical developments. The safest assignments of three-dimensional solution conformations using CD data are still those that are based on biomolecules for which the solid state X-ray structural data are available. These interpretations of course must presume that the usual extrapolation of a solid state structure to an equivalent structure in solution is valid. And for the systems investigated, the extrapolation appears to hold. Another problem that is addressed in detail is the analytical empiricism that is involved in experiments to determine the proportions of α-helix to β-sheet, etc., secondary structures using spectral data. Every conceivable procedure that has been tried, up to and including chemometric neural networking algorithms, is described in Chapter 3. The major obstacle to the analyses is, of course, that there are no reference or basis spectra for the individual structural forms.

The limitations of theoretical models that would allow one to use spectral information to assign a conformation are discussed in essentially every chapter without apology and with the appropriate optimism that the problems will be overcome in the not too distant future.

Confidence in believing in this optimism is derived from my readings of Chapters 16, 17, and 19 which deal with the continuing evolution of CD spectroscopy in the less familiar ranges of the electromagnetic spectrum. Until quite recently chiroptical methods were limited by technology to the range of electronic spectra, i.e., the visible and near-UV. Chapter 16 (by Kiederling) on vibrational circular dichroism (VCD) and Chapter 19 (by Barron) on Raman optical activity (ROA) describe the rapid developments that are being made in the vibrational (infrared) range. And in Chapter 17 (by Sutherland), which, to this reviewer, is perhaps the most fascinating chapter of them all, the potential for applying CD in the spectral range of soft X-rays is described. These subjects are appropriately placed at the end of the text where the justifiable speculations expressed by each author leaves a reader filled with anticipation that at long last an experimental method might well be within reach with which *absolute* molecular conformations can be determined, making CD more than competitive with NMR for large biomolecules.

The editor and authors have done a very commendable job in assembling a compendium of information, illustrated with real experimental data, that will endure for years to come as a special service to, and/or an introduction for, old and new investigators alike to the area of CD spectroscopic methods as they apply to the determination of the solution conformations of biomolecules.

Neil Purdie, *Oklahoma State University*

JA965689F

S0002-7863(96)05689-2

Physical Properties of Polymeric Gels. Edited by J. P. Cohen Addad (University Joseph-Fourier). Wiley: New York. 1996. xii + 311 pp. $89.95. ISBN 0-471-93971-4.

The past three decades has witnessed a revolution in the understanding of the static and dynamic properties of polymers in solution. While classical theories, summarized in the well-known textbooks of Flory, Tanford, and Yamakawa, are still of great value, more accurate understanding has been attained using the field and scaling approaches put forth by Edwards, de Gennes, and others. These modern theoretical advances have been complemented by relatively recent experimental techniques such as neutron scattering and NMR which can probe microscopic behavior. A number of books published in the past twenty years summarize current understanding. Unfortunately, most of these treatments have dealt mostly with solutions of polymer chains and have given short shrift to polymer gels, which are cross-linked networks of such chains swollen in a solvent. Classical theories of gels combine aspects of polymer solution theories with rubber elasticity theories, which have also been well reviewed in numerous texts. It is now known, however, that facile combination of network and solution theories is imprecise in many cases, and that new theoretical concepts are needed to fully understand gel behavior on both macroscopic and microscopic levels.

Given that a large primary literature on the physical chemistry of cross-linked polymer gels has been accumulating, the present book is a welcome contribution. The summary of the present understanding presented will be useful not only to basic scientists, but also to those who use gels as materials for separations, medical and pharmaceutical applications, and chemomechanical actuators.

Despite the general title, the book's scope is restricted mostly to properties of highly swollen gels near equilibrium. Left out are descriptions of the remarkable first-order swelling/collapse phase transitions that some gels exhibit in response to changes in their environment, as well as the kinetics of gel response to such changes. This need not be taken as a criticism of the present book, as a monograph on these other topics has been published recently. Moreover, it becomes clear to the reader that even within the restricted domain of coverage, there is plenty to learn and a plethora of unanswered questions.

The book contains five contributed chapters which can be read separately. The first chapter by J. F. Joanny provides a concise summary and comparison of the classical Flory−Huggins polymer solution theory and the more recent scaling theories developed by de Gennes and colleagues. While this chapter does not deal with gels *per se*, it is useful since these theories show up later in the book. The second chapter, by U. P. Schröder and W. Oppermann, reviews the swelling and elastic properties of polyelectrolyte gels within the framework of the most commonly utilized model in the literature, in which the classical Flory−Rehner theory describing the swelling of nonionic gels is combined with the Donnan theory of ionic swelling pressure. Corrections for the finite extensibility of polymer chains and for counterion "condensation" are included. It is shown that this model can be fit to data from a variety of polyelectrolyte gels by choosing reasonable values of model parameters. As pointed out by the authors however, various aspects of the theory must be regarded as approximate and may not be correct in all domains.

The third chapter, by J. P. Cohen-Addad, is an extensive review of NMR as a probe of gel structure and dynamics. This chapter provides derivations of the equations needed to apply NMR techniques, along with a wealth of structural/dynamical data obtained by NMR for various gel chemistries, extents of gelation, and degrees of swelling.

The process of gelation is the topic of the fourth chapter, by M. Adam and D. Lairez. It has long been known that percolation concepts are relevant to gel formation. Near the threshold of formation of an infinite gel network, scaling theories with roots in the study of critical phenomena apply. In this chapter the theory is presented and compared against data gathered using scattering and rheological techniques.

The final chapter, by J. Bastide and S. J. Candau, reviews the state of understanding of gel structure, as obtained using laser and neutron scattering techniques. This masterfully written chapter exposes the inadequacy of theoretical approaches which simply combine polymer solution theories with rubber elasticity theories. The structure factor of gels shows at least two characteristic length scales, one of which can be assigned to the characteristic distance between cross-link points, and a longer distance characteristic of larger scale organization. The presence of this second scale indicates that gels cannot be viewed simply as networks of chains with the same properties as they would have in solution. A number of theories of the structure factor are presented and evaluated; at present no single theory can account for all observations.

This volume may be regarded as a summary of current understanding of polymer gels, which is not complete. The book will be a useful handbook for researchers in the field since it explains the theory behind various experimental approaches, presents experimental evidence, and relates the latter to current theories of gel properties.

Ronald A. Siegel, *University of California, San Francisco*

JA965639A

S0002-7863(96)05639-9

Principles of Nonlinear Optical Spectroscopy. By Shaul Mukamel (University of Rochester). Oxford University Press: New York. 1995. xviii + 543 pp. $65.00. ISBN 0-19-509278-3.

In recent years, optical experiments probing the dynamics of molecules on ultrafast time scales have become possible, and have substantially increased our understanding of the fundamental microscopic processes underlying many chemical transformations. In order to understand such experiments completely, one must turn to the study of nonlinear optics. In addition, the possibility of using novel materials in optical communications has contributed to a growing interest in the study of nonlinear optics in the chemical community. Professor Shaul Mukamel, a well-known and accomplished theoretical physical chemist, has written an up-to-date and comprehensive monograph/textbook on nonlinear optical spectroscopy. Although the focus is theoretical, the attention paid to describing modern experiments is noteworthy.

Beginning with an introduction to density matrices and relaxation theory, he introduces nonlinear response functions and optical susceptibilities, using both the more standard methods and the Liouville space method that he has used so effectively in his own research. Early on, he introduces semiclassical approaches that are amenable to computer simulation, and shows the connection to the quantum mechanical approaches.

After these theoretical developments, he then goes on to describe and analyze a large number of nonlinear optical experiments, such as fluorescence, spontaneous and coherent Raman spectra, photon echoes, and pump−probe and hole-burning spectroscopies. In the final chapters, Mukamel reviews the theory of the nonlinear response of molecular aggregates, including cooperative and many body effects.

This book is unusual in its completeness: the theoretical development assumes only a standard quantum mechanics course, but goes all the way to the most recent developments; the attention to experiments and what can be learned about molecular dynamics from them are as deep and definitive as the theory. I can recommend this book wholeheartedly both as a textbook in a graduate course in modern fast spectroscopy and as a reference monograph for researchers in the field.

Robert J. Silbey, *Massachusetts Institute of Technology*

JA965513D

S0002-7863(96)05513-8

Strategies in Size Exclusion Chromatography. Edited by Martin Potschka (Scientific Consultant) and Paul L. Dublin (Indiana University-Purdue University). ACS: Washington, DC. 1996. xiii + 415 pp. $109.95. ISBN 0-8412-3414-0.

ACS Symposium Series No. 635. Developed from a symposium sponsored by the Division of Polymer Chemistry, Inc., at the 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2−6, 1995. This book examines size exclusion chromatography technology from both the detector-focused and column-focused approaches. It provides fundamental information on the mechanism of size exclusion chromatography separations. It addresses special topics in size exclusion chromatography including characterization of copolymers, inverse size exclusion chromatography, aggregating polymers, polysaccharides, and proteins.

JA965750G

S0002-7863(96)05750-2