THEORETICA CHIMICA ACTA

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Book reviews

S. Wilson: Electron Correlation in Molecules. Oxford: Clarendon 1984, 281 pp

To construct accurate molecular wave functions and energies, electron correlation has to be taken into consideration. In giving an up-to-date review of the electron correlation problem S. Wilson at the same time describes the present status of *ab initio* quantum chemistry. The material is presented in a simple and clear fashion so that even a beginner (i.e. one who is not yet fully familiar with, for example, the Born-Oppenheimer approximation or the Hartree-Fock model) can read and learn from it.

Nevertheless, those already initiated in *ab initio* quantum chemistry will appreciate this book even more. Practically all of the topics relevant to electron correlation are discussed, with particular emphasis being placed on the author's pet method, "many-body perturbation theory" (MBPT). Within the space available, it would hardly be possible to deal painstakingly with the formalism of MBPT and other difficult subjects. The author prefers to give the reader a feeling for the important aspects of the theory. For example, there is a well-presented section of Jucys' graphical spin algebra, but this can hardly be understood by someone who is not familiar with the traditional theory of angular momentum. The practical aspects of the theory are, however, not neglected. There is a very careful discussion of the choice of the orbitals basis, of the problem of truncation of CI expansions etc., even of the prospective role of vector computers in quantum chemical calculations. It was a pleasure to read this book, and there is only one point in which I would tend to disagree. The author's criticism of the CI approach is certainly justified, but it is probably not fair to present MBPT as the only systematic and non-biased approach to electron correlation. There are many possible variants of MBPT, and in order to achieve reliable results some sophisticated manipulation of MBPT is necessary, even if there is no doubt that these manipulations are elegant and promising. S. Wilson's *Electron correlation in molecules* can be recommended to all theoretical chemists who are interested in *ab initio* theory.

Complementary to this book are that of P. Carsky and M. Urban (*Ab initio* Calculations: Methods and Applications in Chemistry. Lect. Notes in Chemistry, vol. 6. Springer 1980), which is often quoted, and that of I. Lindgren and F. Morrison (Atomic Many-Body Theory. Springer Series in Chemical Physics, vol. 73. Springer 1981).

W. Kutzelnigg, Bochum

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Henry F. Schaefer III: Quantum Chemistry, The development of *ab-initio* methods in molecular electronic structure theory. Oxford: Clarendon, 1984, 144 pp. £15

This little booklet consists of the titles and summaries of 149 selected papers (from 1928 to 1983) that are supposed to represent the important steps in the history of *ab initio* quantum chemistry. The selection is very personal and at first glance rather arbitrary. It turns out, nevertheless, to be quite representative provided that one understands *ab initio* quantum chemistry in a restricted sense, namely as the development of computational methods for the construction of good approximate molecular wave functions, and if one agrees with the author that the state of the art is the configuration interaction (CI) method with all its variants such as MC-SCF, coupled-cluster CEPA etc. and that alternative approaches as those based on r_{12}-dependent wave functions, on propagators or on Monte-Carlo techniques are hardly competitive. Properties (especially 2^{nd} order properties), intermolecular forces, or pseudopotentials, are only shortly mentioned, nonadiabatic and relativistic effects, qualitative understanding of the chemical bond, and many other topics are outside the scope of this booklet.

The summaries, written by H. F. Schaefer, are easy to read and instructive. The author puts the main emphasis on the historical context of his "landmark" papers and on tracing back useful ideas.

The ideal reader of Schaefer's booklet is an experimental chemist who uses black-box-type *ab initio* programs but who is not satisfied with this situation and who wants to understand more about the background of the methods to make better use of them. I hope that many of these ideal readers are reached and encouraged to read the original papers.

W. Kutzelnigg, Bochum

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I. Ugi, J. Dugundji, R. Kopp and D. Marquarding: Perspectives in Theoretical Stereochemistry (Lecture Notes in Chemistry, Vol. 36). Berlin: Springer, 1984: 247 pp., paperback U.S. $19.30, DM 54.80

The book, reproduced directly from the computer-edited manuscript (therefore free from any errors) presents in a consistent and logical fashion the authors' unified mathematical theory for constitutional and stereochemical isomerism, based upon the concept of "permutational isomers" first introduced by Ugi et al. in 1970. This concept, analogous to, but distinct from, Ruch's double coset formalism in which both the ligands and the skeleton receive labels, may also be applied to non-rigid molecules and is independent of the precise geometry of the skeleton (which does not receive any labels, and in reality has seldom the idealized geometry normally ascribed to it).

The book is divided into three parts, totalling eight chapters: part I, the permutational approach to stereochemistry; part II, the mathematical theory of the chemical identity group; part III, application of the theory of the chemical identity group to actual current stereochemical problems. The second part is structured mathematically with definitions, lemmas, theorems and proofs, but the other parts are written in common chemical style. In order to facilitate the reading by chemists, frequent cross-references among various chapters are included, and an appendix explains the mathematical terms (e.g. normal subgroups, cosets, etc.).

For several years, the *b*ond and *e*lectron (BE) matrices introduced by Ugi and his coworkers proved their usefulness in chemical information. Chapter VIII presents an integrated nomenclature and documentation system based on BE matrices and the authors' CANON algorithm which specifies both constitutional and steric features of molecules and avoids some of the drawbacks extant in traditional systems which are discussed critically. In addition, the system described here is easily implemented on a computer.

A notable feature of the book is its rich and recent bibliography (although some historically relevant references from the older literature are also included); some of the cited papers, like an important one by Mislow and Siegel, were consulted in manuscript form and are quoted as being in press.

The reviewer spotted just one recurrent awkward phrase: for "so well as..." one should read "as well as...". In general, the style is clear and very readable, and the printing conditions are excellent. It is a sad thing that the book is dedicated to the memory of one of the authors, professor Dieter Marquarding, who died in 1982 at the age of 47.

The book is addressed to organic, inorganic and theoretical chemists or advanced students, and to all those who wish to become acquainted with modern thinking in chemistry and are not afraid of having to learn a few new terms and to become familiar with mathematical concepts.

Alexandru T. Balaban
Department of Organic Chemistry, The Polytechnic Institute, Bucharest, Romania

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J. W. Perram (ed.): The Physics of Superionic Conductors and Electrode Materials. NATO ASI Series B, Vol. 92. (ISBN 0-306-41271-3). New York and London: Plenum Press 1983, 281 pp

The physics - and chemistry - of ionic conductors is an area of ever increasing research interest, not least because of the potentially rich technological applications envisaged for these systems. This volume, the outcome of a NATO Advanced Study Institute, describes in detail how recent computational advances in the theory of condensed matter can be applied to elucidate and quantify the mechanism of conduction in ionically conducting solids. It is therefore a book primarily for theoreticians, but with sufficient balance in the level of presentation that it should appeal to a wide audience, including those not experienced in the area.

The principal focus of the book is the application of molecular dynamics and Monte Carlo techniques to the study of superionic conductors, together with concomitant theoretical problems associated with the use of lattice sums in simulations of ionic and dipolar systems. Within this framework a broad range of material is covered: the evaluation and application of lattice sums; the role of boundary conditions in ionic simulations; the method of molecular dynamics with constraints (applied to polymeric electrolytes); the method of stochastic dynamics, and recent developments and applications of Monte Carlo methods, to name but a few. If one chapter is to be singled out it is that by Rahman and Vashishta, which reviews widely the general methodology of molecular dynamics simulation with particular application to superionic conductors, and which is written in a lucid manner which never loses sight of experimental reality.

Other topics covered include the relation between crystal structure and ionic conductivity, the hopping model of conduction, application of simulation methods to the problem of melting and application of irreversible thermodynamics to mass transport in ionic conductors.

The volume is recommended both as a work of reference for experienced practitioners and as an introduction to the field for aspiring (but educated) novices.

David E. Logan

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