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Recensiones

R. Lefebvre and C. Moser: Correlation Effects in Atoms and Molecules, Advances in Chemical Physics XIV. London-New York: Wiley 1969. pp. X + 545, $ 29.50.

This volume contains lectures of an Advanced Summer Institute on Correlation Effects in Atoms and Molecules held in Frascati, Italy, in 1967. The contributors are experts on the correlation problem. The contents of their articles are as follows.

R. K. Nesbet suggests that a hierarchy of nth order Bethe-Goldstone equations is particularly advantageous to solve the correlation problem. He emphasises the practical aspect of his method in terms of computational implementation. He supports this by preliminary calculations on first-row atoms which show that higher-order terms in the energy series are negligible and the series converges adequately to second or third order. J. Čišek describes the correlation problem in the language of quantum field theory. He discusses the use of cluster expansions and diagram techniques in calculations of correlation effects in atoms and molecules. In contrast to Sinanoglu, he pursues a coupled pair-many-electron theory. Group theoretical means are employed by B. R. Judd to study effective many-electron operators for configurations of equivalent electrons. His method is an extension of Racah's work on the classification of many-particle eigenfunctions to many-particle operators. The study shows a considerable increase in complexity when going from second-order to third-order perturbation theory. Here a group theoretical description can no longer reduce the number of operators to a *few* parameters. Hence it is less profitable for effective three-electron operators. H. P. Kelly reviews applications of many-body diagram techniques in atomic physics. An analysis of calculations of correlation energies and transition probabilities in atoms is presented. Diagrams for multiple perturbations and scattering are given. A. P. Jucys develops the Hartree-Fock equations in multi-configuration form. Simplifications of these equations and some results for atoms are discussed. A. P. Jucys and V. A. Kaminskas apply what they call "the extended method of calculation" to first-row atoms. The method uses different radial functions for different electrons. The correlation energy of a non-uniform electron gas is the topic of K. A. Brueckner's article. Again diagram technique is used to characterize energy contributions. O. Sinanoğlu reviews his unlinked cluster approach in the light of recent developments. Various types of correlation in excited states are discussed and numerical values for $1s^2 2s^n 2p^m$ atomic configurations are given. Correlation between localized orbitals is investigated. The consequences for semiempirical theories are presented. In particular, the geminal approach is discarded because of large $2s2p$ intershell correlation. In a number of lengthy footnotes the author evaluates other work in the area of correlation. P. O. Löwdin discusses some aspects on the correlation problem and possible extensions of the independent-particle model. Wave and reaction operators are used as tools. Symmetry dilemma, projected Hartree-Fock method and multi-configuration SCF method are topics of this paper. F. Grimaldi investigates the effect of mono- and di-excitations in extensive configuration interaction calculations on diatomic molecules. It is interesting to see that the coupling between mono- and di-excitations has an important influence on one-electron properties like dipole moments. P. G. H. Sandars makes a case for the usefulness of the linked cluster expansion in treating configuration intereaction in open-shell atoms. The emphasis is on various theorems in diagram techniques and their derivation. The volume closes with two articles by V. V. Tolmachev on the abstract theory of the field-theoretic form of the perturbation theory for many-electron atoms and its applications.

To characterize this volume briefly, one might say that quantum field theory with its diagram techniques has influenced the major portion of the articles. Linked and unlinked cluster expansions are used with the emphasis on methodology. Only few results of calculations are available to support one or the other approach. Also many of the topics have been described and reviewed before. Nevertheless, as a unified view this volume will be appreciated by everybody interested in knowing what to expect beyond the Hartree-Fock approximation.

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All-Valence Electrons SCF Calculations of Large Organic Molecules by Gilles Klopman and Brian O'Leary. Topics in Current Chemistry, Vol. 15, No. 4. Berlin-Heidelberg-New York: Springer 1970. 89 pp., 4 Figs., 37 Tables. $10.50.

Professors Klopman and O'Leary have prepared a concise and complete review of modern approximate self consistent field molecular orbital methods. This is an exceptionally fine contribution to the literature of quantum chemistry and fulfills an acute need where no other equivalent presentation is available. A short introductory chapter places their effort in proper perspective, followed in Chapter II by a formal development of spin-restricted matrix Hartree-Fock theory. Chapter III develops the approximate methods including CNDO, INDO, MINDO and PNDO, including a detailed discussion of contributions to the parametrization of the methods by various research groups. This chapter ends with very useful summaries of the methods in tabular form, listing scope of methods (objectives, successes, failures, and source of programs), approximations used for core integrals and electron repulsion integrals, matrix element expressions, and electronic energy expressions. Chapter IV is organized around molecular properties, and gives a comparison between calculated and observed values for ionization potentials, heats of formation, dipole moments, molecular geometries, force constants, electronic spectra, nuclear magnetic resonanec spectra and electron spin resonance spectra using the most appropriate approximate method in each case. This book is highly recommended as a reference for quantum chemists and should find wide use as a supplementary text in graduate and undergraduate quantum chemistry courses. At a price of $ 10.50 paperbound in the U.S.A., this book is rather expensive, but so is everything else these days.

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