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Book Reviews

G. L. Malli (ed.): Relativistic Effects in Atoms, Molecules, and Solids. Proceedings of a NATO Advanced Study Institute at UBC, Vancouver, August 1981, Series B, Vol. 87. New York and London: Plenum Press 1983, x + 544 pp

During the past decade the significance of relativity to the chemistry of most elements except the lightest ones has generally become apparent. After a couple of local workshops at various places, two international conferences in this field were held in 1981 and 1982. With some delay the Proceedings of both have now become available. The Vancouver volume covers a broad spectrum of articles, reviewing the state of art of relativistic quantum chemistry in 1981. The editor has to some extent succeeded in arranging the partly overlapping articles in a logical order.

Foundations of the basic Dirac-Breit equations are given by Sucher (pp. 1–53), Grant (pp. 73–88) and Keller (pp. 489–499). A different perturbative approach is advocated by Detrich and Roothaan (pp. 169–182). Theory and results of relativistic calculations on atoms are presented by Grant (pp. 55–71, pp. 89–113), Desclaux (pp. 115–143) and Mohr (pp. 145–167). As in the nonrelativistic case, the sophistication of the formalism and the accuracy of numerical results contrasts with the simple first-order techniques of SCF-procedures still in use in atomic physics.

Hartree-Fock-Roothaan formalisms for molecules are derived in a straightforward manner by Malli (pp. 183–211) and Ladik *et al.* (pp. 305–333), but the problems of appropriate basis sets, SCF-convergence and variational stability remain open. Useful numerical results are obtained only after the introduction of further simplifications. A comparatively rigorous pseudopotential formalism is presented by Pyper (pp. 437–487) whereas the approach of Malli and Ishikawa (pp. 363–382) lacks the simplifications only justifying the inherent approximations. Numerical results on a diversity of molecular systems are discussed by Desclaux (pp. 213–225) using the one-center approximation, by Hay (pp. 383–401) and Pitzer (pp. 403–420) using effective core potentials, and by Yang (pp. 335–361) and Ziegler (pp. 421–436) using the statistical exchange approximation.

Generalisations and trends in the periodic systems are given, but the explanations sometimes do not distinguish between significant first-order indirect and small second-order direct relativistic effects. Relativistic modifications of the band structure of solids are reviewed by Koelling and MacDonald (pp. 227–304). In addition, 20 lectures are represented by extremely brief abstracts.

Representing written lectures of a summer school, several articles are more readable than the original literature, which is cited extensively in most of the papers. The book is quite useful since it touches most aspects of relativistic quantum chemistry in one volume.

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S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki (eds.): Physical Sciences Data 16, Gaussian Basis Sets for Molecular Calculations. Amsterdam, Oxford, New York, Tokio: Elsevier Publishing Company 1984, 426 pp

This contribution is an extension of the editor's longstanding research on the construction of atomic basis sets for use in molecular calculations. It consists of a short introduction into the general problematics of the optimization and use of various types of basis sets, both of Gaussian and of Slater type, and concludes with over 400 pages of tables of data for all atoms from Lithium ($Z=3$) to Radon ($Z=86$). The Introduction begins with definitions of terms in standard use, such as minimal basis set, primitive and contracted Gaussians and their relationship to Hartree–Fock orbitals, as well as to Slater-type basis sets. The actual optimization of the present basis sets proceeds in four steps, the first three of which involve generation of numerical Hartree–Fock atomic radial functions, least-squares fitting in terms of linear combinations of primitives, and finally refining cycles of the least-squares minimization. The final optimization is then accomplished by using the least-squares basis functions in atomic SCF calculations and minimizing the total SCF energy with respect to further variations in their exponents and contraction coefficients. The introduction then concludes with remarks about the choice of expansion patterns and details of the manner in which higher-order spherical harmonics are most conveniently represented in Gaussian type orbitals, as well as a coherent discussion of the basis set superposition error and the counterpoise method.

The second chapter deals with more specific information as to how best to employ the tabulated basis set information which comprises the main part of the book. The tables themselves contain the standard data regarding expansion pattern, total, kinetic and potential energies, exponents and contraction coefficients and SCF orbital energies and $\langle r^N \rangle$ expectation values. Details of how the various minimal basis sets can be split into larger numbers of component functions for increased flexibility, as well as how they may be augmented by various polarization and diffuse functions to obtain additional accuracy in both SCF and subsequent correlated wavefunction treatments.

Especially with this introductory material at hand, the reader will find the tables of basis set information to be very conveniently organized. The first table gives one- and two-component polarization functions for all neutral atoms in the Li-Ra range plus a few key ionic species. These data are followed by an index of the ensuing basis sets, which allows the user quick access to the information for a given atom or ion of current interest. The book should serve as an essential reference for researchers in the field of molecular calculations, especially for problems dealing with heavy atoms in the periodic table.

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