

PREFACE

The majority of theoretical treatments of electronic behavior are based upon the Schrödinger equation. The Schrödinger equation incorporates the major postulates of quantum mechanics, the assumption that energy states are quantized and the recognition that small particles have wave-like properties. It ignores effects explained by the other theory of non-classical mechanics, the theory of relativity, but these effects are minor when the electronic structures to be studied are those of molecules which contain only light atoms. The small relativistic effects which are important for light atoms, spectroscopic fine structure effects for example, may be incorporated with perturbation theory. This approach rapidly becomes unsatisfactory as heavy atoms and molecules which contain heavy atoms come under consideration. For heavy-atom species it is necessary to discard the Schrödinger equation in favor of the Dirac equation. Relativistic effects, minor in light atoms, increase in magnitude rapidly as atomic number increases. Such effects account for a significant fraction of the chemical bond energies in molecules which possess second row transition elements and larger.

Relativistic effects are responsible for several well-known chemical phenomena. Among these are the lanthanide contraction; the disparity in properties between Au and its smaller group members, Ag and Cu; the special stability of Hg_2^{++} ion; and the fact that Hg is a liquid under standard conditions. They all point up the fact that a general theory of atomic and molecular electronic structure, applicable uniformly to all elements of the periodic table, must be based upon the Dirac equation rather than the Schrödinger. The Dirac equation, like the Schrödinger, can be exactly solved only for one-electron problems. Atomic and molecular wave functions are approximate, and an approximation must have certain qualities in order for it to be a useful one.

In the last two decades, a great deal of effort has been directed toward developing quasirelativistic and fully relativistic many-electron theory formulated in particular with discrete basis expansion methods. Construction of an effective many-body Hamiltonian that accurately accounts for both relativistic and electron correlation effects in many-electron systems is a challenge. It is only in the past 15–20 years that relativistic quantum

chemistry has emerged as a field of research in its own right. It seems certain that relativistic many-electron calculations of molecular properties will assume increasing importance in the years ahead as relativistic quantum chemistry finds wider range of application. The applications of relativistic quantum chemistry are indeed manifold. This volume is concerned with the determination of electronic structures for heavy atoms and molecules which contain heavy atoms where relativistic effects are not negligible. With the increasing use of relativistic quantum chemical techniques in chemistry, there is an obvious need to provide experts' reviews of the methods and algorithms. This volume has the ambitious aim of disseminating in a single volume aspects of relativistic many-electron theories and their exciting developments by practitioners. Together, the nine chapters provide an in-depth account of the most important aspects of contemporary research in relativistic quantum chemistry, ranging from quasirelativistic effective core potential methods to relativistic coupled cluster theory.

In the first chapter of the present volume, M. Dólg and X. Cao provide a comprehensive review of the energy-consistent pseudopotential variant of the relativistic effective core potential method. In Chapter 2, E. Miyoshi, Y. Sakai, Y. Osanai, and T. Noro provide a detailed description of recent developments in relativistic model core potential methods, and outline how to determine effective core potential parameters and valence basis sets. In Chapter 3, A. B. Alekseyev, H.-P. Liebermann and Robert J. Buenker describe two computational methods for carrying out configuration interaction calculations in which spin-orbit and other relativistic effects are included in the Hamiltonian by means of effective core potentials. Various one and two electron spin-orbit coupling Hamiltonians are discussed, along with symmetry properties of their matrix elements by D. G. Fedorov, M. W. Schmidt, S. Koseki, and M. S. Gordon in Chapter 4. Chapter 4 covers both theoretical methods and chemical applications. A. Wolf, M. Reiher, and B. A. Hess provide in Chapter 5 a masterly review of the generalized Douglas-Kroll transformation, a transformation to two-component electron-only formulations by suitably chosen unitary transformations. R. Fukuda, M. Hada, and H. Nakatsuji review their generalized UHF theory in the framework of two-component quasirelativistic molecular orbital theory in Chapter 6. In Chapter 7, T. Nakajima, T. Yanai, Y. Ishikawa and K. Hirao provide a detailed description of new

four-component Dirac-Hartree-Fock and Dirac-Kohn-Sham methods for heavy-atom-containing polyatomics that employ highly efficient computational schemes utilizing generally contracted spherical harmonic Gaussian spinors for rapid integral evaluation. Two-component quasirelativistic Hamiltonians, RESC and higher-order Douglas-Kroll, are also described, and illustrative calculations are shown. O. Matsuoka and Y. Watanabe give a brief overview of their four-component relativistic atomic and molecular program suite, PROPHET4R, in Chapter 8. In Chapter 9, W. Liu, F. Wang, and L. Li give an overview of the Beijing Density Functional Program package that can perform nonrelativistic one-component, quasi-relativistic two-component, and four-component relativistic density functional calculations. Relativistic coupled cluster calculations are computationally demanding. Chapter 10 details such approaches by U. Kaldor, E. Eliav, and A. Landau, i.e. the solution of the matrix DF SCF equations by expansion in basis sets of Gaussian functions and its refinement by Fock-space relativistic coupled cluster (CC) theory.

We owe a considerable debt to our publishers who have been helpful and understanding. In particular, we would like to thank Mr. Suwarno who has been most generous with his advice.

February 2003

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