Book Reviews

Relativistic Effects in Chemistry Part B, Applications. By Krishnan Balasubramanian (Arizona State University). Wiley: New York. 1997. xii + 527 pp. $89.95. ISBN 0-471-17991-4.

This book, the second of two volumes dealing with the effects of relativity in chemistry, describes applications, mostly based on effective core potential methods, to a range of molecular systems. The book consists of four chapters each developed from reviews published previously by Balasubramanian. Throughout the volume the emphasis is on the work carried out by Balasubramanian and his colleagues using effective core potential methods.

Even today, there is the tacit assumption in the vast majority of published molecular electronic structure calculations that the physical consequences of the special theory of relativity are completely negligible, except under the most extreme conditions. Indeed, in 1929, P. A. M. Dirac wrote (*Proc. R. Soc.* **1929**, *A123*, 714) "... quantum mechanics is now complete, the imperfections that still remain being in connection ... with relativity ideas" and then went on to claim that these difficulties "are ... of no importance in the consideration of atomic and molecular structure, and ordinary chemical reactions...". It was not until 1978, almost fifty years later, that P. Pyykkö (*Adv. Quantum Chem.* **1978**, *11*, 353) pointed out to chemists that "for a hydrogen-like atom having $Z = 80$, we see that the binding energy reaches ... about 17% of the rest mass" and made them aware of the potential inadequacies of nonrelativistic formulations of the electronic structure problem. For the hydrogen-like ununbium (Uub), the heaviest atom discovered to date, the binding energy is over 33% of the electron rest mass!

The chemical consequences of relativity, which became apparent during the 1980s, have now entered inorganic chemistry textbooks (Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. Mackay, K. M.; Mackay, R. A. *Introduction to Modern Inorganic Chemistry*, 4th ed.; Prentice Hall: Englewood Cliffs, NJ, 1989). In orbital models, the largest relativistic effects are associated with the tightly bound core orbitals, which contract and become more tightly bound. Valence orbitals undergo more complex "sympathetic" adjustments which may have the same magnitude as the adjustments in the core orbitals. Valence orbitals which penetrate as far as the nucleus display contractions and increases in binding energy of similar proportions to inner-shell electrons. Less penetrating orbitals are modified by the increased screening of the core by the relativistic contraction. This effect dominates the behavior of d, f, ... orbitals. Fine structure effects, which in nonrelativistic formulations are attributed to "spin−orbit" interactions, stabilize $p_{1/2}$ orbitals relative to $p_{3/2}$ orbitals.

As early as 1935, Swirles (*Proc. R. Soc.* **1935**, *A152*, 625; *A157*, 680) demonstrated the practical implementation of Dirac−Hartree−Fock theory in atomic structure calculations using the finite difference techniques which are tractable for one-center problems. For molecules the use of the algebraic approximation, i.e., finite basis set expansions, is ubiquitous in nonrelativistic studies. Indeed, it is almost obligatory. But, in relativistic formulations the practical implementation of the algebraic approximation leads to technical problems which were only solved during the early 1980s. Matrix Dirac−Hartree−Fock calculations provide not only approximations for the occupied spinors but also a representation of the complete spectrum, including both positive energy and negative energy branches, which is an essential ingredient of treatments of electron correlation effects that is not readily available from finite difference studies. Many-body perturbation theory, and the quantum electrodynamics from which it was originally developed, provides a natural vehicle for the description of correlation effects both within the "no-virtual-pair" approximation and beyond.

The technical difficulties associated with practical ab initio relativistic electronic structure studies dictated that most studies of the effects of relativity in molecules carried out during the 1980s were based on semiempirical approaches. Of these, the effective core potential methods have been among the most widely used. It is not easy to see how the relativistic dynamics of valence electrons penetrating the core region can be estimated reliably using this approach. Nevertheless, calculations employing "relativistic" effective core potentials have given many tantalizing glimpses of the effects of relativity in molecular systems, and this work provides, within a single volume, a survey of many of these insights.

The first chapter deals with small transition metal clusters. Developed from a review of small coinage metal clusters published in 1989, it contains new material on larger clusters and on Pt, Pd, Rh, and Ir clusters. For the coinage metals, Cu, Ag, and Au, clusters of up to six atoms are considered. The palladium and platinum clusters Pd_2, Pt_2, Pd_4, and Pt_4 are discussed and then Rh_3 and Ir_3. Fifteen of the 25 figures and 34 of the 39 tables in this chapter are taken from work of Balasubramanian and his collaborators. The second chapter, developed from a review published in 1989, is devoted to heteronuclear diatomics of main group p-block elements. Spectroscopic properties and potential energy curves of heavy diatomic hydrides XH for X = Ga, Ge, As, Se, Br, In, Sn, Sb, Te, I, Tl, Pb, and Bi, together with the ions SeH^+, HBr^-, HI^-, and BiH^+, are considered in the first part. Attention is then turned to the heavy halides XF for X = Tl, Pb, Bi, and Sb; XCl for X = Tl, Pb, and Sn; XI for X = Bi and Pb; and XBr for X = Pb, Sn. In the third part, the species XO are considered for X = Sn, Pb, Sb, and Bi together with SnS and PbS. A comparison of the electronic properties of these diatomic species completes this chapter. Over 90% of the publications cited were originally published prior to 1990.

Chapter 3 covers main group clusters, which were reviewed by Balasubramanian in 1990. Spectroscopic properties and potential energy curves for the following heavy homonuclear dimers are discussed: Ga_2, Ge_2, As_2, Se_2, Br_2, Br_2^+, In_2, Sn_2, Sb_2, Te_2, I_2, I_2^+, Tl_2, Tl_2^+, Pb_2, and Bi_2. Attention is then focused on the electronic structure of mixed clusters, such as Ga_xAs_y and In_xP_y, and then the trimers Ga_3, In_3, Ge_3, and Sn_3, the group V trimers (P_3−Bi_3), and Se_3, Te_3, and Po_3. Less than 6% of the bibliography for this chapter arises from work published after 1990. The final chapter is based on a review published by Balasubramanian in 1994 on molecules containing lanthanides and actinides where relativistic effects are known to be most important. Sections deal with the lanthanide hydrides, diatomic lanthanide and actinide halides, lanthanide oxides, and selected lanthanide and actinide polyatomic molecules. A discussion of lanthanides and actinides trapped in carbon cages completes the chapter. The author writes that the book "is not theoretically demanding and does not contain any sophisticated relativistic quantum mechanical formalism. It can be read independently of Part A, ...". However, many acronyms are used, e.g., NREP, RECP, CASSCF, FOCI, SOCI, CPF, etc. The book would have benefited greatly from a glossary of abbreviations and acronyms employed.

The late 1980s and 1990s saw the development of reliable, relativistic ab initio molecular electronic structure algorithms formulated within the algebraic approximation. Continuing improvements in computer hardware, in terms of both performance and cost, and algorithms for exploiting it are gradually reducing the "quasiempirical" element of both nonrelativistic and relativistic ab initio molecular electronic structure calculations associated with basis set truncation. The future will certainly see the application of these more rigorous methods to systems such as those described in this volume which will, therefore, serve as a useful reference.

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JA975596D

S0002-7863(97)05596-0