Theor Chem Acc (2007) 117:459–460
DOI 10.1007/s00214-006-0160-y

BOOK REVIEW

Relativistic electronic structure theory. Part 2. Applications, edited by P. Schwedtfeger (Elsevier: Amsterdam 2004)

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Published online: 12 August 2006

The last three decades have seen considerable advances in the theory and implementation of quantum mechanical methods, both relativistic and nonrelativistic. Coupled with the remarkable advances in computing technology, high-level calculations can now be performed that accurately interpret experimental results, and in some cases even rival experiments. Although the relativistic methods have tended to lag the nonrelativistic methods, they are in routine use in many places.

The two volumes of "Relativistic Electronic Structure Theory" embody the culmination of efforts, in relativistic method development and offer a wide overview of the state of the art in relativistic computations on atoms, molecules, and solids. The second volume is devoted to applications (backed with the necessary theory), and ranges from QED and parity-violation effects to the properties of solids.

The volume opens with an overview of the chemistry of the heaviest elements—the actinides and transactinides—covering both experiment and theory, and showing how relativistic atomic and molecular calculations have helped to elucidate and inform the experiments on superheavy elements whose half-lives are less than a second and for which the challenge of obtaining experimental data is formidable.

The theme of property prediction for superheavy elements continues in the following chapter with a review of highly accurate calculations on atoms, where the surprising trends due to relativity in the seventh period are illustrated: the change of ground state for the noble metals from $d^{10}s^1$ for Au to d^9s^2 for Rg, the large increase in IP from Pb to E114, and the existence of an electron affinity for the heaviest rare gas (E118).

High accuracy is also the subject of Chapter 3, which reviews state-of-the-art calculations for a few electron atoms that include all the smaller effects that are necessary to produce results within experimental accuracy: the Breit interaction including retardation, QED effects, and finite nuclear size effects.

Small effects, this time coming from the electroweak force, are the focus of the following chapter on parity-violation effects in molecules. The chapter necessarily delves into the standard model of particle physics, but the presentation is very clear, and the implications for chiral chemistry are well illustrated.

Two chapters deal with other properties originating in the nucleus: Chapter 5, on electric field gradients and nuclear quadrupole moments, and Chapter 9 on relativistic effects in NMR chemical shifts. Chapter 5 addresses the contributions to electric field gradients from the partitioning of the relativistic or quasirelativistic Hamiltonian into spin-free and spin-orbit effects, and also the neglect of the "picture change" in the quasirelativistic calculations. Chapter 9 also provides insight into the contribution of the various terms of the relativistic Hamiltonian to chemical shifts and spin–spin coupling constants, addressing both the heavy-atom light-atom (HALA) and the heavy-atom heavy-atom (HAHA) effects.

The intervening chapters (6, 7, and 8) describe the results of methods that replace the core with an effective potential. The chapter on two-component RECP methods first assesses the methods against all-electron calculations, and then describes some interesting results for diatomic molecules and polyatomic molecules of superheavy elements. The succeeding chapter on AIMP

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methods presents applications of lanthanide and actinide ions in solids using an embedding potential, including spin-orbit effects. The third of these chapters describes the use of pseudopotentials for excited states, especially including spin-orbit effects, and presents a range of applications including spectroscopy of various metal diatomics, actinyls, ionic impurities in crystals, and finally the use of zero-electron PPs for spectroscopy in rare gas matrices.

The final three chapters turn to applications of relativistic density functional theory. Chapter 10 covers small molecules, comparing a variety of one-, two-, and four-component DFT calculations with experiment and with high-level wave function calculations. Chapter 11 describes the use of the Douglas–Kroll–Hess approach in DFT applied to molecules and materials, from small molecules through larger coordination complexes to large metal clusters and simulations of surface interactions. Both chapters examine the difficulty that DFT has with open-shells and spin-dependent interactions. The final chapter presents solid-state calculations using relativistic DFT methods, applied to the prediction of lattice constants, band structures, and magnetic properties of ground states.

As can be expected in a contributed volume of this nature, the presentation and depth of the theoretical treatment and the scope of the applications vary considerably. Some chapters have a minimal treatment of the theoretical background and spend most of their time on the presentation of results and analysis of trends; others have an extensive treatment of the theoretical background—sometimes of necessity due to the nature of the subject—with a fairly small range of applications. Each chapter, however, meets the goal of illustrating some aspect of the application of relativistic electronic structure theory to a problem of experimental interest and of illuminating the importance of a relativistic treatment.

This book is a valuable resource for any worker in electronic structure theory, both for its insight into the utility of a variety of relativistic methods, and for its assessment of the contribution of relativity to a wide range of experimental properties.