Theor Chem Account (2008) 119:523–524
DOI 10.1007/s00214-007-0399-y

BOOK REVIEW

Dyall K G, Fægri K, Jr.: Introduction to Relativistic Quantum Chemistry

Oxford University Press, 2007, 530pp., $95.00

Christopher J. Cramer

Received: 14 November 2007 / Accepted: 15 November 2007 / Published online: 27 November 2007

Einstein's formulations of special and general relativity are rightly hailed as being amongst the greatest scientific achievements in human history. With that as background, it is surprising that the everyday consequences of relativity tend to be poorly covered in modern Chemistry curricula—typically being limited to rather brief discussions of relativistic orbital contractions in inorganic chemistry and a murky linking of spin to relativity in introductory quantum mechanics. Dyall and Fægri, in contrast, offer in-depth developments of quantum theories for particles, atoms, and molecules, that are consistent with the requirements of relativity, and they do so within the context of a modern science where computational implementation of these theories permits accurate calculations to be compared to experiment or employed for prediction.

It was hard while reading this book not to be reminded of the classic work of Szabo and Ostlund, *Modern Quantum Chemistry* (Macmillan 1982), which was written as an introduction to *non*-relativistic electronic structure theory. Both texts proceed from first-principles beginnings and develop increasingly sophisticated treatments (and concomitant approximations) with the goal of moving in a logical way from an older foundation to a modern pinnacle. Both are written in lucid and flowing prose and clearly reflect considerable care on the part of the authors to maintain a seamless connectivity of topics and concepts. Finally, both pay attention to the practicalities of computational implementation whenever appropriate.

That being said, Dyall and Fægri face a considerably more challenging task with respect to the physical and, especially, mathematical background required for their presentation. They begin with a brisk review of the principles of special relativity and the consequences of Lorentz invariance for electromagnetic interactions, introducing the necessary four-dimensional operators, gauge transformations, and other concepts in short order. The construction and solution of the quantum mechanical free-particle Dirac equation is then presented and its four-component nature discussed. The next two chapters, dealing with quantum electrodynamics and double group symmetry might arguably have been better left as advanced topics to be treated at the end of the text (the reader who has never before encountered quaternions may be forgiven for feeling daunted), but each has key implications for the development of practical computational algorithms in chemical systems, so one can understand the authors' choice to address these issues early. Armed with these tools, the relativistic spinors of the one-electron atom are derived and particularly useful comparisons that highlight similarities and differences in the relativistic and non-relativistic solutions are made. Part II of the book concludes with the development of relativistic mean-field theory for the many-electron case.

Without going into extensive additional detail, the remainder of the book is devoted to detailed discussions of practical (matrix) operator representations, the demands on one-particle basis sets, methods for including electron correlation, relativistic density functional theory, and an extremely thorough discussion of approximate techniques for including various orders of relativistic effects in practical one-, two-, and four-component technologies, including inter alia relativistic effective atomic core potentials, perturbation theory, the zero-order regular approximation, and the Douglas-Kroll-Hess model. A set of 12 appendices provides additional detail for some of the mathematical manipulations and useful reference material.

However, while the book is mathematically, and perhaps physically, enormously comprehensive, it is, given its title,

C. J. Cramer (✉)
Department of Chemistry, University of Minnesota,
207 Pleasant Street SE, Minneapolis, MN 55455-0531, USA
e-mail: cramer@umn.edu

surprisingly short on chemistry. A chapter is devoted to molecular properties, including magnetic properties like NMR where relativistic effects can be particularly large, but the discussion is entirely formal, with no presentation of actual data, whether experimental or computational. Only very slightly more connection to chemistry is provided in a final chapter dedicated to molecular bonding and structure. At the outset of this last chapter, the authors demur that a listing and discussion of examples would become obsolete so quickly that it would have no value, and advise the reader to consult modern reviews, but this suggestion is not particularly satisfying. Perhaps consistent with this preference for physics over chemistry, the text contains only 5 figures in its 500+ pages, and a similarly small number of tables presenting data.

For those primarily interested in methodological aspects, the theoretical development is careful and explained in detail. Making the comparison to Szabo and Ostlund again, however, there is little or no reduction to practice as there was in that earlier text dedicated to non-relativistic quantum chemistry. Thus, one is not led through the computation of particular matrix elements, for instance (although the relevancies of different relativistic terms *are* generally carefully described in terms of their dependence on inverse powers of the speed of light, which is qualitatively very useful). Some such actual manipulations might help to illuminate more clearly the connection between two-spinor and four-spinor formalisms, these being switched between sufficiently frequently that the motivation can be sometimes opaque.

Notwithstanding these minor reservations, I consider this to be an excellent and surprisingly affordable text. Above and beyond the copious scientific content and the clear exposition, the authors and publisher have obviously been extremely careful in the production process—the equations and text appear essentially error-free. Anyone looking for a comprehensive and practical reference with respect to relativistic quantum theory will be well served by this volume.

Christopher J. Cramer