Markus Reiher, Alexander Wolf

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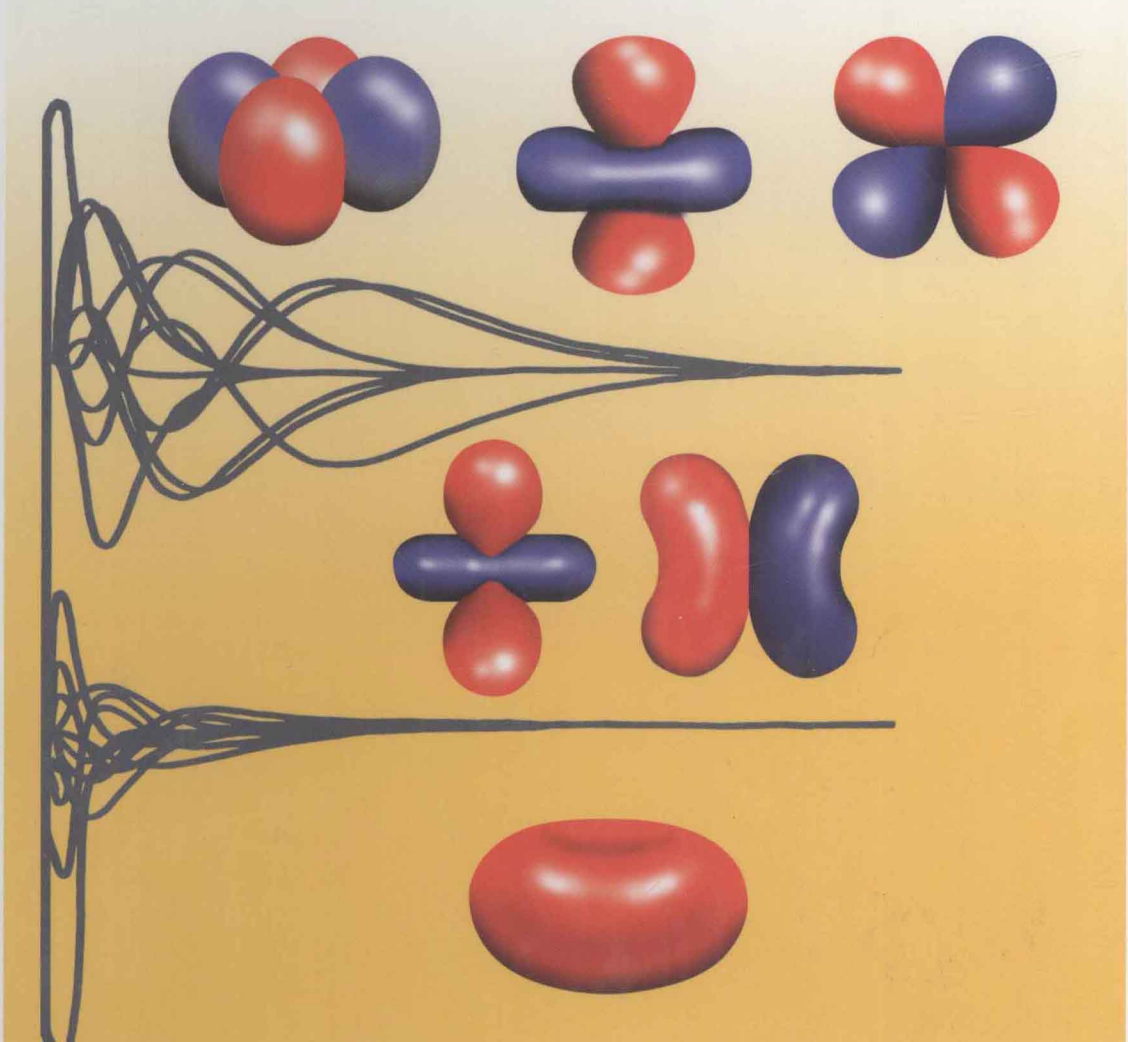
Relativistic Quantum Chemistry

The Fundamental Theory of Molecular Science



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The Fundamental Theory of Molecular Science

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Further Reading

P. Comba, T. W. Hambley, B. Martin

Molecular Modelling of Inorganic Compounds

2009
ISBN: 978-3-527-31799-8

H.-D. Höltje, W. Sippl, D. Rognan, G. Folkers

Molecular Modeling

Basic Principles and Applications

2008
ISBN: 978-3-527-31568-0

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Preface

A relativistic consistent quantum-theoretical description of electronic bound states in atoms was first introduced in atomic physics as early as the late 1920s and has been pushed forward since that time. It was believed, however, that effects stemming from Einstein's theory of relativity were of little or even no importance to chemistry. This changed in the 1970s when it was recognized by Pyykkö, Pitzer, Desclaux, Grant and others that several 'unusual' features in heavy-element chemistry and spectroscopy can only be explained in terms of so-called relativistic effects. *Relativistic effects* denote the deviation of results obtained in a theoretical framework which is in accordance with Einstein's theory of special relativity from nonrelativistic Schrödinger quantum mechanics. Since then, the development of quantum chemical methods for the description of *relativistic* electronic structures has made huge progress — particularly since the late 1980s.

Current relativistic electronic structure theory is now in a mature and well-developed state. We are in possession of sufficiently detailed knowledge on relativistic approximations and relativistic Hamiltonian operators which will be demonstrated in the course of this book. Once a relativistic Hamiltonian has been chosen, the electronic wave function can be constructed using methods well known from nonrelativistic quantum chemistry, and the calculation of molecular properties can be performed in close analogy to the standard nonrelativistic framework. In addition, the derivation and efficient implementation of quantum chemical methods based on (quasi-)relativistic Hamiltonians have facilitated a very large amount of computational studies in heavy element chemistry over the last two decades. Relativistic effects are now well understood, and many problems in contemporary relativistic quantum chemistry are technical rather than fundamental in nature.

We aim to present coherently all its essential aspects in textbook form using a homogeneous notation throughout the book. The greatest challenge of this endeavor is to give a description of the whole theory ranging from the fundamental physical concepts to the final application of the theory to issues of chemical relevance like molecular structure, energetics, and properties. The

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presentation will be concise and focus on the essential ideas as well as on analytical results rather than on too many of the unavoidable technical details, which might blur the view on the physics and concepts behind the calculations. To illustrate these important points in more detail:

(i) It is the nature of approximate relativistic many-electron theories that a large number of effective Hamiltonians may be deduced (defining thus a plethora of different relativistic quantum chemical approaches), though this is neither advantageous nor desirable because of the huge amount and variety of numerical data whose accuracy may be difficult to assess. Instead a rather small number of well-justified approximate Hamiltonians should suffice as we shall see.

(ii) In a similar manner, so-called relativistic effects are discussed *in extenso* in chemistry although these effects are, of course, purely artificial in nature since any fundamental physical theory has to be based on the principles of special relativity. The errors introduced by a nonrelativistic approximate description, which do not occur in a relativistic framework and which cannot in principle be measured in experiments, are called relativistic effects. However, this definition of relativistic effects may only be useful to address surprising observations in the chemistry of homologous compounds when the properties of a heavy-element compound deviate from those of its lighter homologs as in the most prominent cases of the *liquid* state of mercury at ambient conditions and of the *yellowish* color of gold.

Nevertheless, technical details of implementations as well as a moderate amount of discussion of these relativistic effects will be covered by this book as these are needed in practice when actual calculations are to be performed and their results interpreted. In addition, technical and implementational issues are incorporated to demonstrate how the relativistic many-particle equations are actually solved and what effort is required for this.

Because of the wide range of topics covered by this book it was appropriate to start with an introductory chapter, in order to prepare the ground for a convenient perception of structure and material presented in this book. While writing the book we realized that there was no space to present various aspects of our topic in sufficient depth. Still, our main goal was to present in great detail all essential ideas and how they are connected. Since this has always been the guideline for our own research, we may have put the focus too much on what we always have considered to be important throughout the past decade. At least we tried to derive as much as possible of the material presented from scratch to make this book as original as possible. In order to compensate for deficiencies that certainly result from our specific choice of material and its presentation we provide references to selected papers from

the original literature. Although we included a considerable number of such references, it is hardly possible to provide a complete list of references as this would comprise several thousands of papers. Fortunately, Pekka Pyykkö made a huge effort to set up a complete data base of references, first published as a series of books [1–3] and since the mid-1990s also available online on the internet [4]. And, we may draw the reader's attention to reviews by leading experts in the field as collected by Schwerdtfeger [5, 6] and by Hess [7]. Of course, this book provides all the basic vocabulary and knowledge required to dig more deeply into the literature.

Finally, it is a pleasure to mention that our view of relativistic many-electron theory has been shaped over a period of more than a decade in which we had the opportunity to sharpen our understanding by comparison with the views of colleagues who shared their knowledge to various extents with us; these are (in alphabetical order): PD Dr. D. Andrae, D. Dath, Prof. E. Eliav, PD Dr. T. Fleig, Prof. L. Gagliardi, Prof. B. A. Hess, Prof. H.-J. Himmel, Prof. J. Hinze, Prof. J. Hutter, Prof. H. J. Å. Jensen, Prof. G. Jeschke, Prof. U. Kaldor, Dr. D. Kędziera, Prof. B. Kirchner, Dr. T. Koch (it took only 13 years), Dr. A. Landau, Prof. R. Lindh, Prof. P.-Å. Malmqvist, Prof. B. Meier, Prof. F. Merkt, Prof. U. Müller-Herold, Prof. F. Neese, Dr. J. Neugebauer, Prof. P. Pyykkö, Prof. M. Quack, Prof. R. Riek, Prof. B. O. Roos, Prof. K. Ruud, Prof. V. Sandoghdar, Dr. T. Saue, Prof. W. Scherer, Prof. W. H. E. Schwarz, Prof. P. Schwerdtfeger, Prof. H. Siedentop, Dr. R. Szmytkowski, Prof. W. van Gunsteren, Prof. C. van Wüllen, Prof. L. Visscher, and Prof. M. Westerhausen.

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Markus Reiher and Alexander Wolf *Zürich, June 2008*

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