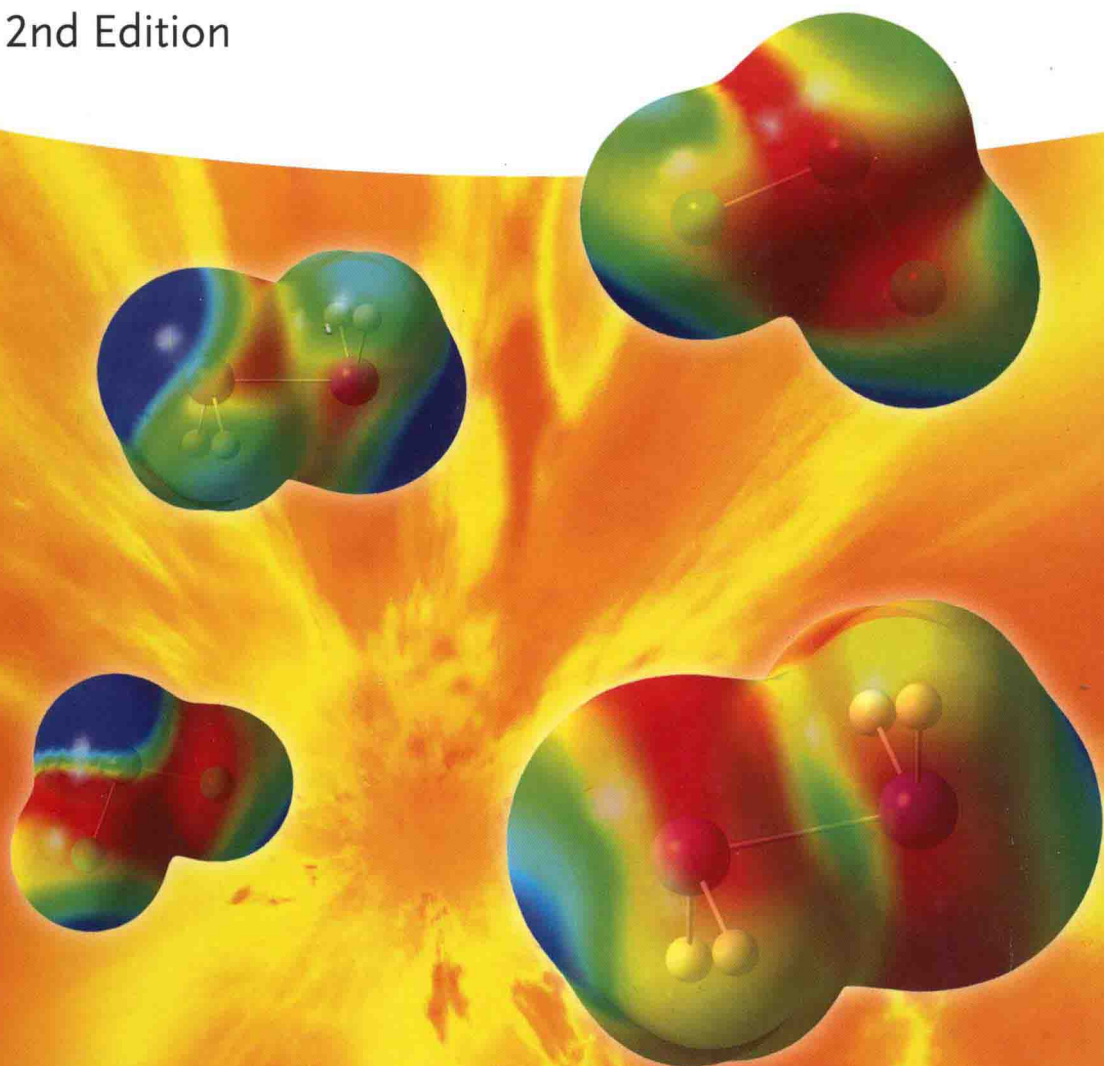


Markus Reiher, Alexander Wolf

Relativistic Quantum Chemistry

The Fundamental Theory of Molecular Science

2nd Edition



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To Carmen and Barbara.

Preface

Preface to the Second Edition

In this second edition of our book *Relativistic Quantum Chemistry*, we have taken the opportunity to refine the presentation of the original material at several places throughout the book in order to enhance the understanding of the train of thought and of the material presented. We have continued to focus on the physical principles of the theory and to discuss how they can be exploited in actual calculations. We have attempted to make the text even more concise and understandable in order to improve on how the formalism transports the physical content and on the step-by-step understanding of the mathematical derivations.

After publication of the first edition in January 2009, we also spotted a number of misprinted equations that required corrections (a correction list for these equations in the first edition has been made available on our web-pages www.reiher.ethz.ch). Some of these issues were brought to our attention by colleagues and especially by our students and co-workers, who were engaged in exercise classes held on the subject at ETH Zürich. In particular, we are grateful to Dr. Katharina Boguslawski, Arndt Finkelmann, Dr. Sam Fux, Moritz Haag, Mickael Hubert, Dr. Christoph Jacob, Prof. Bogumil Jeziorski, Dr. Stefan Knecht, Tobias Krähenmann, Dr. Vincent Liegeois, Dr. Koni Marti, Dr. Edit Mátyus, Dr. Daoling Peng, Dr. Maren Podewitz, Prof. Trond Saue, Benjamin Simmen (who also produced Fig. 8.1 for this edition according to the presentation in Ref. [1]), and Thomas Weymuth.

We have updated the material considering the latest developments in the field over the past five years. These developments comprise both computational and more fundamental advances such as exact two-component approaches and the study of explicitly correlated two-electron wave functions in the context of the Brown–Ravenhall disease, respectively. Other topics, such as relativistic density functional theory and its relation to nonrelativistic spin-

density functional theory, have been extended and worked out in more detail compared with the first edition. The list of references has been extended by almost two hundred entries, most of which reflect recent original work in the field.

The high activity in the field has also been documented in numerous review articles (and books) that have been published on various topics after publication of the first edition of this book (see Refs. [1–28] for an (incomplete) list). All of these presentations have a different focus and emphasize different principles, which makes them an interesting read.

The habit in research papers of writing equations in Hartree atomic units is somewhat unfortunate. It eliminates most of the relevant fundamental physical constants and makes the extraction of units or a simple consistency check in terms of units difficult. As it was already our intention to bring the natural constants back into all equations, we deemed it useful to have a new appendix which explicitly provides a list of the most relevant physical quantities, their dimensions and units, and references to central equations in the text in which they appear.

For producing figures for the new title picture of the book, we are very grateful to Dr. Nick Sablon. Nick generated the graphics material from data presented in Ref. [29]. The four inlays show the relativistic effect on the Fukui function, which was calculated for PbCl_2 and Bi_2H_4 within Schrödinger- (left) and Dirac-based (right) quantum mechanics in Ref. [29].

Finally, we are grateful to our contact persons at Wiley-VCH, namely to Dr. Eva-Stina Müller for making the second edition possible and to Dr. Martin Graf-Utzmann for his patience.

Markus Reiher and Alexander Wolf

Zürich, September 2013

Preface to the First Edition

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 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 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 [30–32] and since the mid-1990s also available online on the internet [33]. And, we may draw the reader's attention to reviews by leading experts in the field as collected by Schwerdtfeger [34,35] and by Hess [36]. 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.

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Markus Reiher and Alexander Wolf

Zürich, June 2008

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