

PREFACE

Relativistic effects are responsible for a number of well-known chemical phenomena. For instance, the effect on the adsorption energy of carbon monoxide on platinum low-index surfaces is so pronounced that the adsorption energy cannot be described by non-relativistic theory based on the Schrödinger equation. Relativistic effects on Pt–C bond shortening and CO adsorption energy obtained in calculations that include the relativistic correction, and corresponding calculations that exclude the correction, are found dramatic. The adsorption energy increases by about 50% when relativity is included. They point up the importance of accounting for relativistic effects in a general theory of atomic and molecular electronic structure.

In the last 3 decades, a great deal of effort has been expended to develop quasi-relativistic and fully relativistic electronic structure theory to account for these chemical phenomena. With the increasing use of quasi-relativistic and fully relativistic quantum chemical calculations on heavy-atom-containing molecules, there is an obvious need to provide experts' reviews of the concept and computational methods. This volume has the ambitious aim of addressing both experimentalists and theoreticians interested in the area of relativistic effects in atomic and molecular systems and processes and in their consequences for the interpretation of the heavy element's chemistry. The book will include chapters covering basic theory, computational methods, and experimental aspects of interest for chemists. It describes the essential details of the theoretical methods to account for relativistic effects and place them into the context of modern applications, of broad interest to experimentalists and theoretical chemists in both academia and industry.

All the authors are renowned experts in their fields and many topics covered in this volume represent the forefront of today's science.

The leading chapters of the book will concentrate on theory at the intermediate level, starting with the explanatory article intended to show the importance of the relativistic theory and relativistic 'thinking' in chemistry and molecular physics. This introductory chapter will outline the basic features of the transition from non-relativistic to relativistic methods and will be followed by several chapters explaining the most promising recent development in relativistic theories for chemistry and their computational implementations. These chapters cover the all-electron methods in the framework of the two- and four-component relativistic approaches, the relativistic density functional approaches, and more approximate techniques based on the idea of relativistic pseudopotentials.

The several chapters are focused on the relativistic methods for molecular calculations and the problems discussed include relativistic two-component theory, density functional theory, pseudopotentials and correlations. These chapters will be mostly addressed to experimentalists with only general background in theory and to the computational chemists without training in relativistic methods. The reliability of different methods used in relativistic calculations on heavy molecules will be thoroughly discussed. This should bridge the gap between recent developments in relativistic computational methods and their understanding and use by experimentalists. A separate chapter will focus on the interplay between relativistic effects and electron correlation. Both these effects need to be accounted for in calculations aiming at high reliability of the computed data.

In contrast to recently published books on relativistic theories for atoms and molecules, the present volume is developed at the intermediate level to be of interest for broader audience. The different chapters in the volume are explanatory rather than formal and primarily address the understanding of relativistic computational methods. The book is designed for those who are not highly versed in these methods and are willing to acquire the basic knowledge of the relativistic computing and associated problems of importance for the heavy element chemistry. The discussion of the possible future applications of relativistic computational methods in modeling of new materials, design of efficient catalysts, and in biochemistry-oriented spin-forbidden photochemical processes is provided in a chapter. The book is designed to address equally well needs of students, postgraduates, and researchers.

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