

PREFACE

When ten years ago the World Scientific Publishing Company invited me to edit a volume on Computational Chemistry, I was very thrilled about the project. A few years earlier, in 1992, we started an annual conference series “Conferences on Current Trends in Computational Chemistry” (CCTCC) that has been attended by a broad group of advanced professionals and students interested in this area of research. From my interactions with the speakers and participants of these series of meeting I gained an impression that the books focusing on reviews of current computational techniques and their applications, that are delivered in a timely manner and are affordable for budget-oriented graduate students, would be a good addition to the published literature. Some colleagues shared my enthusiasm and provided their reviews for the first volume of this series that was published in 1996.

Ten books and ten years later, we are delighted to present you the decennial volume of the series. This volume will be released just few months prior to the 15th CCTCC conference that is scheduled for November 2006. There have been important developments during this decade — computers are more powerful and faster, code features are enhanced and more efficient, and studied molecules are larger and can be studied not only in vacuum but also in an environment of a solvent or in crystal. In addition, the chemical and physical community celebrated the 1998 Nobel Prize that was awarded to two leading computational experts. It was not by chance that Walter Kohn and John A. Pople have been recognized by the Nobel Committee for their contributions to the development of efficient computational methods for quantum chemistry.

The messages that the community is receiving from the administration are also very encouraging. This year John H. Marburger III, the director of the White House Office of Science, announced that “computational science — the use of advanced computing capabilities to understand and solve complex problems — is now critical to scientific leadership, economic competitiveness and national security”. The US President’s Information Technology Advisory Committee in their recent report consider computational science a key technology field of the 21st century because it allows researchers to study complex processes and phenomena that are experimentally difficult to characterize. As a result, they recommend that advances in computational sciences and the development of supercomputer infrastructures be supported.

These optimistic news indicate that our volumes are well-timed and not only present the reviews of current advances in computational methodologies and applications for advanced specialists already involved in these research areas but will also contribute towards the education and training of a new generation of professionals necessary to cover these fast developing areas of computational science. Since each volume covers not just one subject but a broad range of methods and applications, the series provides a balanced mix of general topics and reviews of new findings.

As expectations on the outcomes of applications of current computational chemistry methods are rising, the researchers use such techniques to study larger systems and to anticipate more accurate results. This is impetus for the development of more efficient methods based on the first-principle multi-level simulations appropriate for complex species. Among such methods, the Density Functional Theory (DFT) has received the most attention in the last decade. The first chapter of this volume written by T. Wesołowski reveals an alternative formalism of the DFT method based also on Hohenberg-Kohn theorems. In this formalism, the orthogonal orbitals are used not for the whole system but only for subsystems. The orbitals are derived from the Kohn-Sham type of one-electron equations in which all terms representing the interactions between the subsystems are expressed as universal functionals of electron density. The chapter reviews the formal aspects of the density functional approaches, the development and testing of the density functionals and the possible use of the orbital-free embedding in multi-scale modeling. It also contains numerous examples, including applications for condensed phase species.

The next chapter presented by M. R. Pederson, K. Park and T. Baruah covers the applications of Density Functional Theory in the investigations of molecular magnets. A class of molecules containing collections of spin-polarized ions is often referred to as molecular magnets. There are two groups in these systems that behave very differently when exposed to magnetic fields. One group relates to molecules containing metal centers for which the spin-orbit interaction is quite small. The second group corresponds to molecules containing strongly coupled metal centers and non negligible spin-orbit interactions. The authors describe how density-functional theory may be used to study this class of molecules which has received significant experimental attention lately, because it exhibits the phenomenon of

resonant tunneling of magnetization. This phenomenon is fundamentally interesting, and has the potential to be technologically useful. The examples provided in the chapter show that the magnetism in these molecules can be influenced by applied magnetic fields, by the addition of extra electrons and by changes in hydrogen bonding. The discussion includes numerical details in addition to the underlying theoretical framework.

Another example of the theory development is given in the chapter by P. Čársky and R. Čurík. Their focus is the development of a simple but rigorous *ab initio* computational method that can be applied to vibrationally inelastic electron scattering by polyatomic molecules. Vibrational electron energy loss spectroscopy (EELS) is becoming a useful tool in providing information concerning the excited states of molecules and the electronic structure of negative ions and their unimolecular decomposition. Since the theoretical basis of the EELS are much less developed than those of vibrational or rotational spectroscopy, this chapter, which presents a discussion of the theory and examples of the applications, provides necessary information for those interested in the development and applications of EELS.

The next chapter reviews the reactions of free atoms and radicals which play an important role in the modeling of complex processes occurring in the polluted atmosphere and in combustion chemistry. J. Jodkowski discusses the computational models of the reaction rate theory most frequently used in the theoretical analysis of gas-phase reaction kinetics and presents examples of the reactions of reactive components of the polluted atmosphere, such as O₂, NO_x, OH, NH₂, alkyl radicals, and halogen atoms. Kinetic parameters of the reactions under investigation are provided in an analytical form convenient for kinetic modeling studies. The presented expressions allow for a successful description of the kinetics of the reaction systems in a wide temperature range and could be used in kinetic studies of related species.

Hydrogen bonding is a unique interaction with crucial importance for chemical and bio-chemical reactions including life processes. The number of studied aspects of H-bonding is large and continuously increases due to newly revealed features. One of the current aspects of hydrogen bonding is associated with the experimental NMR studies of this phenomenon. There are three spin-spin couplings that can arise between the atoms which form the X-H-Y hydrogen bond. Coupling constants have signs associated with them which have been determined

experimentally for a few hydrogen-bonded complexes. Until recently, the only model used to predict these signs was the Dirac Vector Model that often fails, even for simple molecules. J. E. Del Bene and J. Elguero, based on the results of rigorous calculations carried out using the *ab initio* equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method, provide generalizations concerning the signs of the one- and two-bond-reduced coupling constants. These generalizations make possible the prediction of the signs of the corresponding spin-spin coupling constants (J) measured experimentally, taking into account the magnetogyric ratios of the pair of coupled atoms. The chapter provides discussion of the theoretical methods and obtained results and covers the details of the newly-proposed Nuclear Magnetic Resonance Triplet Wavefunction Model (NMRTWM) that offers insight into the signs of the reduced coupling constants.

In addition to H-bonding there are many interesting aspects of biological reactions that benefit from computational studies. In the last chapter of this volume, J. V. Burda, J. Šponer, and J. Leszczynski present a review of a biologically important process: activation of cisplatin and its analogs. Cisplatin (cis-dichlorodiammineplatinum cisDDP) is one of the most frequently explored platinum compounds since Rosenberg's discovery of its anticancer activities. The mechanisms of the function of this drug are not fully understood. The chapter covers a review of the theoretical studies that are devoted to the first step of such activation. The complex nature of such a process that includes ligand replacement by water molecules is discussed.

I would like to thank all of the authors for their excellent contributions and fruitful collaboration on this book and all volumes of the series. The very efficient technical assistance of Dr. Manoj K. Shukla in putting together this volume is greatly appreciated. I have had many opportunities to discuss various aspects of this project with the most important part of the community — the readers. As always, I value your feedback. Your comments are very important to me. So please feel free to e-mail your suggestions to jerzy@ccmsi.us.

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