

Preface

Just at the turn of a new century, the further evolution of Computational Chemistry deserves serious consideration. We have learned from its rapid progress in the previous years that even courageous predictions can become too conservative after a few decades. There is no doubt that this discipline will contribute towards a better understanding of classical chemical problems. One may safely assume an even more comprehensive incorporation of Computational Chemistry into the future developments of a wide variety of fields and applications in the different areas of science and technology. As the twenty-first century unfolds, computational techniques are expected to impact the fields of material and environmental sciences and molecular biology as well as the development of new drugs, just to mention a few of the most obvious applications.

The aim of this series of books is to bring together a broad spectrum of expertise into a frank and direct treatise on the state of the present day developments and applications of computational techniques. Every contribution is designed to be accessible to a broad range of scientists interested in the application of computers to problems at the level of atoms and molecules.

The current volume includes six chapters. The chapters incorporate the views of leading experts on the current status of computational chemistry methods and describe the challenges and opportunities of their applications. The first chapter by Piotr Piecuch and Karol Kowalski addresses the new developments in Coupled-Cluster (CC) theory. The homotopy method is used to obtain complete sets of solutions of nonlinear CC equations. The correspondence between multiple solutions of the CCSD, CCSDT, and full CI equations is established, and the application of new approaches in modeling molecular systems is discussed. A new approach to electron correlation in atoms and molecules, termed the method of moments of CC equations (MMCC), is presented. This new method has the potential of surpassing the

existing techniques and of being successfully applied to challenging cases. For example, this MMCC method has been proven to satisfactorily describe quasi-degenerate states and bond breaking.

The second chapter by Charles A. Weatherford and Burke Ritchie reviews the computational theory for the time-dependent calculations of a solution to the Schrodinger equation for two electrons and focuses on the development of propagators to the solution. Long- and short-time propagators are needed to model atomic and molecular dynamics in rapidly varying time-dependent fields, to extract eigenvalues and eigenvectors for large systems by time-dependent spectral methods, and for defining the dynamics of reactions.

The volume also features a discussion of a new scheme, the Self Consistent Field for Molecular Interactions (SCF-MI) method, for modifying Roothaan equations in order to avoid basis set superposition errors (BSSE). This method is especially suitable for computations of intermolecular interactions. The details of the theory along with examples of applications to nucleic acid base pair complexes is revealed by Ermanno Gianinetti, Ida Vandoni, Famulari, and Mario Raimondi. This chapter is complemented nicely by the following contribution from Jiri Sponer, Pavel Hobza, and Jerzy Leszczynski who have reported the current status of the computational studies involving aromatic stacking and hydrogen bonding interactions among nucleic acid bases. Aromatic stacking of nucleic acid bases is one of the key concepts in determining the structures and dynamics of nucleic acids. Only recently have advances in computer hardware and software finally allowed for the application of state-of-the-art quantum-mechanical approaches with inclusion of electron correlation effects to study aromatic base stacking, thereby providing an ultimate qualitative description of this phenomenon. The authors conclude that base stacking is in principle one of the best described interactions in current molecular modeling of DNA fragments. It allows for the study of base stacking in DNA using large-scale classical molecular dynamics simulations. The neglect of cooperativity of stacking and amino group pyramidalization appears to be the most serious approximation of the currently used force field form.

The next chapter by Thanh N. Truong and Dilip K. Maity reveals the possibility of calculating the kinetics of chemical reactions in biological systems from the first principles. Based on variational state theory augmented by multidimensional semiclassical tunneling approximation for calculating thermal rate constants, the development efforts of a general methodology are presented. This approach is successfully applied to the isomerization of free

base poryphyrin. There are also prospects of using it in the kinetic study of biological systems.

The properties of small molecular systems could be predicted by current nonempirical methods with experimental accuracy. In the sixth chapter, Jozef S. Kwiatkowski and Jerzy Leszczynski review the results of rigorous ab initio studies of the series of derivatives of methane, silane, and germane. The presented molecular and vibrational parameters are congruous with the experimental data for these systems. In addition, the theoretical approach allows for the prediction of the effects of halogeno- substitutions on their structures and properties.

We hope that you will find the contents of this volume informative and stimulating. Your comments and suggestions are readily accepted at jerzy@tiger.jsums.edu.

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