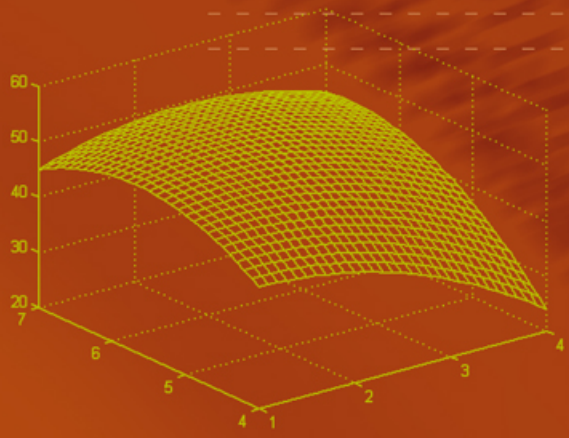
K. I. Ramachandran
G. Deepa
K. Namboori

Computational Chemistry and Molecular Modeling

Principles and Applications



Springer

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Dr. K. I. Ramachandran
Dr. G. Deepa
K. Namboori
Amrita Vishwa Vidyapeetham University
Computational Engineering and Networking
641 105 Ettimadai
Coimbatore
India
ki_ram@ettimadai.amrita.edu
os_deepa@ettimadai.amrita.edu
n_krishnan@ettimadai.amrita.edu

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Dedicated to the lotus feet of
Our Beloved Sadguru and Divine Mother
Sri MATA AMRITANANDAMAYI DEVI

Preface

Computational chemistry and molecular modeling is a fast emerging area which is used for the modeling and simulation of small chemical and biological systems in order to understand and predict their behavior at the molecular level. It has a wide range of applications in various disciplines of engineering sciences, such as materials science, chemical engineering, biomedical engineering, etc. Knowledge of computational chemistry is essential to understand the behavior of nanosystems; it is probably the easiest route or gateway to the fast-growing discipline of nanosciences and nanotechnology, which covers many areas of research dealing with objects that are measured in nanometers and which is expected to revolutionize the industrial sector in the coming decades.

Considering the importance of this discipline, computational chemistry is being taught presently as a course at the postgraduate and research level in many universities. This book is the result of the need for a comprehensive textbook on the subject, which was felt by the authors while teaching the course. It covers all the aspects of computational chemistry required for a course, with sufficient illustrations, numerical examples, applications, and exercises. For a computational chemist, scientist, or researcher, this book will be highly useful in understanding and mastering the art of chemical computation. Familiarization with common and commercial software in molecular modeling is also incorporated. Moreover, the application of the concepts in related fields such as biomedical engineering, computational drug designing, etc. has been added.

The book begins with an introductory chapter on computational chemistry and molecular modeling. In this chapter (Chap. 1), we emphasize the four computational criteria for modeling any system, namely stability, symmetry, quantization, and homogeneity. In Chap. 2, "Symmetry and Point Groups", elements of molecular symmetry and point group are explained. A number of illustrative examples and diagrams are given. The transformation matrix for each symmetry operation is included to provide a computational know-how. In Chap. 3, the basic principles of quantum mechanics are presented to enhance the reader's ability to understand the quantum mechanical modeling techniques. In Chaps. 4–10, computational techniques with different levels of accuracy have been arranged. The chapters also

cover Huckel's molecular orbital theory, Hartree-Fock (HF) approximation, semi-empirical methods, ab initio techniques, density functional theory, reduced density matrix, and molecular mechanics methods.

Topics such as the overlap integral, the Coulomb integral and the resonance integral, the secular matrix, and the solution to the secular matrix have been included in Chap. 4 with specific applications such as aromaticity, charge density calculation, the stability and delocalization energy spectrum, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), bond order, the free valence index, the electrophilic and nucleophilic substitution, etc. In the chapter on HF theory (Chap. 5), the formulation of the Fock matrix has been included. Chapter 6 concerns different types of basis sets. This chapter covers in detail all important minimal basis sets and extended basis sets such as GTOs, STOs, double-zeta, triple-zeta, quadruple-zeta, split-valence, polarized, and diffuse. In Chap. 7, semi-empirical methods are introduced; besides giving an overview of the theory and equations, a performance of the methods based on the neglect of differential overlap, with an emphasis on AM1, MNDO, and PM3 is explained. Chapter 8 is on ab initio methods, covering areas such as the correlation technique, the Möller-Plesset perturbation theory, the generalized valence bond (GVB) method, the multi-configurations self consistent field (MCSCF) theory, configuration interaction (CI) and coupled cluster theory (CC).

Density functional theory (DFT) seems to be an extremely successful approach for the description of the ground state properties of metals, semiconductors, and insulators. The success of DFT not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes. The chapter on density functional theory (Chap. 9) covers the entire applications of the theory.

Chapter 10 explains reduced density matrix and its applications in molecular modeling. While traditional methods for computing the orbitals are scaling cubically with respect to the number of electrons, the computation of the density matrix offers the opportunity to achieve linear complexity. We describe several iteration schemes for the computation of the density matrix. We also briefly present the concept of the best n-term approximation.

Chapter 11 is on molecular mechanics and modeling, in which various force fields required to express the total energy term are introduced. Computations using common molecular mechanics force fields are explained.

Computations of molecular properties using the common computational techniques are explained in Chap. 12. In this chapter, we have included a section on a comparison of various modeling techniques. This helps the reader to choose the method for a particular computation.

The need and the possibility for high performance computing (HPC) in molecular modeling is explained in Chap. 13. This chapter explains HPC as a technique for providing the foundation to meet the data and computing demands of Research and Development (R&D) grids. HPC helps in harnessing data and computer resources in a multi-site, multi-organizational context effective cluster management, making use of maximum computing investment for molecular modeling.

Some typical projects/research topics on molecular modeling are included in Chap. 14. This chapter helps the reader to familiarize himself with the modern trends in research connected with computational chemistry and molecular modeling.

Chapter 15 is on basic mathematics and contains an introduction to computational tools such as Microsoft Excel, MATLAB, etc. This helps even a non-mathematics person to understand the mathematics used in the text to appreciate the real art of computing. Sufficient additions have been included as an appendix to cover areas such as operators, HuckelMO hetero atom parameters, Microsoft Excel in the balancing of chemical equations, simultaneous spectroscopic analysis, the computation of bond enthalpy of hydrocarbons, graphing chemical analysis data, titration data plotting, the application of curve fitting in chemistry, the determination of solvation energy, and the determination of partial molar volume.

An exclusive URL (http://www.amrita.edu/cen/ccmm) for this book with the required support materials has been provided for readers which contains a chapterwise PowerPoint presentation, numerical solutions to exercises, the input/output files of computations done with software such as Gaussian, Spartan etc., HTML-based programming environments for the determination of eigenvalues/eigenvectors of symmetrical matrices and interconversion of units, and the step-by-step implementation of cluster computing. A comprehensive survey covering the possible journals, publications, software, and Internet support concerned with this discipline have been included.

The uniqueness of this book can be summarized as follows:

1. It provides a comprehensive background theory for molecular modeling.
2. It includes applications from all related areas.
3. It includes sufficient numerical examples and exercises.
4. Numerous explanatory illustrations/figures are included.
5. A separate chapter on basic mathematics and application tools such as MATLAB is included.
6. A chapter on high performance computing is included with examples from molecular modeling.
7. A chapter on chemical computation using the reduced density matrix method is included.
8. Sample projects and research topics from the area are included.
9. It includes an exclusive web site with required support materials.

With the vast teaching expertise of the authors, the arrangement and designing of the topics in the book has been made according to the requirements/interests of the teaching/learning community. We hope that the reader community appreciates this. Computational chemistry principles extended to molecular simulation are not included in this book; we hope that a sister publication of this book covering that aspect will be released in the near future. We have tried to make the explanations clear and complete to the satisfaction of the reader. However, regarding any queries, suggestions, corrections, modifications and advice, the readers are always welcome to contact the authors at the following email address: n_krishnan@ettimadai.amrita.edu.

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K. I. Ramachandran

Gopakumar Deepa

Krishnan Namboori P.K.

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