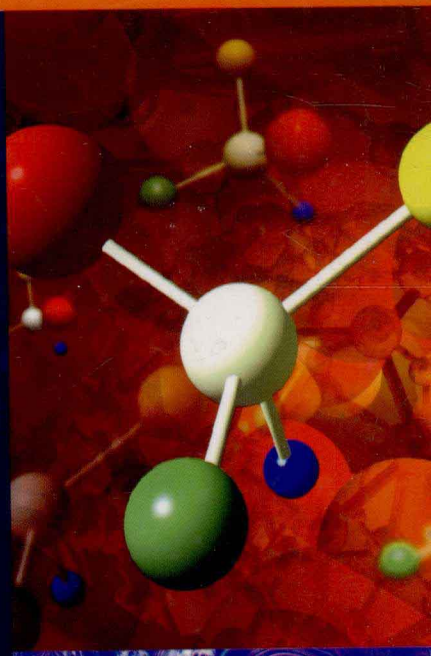
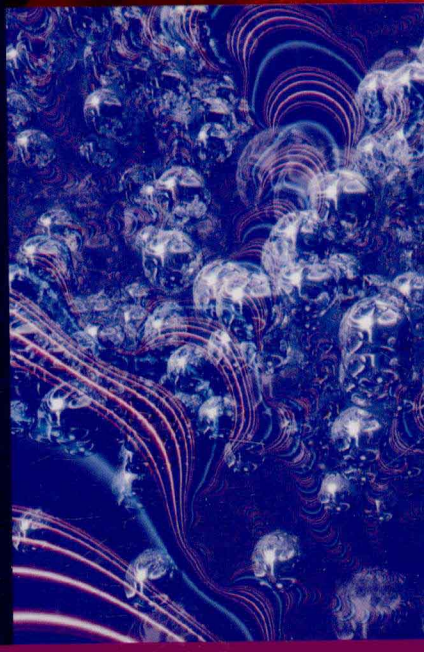
4th Edition

Quantum Chemistry





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New Age Science

Quantum Chemistry

FOURTH EDITION

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Foreword

Qauntum Mechanics, Thermodynamics and Kinetics are important theoretical tools for understanding the behaviour of chemical systems. Quantum Mechanics yields vital information about structural chemistry of atoms and molecules including chemical bond. Hence, the subject becomes quite basic for the entire spectrum of chemical studies.

It is a fairly detailed and comprehensive text. The subject matter has been divided into four parts. Part I dealing with Fundamental Principles of Quantum Mehanics along with its formalims. Part II deals with Applications to some Simple Systems such as translational, vibrational and rotational motion of hydrogen and hydrogen-like atoms. Polyelectronic atoms are discussed in Part II along with the mathematical background relating to approximation methods and the Theory of Angular Momentum. Part III deals with Atomic Structure. Part IV deals with Molecular Structure and Chemical Bond for diatomic as well as polyatomic molecules. Principles of Symmetry and Group theory have been discussed in a separate chapter. Basic methematical principles relating to Determinants, Matrices and Vectors have been presented in appendices.

Professor Prasad has had a long teaching experience and hence the subject matter has been presented as clearly as possible. An important feature of the book is that detailed steps of mathematical derivations have been given which are likely to prove useful to teachers and students alike. Similar is the case with problems, sufficient hints for which have been provided. Problems have been suitably chosen.

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Preface to the Fourth Edition

P. Divac had said that the whole of chemistry is implicit in the laws of quantum mechanics. The year 1927 may be marked as the date of birth of quantum chemistry when Heitler and London, for the first time, applied the quantum laws to develop a theory of covalent bond. Subsequent developments related to atomic and molecular structure and chemical bonding, especially the molecular orbital theory, enabled quantum chemistry to evolve as a potential subdiscipline permeating almost every branch of chemistry.

The early development in quantum mechanics followed two very different mathematical lines. Schrödinger, to explain observed discreteness in atomic phenomenon, formulated the idea of 'quantum states' based on 'wave function' which is continuous, and operators. Heisenberg on the other hand, adopted the idea of discrete quantum jumps as the essential feature of atomic phenomenon and used vectors and matrices to represent the observed quantum transitions. However, it soon became evident that the two approaches were equivalent as the operators of the Schrödinger theory appear as matrices and the wave functions as representatives of vectors.

The present book which has pedagogical orientation deals with Schrödinger's 'wave mechanics', now popularly called quantum mechanics, and its applications to atomic structure and chemical bonding. The text begins with a brief review leading to Planck's quantum theory followed by concept of wave function and formal laws of quantum mechanics (chapters 1, 2, and 3). Applications to simple systems including hydrogen atom are described in chapters 4 to 7. Structure of polyelectronic atoms (chapter 9) is preceded by approximate methods of solving Schrödinger equation (chapter 8) and followed by theory and significance of angular momentum in atomic structure (chapter 10). The two theories of molecular orbital and valence bond for diatomic and polyatomic molecules are elaborately dealt with in chapters 12 and 13. The intervening chapter 11 deals with molecular symmetry and group theory, a necessary prerequisite for molecular orbital theory specially for polyatomic molecules. An alternative approach to energy calculation based on electron density rather than wave function is given in a small chapter 14 under the caption 'Density Functional Theory'. Every chapter, except the last one, ends with problems for which hints are provided.

The author has taken care to keep the language simple and presentation unambiguous. Further, the reader may find that a background of advanced mathematics is not a prerequisite in following the material presented in this book. Necessary mathematical details, wherever needed, have been explained in the text. Mathematical appendices provided at the end of the text are also useful aids.

The author invites critical comments from the readers and learned experts on the subject.

—Author

Preface to the First Edition

Dirac had once said that the whole of chemistry is implicit in the laws of quantum mechanics. Today, quantum mechanics is accepted as a legitimate tool for the study of almost all chemical phenomena as well as molecular and atomic properties.

Though the scope of quantum chemistry is unlimited, the author has restrained himself from being too ambitious, but has taken care to ensure that the prepared text covers all the topics being commonly taught today. The material presented in this book is divided into four parts and thirteen chapters. Part I begins with the developments leading to the formulation of quantum theory (Chapter one). This is followed by descriptions of the theory of matter waves and the quantum mechanical laws in Chapters two and three, respectively. Having gained familiarity with the concepts of operators, eigenvalue, eigenfunction, expectation values, normalization, orthogonality etc., in Part I, the reader will pass on to Part II of the book where applicability of these principles to simple system, viz., particle in a box, harmonic oscillator, a rotating particle and one-electron atomic systems (Chapters 4–7) is discussed. Part III begins with approximation methods of finding wave functions and energies. The quantum mechanics of polyelectronic atoms including the HF SCF theory and the theory of angular momentum of electrons in atoms are treated in Chapter 9 and 10, respectively. Part IV comprising three chapters deal mainly with theories of chemical bond. Principle of symmetry, group theory and their relation to quantum mechanics, which are known to have wide applications in molecular structure, are treated first (Chapter 11) in this part of the book. These are followed by molecular orbital and valence bond treatments of diatomic molecules (Chapter 12) and polyatomic molecules (Chapter 13) wherein the importance and applicability of symmetry principles have been demonstrated. The material in the last two chapters has been presented in such a manner that the reader is able to see the parallel nature of the two theories of bonding and is able to compare the two approaches.

Exposition of principles in each chapter has been extensively backed by exercises and problems for which hints are also provided.

—Author

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PART I

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