面向21世纪课程教材

Textbook Series for 21st Century

Molecular Structural Theory

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HIGHER EDUCATION PRESS

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内容提要

本书是面向21世纪课程教材，填补了我国化学专业英语教材的空白。全书共九章：量子理论、原子、双原子分子、对称性与群论、多原子分子、共轭分子、过渡金属化合物、簇合物和团簇、固体。

本书体系完整，层次分明，逻辑性强，文字流畅，内容先进。可作为理科化学各专业结构化学英语教材，也可供师范院校和工科院校有关专业参考使用。

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Preface

This book is designed for undergraduate chemistry majors. There are many textbooks of structural chemistry published in Chinese or foreign languages. My impression is that authors abroad pay much of their attention to the backgrounds of principles, the developments of related concepts, and the formation of qualitative pictures. They hold the opinion that "our understanding of valence and electronic properties must be in terms of simple physical models which can readily be visualized rather than in terms of numbers gushing from a computer!" (McWeeny R, "Coulson's Valence", 3rd edition, Oxford, 1979, pp. 22～24). In contrast, Chinese authors pay much of their attention to the detailed discussion of principles and the logical reasoning. For example, the formulation of Schrödinger equation on the basis of several axioms and a special chapter of sophisticated group theory can always be found in a typical textbook published in China.

These two different modes, if combined, may improve our teaching. If so, the readers can learn not only how to think and reason in a strict way, but also how to understand the relations between the molecular structure and behavior. For this purpose, in this book the author lays emphasis on qualitative and also simply quantitative descriptions.

Molecular structural theory aims to recognize and explain the formation of molecules, including: (1) why and how the atoms form various molecules; (2) why atoms form compounds in definite proportions, showing the saturation of valence; (3) how the geometrical arrangement and accordingly, the special physical and chemical properties are determined by the composition and connectivity of molecules. The discussions on these three problems construct the main parts of this book, being usually called as "the theory of chemical bonds".

The modern theory of chemical bonds is, historically, based on the principles of quantum mechanics. It involves many fundamental concepts, such as wave-particle dualism, probability waves, and the quantization of physical quantities, which

may be hard to be understood by an ordinary undergraduate chemistry major. To circumvent this, the author introduces the Schrödinger equation in comparison with the classical Maxwell wave equation instead of the axiom formulation. This seems to be an efficient way, as we have found in the teaching practices, to help the students to understand the basic concepts more easily.

The electronic structure of the hydrogen atom is stressed in this book for introducing several basic concepts in the modern chemical bonding theory, such as quantized energy levels, the classification of wave functions, nodes and angular distribution. Therefore, we do not display the whole sophisticated process of solving the Schrödinger equation, instead we focus on the discussion of its results, e.g., the energy levels and atomic orbitals.

In this book, a special chapter (Chapter 4) is presented to introduce the basic concepts of group theory, while its applications can be found in almost all the succeeding chapters. Such an arrangement, we hope, can help the readers to realize that group theory is a very useful tool in molecular structural theory and that it can be easily be mastered.

This book mainly deal with various molecules, involving with diatomic, polyatomic, conjugated molecules and transition-metal compounds. The introductions of clusters and solids are also included here for the purpose of reflecting the recent developments in the theory of chemical bonding.

Each chapter has its own emphasis. Chapters 1 and 2 open with a review of the elementary concepts and quantities of the atomic world. The nature of bonding in the simplest molecules H_2 and H_2^+ is discussed in depth in Chapter 3. Chapter 3 also introduces how to analyze the energy sequence of diatomic molecules on the basis of correlation diagram. By the group theory (introduced in Chapter 4) and the elementary theory of chemical bonding, Chapter 5 goes into description and behavior of polyatomic molecules. The stability and reactivity of the conjugated molecules are discussed by computing and comparing the π energy levels in Chapter 6. Chapter 7 treats the spectra and magnetism of transition-metal compounds in terms of the split of d states. In Chapter 8, the three-center bonds and the well-known empirical rules, such as octet rule and the 18-electron rule, are reviewed. Chapter 9 shows how to understand the energy band and Peierls distortion in solids in the view point of chemical bond. For the purpose of further reading, references including monographs and review articles are also listed.

In order to unite the theory and its applications, all descriptions of theories are

exemplified by some typical molecules. Taking Chapter 4 as an example, molecule NH_3 is used in discussions throughout all that chapter. This is also embodied in the design and selection of exercises behind each chapter. This book not only describes recent accomplishments but also reviews some traditional rules with cautions, because the later is a basis for recognition and development of new areas in molecular structural theory. In addition, the similarity of molecules is well used in organizing this book. Specific characters in different systems lead to individual chapters while general characters of chemical bonding knit all chapters into a coherent structure without too much repetition.

Millions of molecules appeal for in depth studies in chemistry. Facing up to the innumerable experimental facts and research ideas, chemistry needs theoretical rationalization. Theoretical chemistry is an essential component of our discipline. We can enter a higher scientific level through renewing our knowledge and enriching our experience. The well-known theoretical chemist Roald Hoffmann said: "... the most important role of theory in chemistry is to provide a framework in which to think, to organize experimental knowledge." That is also one of my purpose on writing this book.

The author would like to express his special gratitude to Prof. Chen Yi, Deputy President of Nanjing University. This book was originally a lecture note when Prof. Chen invited me to offer the course "structural chemistry" at Nanjing University in the fall of 1991. Many thanks are to Prof. Jiang Dongcheng, Yao Tianyang and Wang Guoxiong for their beneficial discussions. Thanks are also to Mr. Yang Xingshui, Mr. Liu Jun, and Mr. Shao Yihan for their helps in the course of the preparation of the manuscript.

The author greatly appreciates the readers who have given or will give their valuable comments and suggestions for the improvement and extension of this book. Finally, I wish to record thanks to my friends of Higher Education Press (Beijing) for their patient cooperation.

Jiang Yuansheng
November, 1996

Preface to English Edition

This book is translated from a Chinese book, *Jiegou Huaxue* (Higher Education Press, 1997, Beijing).

As early as 1996, when the Chinese work was sent to the press, several friends suggested me to translate the book into English. Sun Jingli (Prof. of Theoretical Physics of Nanjing University, retired), my another friend, enthusiastically showed that he was willing to offer the first draft of English translation for the book. The preceding four chapters in the book were revised on the basis of his translated draft. During the course, Ph. D. candidate Shao Yihan and Prof. Liu Zhimo of Foreign Language also made tremendous efforts. The later five chapters, which contain a large amount of chemical information, were finished by my own self, and, Dr. Ma Jin examined and revised these chapters. She also carefully read the entire manuscript, revised and unified terminology and symbols. Ph. D. candidate Wu Jian assisted me in typing. To all of these people the author expresses his sincere thanks.

In particular, the author wishes to show his gratitude to Prof. Jiang Dongcheng, Ms. Yin Jizu, Mr. Xia Luhui of Higher Education Press and Prof. Chen Yi, Prof. Yao Tianyang of Nanjing University. Without their help and encouragement, this book would not have been published.

Jiang Yuansheng
November 30, 1998

Jiang Yuansheng, graduated from Chemistry Department of Wuhan University in 1953, is a Professor of Chemistry at Nanjing University. Later he continued the post graduate on Physical Chemistry at Jilin University. During 1960s, he was engaged in the field of theoretical polymer chemistry, then changed to the study of Ligand Field Theory. Since the mid-70s, Jiang has devoted himself to the chemical graph theory and applications in conjugated molecules. Jiang is also interested in computational quantum chemistry and has got achievements in clusters and solids. He undertook the cooperative monographs: *Theoretical Method of Ligand Field Theory* and *Graph Theoretical Molecular Orbitals*, and twice won the First Class National Natural Science Prices (1982, 1987). In 1991, Jiang was elected as a member of Chinese Academy of Sciences.

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Contents

Chapter 1

Quantum Theory

The aim of physical chemistry is to investigate the fundamental principles of chemical phenomena, and as it is, in a long period of time study has been limited to the macroscopic behaviors of matter. As a result, the laws of thermodynamics were formulated, and they have been used successfully for solving problems of state equilibrium and thermal effects.

The study of microscopic phenomena began in the early years of the 19th century. Theory of atoms was first proposed by Dalton, and then Avogadro proposed the molecular theory of compounds. At the beginning of this century, the electron mass ($\sim 10^{-27}$ g) was measured by Thomson and Millikan. moreover, Rutherford suggested a nuclear model of atomic structure. According to this model, electrons travel in the orbits around the nucleus, just as planets in the solar system do. These great discoveries and theories enable us to study how chemical phenomena are controlled by particles though much smaller than atoms. Such particles are, for example, electrons and nuclei. In the spirit of the principle that interparticle forces determine orbits of particles, one can explain how electrons transfer and also can get a microscopic picture