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Fundamentals of Quantum Chemistry

SECOND EDITION

James E. House

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Second Edition

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Illinois State University

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Fundamentals of Quantum Chemistry

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Preface to the Second Edition

This second edition of *Fundamentals of Quantum Chemistry* is an expansion of the successful first edition, which was published as *Fundamentals of Quantum Mechanics* (1998). My goal, then and now, was to provide a clear, readable presentation of the basic principles and application of quantum mechanical models for chemists while maintaining a level of mathematical completeness that enables the reader to follow the developments. The title has been changed to more accurately represent the book to a readership with a chemical rather than a physical specialization. Of course, much of the material is equally applicable to both audiences, and the complete contents of the first edition are retained herein.

The second edition differs from the first in several ways.

1. A new chapter on molecular orbital calculations (extended Hückel and self-consistent field), which introduces some of the basic ideas and terminology of the topic, has been included.

2. Several new topics, as sections or part of sections, have been included. These include the photoelectric effect, the perturbation treatment of the helium atom, orbital symmetry and chemical reactions, and molecular term symbols.

3. A significant number of additional figures and minor improvements to existing figures have been added.

4. A significant number of new exercises have been included.

5. Answers are now provided for selected problems at the back of the book.

6. Last but not least, the entire text has been carefully and extensively edited to increase the clarity of the presentation and to correct minor errors.

I believe that these changes will enhance the relevance of the book for a wide range of readers.

It is a pleasure to acknowledge the outstanding guidance and support of Jeremy Hayhurst, Angela Dooley, and Nora Donaghy of Academic Press. Working with them again has been a pleasant experience that I hope to repeat. As in my other book writing ventures, the support and encouragement from my wife, Kathleen A. House, have been invaluable.

Preface to the First Edition

A knowledge of quantum mechanics is indispensable to understanding many areas of the physical sciences. In addition to courses dealing specifically with quantum mechanics, some coverage is devoted to quantum mechanics in many other courses to provide background for the study of certain specific topics. An enormous number of advanced texts in quantum mechanics and quantum chemistry exist for the advanced student or specialist. However, there are few books that deal with quantum mechanics on an elementary level to provide the type of survey needed by nonspecialists to understand the basis of experiments and theories in their fields. My experience in teaching several of these peripheral courses leads me to believe that many students at several levels need some exposure to the main ideas of quantum mechanics. I am also convinced that it is profitable for many students to obtain that exposure from a book that is not intended for study of the subject at an advanced level. Because of this, I have tried to write the book that I wish I had had at the beginning of my study of quantum mechanics.

In my teaching, I encounter a large number of students in chemistry at the undergraduate and M.S. levels who need to review basic quantum mechanics. By actual survey, the vast majority of these students stopped their preparation in mathematics after the required two semesters of calculus. This is typical of students who do not plan to take more specialized courses in quantum mechanics and quantum chemistry. The situation is somewhat similar for students at certain levels in biological sciences, physics, and engineering. The purpose of this book is to provide a minimal background in quantum mechanics quickly and concisely for anyone who needs such a survey. It should also be suitable as a review of the subject for those who are no longer students but who need (or want!) to know some quantum mechanics.

With this audience in mind, this book has been kept to a level that makes it usable by persons of limited background in mathematics. It is presumed that the reader is familiar with basic physics and calculus, but no other background is assumed. In fact, this is one of the intended strengths of this volume, and a few mathematical topics are included in considerable detail to bring the reader along with elementary topics in differential equations, determinants, etc. In this sense, the book is a tool for self-teaching. Of course, no small book can cover quantum mechanics in either depth or breadth. The choice of topics was based on the applicability and relevance of the material to the larger fields of the physical sciences. Much of applied quantum mechanics is based on the treatment of several model systems (particle in a box, harmonic oscillator, rigid rotor, barrier penetration, etc.). These models form the content of much of the survey of quantum mechanics presented here.

After working through this book, the reader will have some familiarity with most of the important models of quantum mechanics. For those whose needs exceed the presentation here or whose appetite for quantum mechanics has been whetted, references are included at the end of each chapter.

It is hoped that this book will meet the needs of a wide audience. First, it should be a useful supplement for a variety of courses in the physical sciences. Second, it should serve as a tool for self-study and review by persons who have ended their formal education. Finally, this book should be a useful lead-in for students (especially those of limited mathematical background) preparing to study the more advanced works in the field. As stated earlier, my aim was to write the book that I wish I had had to start the learning of quantum mechanics.

Debra Feger-Majewski, Dustin Mergott, Sara McGrath, Anton Jerkovich, Ovette Villavicencio, Matt Lewellen, and Jeff Zigmant used some of this material in a preliminary form and made many useful suggestions. The reviews of the manuscript provided by Dr. Clarke W. Earley and Dr. Earl F. Pearson have contributed greatly to this book. Further, David Phanco, Garrett Brown, Jacqueline Garrett, and Michael Remener have made the development and production of this book a pleasant and rewarding experience. Finally, the patience and understanding of my wife, Dr. Kathleen A. House, during the writing of this book are gratefully acknowledged. Her

assistance with graphics production and her careful reading of the entire manuscript have contributed greatly to this book, and her encouragement since the inception of this project has helped make yet another dream come true.

Contents

▶ Chapter 1

The Early Days

Quantum mechanics is a branch of science that deals with atomic and molecular properties and behavior of matter on a microscopic scale. While thermodynamics may be concerned with the heat capacity of a gaseous sample, quantum mechanics is concerned with the specific changes in rotational energy states of the molecules. Chemical kinetics may deal with the rate of change of one substance into another, but quantum mechanics is concerned with the changes in vibrational states and structures of the reactant molecules as they are transformed. Quantum mechanics is also concerned with the spins of atomic nuclei and the populations of excited states of atoms. Spectroscopy is based on changes of quantized energy levels of several types. Quantum mechanics is thus seen to merge with many other areas of modern science.

A knowledge of the main ideas and methods of quantum mechanics is important for developing an understanding of branches of science from nuclear physics to organic chemistry. This book attempts to develop that familiarity for persons from all of the sciences.

The modern applications of quantum mechanics have their roots in the developments of physics around the turn of the century. Some of the experiments, now almost 100 years old, provide the physical basis for interpretations of quantum mechanics. The names associated with much of this early work (e.g., Planck, Einstein, Bohr, de Broglie) are legendary in the realm of physics. Their elegant experiments and theories now seem almost commonplace to even beginning students, but these experiments were at the forefront of scientific development in their time. It is appropriate, therefore, for this book to begin with a brief review of a few of the most important of these early studies.

1.1 Blackbody Radiation

When an object is heated to incandescence it emits electromagnetic radiation. The nature of the object determines to some extent the type of radiation that is emitted, but in all cases a range or distribution of radiation is produced. It is known that the best absorber of radiation is also the best emitter of radiation. The best absorber is a so-called "blackbody," which absorbs all radiation and from which none is reflected. If we heat this blackbody to incandescence, it will emit a whole range of electromagnetic radiations whose energy distributions depend on the temperature to which the blackbody is heated. Early attempts to explain the distribution of radiation using the laws of classical physics were not successful. In these attempts it was assumed that the radiation was emitted because of vibrations or oscillations within the blackbody. These attempts failed to explain the position of the maximum that occurs in the distribution of radiation; in fact, they failed to predict the maximum at all.

Since radiation having a range of frequencies (ν, Greek "nu") is emitted from the blackbody, theoreticians tried to obtain an expression that would predict the relative intensity (amount of radiation) of each frequency. One of the early attempts to explain blackbody radiation was made by W. Wien. The general form of the equation that Wien obtained is

$$f(\nu) = \nu^3 g(\nu/T), \tag{1.1}$$

where $f(\nu)$ is the amount of energy of frequency ν emitted per unit volume of the blackbody and $g(\nu/T)$ is some function of ν/T. This result gave fair agreement with the observed energy distribution at longer wavelengths but did not give agreement at all in the region of short wavelengths. Another relationship obtained by the use of classical mechanics is the expression derived by Lord Rayleigh,

$$f(\nu) = \frac{8\pi\nu^3}{c^3}kT, \tag{1.2}$$

where c is the velocity of light (3.00×10^8 m/s) and k is Boltzmann's constant, 1.38×10^{-16} erg/molecule.

Another expression was found by Rayleigh and Jeans and predicts the shape of the energy distribution as a function of frequency, but only in the region of short wavelengths. The expression is

$$f(\nu) = \frac{8\pi\nu^3}{c^3}\left(\frac{hkT}{h\nu}\right) = \frac{8\pi\nu^2 kT}{c^3}. \tag{1.3}$$

Therefore, the Wien relationship predicted the intensity of high-ν radiation, and the Rayleigh–Jeans law predicted the intensity of low-ν radiation emitted from a blackbody. Neither of these relationships predicted a distribution of radiation that goes through a maximum at some frequency with smaller amounts emitted on either end of the spectrum.

The problem of blackbody radiation was finally explained in a satisfactory way by Max Planck in 1900. Planck still assumed that the absorption and emission of radiation arose from some sort of oscillators. Planck made a fundamental assumption that only certain frequencies were possible for the oscillators instead of the whole range of frequencies that were predicted by classical mechanics. The permissible frequencies were presumed to be some multiple of a fundamental frequency of the oscillators, ν_0. The allowed frequencies were then $\nu_0, 2\nu_0, 3\nu_0, \ldots$. Planck also assumed that energy needed to be absorbed to cause the oscillator to go from one allowed frequency to the next higher one and that energy was emitted as the frequency dropped by ν_0. He also assumed that the change in energy was proportional to the fundamental frequency, ν_0. Introducing the constant of proportionality, h,

$$E = h\nu_0, \tag{1.4}$$

where h is Planck's constant, 6.63×10^{-27} erg s or 6.63×10^{-34} J s. The average energy per oscillator was found to be

$$\langle E \rangle = \frac{h\nu_0}{\left(e^{h\nu_0/kT} - 1\right)}. \tag{1.5}$$

Planck showed that the emitted radiation has a distribution given by

$$f(\nu) = \frac{8\pi\nu_0^3}{c^3}\langle E \rangle = \frac{8\pi\nu_0^3}{c^3}\frac{h\nu_0}{e^{h\nu_0/kT} - 1}. \tag{1.6}$$

This equation predicted the observed relationship between the frequencies of radiation emitted and the intensity.

The successful interpretation of blackbody radiation by Planck provided the basis for considering energy as being quantized, which is so fundamental to our understanding of atomic and molecular structure and our experimental methods for studying matter. Also, we now have the relationship between the frequency of radiation and its energy,

$$E = h\nu. \tag{1.7}$$