QUANTUM STATES OF ATOMS, MOLECULES, AND SOLIDS

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M. A. M.— *To my parents, Janice and Alfred Morrison*
T. L. E.— *To my parents, V. Lambert and Ruby O. Estle*
N. F. L.— *To my parents, Hattie and Walter Lane, my wife, Joni Sue, and my children, Christy and John*

Preface

This book will show you some of what you can do with quantum mechanics. In it the methods of quantum theory are applied to simple atomic, molecular, and solid systems. We have tried to stress, via a unified presentation of the quantum theory of matter, the underlying concepts and principles of that theory. An opportunity is provided, through exposition and problems, for you to develop skills in applying some of the more important tools of quantum mechanics to physically important systems. Ultimately we seek to lay a foundation for further study at a more advanced level in each of the three fields touched on: atomic physics, molecular physics, and solid-state physics. Consequently, we emphasize and explicate in considerable detail a few fundamental concepts central to these fields.

The overall plan is rather straightforward. Important ideas or methods are presented in the simplest possible context; an effort is made to avoid nonessential mathematical or physical complications. Thus we often use one- or two-dimensional systems, or "models," where appropriate. After the basic ideas have been presented and illustrated by means of one or more examples, we begin to add additional features, gradually working toward more realistic three-dimensional problems. We believe that it is easier to tackle mathematically and physically sophisticated problems if one has a firm grasp of the basic principles involved; then no matter how complex and involved a problem may be, it can always be related conceptually to a simple and familiar model.

For example, in Part Two (on molecules) we begin with an introductory chapter and a rather thorough discussion of the Born-Oppenheimer approximation, which underlies most molecular theories. Then we move into a study of a one-dimensional, symmetric double square well, a model of a homonuclear diatomic molecule. Using this and other models of one- and two-dimensional "molecules," we discuss molecular symmetries and the LCAO:MO method, drawing on qualitative pictures of molecular orbitals

and correlation diagrams for insight. These discussions ultimately lead to an examination of the full problem of electronic states of three-dimensional multielectron molecules (Chapter 16). A somewhat similar approach is adopted in Part Three and in the latter chapters of Part One.

We have chosen to concentrate on the electronic states of atoms, molecules, and solids, a choice that enables us to suggest similarities in the three areas of physics treated (e.g., the orbital approximation). The book is divided into three parts: Electrons in Atoms, Electrons in Diatomic Molecules, and Electrons in Crystalline Solids. Although the book was prepared as a continuous whole, we have tried to write each part so that it could be studied independently of previous material. Of course, the reader who studies molecular physics (Part Two) must also know some atomic physics. However, it is not necessary to have read our discussion of atomic physics. Whenever we draw on earlier sections of our text, appropriate references are provided, and those few earlier sections to which we send you can be read apart from surrounding discussions. (Although the emphasis in Parts Two and Three is on electronic states, the former contains a chapter on nuclear motion and the latter one on applications and lattice vibrations.) A few sections are starred (*). These are supplementary in nature and can be omitted on a first reading. Starred sections tend to be more difficult and contain fewer intermediate steps than unstarred sections.

Our book is aimed at students of physics, chemistry, or engineering who have had some sort of introduction to quantum mechanics, such as that usually contained in a one-semester course at the sophomore-junior level. The first chapter provides a summary and (brief!) review of the material with which our reader should be familiar: the time-dependent and time-independent Schroedinger equations, the solution of the latter for a few simple one-dimensional systems (square wells, harmonic oscillators, etc.), and a few basic definitions (expectation value, Hamiltonian, commutator, and the like). The Suggested Readings in Chapter 1 and the Bibliography at the end list other useful introductory books. Aside from assuming this minimal background, every effort has been made to keep this text self-contained. A year or two of early college math and physics should equip the reader to make it through our book with a minimum of anguish.

And now a word about the problems: *important!* We know that every book tells you how essential its problems are, but we, too, must adopt that cliché. For it is true: there is no way to learn how to apply quantum mechanics except to do problems in quantum mechanics. Throughout the book, you will find both "exercises" and "problems." The former tend to be straightforward manipulations of the sort usually prefaced by "it can be shown that. . . ." We have tried to keep the number of such exercises to a minimum and actually to include in the text steps in derivations where the truth of the matter is that "it can be shown (but only with some difficulty)."

The problems, which appear at the end of each chapter, are another matter. They are designed to help you understand the principles expounded in the text, to extend the text material a little to other topics, and to isolate and clarify possible points of confusion. They are designed to be a learning tool, and hence they usually contain intermediate steps. We would like to encourage you as forcefully as possible to try these problems, many of them.

This material has been developed and tested over the past six years in courses at Rice University; at least one group of students has been exposed to each problem and exercise. The book as written was designed to be used in "traditional" course with lectures, homework, tests, and so on, in "self-paced" courses, and in independent self-study and has been tried in each of these modes. Each problem comes with a "rating" of one to four stars: * = easy, ** = average, *** = a little challenging, **** = difficult. These ratings are based largely on our students' evaluation; hopefully, they will provide some guidelines for student and teacher alike. Further problems and discussions can be found in the references mentioned in the Suggested Readings.

Surely few authors have been as fortunate as we in having so much able and willing outside assistance. To name everyone who contributed in some way would take several pages, and our editor will not allow that. First, we should express our gratitude to the Physics Department at Rice University, which provided an environment in which this book could be written, classes for us to experiment on, moral support, and secretarial help when possible. We also owe a debt to the long-suffering students and tutors of the junior and senior quantum courses at Rice, who at one time or another used this book in manuscript form and readily offered much useful criticism and advice for its improvement, to Professors G. K. Walters, Ian Duck, and J. P. Hannon, who used the text in their classes, and to Lee Collins, Jim Black, Horace Mitchell, and Alan Haggard, who carefully read earlier versions of the manuscript, caught many errors, and offered a number of invaluable suggestions. We would like to thank William Grimshaw, our editor at Prentice-Hall, for his patience and assistance, and Mary Comerford, who cheerfully and skillfully typed her way through more drafts and revisions than any of us wish to recall. In addition, we apologize and would like to express our thanks to anyone we have left out.

Finally, we are pleasantly surprised to find that after six years of working with this material, we still like it. We believe that atomic, molecular, and solid-state physics are interesting and exciting subjects and that learning about them can, in its own way, be fun. We hope some of this feeling is communicated to you.

Houston, Texas

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ONE

ELECTRONS IN ATOMS

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Recollections of Quantum Theory: A Survey Chapter

"How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, *must be the truth."*
Arthur Conan Doyle, Sherlock Holmes to Dr. Watson in "The Sign of Four," The Complete Sherlock Holmes *(Garden City, N.Y.: Doubleday & Company).*

Throughout the nineteenth century great strides were made in the study of classical physics, and by the early 1900s a complacent mood had settled over physicists. Newtonian mechanics had been carried forward by Hamilton and Lagrange to the point where it appeared not only correct but also quite beautiful. Moreover, the electromagnetic theory of James Clark Maxwell masterfully dealt with problems involving electric and magnetic fields. Little did most of the scientists of this era realize that this mood was about to be shattered, that a series of experiments and comparisons of observations to theory would shortly reveal gaping holes in physical theory as it applied to the microscopic realm, and that a series of papers by Einstein, Schroedinger, de Broglie, Heisenberg, and others was about to burst on the scene causing shock waves whose reverberations would be felt throughout the twentieth century. For theirs was to become a new physics called *quantum mechanics* and was

destined to revise radically man's thinking about the physical world and his relation to it.

However, a history of the development of quantum physics cannot be presented here; such a digression would lead us too far from our goals. Nor shall we seek to present a pedagogically sound discourse on the principles of quantum theory; a number of other books have already done so.[1] Rather we shall briefly survey the principal concepts, methods, and results of elementary nonrelativistic quantum theory. These results are not to be taken lightly, for they constitute the theoretical foundation on which the rest of this book is constructed. This brief treatment is simply a review and summary of important material, most of which should already be familiar to the reader and which can be skimmed by anyone who is not enthralled by summaries. We shall refer to and explicate results from this chapter as needed in later work.

1.1 THE WAVE-PARTICLE DUALITY

At the heart of quantum physics is a revolutionary concept of the nature of matter. Until the advent of quantum mechanics, particles had been thought of as entities possessing well-defined positions, momenta, energies, and so on, and as obeying the laws of classical mechanics. Then came the wave theory of matter and its consequences as set forth by Heisenberg, who demonstrated that the nature of the universe prohibits us from determining simultaneously the position and momentum of a particle to an aribitrary degree of precision. This disconcerting notion is expressed mathematically by the *Heisenberg uncertainty principle*:[2]

$$\Delta p_x \, \Delta x \gtrsim \hbar, \qquad \Delta p_y \, \Delta y \gtrsim \hbar, \qquad \Delta p_z \, \Delta z \gtrsim \hbar, \tag{1.1}$$

where Δp_x is the uncertainty in the x component of linear momentum, Δx is the uncertainty in the x component of position, and so on. The constant $\hbar$ is

$$\hbar \equiv \frac{h}{2\pi}, \tag{1.2}$$

where h is *Planck's constant*,[3]

$$h = 6.6257 \times 10^{-27} \text{ erg-sec.} \tag{1.3}$$

[1] See the Suggested Readings at the end of this chapter for references to histories and elementary texts.

[2] A similar relationship holds for energy and time, $\Delta E \, \Delta t \gtrsim \hbar$.

[3] See Appendix 1 for a table of fundamental constants.