QUANTUM MECHANICS

THIRD EDITION

LEONARD I. SCHIFF

QUANTUM MECHANICS

THIRD EDITION

LEONARD I. SCHIFF
Professor of Physics
Stanford University

McGRAW-HILL BOOK COMPANY
New York
St. Louis
San Francisco
Toronto
London
Sydney

QUANTUM MECHANICS

Library of Congress Catalog Card Number 68-25665
55287

34567890 MAMM 7543210

PREFACE

This volume has a threefold purpose: to explain the physical concepts of quantum mechanics, to describe the mathematical formalism, and to present illustrative examples of both the ideas and the methods. The book is intended to serve as a text at the graduate level and also as a reference book. It is assumed that the reader is reasonably familiar with classical mechanics, electromagnetic theory, atomic structure, and differential equations; prior acquaintance with matrices or group theory is not necessary. In addition, he should have had some contact with complex variables (for Chap. 9) and the special theory of relativity (for Chap. 13).

The author believes that the analytical methods employed in the book will satisfy most theoretical physicists even though no attempt is made to achieve mathematical rigor. For example, there is little or no discussion of the justification for the interchange of sum, derivative, and integral operations or for the use of the δ function. On the other hand, the physical reasons for the nature of the results obtained are investigated wherever possible.

Problems are given at the end of each chapter. They are often used to illustrate or amplify points discussed in the text. Original theoretical papers are referred to throughout the book; the list is representative rather than exhaustive. Experimental results are, for the most part, quoted without reference, since the large amount of documentation required for an adequate survey seems out of place in a book on theoretical physics. Several other books and review articles on quantum mechanics and related subjects are referred to for more detailed discussions of particular topics.

The scope of this volume is best outlined if the book is divided into three parts. The first three chapters constitute an introduction to quantum mechanics, in which the physical concepts are discussed and the Schrödinger wave formalism is established. The next nine chapters present exact solutions of the wave equation for both bound-state and collision problems, the Heisenberg matrix formalism and transformation theory, symmetry, approximation methods, the scattering matrix, particle identity, radiation theory, and some applications to atomic systems. Since Chaps. 5 to 12 include most of the material given in a first-year graduate course, it seems desirable to include a semiclassical treatment of electromagnetic radiation (Chap. 11) even though some of the results are obtained again in Chap. 14. The last two chapters are an introduction to relativistic particle theory and to quantized fields.

The first edition of this book was completed 20 years ago, and relatively few changes were made in the second edition. Thus the present revision is of necessity extensive; at the same time it is intended to retain the comprehensiveness of the original volume without a substantial increase in length. The principal additions are a section on complex potentials and the reciprocity and optical theorems (Sec. 20); a much fuller account of matrices and transformation theory (Chap. 6); a new chapter that discusses geometrical and dynamical symmetries and includes a fairly detailed account of angular momentum (Chap. 7); a considerably expanded treatment of approximation methods for bound-state and collision problems, including the scattering matrix and its applications, analytic properties, and dispersion relations (Chaps. 8 and 9); and a new section on the density operator and matrix (Sec. 42). The principal topics dropped from the second edition are the variational treatment of scattering, the theory of the Cerenkov effect, and the quantization of the Dirac equation; also, the last two sections of the second edition are somewhat condensed and combined into one (Sec. 57) in the present volume. Some changes in notation have been made to conform to current usage, and a table of the numerical values of some physical quantities has been added inside the back cover.

The author wishes again to record his indebtedness to the late Prof. J. R. Oppenheimer and to Prof. Robert Serber in connection with the preparation of the first edition of this book. He is also grateful to several of those who have studied and taught from the earlier revision for their many helpful suggestions. In particular, Prof. E. H. Wichmann prepared a thorough review of the second edition that contributed substantially to the present volume. The author also thanks the many students who studied from the various drafts of the third edition for their comments, and especially Prof. J. D. Walecka for his constructive criticism of particular sections.

Leonard I. Schiff

CONTENTS

1

The Physical Basis of Quantum Mechanics

At the present stage of human knowledge, quantum mechanics can be regarded as the fundamental theory of atomic phenomena. The experimental data on which it is based are derived from physical events that lie almost entirely beyond the range of direct human perception. It is not surprising, therefore, that the theory embodies physical concepts that are foreign to common daily experience. These concepts did not appear in the historical development of quantum mechanics, however, until a quite complete mathematical formalism had been evolved. The need for quantitative comparison with observation, which is the ultimate test of any physical theory, in this case led first to the formalism and only later to its interpretation in physical terms.

It seems desirable in introducing the subject of quantum mechanics to depart from the historical order and preface the mathematical development with a discussion of the physical concepts.[1] In this chapter we first review briefly the experimental background and the ideas of the old

[1] For a detailed study of the historical development, see M. Jammer, "The Conceptual Development of Quantum Mechanics" (McGraw-Hill, New York, 1966).

quantum theory, then discuss the newer physical concepts of uncertainty and complementarity, and finally lay the groundwork for the formalism that will be developed in its most familiar form in Chap. 2. No attempt will be made to deduce the structure of the formalism from the fundamental experiments; we shall try to make the theoretical development seem plausible rather than unique. The justification for the theory, then, will rest on the agreement between deductions made from it and experiments, and on the simplicity (in principle more than in practice) and consistency of the formalism.

1□EXPERIMENTAL BACKGROUND

Experimental physics prior to 1900 had demonstrated the existence of a wide variety of phenomena, which for the most part were believed to be explicable in terms of what we now call *classical* theoretical physics. The motions of mechanical objects were successfully discussed in terms of Newton's equations on both celestial and terrestrial scales. Application of this theory to molecular motions produced useful results in the kinetic theory of gases, and the discovery of the electron by J. J. Thomson in 1897 consisted in showing that it behaved like a newtonian particle. The wave nature of light had been strongly suggested by the diffraction experiments of Young in 1803 and was put on a firmer foundation by Maxwell's discovery in 1864 of the connection between optical and electrical phenomena.

INADEQUACY OF CLASSICAL PHYSICS

The difficulties in the understanding of experimental results that remained at the beginning of this century were largely concerned with the development of a suitable atomic model and with the late discoveries of x-rays and radioactivity. However, there were also difficulties associated with phenomena that should have been understood but actually were not: such things as the spectral distribution of thermal radiation from a blackbody, the low-temperature specific heats of solids, and the appearance of only 5 degrees of freedom in the motion of a free diatomic molecule at ordinary temperatures.

The beginning of an understanding of the second class of difficulties was made by Planck in 1900, when he was able to explain the blackbody spectrum in terms of the assumed emission and absorption of electromagnetic radiation in discrete *quanta*, each of which contains an amount of energy E that is equal to the frequency of the radiation ν multiplied by a universal constant h (called *Planck's constant*):

$$E = h\nu \tag{1.1}$$

This quantum idea was later used by Einstein in accounting for some of the experimental observations on the photoelectric effect. In this way the dual character of electromagnetic radiation became established: It sometimes behaves like a wave motion and sometimes like a stream of corpuscular quanta.

At about this time, the existence of discrete values for the measurable parameters of atomic systems (not only of electromagnetic radiation) became apparent through Einstein's and Debye's theories of the specific heats of solids, Ritz's classification of spectral lines, the experiment of Franck and Hertz on the discrete energy losses of electrons on collision with atoms, and (somewhat later) the experiment of Stern and Gerlach, which showed that the component of the magnetic moment of an atom along an external magnetic field has discrete values.

SUMMARY OF PRINCIPAL EXPERIMENTS AND INFERENCES

The theoretical physics of the first quarter of this century thus contained two important inferences, obtained from the experiments and their interpretations, that had not existed in 1900: the dual character of electromagnetic radiation and the existence of discrete values for physical quantities. The relations between the principal experimental conclusions and the theoretical inferences are shown schematically in Table 1; for a more detailed discussion and a bibliography, reference should be made to a book on atomic physics.[1]

A third theoretical inference appeared in 1924 with the suggestion by de Broglie that matter also has a dual (particlelike and wavelike) character; he assumed that the relation between the momentum p of any particle and the length λ of the corresponding wave is[2]

$$\lambda = \frac{h}{p} \tag{1.2}$$

Up to that time all the evidence had indicated that matter was composed of discrete newtonian particles; in particular, sharp tracks of charged particles such as electrons and helium nuclei had been observed in expansion cloud chambers like that invented by C. T. R. Wilson in 1911. Shortly after this, however, Davisson and Germer (1927) and G. P. Thomson (1928) independently observed the diffraction of electrons by crystals and thus confirmed de Broglie's principal supposition.

[1] See, for example, F. K. Richtmyer, E. H. Kennard, and T. Lauritsen, "Introduction to Modern Physics" (McGraw-Hill, New York, 1955); M. Born, "Atomic Physics" (Hafner, New York, 1951); G. P. Harnwell and W. E. Stephens, "Atomic Physics" (McGraw-Hill, New York, 1955).

[2] Equation (1.2) is also valid for light quanta, as may be seen by dividing both sides of Eq. (1.1) by the velocity of light, c; for a directed beam of light $p = E/c$ and $\lambda = c/\nu$.

Table 1 Relations between experimental interpretations and theoretical inferences

Diffraction (Young 1803, Laue 1912)	Electromagnetic waves
Blackbody radiation (Planck 1900) Photoelectric effect (Einstein 1904) Compton effect (1923) Combination principle (Ritz-Rydberg 1908)	Electromagnetic quanta
Specific heats (Einstein 1907, Debye 1912) Franck-Hertz experiment (1913) Stern-Gerlach experiment (1922)	Discrete values for physical quantities

2☐THE OLD QUANTUM THEORY

What is now called the *old quantum theory*[1] was initiated by the work of Planck on blackbody radiation and was carried farther by Einstein and Debye. However, only after Rutherford's discovery in 1911 that an atom consists of a small, massive, positively charged nucleus surrounded by electrons could the theory be applied to a quantitative description of atoms.

BOHR-SOMMERFELD QUANTIZATION RULES

The first step in this direction was taken by Bohr in 1913, when he made two postulates concerning the electronic or extranuclear structure of an atom. The first of these was that an atomic system can exist in particular stationary or quantized states, each of which corresponds to a definite energy of the system. Transitions from one stationary state to another are accompanied by the gain or loss, as the case may be, of an amount of energy equal to the energy difference between the two states; the energy gained or lost appears as a quantum of electromagnetic radiation, or as internal or kinetic energy of another system. The second postulate (in agreement with that of Planck and Einstein) was that a radiation quantum has a frequency equal to its energy divided by Planck's constant h.

These two postulates by themselves provided some insight into the Ritz combination principle and the Franck-Hertz experiment. To obtain specific results for hydrogen, Bohr proposed a simple rule for the selection of the circular orbits that are to constitute stationary states: The angular momentum must be an integral multiple of $h/2\pi$. A more general quantization rule was discovered independently by W. Wilson (1915) and by

[1] For a more detailed discussion than is presented in this section, see the books cited above, and L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," chap. II (McGraw-Hill, New York, 1935).