

THE FUNDAMENTAL PRINCIPLES OF QUANTUM MECHANICS

With Elementary Applications

BY
EDWIN C. KEMBLE
Professor of Physics,
Harvard University

INTERNATIONAL SERIES IN PHYSICS

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FIRST EDITION

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PREFACE

This volume was originally intended to be an expansion of a summary of the elements of quantum mechanics written some years ago for the *Reviews of Modern Physics* by the author in collaboration with Professor E. L. Hill. The point of view is essentially the same as in the summary, but as the present work has grown in my hands it has lost most of its resemblance to the initial pattern.

The method of approach was dictated by the desire to meet the needs of graduate students of physics. For this reason the argument is inductive in form and applications of the theory have been interwoven with the development of the basic mathematical structure. In order to minimize the necessity for frequent consultation of mathematical reference books, a good deal of background mathematical material is included in Chap. IV.

In reading other treatises on quantum theory I have frequently been distressed by the tendency to gloss over the numerous mathematical uncertainties and pitfalls which abound in the subject. From the standpoint of the beginner there is much to be said for this practice of minimizing the defects of the theory in order to exhibit its main outlines in a compact and attractive form. Nevertheless it has seemed to me that a book which deliberately called attention to the weak spots in the argument would be of considerable value to teachers and to students of the more mature type. The work of the mathematician von Neumann provides a masterly antidote to the lack of rigor characteristic of the average physicist, but by common consent this work is too difficult for any but the most mathematical students of this subject. Hence I have been led to try my hand at bridging the gap between the exacting technique of von Neumann and the usual less rigorous formulations of the theory. In carrying this project through I have restricted the discussion to such elementary mathematical methods as are the common property of physicists today. The reader must judge my success in avoiding the Scylla of sloppy thinking and the Charybdis of tedious complexity. Fine print, starred sections, and appendices indicate portions of the material which may well be omitted or briefly scanned on first reading.

A feature of the present volume on the physical and philosophical side is its consistent emphasis on the operational point of view and on the fundamental importance of Gibbsian assemblages of independent systems in the physical interpretation of the mathematical formalism.

A considerable collection of references indicates the author's indebtedness to the ideas of others, but the list is by no means exhaustive. I have borrowed freely from other books and am particularly indebted to those of von Neumann, Dirac, and of Born and Jordan.

It is a pleasure to thank my colleagues and former colleagues, Dr. Eugene Feenberg, Dr. W. H. Furry, Professor J. C. Slater, and Professor J. H. Van Vleck for invaluable suggestions and generous assistance. I am particularly indebted to Professor Van Vleck for reading the entire manuscript and for his constant encouragement. Dr. Montgomery H. Johnson is responsible for much of the work on the continuous spectrum in Sec. 31, while Dr. Bela Lengyel and Dr. Charles H. Fay have at various times spent long hours in checking equations and other technical assistance. The author is very grateful to the librarian of the Harvard Physics Laboratory, Mrs. Miner T. Patton, for her cheerfulness and accuracy in the repeated typing of successive editions of the manuscript.

To the Milton Fund of Harvard University I am indebted for a generous grant for technical help in preparing the manuscript for the printer.

EDWIN C. KEMBLE.

PEACHAM, VERMONT,
August, 1937.

NOTATION

The number of different physical and mathematical quantities to be represented by separate symbols in this book is embarrassingly large in comparison with the available letters of the Roman and Greek alphabets. For this reason the establishment of a one-to-one correspondence of symbols and meanings has proved impracticable. The author has endeavored to keep the notation consistent within each chapter and, with a few exceptions which should not be confusing, has used only one symbol for each well-defined and recurrent meaning.

The following notes may be of use to the reader who attempts to dip into the middle of the book.

An asterisk * used as a superscript denotes the complex conjugate of the number or function in question.

Ordinarily the symbol Ψ denotes a time-dependent wave function, while ψ indicates the time-free space factor of a monochromatic or single-energy Ψ . At times ψ is also used for the instantaneous form of a general wave function.

Vectors are indicated by superior arrows.

Three-dimensional vector and scalar products are indicated by the conventional \times and \cdot , e.g., $\vec{A} \times \vec{B}$ and $\vec{A} \cdot \vec{B}$.

The scalar products of many-dimensional complex vectors and of functions are denoted by heavy parentheses, e.g.,

$$\begin{aligned}\vec{(A, B)} &= \sum_k A_k B_k^*, \\ (\psi(x), \varphi(x)) &= \int \psi \varphi^* dx.\end{aligned}$$

In Chap. IV the *norm* of a function f , viz., (f, f) , is indicated by Nf , while the *magnitude*, or square root, of the norm is indicated by $\|f\|$.

$\Sigma \alpha'$ denotes a mixed process of summation and integration over all eigenvalue points in α' -space. Cf. p. 246.

Matrices are denoted by boldface type or by a typical element enclosed in double vertical rules. Thus,

$$\mathbf{H} = \|H(m, n)\|.$$

The *first* of the two indices of the typical element of an ordinary two-dimensional matrix indicates the *row*, while the *second* denotes the *column*.

The Dirac notation for an eigenfunction of α in x' -space, viz., $(x'|\alpha')$, is introduced in Sec. 36*b*, while the Dirac notation for matrix elements, e.g., $(\beta''|\gamma|\beta')$, appears in Sec. 44*d*. The Dirac symbolism is employed only at points where it is particularly convenient.

REFERENCE ABBREVIATIONS

- D. P. *Differentialgleichungen der Physik*, Riemann-Weber, Braunschweig, edition of 1927.
- E. Q. *Elementare Quantenmechanik*, M. Born and P. Jordan, Berlin, 1930.
- M. G. Q. *Mathematische Grundlagen der Quantenmechanik*, J. v. Neumann, Berlin, 1932.
- M. M. P. *Methoden der Mathematischen Physik I*, R. Courant and D. Hilbert, Berlin, 2d ed., 1931.
- P. Q. M. *The Principles of Quantum Mechanics*, P. A. M. Dirac, Oxford, 1st ed., 1930; 2d ed., 1935.
- Q. M. *Quantum Mechanics*, E. U. Condon and P. M. Morse, New York, 1929.
- T. A. S. *The Theory of Atomic Spectra*, E. U. Condon and G. H. Shortley, Oxford, 1935.

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* An asterisk before the number of a section or subsection indicates that the section or subsection so marked may be omitted or skimmed to advantage on first reading.

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