

QUANTUM
MECHANICS
VOLUME I:
FUNDAMENTALS

Quantum Mechanics

Volume I: Fundamentals

Preface

In 1961–1962 I taught the graduate quantum mechanics course at Harvard, and unwittingly prepared a detailed set of handwritten notes for distribution to the students. Having heard of this, the Pied Piper from Benjamin appeared. Little did he or I suspect that his enticing tune would lead to a two-volume tome.

This volume is intended as a text for a first-year graduate quantum mechanics course. The great majority of students entering graduate school today have had a term or more of introductory quantum theory. The lectures I have given at Cornell and Harvard therefore assumed that the audience had at least a nodding acquaintance with the phenomenological and epistemological background, the Schrödinger equation, and its application to very simple systems. This book is written in the same spirit. It is self-contained, and in principle it can be read by someone who has not heard of Planck's constant. But only a very gifted student could expect to digest it comfortably without any previous exposure to the quantum theory.

As for other prerequisites, I should like to emphasize that I do *not* assume a knowledge of group theory, functional spaces, or classical mechanics beyond Hamilton's equations. Except for Sec. 3, which can be skipped without destroying the continuity of the argument, only ele-

Preface

mentary electromagnetic theory is necessary until Chapt. VIII. On the other hand, I do assume some knowledge of vector analysis, linear algebra, ordinary differential equations, Fourier analysis, and analytic functions. The general level of mathematical rigor is typical of most of current theoretical physics.

In the courses I have taught, and also in this book, I have tried to meet several, occasionally conflicting, goals. On the one hand, quantum mechanics underlies essentially all current thinking in physics, and the serious student must therefore master the conceptual and mathematical foundations of the subject if he is not to be a mere technician. On the other hand, quantum mechanics is also an exceedingly complicated and rapidly proliferating technique used by many physicists in their day-to-day work. It is therefore some combination of philosopher and artisan that I have in mind—a “quantum mechanic.”

Insofar as “fundamentals” are concerned, I have emphasized the theory of the measurement process, and symmetry principles. The analysis of measurements, and its relationship to the statistical interpretation, are usually overlooked in courses on quantum mechanics. While it is true that measurement theory cannot be appreciated by the novice, it can be understood by hard-thinking students who are able to master the more technical portions of the subject. Here I do not mean to imply that measurement theory is easy. Far from it. As for symmetry, or lack thereof, no apologies are necessary because recent developments have repeatedly shown that this is a subject that one can ill afford to ignore. No matter how much one has studied invariance principles and their consequences, there always appear to be sensational surprises that reveal the superficiality of one's understanding.

In the applications of the general theory I have tried to find examples that really do justice to the technique used. It was also my intention to illustrate every important technique with an application of genuine practical interest. Unfortunately I found it rather inconvenient to meet these objectives completely within the compass of Volume I. For example, the Wigner-Eckart theorem and the angular momentum decomposition of the electromagnetic field are not applied until Volume II (containing Chaps. X–XIII). But by and large I believe I have illustrated the theory with realistic applications, or, as in Sec. 15, with artificial examples of sufficient complexity to reveal the essential ingredients of a practical calculation.

A few remarks concerning the organization of the book are in order here. If logic and efficiency were the only considerations, I would begin straightaway with Dirac's abstract formulation. But most students appear to find this too difficult, and I therefore develop the wave-mechanical formulation first. Once students have had the opportunity to master

this approach by applying it to several problems of moderate complexity, they are far more receptive to the abstract approach, and also in a better position to appreciate its power and elegance. In the remainder of the course (i.e., following Chapt. IV) I always use Dirac's mode of thought and notation. The applications treated in this volume are almost exclusively concerned with systems having a small number of degrees of freedom. In thinking about such systems one is not forced to make drastic approximations *ab initio*, and much confusion between basic principles and approximation methods is thereby avoided. The theory of systems with many degrees of freedom has, on the whole, been relegated to Volume II. That volume will contain discussions of radiation theory, quantum statistics and the many-body problem, and more advanced topics in collision theory.

Here I should like to interject a few suggestions to those who set out to learn this subject by themselves, without the crutch of a lecture course. There are a number of topics of more than average technical complexity that can be deleted in a first approach to the subject. Some of these have been set in small type and are also marked off by the symbol •. But even larger portions can be saved for later consumption. For example, Sec. 3 can be read just prior to Chapt. VIII. Section 17 on the Coulomb field contains a good deal of rather intricate analysis; readers who do not feel at home off the real axis might do well to substitute a treatment along more conventional lines. The advice in the footnote at the beginning of Sec. 20 should be heeded by beginners. The bulk of Sec. 34, and essentially all of Sec. 49, can safely be skipped. But the problems should not be skipped under any circumstances. It is impossible to know whether one has understood the theory unless one has solved problems. Some of the problems in this book are rather difficult, and one should not be dismayed if several long days are required for their solution.

In citing the literature I have used a set of rather arbitrary rules. The papers from the Heroic Age are not referred to, unless they contain further information that the reader might find useful. On the other hand, more modern articles whose existence may be unknown to the student are frequently cited. On several occasions I have purposely used published material in the problems without stating a reference. The abused authors are R. J. Glauber, J. V. Lepore, J. Schwinger, and Y. Yamaguchi and Y. Yamaguchi. The wave packet treatment of collisions described in Sec. 12.2 is due to F. E. Low.

KURT GOTTFRIED

Ithaca, New York
December 1965

I also wish to thank Alan Ghodas and Velina Ray for diligent help in preparing the manuscript and correcting proofs, and all the good people at W. A. Benjamin, Inc. for their remarkable patience. A large portion of the manuscript was prepared while I held a Jean Simon Guggenheim Fellowship at CERN; I should like to thank the Guggenheim Foundation for its generous support, and Leon Van Hove and Victor Weisskopf for the warm hospitality extended to me in Geneva. Finally, I am very indebted to my wife for encouragement and support throughout the entire process that have gone into the writing of this book.

Acknowledgments

By far the most pleasant task in writing a book is the compilation of acknowledgments. Above all I should like to express my debt to the men who have taught me this subject, both by the spoken and written word. As a student I was very fortunate to hear lectures by three outstanding teachers, J. D. Jackson, J. Schwinger, and V. F. Weisskopf. Schwinger's approach made an especially deep impression on me, and I frequently consulted my voluminous notes from his course in preparing my own lectures. A brief glance at this book also reveals that I have been greatly influenced by Dirac's classic monograph, and by Pauli's *Handbuch* article. In truth, portions of Chaps. I, II, and IV are merely expanded translations of Pauli's work, "a poor man's Pauli." I have also received advice and criticism from a number of friends, colleagues, and students. On innumerable occasions Jeffrey Goldstone has shared his exceptional understanding of the foundations of this subject with me; these conversations had a marked effect on the final shape of Secs. 20 and 27. I have also benefited from many suggestions and comments by David Jackson, Paul Martin, and Charles Schwartz. Wendell Furry kindly read and commented on Chapt. IV. Some of the views and ideas expressed in Secs. 20.3 and 56.2 grew out of stimulating conversations with Donald Yennie.

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K. G.

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Quantum Mechanics

• *Volume I: Fundamentals, 1966*
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Volume II: Systems with Many Degrees of Freedom
In preparation

7. Eigenfunctions
 1. Stationary states 2. The spectrum of the Hamiltonian 3. Orthogonality and completeness 4. Linear vector spaces 5. Simultaneous eigenfunctions and compatible observables 6. Probability amplitudes

8. The Classical Limit
 1. Ehrenfest's theorem 2. The relationship between the Schrödinger and Hamilton-Jacobi equations 3. The semiclassical approximation for stationary states

III. Illustrative Solutions of Schrödinger's Equation

9. Separation of Variables in the Two-Body Problem
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10. Eigenvalues and Eigenfunctions of the Angular Momentum Operators
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11. Free-Particle Wave Functions
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12. Scattering Theory
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13. The Born and Eikonal Approximations
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from classical physics. It is not that physics is not applicable to the range of phenomena which are now being investigated. The range of this investigation in classical physics has been carefully defined, the stage upon which the new theory is to appear will be set. Our task of argument will not follow the usual lines; instead it will draw first on the wisdom of classical physics, and then on the wisdom of the new theory, and lastly on the wisdom of the new theory, and lastly on the wisdom of the new theory.

I

Development Aspects of the Electromagnetic Field

Uncertainty and Complementarity

During the first decade of this century it became increasingly clear that classical physics could not account for some of the most significant features of the newly discovered atomic phenomena. The inadequacy of classical theory was strikingly emphasized by the partial success of the ideas proposed by Planck, Einstein, and Bohr. This "old quantum theory" was a diabolically clever hodge-podge of classical laws and seemingly unrelated *ad hoc* recipes. The creation of quantum mechanics in the period 1924-1928 restored logical consistency to its rightful place in theoretical physics. Of even greater importance, it provided us with a theory that appears to be in complete accord with our empirical knowledge of all nonrelativistic phenomena. On the other hand, the new theory brought with it a most profound revolution in the concepts, and to some extent even the aims, of physics.

We shall begin our study of quantum mechanics by analyzing some of the microscopic phenomena to which we have alluded. This analysis will force us to the conclusion that some of the most "obvious" and dearly cherished notions abstracted from our vast experience of macroscopic phenomena are simply inapplicable to the microcosm. We shall see that this failure of classical physics is not merely a matter of quantitative disagreements with experiments. The problem is much more fundamental

because *classical physics does not even provide an appropriate language for describing certain microscopic phenomena in purely qualitative terms*. Once the extent of this breakdown of classical physics has been carefully delineated, the stage upon which the new theory is to appear will be set. Our train of argument will not follow historical lines; instead it will draw heavily on the wisdom of hindsight. The historical development of the theory is a long and fascinating story that falls outside the scope of this book.*

1. Nonclassical Aspects of the Electromagnetic Field

The study of interaction between light and electrons provided most of the important clues in the development of the quantum theory, and so we shall first address ourselves to this topic. Consider an electromagnetic wave packet of mean wave vector \mathbf{k} having a spatial extension considerably in excess of $1/k$, i.e., a fairly monochromatic packet.† According to classical electrodynamics the energy and momentum carried by this packet depend on the mean intensity of the field. The classical theory asserts that after this packet has interacted with an electron, the field will consist of an outgoing spherical wave, as well as a packet of slightly depleted intensity proceeding in the initial direction $\hat{\mathbf{k}}$. Furthermore, classical theory predicts that if the electron was initially at rest, it will possess a momentum in the direction $\hat{\mathbf{k}}$ after the collision. Let us now compare these predictions with the experimental facts originally obtained by Compton in a study of X-ray scattering. His experiments revealed that (a) electrons frequently acquire a momentum transverse to $\hat{\mathbf{k}}$; (b) no vestige of the spherically scattered wave is observed: on the contrary, the electromagnetic energy and momentum are concentrated in a spatially confined packet after the collision; (c) the propagation of this scattered packet is correlated in direction with the momentum vector of the scattered electron.

We are obviously faced with a number of glaring disagreements with classical electrodynamics. In fact, as Compton himself recognized, one can retrieve some of the experimental results by invoking the photon

* For an account of developments preceding 1926, see Whittaker. Pauli's footnotes provide an outline history for the period 1925-1932. (When only an author's name appears in a citation, see the Bibliography for a detailed reference.)

† If $\hat{\mathbf{k}}$ is a unit vector in the direction of propagation of a plane wave, then $\mathbf{k} = \hat{\mathbf{k}}/\lambda$, where $2\pi\lambda$ is the wavelength. We shall always use the notation $\hat{\mathbf{a}}$ for a unit vector in the direction of \mathbf{a} .

1. Nonclassical Aspects of the Electromagnetic Field

concept introduced long before by Einstein in his theory of the photo-effect. That is, one treats the incident field as an assembly of particles (photons) that can scatter from the electrons like billiard balls. The energy E and momentum \mathbf{p} which one ascribes to these particles are related to the mean circular frequency ω and wave vector \mathbf{k} of the electromagnetic disturbance by

$$E = \hbar\omega, \quad \mathbf{p} = \hbar\mathbf{k}, \quad (1)$$

where \hbar ($= 1.054 \times 10^{-27}$ erg sec) is Planck's constant.* The conservation laws of energy and momentum, in conjunction with (1), correctly determine the frequency and propagation vector of the scattered packet in terms of the momentum vector of the scattered electron. We should note here that the electrodynamic dispersion law $\omega = ck$, where c is the velocity of light, implies that $E = pc$. One therefore speaks of the photon as a particle with vanishing rest mass.

Let us examine the novel features of Compton's "explanation" in more detail. In the first instance we note that the relations (1) constitute a most remarkable liaison between two families of concepts that are quite unrelated in classical physics—that of particles and that of waves. Here we may already catch a glimpse of Bohr's *Complementarity Principle*, which, among other things, asserts that in the atomic domain it is not possible to describe phenomena by any single classical concept. Concerning this point, *the wave-particle duality*, we shall have much more to say shortly. Let us first emphasize another striking feature of the Compton experiment. That is, *there is a stochastic aspect to the actually observed course of events*, because there does not appear to be any imaginable way in which the experimenter can control or predict the momentum that an electron will acquire in any single collision. The only reproducible experimental quantity is the probability distribution for the magnitude and direction of the momentum transfer. The naive theory of the Compton effect based on (1) also involves this probabilistic aspect, because it only gives the momentum of the scattered light in terms of the momentum of the scattered electron. In fact, this naive theory is clearly *incomplete*, because it cannot predict the probability distribution referred to above. On the other hand, the classical theory is not only incomplete; it is *wrong*, for it does not contain any stochastic element. Rather, it asserts that the momentum transfer is uniquely determined once the incident light packet is specified.

An immense amount of evidence attesting to the wave nature of light had been collected in the century preceding Compton's work. Can one reconcile the phenomena of interference and diffraction with those of the

* A list of fundamental constants and conversion factors is provided in the appendix.

photo-effect and Compton scattering? In order to answer this question, let us investigate a typical interference experiment. Consider the grating arrangement shown in Fig. 1.1. According to classical theory, the angular separation between maxima is $\Delta\alpha \simeq \lambda/d$, and the angular width of each maximum is $\delta\alpha \simeq (d/D)(\Delta\alpha)$, where λ is the wavelength of the radiation. As a detector we could use a photographic plate, which on detailed examination would reveal a multitude of spots whose density is given by classical wave theory. Each individual spot is actually the

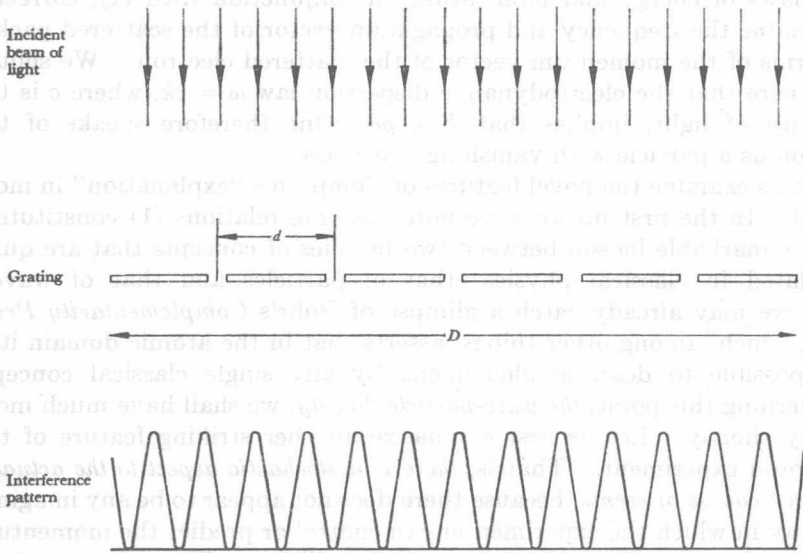


Fig. 1.1. Diffraction grating.

result of a photo-chemical reaction which, as we now know, is triggered by a *single* quantum. This can also be shown by reducing the beam intensity to a point where, on the average, only one quantum is passing through the apparatus at a time. Thus only one chemical reaction in the detector would be triggered at a time.* This is in complete disagreement with the classical theory which predicts that the interference pattern remains unaltered, and that the total intensity is reduced. In the one-photon-at-a-time experiment, we only see one spot at a time. If we make a long exposure so that many photons pass through the apparatus, and fail to resolve the different spots on the photographic plate, we

* Or we could put a cloud chamber behind the screen and observe Compton scattering of the diffracted light.