Principles of Quantum Mechanics

Ramamurti Shankar

Principles of Quantum Mechanics

Ramamurti Shankar

Yale University
New Haven, Connecticut

PLENUM PRESS · NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

Shankar, Ramamurti.
Principles of quantum mechanics.

Includes index.
Quantum theory. I. Title.
QC174.12.S52 530.1'2 79-24490
ISBN 0-306-40397-8

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

Printed in the United States of America

Preface

Publish and perish—*Giordano Bruno*

Given the number of books that already exist on the subject of quantum mechanics, one would think that the public needs one more as much as it does, say, the latest version of the Table of Integers. But this does not deter me (as it didn't my predecessors) from trying to circulate my own version of how it ought to be taught. The approach to be presented here (to be described in a moment) was first tried on a group of Harvard undergraduates in the summer of '76, once again in the summer of '77, and more recently at Yale on undergraduates ('77–'78) and graduates ('78–'79) taking a year-long course on the subject. In all cases the results were very satisfactory in the sense that the students seemed to have learned the subject well and to have enjoyed the presentation. It is, in fact, their enthusiastic response and encouragement that convinced me of the soundness of my approach and impelled me to write this book.

The basic idea is to develop the subject from its postulates, after addressing some indispensable preliminaries. Now, most people would agree that the best way to teach any subject that has reached the point of development where it can be reduced to a few postulates is to start with the latter, for it is this approach that gives students the fullest understanding of the foundations of the theory and how it is to be used. But they would also argue that whereas this is all right in the case of special relativity or mechanics, a typical student about to learn quantum mechanics seldom has any familiarity with the mathematical language in which the postulates are stated. I agree with these people that this problem is real, but I differ in my belief that it should and can be overcome. This book is an attempt at doing just this.

It begins with a rather lengthy chapter in which the relevant mathematics of vector spaces is developed from simple ideas on vectors and matrices the student is assumed to know. The level of rigor is what I think is needed to make a practicing quantum mechanic out of the student. This chapter, which typically takes six to eight lecture hours, is filled with examples from physics to keep students from getting too fidgety while they wait for the "real physics." Since the math introduced has to be taught sooner or later, I prefer sooner to later, for this way the students, when they get to it, can give quantum theory their fullest attention without having to battle with the mathematical theorems at the same time. Also, by segregating the mathematical theorems from the physical postulates, any possible confusion as to which is which is nipped in the bud.

This chapter is followed by one on classical mechanics, where the Lagrangian and Hamiltonian formalisms are developed in some depth. It is for the instructor to decide how much of this to cover; the more students know of these matters, the better they will understand the connection between classical and quantum mechanics. Chapter 3 is devoted to a brief study of idealized experiments that betray the inadequacy of classical mechanics and give a glimpse of quantum mechanics.

Having trained and motivated the students I now give them the postulates of quantum mechanics of a single particle in one dimension. I use the word "postulate" here to mean "that which cannot be deduced from pure mathematical or logical reasoning, and given which one can formulate and solve quantum mechanical problems and interpret the results." This is not the sense in which the true axiomatist would use the word. For instance, where the true axiomatist would just postulate that the dynamical variables are given by Hilbert space operators, I would add the operator identifications, i.e., specify the operators that represent coordinate and momentum (from which others can be built). Likewise, I would not stop with the statement that there is a Hamiltonian operator that governs the time evolution through the equation $i\hbar\partial|\psi\rangle/\partial t = H|\psi\rangle$; I would say the H is obtained from the classical Hamiltonian by substituting for x and p the corresponding operators. While the more general axioms have the virtue of surviving as we progress to systems of more degrees of freedom, with or without classical counterparts, students given just these will not know how to calculate anything such as the spectrum of the oscillator. Now one can, of course, try to "derive" these operator assignments, but to do so one would have to appeal to ideas of a postulatory nature themselves. (The same goes for "deriving" the Schrödinger equation.) As we go along, these postulates are generalized to more degrees of freedom and it is for pedagogical reasons that these generalizations are postponed. Perhaps when students are finished with this book, they can free themselves from the specific operator assignments and think of quantum mechanics as a general mathematical formalism obeying certain postulates (in the strict sense of the term).

The postulates in Chapter 4 are followed by a lengthy discussion of the same, with many examples from fictitious Hilbert spaces of three dimensions. Nonetheless, students will find it hard. It is only as they go along and see these postulates used over and over again in the rest of the book, in the setting up of problems and the interpretation of the results, that they will catch on to how the game is played. It is hoped they will be able to do it on their own when they graduate. I think that any attempt to soften this initial blow will be counterproductive in the long run.

Chapter 5 deals with standard problems in one dimension. It is worth mentioning that the scattering off a step potential is treated using a wave packet approach. If the subject seems too hard at this stage, the instructor may decide to return to it after Chapter 7 (oscillator), when students have gained more experience. But I think that sooner or later students must get acquainted with this treatment of scattering.

The classical limit is the subject of the next chapter. The harmonic oscillator is discussed in detail in the next. It is the first realistic problem and the instructor may be eager to get to it as soon as possible. If the instructor wants, he or she can discuss the classical limit after discussing the oscillator.

We next discuss the path integral formulation due to Feynman. Given the intuitive understanding it provides, and its elegance (not to mention its ability to give the full propagator in just a few minutes in a class of problems), its omission from so many books is hard to understand. While it is admittedly hard to actually evaluate a path integral (one example is provided here), the notion of expressing the propagator as a sum over amplitudes from various paths is rather simple. The importance of this point of view is becoming clearer day by day to workers in statistical mechanics and field theory. I think every effort should be made to include at least the first three (and possibly five) sections of this chapter in the course.

The content of the remaining chapters is standard, in the first approximation. The style is of course peculiar to this author, as are the specific topics. For instance, an entire chapter (11) is devoted to symmetries and their consequences. The chapter on the hydrogen atom also contains a section on how to make numerical estimates starting with a few mnemonics. Chapter 15, on addition of angular momenta, also contains a section on how to understand the "accidental" degeneracies in the spectra of hydrogen and the isotropic oscillator. The quantization of the radiation field is discussed in Chapter 18, on time-dependent perturbation theory. Finally the treatment of the Dirac equation in the last chapter (20) is intended to show that several things such as electron spin, its magnetic moment, the spin–orbit interaction, etc., which were introduced in an ad hoc fashion in earlier chapters, emerge as a coherent whole from the Dirac equation, and also to give students a glimpse of what lies ahead. This chapter also explains how Feynman resolves the problem of negative-energy solutions (in a way that applies to bosons and fermions).

For Whom Is this Book Intended?

In writing it, I addressed students who are trying to learn the subject by themselves; that is to say, I made it as self-contained as possible, included a lot of exercises and answers to most of them, and discussed several tricky points that trouble students when they learn the subject. But I am aware that in practice it is most likely to be used as a class text. There is enough material here for a full year graduate course. It is, however, quite easy to adapt it to a year-long undergraduate course. Several sections that may be omitted without loss of continuity are indicated. The sequence of topics may also be changed, as stated earlier in this preface. I thought it best to let the instructor skim through the book and chart the course for his or her class, given their level of preparation and objectives. Of course the book will not be particularly useful if the instructor is not sympathetic to the broad philosophy espoused here, namely, that first comes the mathematical training and then the development of the subject from the postulates. To instructors who feel that this approach is all right in principle but will not work in practice, I reiterate that it has been found to work in practice, not just by me but also by teachers elsewhere.

The book may be used by nonphysicists as well. (I have found that it goes well with chemistry majors in my classes.) *Although I wrote it for students with no familiarity with the subject, any previous exposure can only be advantageous.*

Finally, I invite instructors and students alike to communicate to me any suggestions for improvement, whether they be pedagogical or in reference to errors or misprints.

Acknowledgments

As I look back to see who all made this book possible, my thoughts first turn to my brother R. Rajaraman and friend Rajaram Nityananda, who, around the same time, introduced me to physics in general and quantum mechanics in particular. Next come my students, particularly Doug Stone, but for whose encouragement and enthusiastic response I would not have undertaken this project. I am grateful to Professor Julius

Kovacs of Michigan State, whose kind words of encouragement assured me that the book would be as well received by my peers as it was by my students. More recently, I have profited from numerous conversations with my colleagues at Yale, in particular Alan Chodos and Peter Mohr. My special thanks go to Charles Sommerfield, who managed to make time to read the manuscript and made many useful comments and recommendations. The detailed proofreading was done by Tom Moore. I thank you, the reader, in advance, for drawing to my notice any errors that may have slipped past us.

The bulk of the manuscript production costs were borne by the J. W. Gibbs fellowship from Yale, which also supported me during the time the book was being written. Ms. Laurie Liptak did a fantastic job of typing the first 18 chapters and Ms. Linda Ford did the same with the last two. The figures are by Mr. J. Brosious. Mr. R. Badrinath kindly helped with the index.

On the domestic front, encouragement came from my parents, my in-laws, and most important of all from my wife, Uma, who cheerfully donated me to science for a year or so and stood by me throughout. Little Umesh did his bit by tearing up all my books on the subject, both as a show of support and to create a need for this one.

New Haven
Connecticut

Ramamurti Shankar
Yale University

Prelude

Our description of the physical world is dynamic in nature and undergoes frequent change. At any given time, we summarize our knowledge of natural phenomena by means of certain laws. These laws adequately describe the phenomenon studied up to that time, to an accuracy then attainable. As time passes, we enlarge the domain of observation and improve the accuracy of measurement. As we do so, we constantly check to see if the laws continue to be valid. Those laws that do remain valid gain in stature, and those that do not must be abandoned in favor of new ones that do.

In this changing picture, the laws of classical mechanics formulated by Galileo, Newton, and later by Euler, Lagrange, Hamilton, Jacobi, and others, remained unaltered for almost three centuries. The expanding domain of classical physics met its first obstacles around the beginning of this century. The obstruction came on two fronts: at large velocities and small (atomic) scales. The problem of large velocities was successfully solved by Einstein, who gave us his relativistic mechanics, while the founders of quantum mechanics—Bohr, Heisenberg, Schrödinger, Dirac, Born, and others—solved the problem of small-scale physics. The union of relativity and quantum mechanics, needed for the description of phenomena involving simultaneously large velocities and small scales, turns out to be very difficult. Although much progress has been made in this subject, called quantum field theory, there remain many open questions to this date. We shall concentrate here on just the small-scale problem, that is to say, on non-relativistic quantum mechanics.

The passage from classical to quantum mechanics has several features that are common to all such transitions in which an old theory gives way to a new one:

(i) There is a domain D_n of phenomena described by the new theory and a subdomain D_o wherein the old theory is reliable (to a given accuracy).

(ii) Within the subdomain D_o either theory may be used to make quantitative predictions. It might often be more expedient to employ the old theory.

(iii) In addition to numerical accuracy, the new theory often brings about radical conceptual changes. Being of a qualitative nature, these will have a bearing on all of D_n.

For example, in the case of relativity, D_o and D_n represent (macroscopic) phenomena involving small and arbitrary velocities, respectively, the latter, of course, being bounded by the velocity of light. In addition to giving better numerical predictions for high-velocity phenomena, relativity theory also outlaws several cherished notions of the Newtonian scheme, such as absolute time, absolute length, unlimited velocities for particles, etc.

In a similar manner, quantum mechanics brings with it not only improved numerical predictions for the microscopic world, but also conceptual changes that rock the very foundations of classical thought.

This book introduces you to this subject, starting from its postulates. Between you and the postulates there stand three chapters wherein you will find a summary of the mathematical ideas appearing in the statement of the postulates, a review of classical mechanics, and a brief description of the empirical basis for the quantum theory. In the rest of the book, the postulates are invoked to formulate and solve a variety of quantum mechanical problems. It is hoped that, by the time you get to the end of the book, you will be able to do the same yourself.

Note to the Student

Do as many exercises as you can, especially the ones marked ★ or whose results carry equation numbers. The answer to each exercise is given either with the exercise or at the end of the book.

The first chapter is very important. Do not rush through it. Even if you know the math, read it to get acquainted with the notation.

I am not saying it is an easy subject. But I hope this book makes it seem reasonable.

Good luck.

Contents

1

Mathematical Introduction

The aim of this book is to provide you with an introduction to quantum mechanics, starting from its axioms. It is the aim of this chapter to equip you with the necessary mathematical machinery. All the math you will need is developed here, starting from some basic ideas on vectors and matrices that you are assumed to know. Numerous examples and exercises related to classical mechanics are given, both to provide some relief from the math and to point out the wide applicability of the techniques you will learn here. The effort you put into mastering this first and very important chapter will be worth your while. The theory of linear vector spaces that you will learn here will not only arm you for this course, but also unify and clarify several ideas, related to vectors and matrices on the one hand, and to functions and operators on the other. Approach this chapter any way you wish, stooped over your desk or curled up in your couch; but in all cases keep some pencils and paper handy to work out the problems.

1.1. Linear Vector Spaces: Basics

Definition 1. A *linear vector space* $\mathbb{V}$ is a set $\{\mathbf{V}^1, \mathbf{V}^2, \mathbf{V}^3, \ldots\}$ of *vectors*, which may be added to each other and multiplied by *scalars* $\{\alpha, \beta, \ldots\}$ in such a way that (a) the operations of addition and scalar multiplication performed on the elements of $\mathbb{V}$ yield only elements of $\mathbb{V}$ (closure); (b) addition and scalar multiplication obey the following axioms.

Axioms for Addition. For arbitrary $\mathbf{V}_i$, $\mathbf{V}_j$, $\mathbf{V}_k$ of $\mathbb{V}$

(i) $\mathbf{V}_i + \mathbf{V}_j = \mathbf{V}_j + \mathbf{V}_i$ (commutativity)

(ii) $\mathbf{V}_i + (\mathbf{V}_j + \mathbf{V}_k) = (\mathbf{V}_i + \mathbf{V}_j) + \mathbf{V}_k$ (associativity)

(iii) There exists a unique null vector $\mathbf{0}$ in $\mathbb{V}$ such that $\mathbf{0} + \mathbf{V}_i = \mathbf{V}_i + \mathbf{0} = \mathbf{V}_i$ (existence of identity element)

(iv) For each $\mathbf{V}_i$ there is a unique inverse $(-\mathbf{V}_i)$ in $\mathbb{V}$ such that $\mathbf{V}_i + (-\mathbf{V}_i) = \mathbf{0}$ (existence of inverse)

Those of you familiar with groups will see that the elements of a linear vector space form a group under addition.

Axioms for Scalar Multiplication. For arbitrary $\mathbf{V}_i$, $\mathbf{V}_j$, α, and β,

(v) $\alpha(\mathbf{V}_i + \mathbf{V}_j) = \alpha\mathbf{V}_i + \alpha\mathbf{V}_j$

(vi) $(\alpha + \beta)\mathbf{V}_i = \alpha\mathbf{V}_i + \beta\mathbf{V}_i$

(vii) $\alpha(\beta\mathbf{V}_i) = (\alpha\beta)\mathbf{V}_i$

There is a simple mnemonic that summarizes these axioms: do what comes naturally.

Definition 2. The domain of allowed values for the scalars $\{\alpha, \beta, \ldots\}$ is called the *field* $\mathbb{F}$ over which $\mathbb{V}$ is defined. If $\mathbb{F}$ consists of all real (complex) numbers, we have a real (complex) vector space. (Appendix A.3 contains a brief introduction to complex numbers.)

Example 1.1.1. As an example of a vector space, let us consider the set of all directed line segments, i.e., the set of arrows of definite length and orientation that we use in physics to represent displacement, velocity, force, etc. As it is, the set does not form a vector space; we must first define addition and scalar multiplication. The addition law we choose is of course the usual one: to add two arrows $\mathbf{V}$ and $\mathbf{V}'$, place the tail of $\mathbf{V}'$ at the tip of $\mathbf{V}$, and then their sum, $\mathbf{V} + \mathbf{V}'$, is given by the arrow running from the tail of $\mathbf{V}$ to the tip of $\mathbf{V}'$ (Fig. 1.1). One may add three or more vectors by using the recipe on two vectors at a time. The null vector $\mathbf{0}$ is defined to be an arrow of zero length, and the vector $(-\mathbf{V})$ is related to the vector $\mathbf{V}$ by a reversal of direction. You may verify that these addition rules obey all the four axioms (i)–(iv).

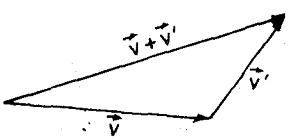

Fig. 1.1. The rule for vector addition. Note that it obeys axioms (i)–(iii).

We next define scalar multiplication. The vector $\alpha\mathbf{V}$ is defined to be the vector $\mathbf{V}$ stretched by a factor α. This definition can be seen to meet the requirements (v)–(vii). Since α is necessarily real (for our definition "stretched by α" to make sense), we have here a real vector space. □

*Exercise 1.1.1.** Consider the set of all entities of the form (a, b, c), where a, b, c are real numbers. These form a vector space with addition and scalar multiplication defined as follows:

$$(a, b, c) + (d, e, f) = (a + d, b + e, c + f)$$
$$\alpha(a, b, c) = (\alpha a, \alpha b, \alpha c)$$

Write down the null vector and the inverse of (a, b, c). Verify that axioms (i)–(iv) are met. Do we have a vector space if a, b, c are required to be positive numbers? Show that vectors of the form $(a, b, 1)$ do not form a linear vector space.

Exercise 1.1.2. By using the axioms prove the following:

(1) $0\mathbf{V} = \mathbf{0}$ (Hint: add $0\mathbf{V}$ to $\alpha\mathbf{V}$)

(2) $\alpha\mathbf{0} = \mathbf{0}$ (Hint: add $\alpha\mathbf{0}$ to $\alpha\mathbf{V}$)

(3) $(-1)\mathbf{V} = (-\mathbf{V})$ [Hint: add $\mathbf{V}$ to $(-1)\mathbf{V}$]

Definition 3. A set of vectors $\{\mathbf{V}_1, \mathbf{V}_2, \ldots, \mathbf{V}_n\}$ is said to be *linearly independent* (*LI*) if there exists no linear relation among them of the form

$$\sum_i^n \alpha_i \mathbf{V}_i = \mathbf{0} \tag{1.1.1}$$

except the trivial one with all $\alpha_i \equiv 0$.

This equation says that no member of the LI set can be written as a linear combination of the others. In contrast, a linearly dependent set admits a relation of the form Eq. (1.1.1) with not all $\alpha_i = 0$. In this case we can express at least one vector as a linear combination of the others. For instance if $\alpha_3 \neq 0$, we can divide by α_3 and rearrange Eq. (1.1.1) to get

$$\mathbf{V}_3 = \sum_{\substack{i=1\\ \neq 3}}^n \alpha_i' \mathbf{V}_i; \; \alpha_i' = \frac{-\alpha_i}{\alpha_3}$$

Definition 4. A vector space is *n dimensional* if it admits at most n vectors that are LI.

We shall denote an n-dimensional space defined over a field F by $V^n(F)$. Thus $V^n(R)$ [$V^n(C)$] is an n-dimensional real (complex) vector space. The dimensionality or field will be omitted wherever irrelevant.