Quantum Mechanics

HENDRIK F. HAMEKA
University of Pennsylvania

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS New York · Chichester · Brisbane · Toronto

To Charlotte

Library of Congress Cataloging in Publication Data:

Hameka, Hendrik F.
Quantum mechanics.

"A Wiley-Interscience publication."
"Based in part on an earlier book, Introduction to quantum theory, which was published in 1967"--Pref.
Includes bibliographies and index.
1. Quantum theory. I. Title.

QC174.12.H35 530.1'2 81-3430
ISBN 0-471-09223-1 AACR2

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Preface

The present book is based in part on an earlier book, *Introduction to Quantum Theory*, which was published in 1967. At that time I intended that the book be used as a text for junior or senior undergraduates in physics and for senior undergraduates and first-year graduate students in chemistry. In the preface I outlined my approach to the teaching of quantum mechanics and the goals that I hoped to achieve in a one-semester course on the subject. Since then the book has been used for 12 years, and I have modified some of my original ideas, either because of my own observations or due to suggestions made by colleagues. In order to describe the present book I quote the relevant parts of the preface to the old book and then discuss the changes in my philosophy and in the new book.

"The approach is semihistorical. First, it is shown how classical mechanics became inadequate for the explanation of certain experimental findings. This is followed by a discussion of the wave nature of free particles from which the Schrödinger equation is more or less derived. In the historical discussion I felt free to omit certain developments that had no pedagogic value, although they might be important from a historical point of view. I tried to keep the discussion closely linked to physical ideas. Whenever there was a conflict between physical understanding and mathematical rigor, I always decided in favor of the former.

"An important consideration in teaching quantum theory at the elementary level is the inadequate mathematical background of the students. In order to understand quantum theory and to apply it, the student must have some knowledge of many branches of mathematics: differential and integral calculus, Fourier analysis, differential equations, vector analysis, complex numbers, matrices and determinants, linear equations and eigenvalue problems, and the theory of special functions. I expect students to be acquainted with elementary differential and integral calculus, but the other mathematical topics listed above are discussed here. Naturally the teacher is free to omit any of them from his discussion if he feels the students are already familiar with them.

"I hope the present work can be used for a variety of courses, particularly junior and senior physics courses and senior and first-year graduate chemistry courses. Its length and contents make it suitable for a one-semester course

designed as a formal introduction to quantum mechanics. It is also suitable for the first half of a two-semester course in quantum chemistry. In this case, it needs to be supplemented by another text for the second semester."

Today, students in physical chemistry need to know more about quantum mechanics than they did in the past. Specifically, time-dependent quantum mechanics and the interaction between radiation and matter are essential for the understanding of newly developed areas in spectroscopy and kinetics. I added these topics to the new book. I also rounded off the chapter on atomic structure. Consequently the new book is about 25% larger than the old book, and it is not possible to cover all its material in one semester. The new version is suitable for a two-semester course rather than a one-semester course in quantum mechanics.

I found that most students appreciate the detailed mathematical derivations in the book. The better qualified students should be familiar with the more elementary derivations, but they still like to be able to review them. Some of the readers criticized the organization of the material; they felt that the relevance of some mathematical discussions to the quantum theory was not immediately clear because they were separated into different chapters. I felt that this criticism was justified, and I rearranged the material so that each mathematical derivation was immediately followed by its quantum mechanical application. I left the chapter on matrices as a separate entity. Usually I do not discuss the matrix algebra while teaching the course, but most students like to have the material available for review purposes.

I revised and expanded the problem sets at the end of each chapter; most of the new problems are taken from exams that I gave. I also added a list of recommended books at the end of each chapter. Naturally these lists are far from complete; they are mostly books that I found useful myself and the selection reflects my personal taste.

Finally, I wish to thank Dr. O. Zamani-Khamiri for her help in correcting the manuscript.

HENDRIK F. HAMEKA

Philadelphia, Pennsylvania
May 1981

Contents

CHAPTER ONE

Preliminaries

1-1 Introduction

A beginning student usually has more difficulty in learning quantum mechanics than classical mechanics, although the complexities of the two theoretical approaches are not widely different. Certain simple systems can be treated exactly in either quantum mechanics or classical mechanics; examples are one-dimensional motion, a particle in a central force field, or some two-particle systems. More complex systems cannot be treated exactly in either classical or quantum mechanics. They may at best be described by means of approximate mathematical methods, which are just as complicated and laborious in classical as in quantum mechanics.

The difficulty in learning quantum mechanics is caused mostly by the fact that everyone is much more familiar with the concepts and everyday applications of classical mechanics than with those of quantum mechanics. For example, in driving a car we must be able to predict the positions of the other cars on the road at future times and we adjust the future positions of our car accordingly by using the steering wheel, the gas pedal, and the brake. All this involves applications of the laws of classical mechanics.

Another example of applied classical mechanics is a baseball game. Every aspect of a baseball game is related to classical mechanics because it involves predictions about the orbit of the ball. A major league baseball player must have an intuitive understanding of classical mechanics because he can judge and anticipate the flight of the ball much quicker and much more effectively than any theoretician can calculate it.

As we go through life, we use the results and the concepts of classical mechanics all the time; we use them when we walk, when we drive a car, when we play, and even when we eat.

The fundamental laws of classical mechanics were first proposed by Newton during the seventeenth century. These same laws were transformed into more sophisticated mathematical form during the eighteenth and nineteenth centuries by Lagrange and Hamilton. They were supplemented by Maxwell during the late nineteenth century in order to describe the behavior of electrically charged particles.

It is not surprising that, when the structure of the atom was first discovered, scientists expected the particles within the atom to obey the same laws of classical mechanics as did all other systems that they had been able to observe. In particular, Lorentz published extensive calculations on the behavior of the electrons within the atom, using a combination of classical mechanics and the Maxwell equations. This work had a certain degree of success; for instance, Lorentz explained the Zeeman effect in this way. However, as more experimental information on atomic structure became available, it showed conclusively that classical mechanics was not valid within the atom. In order to explain all these new experimental observations in a logical and consistent manner, it became necessary to derive a new mechanics.

Since the evidence of experiments and the authority of leading scientists support the necessity of using quantum mechanics for the description of atomic motion, the beginning student has no choice but to accept this situation. Yet emotionally he has difficulty in believing that a baseball game and a hydrogen molecule are governed by different laws of motion, and he clings to the classical concept of electrons orbiting around the nuclei as long as he can. Therefore, before discussing quantum mechanics, we think it is useful to discuss briefly the arguments and experiments that led to the abandonment of classical mechanics for atomic motion. This means that we will use the historical approach in teaching quantum mechanics.

We feel that the historical approach constitutes the best method for teaching quantum mechanics because it provides a smooth transition from the old classical mechanics that we are familiar with to the new quantum mechanics that we wish to learn. We will only discuss those theoretical advances that were important in the development of quantum mechanics because our purpose is to teach the subject and not to give its complete history. Even so, we will mention some old theories that are now obsolete but that were important at the time as long as these theories have pedagogical value.

In these early chapters we also review some of the main features of classical mechanics so that we will be able to recognize where it differs and where it agrees with quantum mechanics.

Throughout the book we explain the various topics in mathematics that are necessary for expressing the physical concepts in classical and quantum mechanics. For example, in Sections 2 and 5 of this chapter we describe some aspects of vector analysis; in Chapter 3 we discuss Fourier analysis; in Chapter 5 we give a brief review of the theory of differential equations, and so on. We feel that this mixing of mathematics and physics makes the book more readable than the other alternative of segregating all mathematics into separate chapters.

1-2 Classical Mechanics

The basic equation of classical Newtonian mechanics for a particle in three-dimensional space is most conveniently expressed in terms of vectors. We

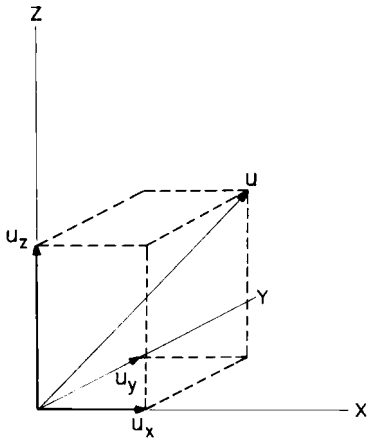

Fig. 1-1 Graphic representation of a vector **u** and its three components u_x, u_y, and u_z.

briefly discuss a few vector properties in this section; some additional vector properties are discussed in Section 5 of this chapter.

A vector **u** can be defined as a directed line segment. It is determined by its three components u_x, u_y, and u_z along the x, y, and z axes (see Fig. 1-1). Therefore, the boldface vector symbol **u** actually represents three quantities, which can be denoted by $\mathbf{u}=(u_x, u_y, u_z)$. The direction of **u** is determined by the three direction cosines, and its magnitude, which is the length of the line segment and which is denoted by $|\mathbf{u}|$ or u, is given by

$$u=\left(u_x^2+u_y^2+u_z^2\right)^{1/2} \tag{1-1}$$

The sum **w** of two vectors **u** and **v**,

$$\mathbf{w}=\mathbf{u}+\mathbf{v} \tag{1-2}$$

is defined such that each component of **w** is the sum of the two corresponding components of **u** and **v**,

$$\begin{aligned} w_x &= u_x + v_x \\ w_y &= u_y + v_y \\ w_z &= u_z + v_z \end{aligned} \tag{1-3}$$

When a vector **u** is a function of a parameter t, that is, each component of **u** is a function of t, we can define the derivative of **u** with respect to t:

$$\frac{d\mathbf{u}(t)}{dt}=\lim_{\Delta t\to 0}\frac{\mathbf{u}(t+\Delta t)-\mathbf{u}(t)}{\Delta t} \tag{1-4}$$

This definition is again equivalent to the three equations:

$$\left(\frac{d\mathbf{u}}{dt}\right)_x=\lim_{\Delta t\to 0}\frac{u_x(t+\Delta t)-u_x(t)}{\Delta t} \quad \text{and so on} \tag{1-5}$$

In classical mechanics we can represent the position of a point particle in three-dimensional space by means of a vector. In Fig. 1-1 we show how the position of the point P is determined by the vector $\mathbf{r}$, which is identical with the line segment OP. The Cartesian coordinates (x, y, z) of the point P are the three components of the vector $\mathbf{r}$. The motion of the point P is described by its orbit, which is the time dependence $\mathbf{r}(t)$ of its position vector $\mathbf{r}$.

The velocity $\mathbf{v}(t)$ of the particle is defined as

$$\mathbf{v}(t)=\frac{d\mathbf{r}}{dt} \tag{1-6}$$

and the acceleration $\mathbf{a}(t)$ of the particle is defined as

$$\mathbf{a}(t)=\frac{d\mathbf{v}(t)}{dt}=\frac{d^2\mathbf{r}(t)}{dt^2} \tag{1-7}$$

The fundamental equation of Newtonian mechanics is

$$\mathbf{F}=m\mathbf{a} \tag{1-8}$$

In other words, if a particle (or a body) is subject to a force $\mathbf{F}$, it will experience an acceleration $\mathbf{a}$ that is proportional to $\mathbf{F}$. The proportionality constant m is defined as the mass of the particle. Clearly, the particle will have zero acceleration $\mathbf{a}=\mathbf{0}$ if it is not subjected to any exterior forces. In that case it will move through space with a constant velocity $\mathbf{v}$.

We may rewrite Eq. (1-8) in a different form by introducing the momentum $\mathbf{p}$ of the particle, which is defined as

$$\mathbf{p}=m\mathbf{v} \tag{1-9}$$

It is easily seen that

$$\mathbf{F}=\frac{d\mathbf{p}}{dt} \tag{1-10}$$

The equations of motion (1-8) and (1-10) may be solved for simple systems, such as one-dimensional motion, a particle in a central force field, and so on. For more complex systems it is useful to make use of a more general mathematical formulation of the laws of motion. This formulation can be derived from Hamilton's principle or the principle of least action, and it leads to a set of differential equations that are known as the Lagrangian equations of motion or the Hamiltonian equations of motion. The latter are quite important in the formulation of quantum mechanics and we feel that it is helpful to discuss them here. However, we do not present the rigorous derivation of Hamilton's equations from the principle of least action; instead we just illustrate their validity for a simple one-particle system.

We consider a system of one particle with mass m moving in a conservative force field. Such a force field is defined by the condition that the three components F_x, F_y, and F_z of the force acting on the particle can all be represented as the derivatives of a single function $V(x, y, z)$ of the position coordinates x, y, and z.

$$F_x = -\frac{\partial}{\partial x} V(x, y, z)$$

$$F_y = -\frac{\partial}{\partial y} V(x, y, z)$$

$$F_z = -\frac{\partial}{\partial z} V(x, y, z) \tag{1-11}$$

Equations (1-11) can be combined into a vector equation,

$$\mathbf{F} = -\nabla V(x, y, z) \tag{1-12}$$

where the three components $(\partial/\partial x)$, $(\partial/\partial y)$, and $(\partial/\partial z)$ are symbolically represented by the vector symbol ∇. Each component of $\mathbf{F}$ is a function of the position coordinates x, y, and z. We write $\mathbf{F}$, therefore, as $\mathbf{F}(x, y, z)$ and we call it a vector field. The quantity ∇V is called the gradient of the function V and we can write Eq. (1-12) also as

$$\mathbf{F}(x, y, z) = -\text{grad } V(x, y, z) \tag{1-13}$$

A vector field that can be expressed as the gradient of a function of position is called an irrotational field; it should be noted that not all vector fields are irrotational.

We will now reformulate the equations of motion (1-10) into the Hamiltonian form. By substituting the set of equations (1-12) we find

$$\frac{dp_x}{dt} = -\frac{\partial V}{\partial x} \qquad \frac{dp_y}{dt} = -\frac{\partial V}{\partial y} \qquad \frac{dp_z}{dt} = -\frac{\partial V}{\partial z} \tag{1-14}$$

We define the kinetic energy T of the particle either in terms of the velocity v or in terms of the momentum p as

$$T = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \tag{1-15}$$

Obviously,

$$\frac{dx}{dt} = v_x = \frac{p_x}{m} = \frac{\partial T}{\partial p_x} \tag{1-16}$$

and we have the three equations,

$$\frac{dx}{dt}=\frac{\partial T}{\partial p_x} \qquad \frac{dy}{dt}=\frac{\partial T}{\partial p_y} \qquad \frac{dz}{dt}=\frac{\partial T}{\partial p_z} \tag{1-17}$$

We next introduce the function

$$H(x, y, z; p_x, p_y, p_z)=T(p_x, p_y, p_z)+V(x, y, z) \tag{1-18}$$

which is called the Hamiltonian function and which is the energy of the particle written as a function of the three position coordinates x, y, and z and of the momentum components p_x, p_y, and p_z. Since T does not depend on x, y, and z, we have

$$\frac{\partial H}{\partial x}=\frac{\partial V}{\partial x} \qquad \frac{\partial H}{\partial y}=\frac{\partial V}{\partial y} \qquad \frac{\partial H}{\partial z}=\frac{\partial V}{\partial z} \tag{1-19}$$

and since V does not depend on $\mathbf{p}$, we have

$$\frac{\partial H}{\partial p_x}=\frac{\partial T}{\partial p_x} \qquad \frac{\partial H}{\partial p_y}=\frac{\partial T}{\partial p_y} \qquad \frac{\partial H}{\partial p_z}=\frac{\partial T}{\partial p_z} \tag{1-20}$$

Hence Eqs. (1-14) and (1-17) can be reformulated as

$$\frac{dx}{dt}=\frac{\partial H}{\partial p_x} \qquad \frac{dy}{dt}=\frac{\partial H}{\partial p_y} \qquad \frac{dz}{dt}=\frac{\partial H}{\partial p_z}$$

$$\frac{dp_x}{dt}=-\frac{\partial H}{\partial x} \qquad \frac{dp_y}{dt}=-\frac{\partial H}{\partial y} \qquad \frac{dp_z}{dt}=-\frac{\partial H}{\partial z} \tag{1-21}$$

In this way the motion of the particle can be derived mathematically from a single function, the Hamiltonian function H. We note that in Eq. (1-21) the coordinates and momenta have been "paired off": the first pair is p_x and x, the second is p_y and y, and the third is p_z and z. We say that the momentum p_x is conjugate to the coordinate x, and so on.

Equations (1-21) are called Hamilton's equations of motion. We use them to show that the Hamiltonian function H is time independent. We have

$$\frac{dH}{dt}=\left(\frac{\partial H}{\partial x}\frac{dx}{dt}+\frac{\partial H}{\partial p_x}\frac{dp_x}{\partial t}\right)+\left(\frac{\partial H}{\partial y}\frac{dy}{dt}+\frac{\partial H}{\partial p_y}\frac{dp_y}{dt}\right)+\left(\frac{\partial H}{\partial z}\frac{dz}{dt}+\frac{\partial H}{\partial p_z}\frac{dp_z}{dt}\right)=0 \tag{1-22}$$

The Hamiltonian function H represents the energy E of the system; since the Hamiltonian function is time independent, the energy of the system remains a constant in time. We call the energy a constant of the motion.

We mentioned already that Hamilton's equations of motion are generally valid; they are valid in different coordinate systems, they are valid for describing N-particle systems, and so forth. For example, they can be used to describe the vibrational motion in polyatomic molecules such as methane, benzene, and so on. We will describe these generalized Hamilton's equations of motion, but we do not derive them.

First, we consider again a particle in three-dimensional space, but now we assume that its position is described by three generalized coordinates (q_1, q_2, q_3) that are determined in a certain way by the Cartesian coordinates (x, y, z). In other words, the coordinates q_i are functions of x, y, and z:

$$\begin{aligned} q_1 &= q_1(x, y, z) \\ q_2 &= q_2(x, y, z) \\ q_3 &= q_3(x, y, z) \end{aligned} \tag{1-23}$$

For example, we may wish to use polar, elliptical, or cylindrical coordinates, instead of the Cartesian coordinates. The transformation of Eq. (1-23) also leads to a new set of momenta (p_1, p_2, p_3) and to a new Hamiltonian:

$$H = H(q_1, q_2, q_3; p_1, p_2, p_3) \tag{1-24}$$

The Hamiltonian equations are now given by

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \qquad (i = 1,2,3) \tag{1-25}$$

We see that the momenta p_i and the coordinate q_i are coupled; we say that p_1 is conjugate to q_1, p_2 is conjugate to q_2, and so on.

The above description is also applicable to systems that are determined by N coordinates $(q_1, q_2, q_3, \ldots, q_N)$ with N either smaller or larger than 3. An example of such a system is the vibrational motion of a polyatomic molecule. Again we introduce a set of momenta $(p_1, p_2, p_3, \ldots, p_N)$, so that p_1 is conjugate to q_1, p_2 is conjugate to q_2, and so forth, and a Hamiltonian function

$$H = H(q_1, q_2, q_3, \ldots, q_N; p_1, p_2, \ldots, p_N) \tag{1-26}$$

The Hamiltonian equations of motion are now given by

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \qquad (i = 1,2,3,\ldots,N) \tag{1-27}$$

If we can solve the Hamiltonian equations, we obtain the solution as a set of expression $q_i(t)$ and $p_i(t)$ as functions of time. However, each of the Eqs. (1-27) contributes an arbitrary integration constant, so that the solution for an N-coordinate system contains $2N$ undetermined parameters. This result agrees