

QUANTUM
MECHANICS



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QUANTUM MECHANICS

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Editors' Preface to the Manchester Physics Series

The first book in the Manchester Physics Series was published in 1970, and other titles have been added since, with total sales world-wide of more than a quarter of a million copies in English language editions and in translation. We have been extremely encouraged by the response of readers, both colleagues and students. The books have been reprinted many times, and some of our titles have been rewritten as new editions in order to take into account feedback received from readers and to reflect the changing style and needs of undergraduate courses.

The Manchester Physics Series is a series of textbooks at undergraduate level. It grew out of our experience at Manchester University Physics Department, widely shared elsewhere, that many textbooks contain much more material than can be accommodated in a typical undergraduate course and that this material is only rarely so arranged as to allow the definition of a shorter self-contained course. In planning these books, we have had two objectives. One was to produce short books: so that lecturers should find them attractive for undergraduate courses; so that students should not be frightened off by their encyclopaedic size or their price. To achieve this, we have been very selective in the choice of topics, with the emphasis on the basic physics together with some instructive, stimulating and useful applications. Our second aim was to produce books which allow courses of different length and difficulty to be

selected, with emphasis on different applications. To achieve such flexibility we have encouraged authors to use flow diagrams showing the logical connections between different chapters and to put some topics in starred sections. These cover more advanced and alternative material which is not required for the understanding of later parts of each volume. Although these books were conceived as a series, each of them is self-contained and can be used independently of the others. Several of them are suitable for wider use in other sciences. Each author's preface gives details about the level, prerequisites, etc., of his volume.

We are extremely grateful to the many students and colleagues, at Manchester and elsewhere, whose helpful criticisms and stimulating comments have led to many improvements. Our particular thanks go to the authors for all the work they have done, for the many new ideas they have contributed, and for discussing patiently, and often accepting, our many suggestions and requests. We would also like to thank the publishers, John Wiley & Sons, who have been most helpful.

January, 1987

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Author's Preface

In writing an undergraduate textbook on quantum mechanics, it is necessary to select severely from this huge subject. Over the years, I have lectured on quantum mechanics at all levels, from introductory undergraduate to advanced postgraduate. Perhaps surprisingly, many of these courses shared a common approach. It is this approach I am presenting here. I am concentrating on general principles and methods. My aim is to display the structure of quantum mechanics clearly. Students who have worked through this book should be able to follow quantum-mechanical arguments in books and (not too advanced) papers, and to cope with simple cases themselves. For this purpose, I employ ideas and methods of wide applicability without taking them to their full generality. For example, symmetry arguments are more prominent and angular momentum is treated from a more general viewpoint than is usual at this level.

The title of this book, Quantum Mechanics rather than Quantum Physics, reflects its emphasis on principles and methods rather than applications. Of course, applications are essential for readers to test their understanding of the formalism and to bring it to life. I have chosen applications from atomic physics. This is an important branch of physics since it underlies molecular and solid state physics. Many of its ideas can, with some modifications, be taken over to other fields such as nuclear or particle physics. It also has the virtue of simplicity: we know the forces which act inside atoms. Although not primarily a book on atomic physics, the applications cover many of the important topics of atomic physics.

No knowledge of quantum mechanics is assumed in this book but the depth of treatment presupposes a certain maturity. It would help most readers to have met some elementary wave mechanics before, making it suitable for third-year UK undergraduate physics courses though good second-year students should find much of it useful and stimulating. In the US, it may be used at senior undergraduate or first-year graduate level. It should also be of interest to experimental research workers who require a good grasp of quantum mechanics without the full formalism needed by the professional theorist. Many good books cater for the latter but very few fill the gap between elementary and advanced accounts. I take as my starting point wave functions instead of the abstract and more general Dirac state vectors, as more appropriate to the introductory level of this book. The elegance and formal simplicity of the Dirac formalism easily create an illusion of understanding. Dirac state vectors are not introduced until Chapter 5 and never used in their full generality, although an account of the Dirac formalism is given in Chapter 12 which can be studied with benefit any time after Chapter 3.

Two features facilitate the use of this book for courses of different length and difficulty. Firstly, a flow diagram (on the inside of the front cover) shows the logical connections of the chapters which make it possible to study chapters in different order and to omit some topics altogether. Secondly, about a quarter of the text forms 'starred' sections, and some material, insufficient to justify a separate section, is printed on tinted background. Material distinguished in either of these ways is not required for the understanding of material later in the book. Typically, I have covered the material in Chapters 1 to 11, including about half the starred sections, in 40 lectures of 50 minutes each.

The problems at the end of each chapter form an important part of the book. Their purpose is to enable readers to test their understanding and to introduce some interesting physics which is enlarged on in the solutions at the end of the book.

I would like to thank the many students and colleagues who, over the years, have influenced my understanding and teaching of quantum mechanics, and in particular Tony Phillips and David Sandiford who read the whole manuscript and suggested many improvements, some of a major kind. I am grateful to Sandy Donnachie for encouraging me to write this book. My special thanks go to my wife Betty for producing the computer-generated graphs and for much other help with the preparation of this book. Without her support, it would never have seen the light of day.

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1

CHAPTER

Basic concepts

As the reader is no doubt aware, classical physics fails to describe the behaviour of atoms and sub-atomic systems. Treating an atom like a solar system scaled down to atomic dimensions and applying classical physics to it in no way predicts the observed phenomena. This should not be surprising. The laws of classical physics were obtained from the study of macroscopic systems, and we have no right to expect these laws to hold for systems many orders of magnitude smaller. Indeed, many of the observed properties of atoms are startlingly at variance with the predictions of classical physics and are intuitively wholly incomprehensible.

Examples of such perplexing behaviour are:

- (i) *Energy quantization* Atoms possess *discrete* energy levels, i.e. the observed values of the energy of an atom do not form a *continuum*, as expected from classical physics. These discrete energy levels show up when atoms make transitions between discrete atomic states with well-separated energies, for example in the Franck-Hertz experiment or in the optical line spectra of atoms.
- (ii) *Angular momentum quantization* In the Stern-Gerlach experiment a beam of atoms, each possessing a permanent magnetic moment, traverses an inhomogeneous magnetic field. Classically, one would expect the atoms to be deflected into a fan-like *continuum* of directions. In fact, they are deflected into a *discrete* number of different directions only. The explanation of this phenomenon, as we shall see, is that the component of the atom's angular momentum

in the direction of the magnetic field is quantized, i.e. it can only assume certain discrete values.

(iii) *Barrier penetration* In the alpha particle decay of heavy nuclei, the alpha particles tunnel through a potential barrier. According to classical mechanics, the alpha particle could not escape from the nucleus as it does not have enough kinetic energy to surmount the barrier. In penetrating the barrier, it passes through a region in which its classical kinetic energy is negative!

From the point of view of classical physics and from our experience with everyday objects, these phenomena appear crazy, i.e. quite unintelligible. In contrast, quantum mechanics is outstandingly successful in providing detailed descriptions of them, in quantitative agreement with experiments. Moreover, quantum mechanics gives correct descriptions (i.e. in agreement with observations) of the properties of atoms, molecules and nuclei, provided relativistic effects are allowed for.

The difficulties of learning and understanding quantum mechanics are largely conceptual. We have no direct experience of atoms and molecules, and we must not visualize them as tiny scaled-down versions of classical macroscopic objects. To argue by analogy in this way is usually totally misleading. These conceptual difficulties lead one to start a systematic account of quantum mechanics with a more abstract mathematical formulation.

In this chapter, I shall develop some of the basic mathematical formalism of quantum mechanics. In Chapter 2 this formalism will at once be applied to some very simple situations to get a feeling for how it all works: to see how the formalism is handled and to illustrate its physical interpretation. In particular, I shall be able, already at this early stage, to give the quantum-mechanical explanations of the three startling unclassical phenomena discussed above. These examples will take us a long way towards a quantum-mechanical way of thinking. One builds up a sort of intuitive picture of what the mathematics means.

The first two chapters are seen to be complementary. The first develops the mathematical formalism, the second shows how it is used and what it means. A reader who has difficulties mastering Chapter 1 on first studying it should proceed to Chapter 2 and then have another go at the first chapter. In order to facilitate the study of Chapter 1, I shall start by considering the very simplest system: a particle of mass m and no internal structure, i.e. a so-called point-particle. Later I shall extend these ideas to many-particle systems and particles with spin.

1.1 THE STATE OF A SYSTEM

In quantum mechanics, the state of a system is specified by a wave function ψ . For a system consisting of a single point particle, ψ is a complex function of the position coordinate \mathbf{r} of the particle and the time t : $\psi = \psi(\mathbf{r}, t)$ specifies the

state of the system at time t . The temporal development of the wave function is given by the equation of motion for the system. For non-relativistic quantum mechanics this is the Schrödinger equation (discussed in section 1.3) which is the quantum-mechanical analogue of Newton's equations in classical mechanics.

It is a fundamental assumption of quantum mechanics that *all* information about a system at a given instant of time t can be derived from the wave function ψ . In the next section we shall see how the physical properties of a system in the state ψ are determined. Here I only wish to remind the reader that for a particle in the state $\psi(\mathbf{r}, t)$

$$P(\mathbf{r}, t) d^3\mathbf{r} = |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r} \quad (1.1)$$

gives the probability that at time t the particle is in a volume element $d^3\mathbf{r}$ at the point \mathbf{r} . The definition of probability at once implies the following normalization condition for ψ :

$$\int |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r} = 1. \quad (1.2)$$

The integration in Eq. (1.2) will be over all space in general. If the particle is confined to a certain region of space (for example, within a box of volume V) then the range of integration in Eq. (1.2) is restricted to this region. Unless otherwise indicated, integrals will always be over all regions of space accessible to the particle, i.e. over the whole configuration space of the system. A wave function satisfying the condition (1.2) is said to be normalized or normed. Later we shall relax the condition (1.2); we shall wish to consider wave functions which cannot be normed in this way. For example, for the plane wave

$$\psi(\mathbf{r}, t) = \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$$

the normalization integral (1.2), taken over all space, diverges. For the present we shall only consider states ψ which can be normed according to Eq. (1.2).

Eq. (1.1) illustrates two basic features of quantum mechanics.

First, according to Eq. (1.1) the position of a particle (at a given time t) is not uniquely determined but only given by a probability distribution even when the particle is in a definite state, i.e. in a state fully specified according to quantum mechanics. This is in contrast to classical mechanics where the properties of a system in a definite state are uniquely determined and probabilities only occur for incompletely specified systems; for example, in statistical mechanics the state of a system is specified by macroscopic average quantities like temperature and density.

Secondly, Eq. (1.1) relates the probability density $P(\mathbf{r}, t)$ which is an observable quantity to the wave function of the system, $\psi(\mathbf{r}, t)$, which is not observable. Nevertheless, wave functions play a central role in quantum mechanics. In

particular, they satisfy the *linear superposition principle*: if $\psi_1 \equiv \psi_1(\mathbf{r}, t)$ and $\psi_2 \equiv \psi_2(\mathbf{r}, t)$ are two possible states of a system, so is

$$\psi = c_1\psi_1 + c_2\psi_2 \quad (1.3)$$

where c_1 and c_2 are complex numbers. For the state (1.3), Eq. (1.1) leads to the probability density

$$P(\mathbf{r}, t) = |\psi|^2 = |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + 2\Re\{c_1^*c_2\psi_1^*\psi_2\}, \quad (1.4)$$

i.e. probabilities are not additive: Eq. (1.4) contains an interference term which stems from the fact that the relation (1.1) between probabilities and wave functions is a quadratic one. This feature is typical of quantum mechanics: observable quantities depend quadratically on the unobservable wave functions, leading to interference effects. Such effects do not occur in classical mechanics. They are, of course, characteristic of all wave motion. For example, light intensities are not additive whereas light amplitudes are. Analogously, one refers to wave functions as probability amplitudes.

From the superposition of amplitudes it follows that the relative phases of different parts of an amplitude [e.g. of ψ_1 and ψ_2 in Eq. (1.3)] are all-important: they affect critically the interference pattern. On the other hand, multiplying all wave functions by the same phase factor $e^{i\alpha}$ (where α is a real number) produces no observable effects.

For electromagnetic waves there are no interference effects if waves without well-defined phase relationships between them are superposed. For example, in a Young double-slit experiment an interference pattern occurs if both slits are illuminated with light from the same source. If this source is replaced by two incoherent light sources, each illuminating one slit only, the interference pattern disappears and the light intensities are additive. In quantum mechanics too, we distinguish these two cases: a system in a *pure state* specified by a wave function, and a system in a *mixed state*, i.e. a system in a mixture of pure states without well-defined phase relationships between them. Such a mixture cannot be specified by a single wave function. The properties of a mixed state follow from those of pure states, as will be illustrated later. We shall mainly be considering pure states and, as is usual, refer to them simply as states.

1.2 OBSERVABLES

In the last section I stated that all physical properties of a system can be derived from its wave function. We must now see how this is done.

Quantities such as the position, momentum or energy of a particle, which can be measured experimentally, are called observables. In classical physics, observables are represented by ordinary variables. In quantum mechanics, observables are represented by operators, i.e. by quantities which operate on a wave function giving a new wave function. If \hat{A} denotes an operator, \hat{A} will

transform a state $\psi(\mathbf{r}, t)$ into another state, called $\hat{A}\psi(\mathbf{r}, t)$.* We shall have explicit examples of operators in a moment. It is of course not possible to derive the operators which represent observables in any fundamental way from classical mechanics. However, a simple prescription exists which establishes the bridge between the classical quantities and the operators. The operators corresponding to the position coordinate \mathbf{r} and the momentum \mathbf{p} of a particle are, respectively, given by

$$\hat{\mathbf{r}} = \mathbf{r}, \quad \hat{\mathbf{p}} = -i\hbar\nabla. \quad (1.5)$$

Thus the operator $\hat{\mathbf{r}}$ is the operation of multiplying a wave function by \mathbf{r} :

$$\hat{\mathbf{r}}\psi(\mathbf{r}, t) = \mathbf{r}\psi(\mathbf{r}, t). \quad (1.6)$$

Similarly the operator $\hat{\mathbf{p}}$ is the operation of taking the gradient of a wave function and multiplying it by $-i\hbar$:

$$\hat{\mathbf{p}}\psi(\mathbf{r}, t) = -i\hbar\nabla\psi(\mathbf{r}, t). \quad (1.7)$$

More generally, the operator corresponding to a function of \mathbf{r} and \mathbf{p} , $F(\mathbf{r}, \mathbf{p})$, is given by

$$\hat{F} = F(\hat{\mathbf{r}}, \hat{\mathbf{p}}) = F(\mathbf{r}, -i\hbar\nabla). \quad (1.8)$$

For example, in classical mechanics the energy of a point particle of mass m , moving in a potential $V(\mathbf{r})$, is given by the Hamiltonian function

$$H(\mathbf{r}, \mathbf{p}) = \frac{1}{2m} \mathbf{p}^2 + V(\mathbf{r}),$$

leading to the energy operator

$$\hat{H} = H(\hat{\mathbf{r}}, \hat{\mathbf{p}}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}). \quad (1.9)$$

I shall take as the fundamental connection between the observable properties of a system and its state the following postulate:

For a system in the normed state $\psi(\mathbf{r}, t)$, the expectation value at time t of the observable A , represented by the operator \hat{A} , is given by

$$\langle \hat{A} \rangle = \int \psi^*(\mathbf{r}, t) \hat{A} \psi(\mathbf{r}, t) d^3\mathbf{r}. \quad (1.10)$$

This expression is the basis of all comparisons between the predictions of quantum mechanics and experiment. Another reason for taking it as the cornerstone of our discussion is that it leads to or suggests many important consequences. Before coming on to these, I want to make some comments on Eq. (1.10).

* Initially and if I want to stress that a quantity is an operator, I shall mark it by a circumflex accent: \hat{A} will denote the operator corresponding to the variable A . Later on, the accent will be omitted, unless doing so could lead to confusion.

Firstly, if for the observable A we take the position coordinate \mathbf{r} , Eq. (1.10) becomes

$$\langle \hat{r} \rangle = \int \mathbf{r} |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r}. \quad (1.11)$$

This result is in agreement with the probability distribution (1.1), which is very comforting.

Secondly, the order of the factors in the integrand of Eq. (1.10) must, in general, not be changed: they must be in the order shown. For example, for the momentum operator $\hat{p} = -i\hbar\nabla$ we have

$$\psi^*(-i\hbar\nabla)\psi \neq -i\hbar\nabla(\psi^*\psi) = -i\hbar[(\nabla\psi^*)\psi + \psi^*\nabla\psi].$$

This is a general feature of operators: they are usually non-commuting quantities: the order of factors matters.

Thirdly and most importantly, Eq. (1.10) is a statistical statement. It says nothing about the result of a single observation but only about the expectation value, i.e. the mean value, obtained from many repeated measurements. Before each of these measurements we must prepare the system to be in the state $\psi(\mathbf{r}, t)$. Averaging over the results of these measurements, we obtain a mean value. It is this mean value which is given by Eq. (1.10). In Chapter 3 we shall return to the problem of how to prepare a system to be in a definite state.

I now come on to consider some of the consequences of Eq. (1.10). In this section, we shall be concerned with the properties of the system at one instant of time only. For the present we can therefore forget about the time dependence of Eq. (1.10), treating ψ and \hat{A} as the state and the operator at the instant of time considered.

Observables such as momentum or energy are real quantities. Hence the expectation value (1.10) must be real for any state ψ :

$$\int \psi^* \hat{A} \psi d^3\mathbf{r} = \int \psi (\hat{A} \psi)^* d^3\mathbf{r} = \int (\hat{A} \psi)^* \psi d^3\mathbf{r}. \quad (1.12)$$

An operator which satisfies condition (1.12) for all states ψ is called *Hermitian* or *self-adjoint*. We conclude that observables must be represented by Hermitian operators.

The condition (1.12) for \hat{A} to be Hermitian is equivalent to the condition that for any two states ψ_1 and ψ_2

$$\int \psi_1^* \hat{A} \psi_2 d^3\mathbf{r} = \int (\hat{A} \psi_1)^* \psi_2 d^3\mathbf{r}. \quad (1.13)$$

To derive this condition, we consider the state

$$\psi = c_1 \psi_1 + c_2 \psi_2 \quad (1.14)$$