An Introduction to Quantum Theory

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The Postulates of Quantum Mechanics

In this chapter the basic concepts of quantum theory are formulated via a self-consistent set of six postulates. These six postulates deal with the following: operator images of physical observables; properties of state vectors and wave functions; the connection with experimental measurements; coordinate-space forms of those operators having classical analogs; the primary dynamical equation of quantum mechanics; and the completeness of the eigenvectors of observables. The postulates are the framework on which the edifice of quantum mechanics is constructed. A separate section is devoted to the statement of each postulate and to a few examples chosen to illustrate or apply it. A comprehensive set of applications is presented in Chapters 6 and 7, where various 1-D systems are used as the vehicles for illustrating the postulates. The basic theory of this chapter is extended and developed in Chapters 8 and 9. Since probability is a key interpretational concept, a brief introduction to this topic is given in an appendix.

We emphasize that our formulation of quantum theory (in this chapter and throughout this book) is restricted to the case of pure states. This is not a major restriction. It means that, when we consider ensembles of individual quantum systems (e.g., single particles, atoms, nuclei, etc.), all of the systems in the ensemble are assumed to be in the same quantum state, not necessarily an eigenstate of a quantal operator. Ensembles for which this assumption does not hold are described by a density operator or density matrix rather than by a pure state; treatments of such cases can be found in references cited later.

5.1. Observables

The first postulate deals with the mathematical imaging of observables by Hermitian operators.

POSTULATE I.

To every physical observable, e.g., position, energy, linear and angular momentum, intrinsic spin, there corresponds a Hermitian linear operator (also denoted an observable) acting on vectors in a separable Hilbert space $\mathcal{H}$. Let $\hat{A}$ be such an observable for some physical system. Its eigenvalues a_n and eigenvectors $|a_n\rangle$ play a special role: the only values of $\hat{A}$ which can be obtained in an ideal measurement are its eigenvalues $\{a_n\}$, while $|a_n\rangle$ is the quantum state of the system when the value of the observable has been measured to be a_n.

Table 5.1 *Physical observables and the mathematical symbols corresponding to their Hilbert-space operators*

Observable	Hilbert-space symbol
Energy	$\hat{H}$
Position	$\hat{Q}_x$ (in 1-D) or $\hat{\mathbf{Q}}$ (in 3-D)
Linear Momentum	$\hat{P}_x$ (in 1-D) or $\hat{\mathbf{P}}$ (in 3-D)
(Orbital) Angular Momentum	$\hat{\mathbf{L}} = \hat{\mathbf{Q}} \times \hat{\mathbf{P}}$
Intrinsic Spin	$\hat{\mathbf{S}}$
Kinetic Energy[a]	$\hat{K} = \hat{\mathbf{P}} \cdot \hat{\mathbf{P}}/(2m)$

[a] Kinetic energy is not an observable classically, but, because it is an operator in quantum mechanics, it is included in this list in order to display its connection to $\hat{\mathbf{P}}$.

This first postulate states that the possible values one can measure for an observable $\hat{A}$ are the eigenvalues of the equation

$$\hat{A}|a_n\rangle = a_n|a_n\rangle. \tag{5.1}$$

Furthermore, if a_n is the measured value of the observable, then $|a_n\rangle$ is the state of that system following the measurement which has yielded a_n. This statement is made under the assumption that only the quantum number a_n is needed to specify the state. We shall see in Chapter 9 how this part of Postulate I is modified when more than one quantum number is needed to specify the state.

Table 5.1 lists both the observables of classical mechanics that have quantal counterparts and the symbols of the Hilbert-space operators that are their mathematical images. Operators such as spin, for which there is no classical equivalent, will be introduced in later chapters. As noted previously, operators are represented by capital letters overlaid with a carat: ˆ; their eigenvalues are generally indicated by the same symbols in lower case, one exception being the energy, the operator for which is $\hat{H}$ whereas the eigenvalue is E, possibly enhanced by sub- or superscripts.

Examples of the operators that image observables and their corresponding eigenvalues and eigenvectors have been encountered in the preceding chapters. The 1-D position operator $\hat{Q}_x$ and its eigenvalue equation (4.47) were introduced in Chapter 4; this led directly to the Dirac delta function, the coordinate representation, and the concept of locality. In Chapter 3 the Hamiltonian operator $\hat{H}$ and the coordinate-space form of the time-independent Schrödinger equation $\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$ for the particle in a 1-D box were explored in detail. The box energy $E_n = n^2\hbar^2\pi^2/(2mL^2)$ and normalized eigenfunction $\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L^2)$ correspond, respectively, to a_n and to the coordinate-space form of $|a_n\rangle$ in Eq. (5.1).

Measurement (detection) implies that the system undergoes an interaction of some kind. Until the system is altered by a subsequent interaction (which may occur as part of a subsequent measurement), it remains in the state $|a_n\rangle$ when a_n is the measured value of the observable $\hat{A}$.

This forcing of the system into state $|a_n\rangle$ via measurement is, however, not always

possible. It will occur only if the detection (or production) apparatus is capable of sufficient discrimination that it selects just the eigenvalue a_n. For example, a_n will be selected if the *resolution* of the apparatus is finer (smaller) than the separation between a_n and $a_{n\pm1}$. Suppose that we have N systems for which $\hat{A}$ is to be measured. If the resolution is fine enough, then the value of $\hat{A}$ for every one of the N systems can be a_n, and in this case each system will be in state $|a_n\rangle$.

Let us next assume that the resolution of the apparatus remains fine enough to isolate each of the eigenvalues, but that the experiment measuring $\hat{A}$ allows each of the N systems to end up with any one of the three values a_{n-1}, a_n, and a_{n+1} in such a way that for each system the state $|\alpha\rangle$ is

$$|\alpha\rangle = \sum_{j=n-1}^{n+1} w_j |a_j\rangle. \tag{5.2}$$

In order for $|\alpha\rangle$ of (5.2) to be a pure state, *both the magnitude and the phase (or relative phase) of each w_j must be known.* An example of (5.2) is Eq. (3.94) with the values $a_2 = a_3 = \sqrt{\frac{1}{2}}$ that led to Eq. (3.99). We emphasize that, whenever a superposition like (5.2) is used to represent a pure state, each w_j is assumed to be known.

Finally, suppose that the apparatus cannot or is not set to discriminate between, say, a_n and $a_{n\pm1}$ (but can distinguish the other a_j from them). In this case, the relative populations of the three eigenvalues among the N systems might be known, but not the relative phase relations between the states $|a_n\rangle$ and $|a_{n\pm}\rangle$. Without knowledge of these phase relations, i.e., if $|w_j|$ but not $\arg w_j$ is known, then (5.2) cannot be used to describe each system. The ensemble is then in a *mixed* state and the appropriate tool for describing this situation is the density operator or density matrix. Discussions of mixed states can be found, e.g., in Baym (1976), Cohen-Tannoudji, Diu, and Laloë (1977), Gottfried (1966), and Sakurai (1994). In Section 6.1, as an application of the 1-D quantum-box eigenvalue problem, we discuss a specific instance wherein a *Gedanken* measurement leads to non-fully-determined w_j's, and we also indicate how full knowledge of the w_j's can be attained.

Many observables, of course, can be measured in such a way as to yield a unique a_n and $|a_n\rangle$. However, in the case of a *continuous* spectrum, a linear superposition analogous to (5.2) *always* occurs. The reason is simple. Let $\hat{B}$ be the observable and $\{b\}$ its continuous set of eigenvalues; the eigenvalue equation is

$$\hat{B}|b\rangle = b|b\rangle. \tag{5.3}$$

In order to measure a single – or "sharp" – value b, itself a point in a continuum, the apparatus must be capable of isolating a point, i.e., of distinguishing a value having no extent or "width." However, all detectors are of finite size and will therefore admit not a single point-value b but a range of them. Corresponding to this measured range of b values will be a linear superposition of the states $|b\rangle$. Suppose that the values of b lie in the closed interval $[b_1, b_2]$. Then in this case the pure quantum state $|\beta\rangle$ will be given by

$$|\beta\rangle = \int_{b_1}^{b_2} db\, w(b)|b\rangle, \tag{5.4}$$

where $w(b)$ is a known weight function.

Equation (5.4) may appear to be a trivial extension of (5.2). Its consequences, rather than being trivial, are of the utmost importance. The reason is that (5.4) converts *non-normalizable*, *continuum* states $|b\rangle$ into normalizable ones. That is, the relation $\langle b'|b\rangle = \delta(b - b')$ – illustrated by the example of the states $|x\rangle$ of the 1-D position operator $\hat{Q}_x$ discussed in Section 4.4, where delta-function normalization was introduced – means that $|b\rangle$ is not a Hilbert space vector: $|b\rangle \notin \mathcal{H}$. The effect of the linear superposition (5.4), on the other hand, will be to produce a *normalizable* state $|\beta\rangle$ as long as the following condition holds:

$$\int_{b_1}^{b_2} |w(b)|^2 \, db = \text{finite}. \tag{5.5}$$

Even when $b_2 = -b_1 = \infty$, the weight functions occurring in physics obey (5.5). The end result is that, via (5.4), $|\beta\rangle \in \mathcal{H}$, in contrast to $|b\rangle$. Thus, whereas a non-normalizable $|b\rangle$ cannot be a quantum state (even though b is a value of the observable $\hat{B}$), a linear superposition of the $|b\rangle$ can be such a state. Despite this, one often works directly with the non-normalizable or *improper* states $|b\rangle$, particularly in the case of collisions, as described in Chapters 7 and 15.

5.2. States, wave functions, and probabilities

The state of a quantum system is a vector in $\mathcal{H}$. As such, it is a highly abstract quantity. Its realization as a wave function makes it easier to work with, and its interpretation in terms of probabilities gives it meaning. These aspects are explored in the present section via application of the second postulate to a system consisting of a single particle. The extension to multi-particle systems is straightforward and is discussed later in this book.

Quantal probabilities are the absolute squares of various scalar products, themselves often referred to as *amplitudes*. Two of these scalar products are so important that they are given the special name of *wave functions*. Wave functions are the scalar product of a Hilbert-space state with the eigenstates of the position operator $\hat{\mathbf{Q}}$ or the momentum operator $\hat{\mathbf{P}}$ and, as such, define the position or momentum representation of the state, or, equivalently, the position (or coordinate) and momentum wave functions (recall Section 4.4). The relevant eigenstates and eigenvalues obey

$$\hat{\mathbf{Q}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle \tag{5.6}$$

and

$$\hat{\mathbf{P}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle, \tag{5.7}$$

where $\mathbf{r}(\mathbf{p})$ is the position (momentum) of the particle. Since $\mathbf{r}$ and $\mathbf{p}$ are continuous, $|\mathbf{r}\rangle$ and $|\mathbf{p}\rangle$ are each normalized to a delta function:

$$\langle \mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r}) \tag{5.8}$$

and

$$\langle \mathbf{p}'|\mathbf{p}\rangle = \delta(\mathbf{p}' - \mathbf{p}). \tag{5.9}$$

To obtain the wave functions, and to formulate Postulate II, we introduce the generic single-particle state, denoted $|\alpha\rangle$. It is a Hilbert-space state, which is *assumed to be*

normalized. The coordinate-space representative of $|\alpha\rangle$ is the scalar product $\langle \mathbf{r}|\alpha\rangle$, which we shall denote by the symbol $\psi_\alpha(\mathbf{r})$:

$$\psi_\alpha(\mathbf{r}) \equiv \langle \mathbf{r}|\alpha\rangle \tag{5.10}$$

is the coordinate-space wave function. Similarly, the momentum-space representative of $|\alpha\rangle$ is the scalar product $\langle \mathbf{p}|\alpha\rangle$, for which we use the special symbol $\varphi_\alpha(\mathbf{p})$:

$$\varphi_\alpha(\mathbf{p}) \equiv \langle \mathbf{p}|\alpha\rangle \tag{5.11}$$

is the momentum-space wave function.

These definitions deliberately avoid the usage $\alpha(\mathbf{r})$ and $\alpha(\mathbf{p})$ because the functions labeled by ψ_a and φ_α are different, while calculus tells us that $\alpha(\mathbf{r})$ and $\alpha(\mathbf{p})$ are the same functions of two different variables. That is, if $\mathbf{s}$ is an arbitrary vector variable,

$$\psi_\alpha(\mathbf{s}) \neq \varphi_\alpha(\mathbf{s}),$$

a result that should be no surprise since $\langle \mathbf{r}|$ and $\langle \mathbf{p}|$ are eigenstates of two different operators. The distinction is essential.

POSTULATE II.

The state of a quantum system is a (normalizable) vector in $\mathcal{H}$. It is labeled by the eigenvalues of all operators for which it is a simultaneous eigenstate, and it may be a linear combination of eigenvectors of quantal operators. Scalar products of a state with other vectors (suitably normalized), in $\mathcal{H}$ or not, yield quantal probability amplitudes, the absolute square of each being a probability or a probability density, as follows.

(a) For a quantum system consisting of a single particle, the position- or coordinate-space wave function $\psi_\alpha(\mathbf{r}) = \langle \mathbf{r}|\alpha\rangle$ is the *probability amplitude* that the particle will be at position $\mathbf{r}$. The *probability* $P_\alpha(\mathbf{r})$ for finding the particle between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ is

$$P_\alpha(\mathbf{r}) = |\langle \mathbf{r}|\alpha\rangle|^2 d^3r \equiv |\psi_\alpha(\mathbf{r})|^2 d^3r; \tag{5.12}$$

hence, $\rho_\alpha(\mathbf{r}) = |\psi_\alpha(\mathbf{r})|^2$ is a standard *probability density*.[1] Corresponding remarks hold for the momentum-space wave function $\varphi_\alpha(\mathbf{p})$. In the case of a particle in 1-D, say x, the analogous quantities are $\psi_\alpha(x) = \langle x|\alpha\rangle$, $P_\alpha(x) = |\psi_\alpha(x)|^2\, dx$, etc.

(b) If the system is in state $|\alpha\rangle$, then the probability amplitude $C_{\beta\alpha}$ for finding it in any other (normalized) quantal state $|\beta\rangle$ is

$$C_{\beta\alpha} = \langle \beta|\alpha\rangle; \tag{5.13}$$

the corresponding (discrete) probability $P_{\beta\alpha}$ is

$$P_{\beta\alpha} = |\langle \beta|\alpha\rangle|^2. \tag{5.14}$$

Neither $|\beta\rangle$ nor $|\alpha\rangle$ need be an eigenstate of a quantal operator.

[1] See Appendix A for a brief treatment of probability theory. The assumption that $|\alpha\rangle$ is normalized to unity, i.e., that $\langle \alpha|\alpha\rangle = 1$, means that the total probability is unity: $\int |\psi_\alpha|^2\, d^3r = 1$.

(c) In the event that a quantal system can evolve to a state $|\alpha,\ t\rangle$ at time t by more than one path, as, for example, in the case of the two-slit experiment with electrons, then, as long as one employs no device that can determine which path was actually followed, $|\alpha,\ t\rangle$ is a linear combination of states $|\alpha_j,\ t\rangle$, where j specifies the particular path:[2]

$$|\alpha,\ t\rangle = \sum_j w_j |\alpha_j,\ t\rangle; \tag{5.15}$$

the constant w_j is a known weight. The amplitude $C_{\beta\alpha}(t) = \langle\beta|\alpha,\ t\rangle$ now becomes a sum of amplitudes $C_{\beta\alpha_j}(t)$ and the probability $P_{\beta\alpha}(t)$ contains interference terms:

$$P_{\beta\alpha}(t) = |\langle\beta|\alpha,\ t\rangle|^2 = \left|\sum_j w_j \langle\beta|\alpha_j,\ t\rangle\right|^2$$

$$= \left|\sum_j w_j C_{\beta\alpha_j}(t)\right|^2. \tag{5.16}$$

On the other hand, the sum in (5.15) collapses to a single term[3] if a determination of the path k that is actually followed is made, in which case $w_j \to \delta_{jk}$.

This postulate is a statement of the probabilistic interpretation of quantum mechanics and each of its three portions has already been exemplified in Section 3.3 via the quantal-box eigenvalue problem. Postion-space probability densities $\rho_n(x)$ (Eq. (3.92)) have been plotted in Fig. 3.8. Parts (b) and (c) of Postulate II are illustrated for the box problem by the superposition wave function (3.94). For instance, corresponding to $C_{\beta\alpha}$ of (5.13) are either of the coefficients a_2 or a_3 in Eq. (3.94): the amplitudes are $a_j = (\Psi_j|\Psi)$, $j = 2$ or 3, and the probability that Ψ_j is present in Ψ is $|a_j|^2$. Furthermore, as noted in the paragraph below Eq. (3.97), $|a_j|^2$ is also the probability that an energy measurement will yield E_j. Finally, since Ψ of (3.94) is a superposition – a coordinate-space version of Eq. (5.15) – the interference noted in connection with (5.16) shows up in the probability density $\rho(x,\ t)$ of (3.98) and (3.99).

Postulate II is a cornerstone of the theory, from which follows both the uncertainty principle of Heisenberg and a limitation on the kinds of questions it is meaningful to ask in a quantum context. It does *not* mean, however, that quantum theory is imprecise – far from it! Consider, e.g., the deuteron, a stable nucleus formed from a neutron (n) and a proton (p). Although one cannot specify the distance between n and p in the ground state of the deuteron – quantum mechanics yields only the probabilities of various separations – it is possible using quantum theory to calculate the average separation, the binding energy, the total angular-momentum eigenvalue, and the values of the magnetic moment

[2] "Path" as used in this context need not refer to a physical path in coordinate space, although this is the typical interpretation. Thus, some "path" which produced the linear superposition (3.94) of box eigenfunctions was followed.

[3] Equation (5.15) represents $|\alpha,\ t\rangle$ as a "wave packet," and this collapse or "reduction" of the wave packet has long been a source of controversy and debate. The interested reader can find discussions in Wheeler and Zurek (1983), Bell (1988), Cini and Levy-Leblond (1990), and Peierls (1991). See also Cushing (1994).

and of the quadrupole moment, all to high accuracy. Thus, the inability to know the values of some quantities that in classical physics are known to arbitrary accuracy does not prevent us from using quantum theory to determine many observables with precision. Furthermore, the agreement between quantum theory and experiment is usually so good that discrepancies are attributed not to a failure of quantum theory itself but typically to neglect of dynamical effects that were deemed for some reason to be negligible – and occasionally to errors in measurement.

The ability to calculate certain observables with great accuracy coupled with the inability to know precisely the values of other observables, e.g., exactly where the electron in an H-atom is located relative to the proton, means that one can draw no detailed picture to represent the spatial configuration of an atom or a nucleus. There is no reliable answer to the question "What does a particular microscopic system really look like?"

This inability to provide a picture or likeness of microscopic "reality" is often an unsettling feature when quantum theory is first encountered. It can be discomforting to realize that one must give up the pictures and/or models that one's eyes and classical physics supply for macroscopic systems. This inability to state in detail (to "describe") what is "out there" when one is discussing a microscopic system, for example the H-atom, naturally leads a newcomer to quantum theory to ask what the phrase "a quantum system is *described* by its state vector" is supposed to mean.

The answer is typically quantal, in that the ordinary meanings of "describe" and of "description" are altered: a quantum description of a system is composed of quantum numbers, probability amplitudes, expectation values of relevant operators, rates of transition to various states, and possibly other quantum features, all derivable from the state vector of the system. A pictorial representation is often used as well, although it is never to be interpreted as "what is actually out there." It is based on the probability of finding the system in some spatial volume, or, in the case of a single particle, finding it at a particular point. In the case of bound states, these probability distributions are usually localized in such a way that the vast majority of the distribution is confined to a relatively small spatial volume. (Recall the distributions for a particle in a box, Figs. 3.8 and 3.9.) For an atom, this results in the electrons being localized as a "charge cloud," as we indicate shortly in the case of the ground state of hydrogen. In general, these charge-cloud distributions for the H-atom provide a basis for understanding the structures of atoms and many molecules; included in the latter case are angles and lengths of chemical bonds (which are measurable quantities). Such visualizations are helpful in gaining a "feel" for the results of often complex computations, i.e., an understanding of the system, and we shall thus "pictorialize" the calculations arising in later chapters of this book. It is in these pictorializations and the construction of quantal models for more complex systems, as opposed to solving the equations, that the physics is often apprehended.

To illustrate the foregoing comments, we consider a realistic example (as opposed to the quantal box): the ground state of the H-atom. The proton, here assumed infinitely massive, is taken as the origin of the coordinate system, so that H becomes a one-particle (i.e., a one-electron) system. It is further assumed that effects due to the intrinsic spin of the electron (discussed in Chapter 13) and to special relativity may be ignored. On ignoring the latter two effects, the quantal energy spectrum of H becomes identical to

that of the simple Bohr theory, viz., $E_n = -\kappa_e e^2/(2a_0 n^2)$. The associated eigenstates are labeled by three quantum numbers, one of which is n. The other two quantum numbers are denoted ℓ and m_ℓ (see Chapter 11 for details); for fixed n, the allowed values of ℓ and m_ℓ are $\ell = 0, 1, 2, \ldots, n-1$ and, for each ℓ, $m_\ell = -\ell, -\ell+1, -\ell+2, \ldots, \ell-1, \ell$. Hence, for this model of hydrogen, the label α in the generic state $|\alpha\rangle$ is replaced by the three integers $n\ell m_\ell$:

$$|\alpha\rangle \rightarrow |n\ell m_\ell\rangle, \text{ non-relativistic hydrogen atom.} \tag{5.17}$$

Correspondingly, the coordinate-space wave function becomes

$$\psi_{n\ell m_\ell}(\mathbf{r}) = \langle \mathbf{r} | n\ell m_\ell \rangle, \tag{5.18}$$

where $\mathbf{r}$ is the position of the electron relative to the proton.

By assumption, $|n\ell m_\ell\rangle$ is normalized, i.e.,

$$\langle n\ell m_\ell | n\ell m_\ell \rangle = 1. \tag{5.19}$$

This implies that

$$\int d^3 r \, |\psi_{nlm_\ell}(\mathbf{r})|^2 = 1, \tag{5.20}$$

a relation that follows from insertion into (5.19) of

$$\hat{I} = \int d^3 r \, |\mathbf{r}\rangle\langle\mathbf{r}|, \tag{5.21}$$

one of several possible resolutions of the identity. Equation (5.20) states that

$$\rho_{n\ell m_\ell}(\mathbf{r}) = |\psi_{n\ell m_\ell}(\mathbf{r})|^2 \tag{5.22}$$

is a normalized probability distribution.

Before specializing to the ground state, we note from Appendix A that normalization of $\psi_{n\ell m_\ell}(\mathbf{r})$ means that the probability $P_{n\ell m_\ell}(V)$ of finding the electron somewhere in a volume V centered on the proton when its state is $|n\ell m_\ell\rangle$ is

$$P_{n\ell m_\ell}(V) = \int_V d^3 r \, |\psi_{n\ell m_\ell}(\mathbf{r})|^2. \tag{5.23}$$

Furthermore, if V is a sphere of radius a, then the probability $P_{n\ell m_\ell}(r \leqslant a)$ that the electron's radial coordinate is less than or equal to a is

$$P_{n\ell m_\ell}(r \leqslant a) = \int_0^a r^2 \, dr \int_{\text{sphere}} d\Omega \, |\psi_{n\ell m_\ell}(r, \theta, \phi)|^2, \tag{5.24}$$

where r, θ, and ϕ are the polar coordinates of $\mathbf{r}$ and $d\Omega = \sin\theta \, d\theta \, d\phi$ is the differential of solid angle. This expression for $P_{n\ell m_\ell}(r \leqslant a)$ is based on an important principle: if the probability density depends on several variables and one (or more) of these is not specified (or measured), then all allowed values of each such variable must be summed on or integrated over in order to obtain the relevant probability. This rule means that, if an observable is not measured, then the probability associated with it will be unity since one of its values must occur. In the present case, any angles θ and ϕ may occur but none is specified, so we sum (integrate) over all of them to get the angle-independent result $P_{n\ell m_\ell}(r \leqslant a)$.

Let us now consider the ground state, for which E_n takes on its smallest value. This occurs for $n = 1$, which means that $\ell = 0 = m_\ell$. Thus the ground state is $|100\rangle$. It is shown in Chapter 11 that the coordinate-space wave function $\langle r\theta\phi|100\rangle$ is

$$\psi_{100}(r\theta\phi) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}, \tag{5.25}$$

a result independent of the polar angles. The Bohr radius a_0 is equal to $\hbar^2/(m_e\kappa_e e^2)$ (Eq. (1.22)), and the factor $[1/(\pi a_0^3)]^{1/2}$ ensures normalization.

Thus, the ground-state wave function is normalized and spherically symmetric (no θ or ϕ dependence). It gives rise to a probability density proportional to $\exp(-2r/a_0)$, whose maximum is at $r = 0$ and that falls to $1/e$ of its $r = 0$ value at $r = a_0/2 \cong 0.25$ Å, as shown in Fig. 5.1. Since the factor r^2 occurs in the volume integral, one often introduces the *radial probability amplitude* $r\psi_{n\ell m_\ell}(\mathbf{r})$, from which one obtains the *radial probability distribution* $\rho^{\text{rad}}_{n\ell m_\ell}(\mathbf{r})$, which in the case of the ground state is

$$\rho^{\text{rad}}_{100}(\mathbf{r}) = |r\psi_{100}(\mathbf{r})|^2. \tag{5.26}$$

Figure 5.2 shows the radial probability density $|r\psi_{100}(r)|^2$ plotted as a function of r. In contrast to $|\psi_{100}(r)|^2$, it is zero at $r = 0$ and its maximum $r_{\max}$ is larger than zero. An

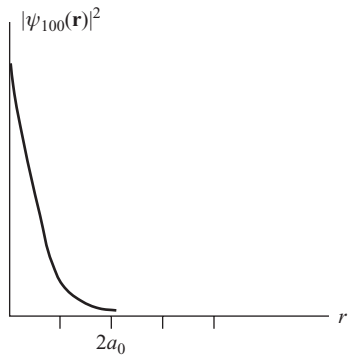

Fig. 5.1 The probability density $|\psi_{100}(\mathbf{r})|^2$ for the ground state of the H-atom.

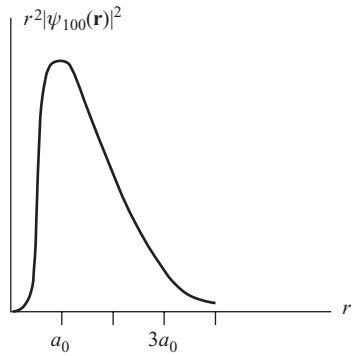

Fig. 5.2 The radial probability distribution $\rho_{\text{rad}}(\mathbf{r}) = r^2|\psi_{100}(\mathbf{r})|^2$ for the ground state of the H-atom.

easy calculation leads to $r_{\max} = a_0$, the radius of the lowest orbit in Bohr's model of hydrogen. Of course, this is not the distance of the electron from the proton, but only the radius at which $\rho^{\text{rad}}_{100}(\mathbf{r})$ is maximal. As shown in Fig. 5.2, the radial probability density $r^2|\psi_{100}(r)|^2$ is concentrated in a spherical shell lying between $r \cong 0.5a_0$ and $r \cong 3a_0$. This shell is the electronic charge cloud noted earlier; it underlies the picture in which the electron in the H-atom is *localized* in the vicinity of a_0 even though it is not *at* the radius a_0. Indeed, a_0 is not even equal to the average or the expected value of r: that quantity, which we denote $\bar{r}$, is larger than a_0; its value will later be shown to be $\overline{r} = 3a_0/2$. This is a further argument against accepting a planetary-orbit picture for the structure of hydrogen (as noted before, the Bohr model is simply not valid). Nevertheless, the values r_n of the nth Bohr orbits play much the same role for $n > 1$ as that in the case $n = 1$: when $n > 1$, then for those states $|n, \ell = n - 1, m_\ell = 0\rangle$, the radial probability distribution $|r\langle r\theta\phi|n, \ell = n - 1, m_\ell = 0\rangle|^2$ has its maximum at $r_{\max} = r_n = n^2 a_0$. Furthermore, for such states the average value $\overline{r}$ will also be greater than r_n, and $\rho^{\text{rad}}_{n\ell m_\ell}(\mathbf{r})$ will continue to be concentrated in a small shell, though not necessarily a spherical one. These points will be established in Chapter 11.

Other probability amplitudes and densities will be evaluated in subsequent sections of this book. In the case of bound states, the probability distributions are usually localized in such a way that the vast majority of the distribution is confined to a relatively small spatial volume. For an atom, this results in the electrons being characterized as a charge cloud. In general, the charge-cloud distributions for the H-atom provide the basis for understanding the structure of heavier atoms and many molecules. Aspects of this are discussed in Chapter 18.

5.3. Measurements/connection with experimental data

Postulates I and II have dealt with some theoretical aspects of observables: their abstract operator images, states of quantum systems as the eigenvectors of quantal operators, and the probabilistic interpretation of states. Postulate III is concerned with experimental aspects of observables: their measurement and the relation of measured values to theoretical predictions. Ideal measurements of eigenvalues play but a limited role here, since measurements are generally not ideal, while the states of quantum systems are not always eigenvectors of the operator whose eigenvalues one might wish to measure. Furthermore, we may wish to compare a measurement with a theoretical prediction, often arising from an approximate calculation. How to connect theory and experiment in these more general situations is the subject of the present section.

Measurements yield numbers. The implication of this seemingly trivial statement is that the final results of a theoretical analysis on some quantum system should include predictions of the numbers that have been or will be obtained in an experiment. These numbers can include energies, lifetimes of decaying states, electric and magnetic moments, etc. On the theoretical side, every such number involves the matrix element of an operator. The simplest example of this is the eigenvalue a_n of an observable $\hat{A}$. Starting with Eq. (5.1),

$$\hat{A}|a_n\rangle = a_n|a_n\rangle,$$

it follows from projecting both sides of this equation onto $\langle a_n|$ that

$$a_n = \langle a_n|\hat{A}|a_n\rangle.$$

Thus, a_n is a diagonal matrix element of the operator $\hat{A}$.

More generally, one can always associate with every experimental measurement the matrix element – not necessarily a diagonal one – of a quantal operator. That is, quantal predictions will involve theoretical quantities of the form $B_{\beta\alpha} = \langle\beta|\hat{B}|\alpha\rangle$, *where* $|\alpha\rangle$ *and* $|\beta\rangle$ *are quantal states and* $\hat{B}$ *is a quantal operator, which may but need not be an observable. Some predictions will be proportional to* $B_{\beta\alpha}$; *others may involve* $|B_{\beta\alpha}|^2$.

In order to relate theoretical predictions to experimental measurements in a relatively simple way, our formulation of Postulate III will be in terms of measurements of an observable $\hat{A}$ when the system is in quantal state $|\alpha\rangle$. This assumption is not too restrictive, since it allows us to deal with a variety of theoretical and experimental possibilities. Furthermore, the basic concepts are readily extended to cases in which measurements involve off-diagonal matrix elements and/or operators that are not observables, as in the cases of 3-D scattering and electromagnetic radiation. We consider experimental aspects first.

Two ingredients (among several) are essential to achieving accurate measurements. First, the apparatus must have sufficient resolution to discriminate between adjacent values of the observable.[4] This ingredient, essential to an ideal measurement, is discussed in Section 5.1. Second, enough counts (observations) must be made that fluctuations away from the desired value are small. That is, one must have good statistics. Our concern here is only with the latter aspect. To achieve it means that N, the number of times the observable is measured, must be large. In the ideal situation $N \to \infty$, just as in the case of the *a priori* determination of the probability of achieving a particular outcome for some event (see Appendix A). This analogy to probability holds in practice as well, since neither in experimental measurements nor in *a posteriori* determinations of the probability of the occurrence of a particular outcome is an infinite number of observations made.

We now assume good statistics, i.e., N large enough that $\sqrt{N} \ll N$. If the N measurements of the observable $\hat{A}$ yield $\{a^{(j)}\}_{j=1}^{N}$, then the "value" of the observable extracted from these measurements is the average $\langle\hat{A}\rangle_\alpha$, defined as

$$\langle\hat{A}\rangle_\alpha = \sum_{j=1}^{N} P_j a^{(j)}, \tag{5.27a}$$

where the subscript α on the LHS of (5.27a) signifies that all N of the systems measured were each in the state $|\alpha\rangle$ when the experiment was performed, while P_j is the probability that the value $a^{(j)}$ will occur. It is often the case that these probabilities are *a priori* equal, i.e., $P_j = N^{-1}$, $\forall\ j$, in which case

$$\langle\hat{A}\rangle_\alpha = \frac{1}{N}\sum_{j=1}^{N} a^{(j)}. \tag{5.27b}$$

[4] By "apparatus" is meant both the devices which generate the probe and those which detect the final systems, including photons. Note also that control of resolution is meant to encompass items such as systematic errors, finite-size effects, various biases, etc.

The relation of the measured average value of (5.27) to that predicted theoretically is given by Postulate III.

POSTULATE III.

Assume that the physical system for which the observable $\hat{A}$ is to be measured is initially prepared in quantum state $|\alpha\rangle$. Then *the theoretical prediction for the average or expected value* $\langle\hat{A}\rangle_\alpha$ *of the observable* $\hat{A}$ *when the system is in state* $|\alpha\rangle$ *is given by the matrix element* $\langle\alpha|\hat{A}|\alpha\rangle$, i.e.,

$$\langle\hat{A}\rangle_\alpha = \langle\alpha|\hat{A}|\alpha\rangle. \tag{5.28}$$

The relation of this quantity to the values $a^{(j)}$ observed in experiments is

$$\langle\alpha|\hat{A}|\alpha\rangle = \langle\hat{A}\rangle_\alpha = \sum_{j=1}^{N} P_j a^{(j)}, \tag{5.29}$$

where an "in-principle" limit of $N \to \infty$ is implied but not observed in practice.

Note the difference between Postulates I and III: the former states that $\{a_n\}$ comprises the entire set of values that an observable $\hat{A}$ can have (for simplicity here, all a_n are assumed discrete), whereas Postulate III, via Eq. (5.29), relates the *average* value obtained in a measurement of $\hat{A}$ to that predicted by theory. Aspects of this are illustrated in the following examples.

Eigenstates

Assume that at least a portion of the spectrum of $\hat{A}$ is discrete, i.e.,

$$\hat{A}|a_m\rangle = a_m|a_m\rangle, \qquad m = 1, 2, \ldots.$$

Let the system on which $\hat{A}$ is to be measured be prepared in state $|a_n\rangle$, i.e., $|\alpha\rangle = |a_n\rangle$. Then $\langle\alpha|\hat{A}|\alpha\rangle = a_n$ and (5.29) becomes

$$a_n = \sum_{j=1}^{N} P_j a^{(j)}. \tag{5.30}$$

One expects not only that $P_j = 1/N$, but also that the results of very accurate measurements will yield $a^{(j)} = a_n \pm \delta a^{(j)}$, where $\delta a^{(j)}$ contains the effects of experimental error, with $\delta a^{(j)}/a_n \ll 1$.

As a specific example, let us consider a particle in the 1-D quantal box: it is not a realistic physical system but displays many of the characteristics of one. Let $|n, t\rangle$ be the Hilbert-space vector whose coordinate-space representation is $\Psi_n(x, t)$ of Eq. (3.91). If the particle's state is $|n, t\rangle$, then the theoretical value of the energy for that state is $E_n = \langle n, t|\hat{H}|n, t\rangle$, where $\hat{H}$ is the relevant Hamiltonian. Were it possible to have N particles in the box, all in state $|n, t\rangle$, and also to measure the average energy of such a system, then a_n on the LHS of (5.30) would be replaced by E_n, while the $a^{(i)}$ on the RHS would be replaced by the measured values of the energy, $E^{(j)}$.

Next, suppose that the state in which the systems are prepared is a linear combination of eigenstates of $\hat{A}$, say

$$|\alpha\rangle = \sum_{n=1}^{n_0} C_n |a_n\rangle, \tag{5.31}$$

with $C_n = \langle a_n|\alpha\rangle$. If there are N systems for which (5.31) is the state, it follows from Postulate II that, of the N systems, $N_n = |C_n|^2 N$ are in eigenstate $|a_n\rangle$, while Postulate III leads to the following theoretical prediction for $\langle \hat{A}\rangle_\alpha$:

$$\begin{aligned}\langle \hat{A}\rangle_\alpha &= \sum_{n=1}^{n_0} |C_n|^2 a_n \\ &= \frac{1}{N}\sum_{n=1}^{n_0} N_n a_n. \end{aligned} \tag{5.32}$$

Equation (5.32) is itself a probabilistically weighted sum. By extending this type of analysis to "preparation" of final states, we shall show below how $|C_n|$ can be extracted – to within experimental error – from certain measurements.

The particle in a quantal box again provides an illustration of the foregoing. Corresponding to $|\alpha\rangle$ of (5.31) is the superposition wave function (3.94), so that the C_n of (5.31) take on the values $C_1 = C_4 = C_j = \cdots = 0$, $C_2 = a_2$, and $C_3 = a_3$. Let us assume that an energy measurement were to be made, with all N particles being in the state $|\alpha\rangle$ of (5.31). Corresponding to $\langle \hat{A}\rangle_\alpha$ is $\langle \hat{H}\rangle_\alpha = \langle\alpha|\hat{H}|\alpha\rangle$; a straightforward calculation yields $\langle \hat{H}\rangle_\alpha \equiv \overline{E} = |a_2|^2 E_2 + |a_3|^2 E_3$. Choosing $a_2 = a_3 = \sqrt{\frac{1}{2}}$, we get $\overline{E} = (E_2 + E_3)/2 = 13\pi^2\hbar^2/(4mL^2)$.

Finally, let us suppose that the prepared state $|\alpha\rangle$ of the system is $|b_m\rangle$, an eigenstate of a second observable $\hat{B}$ that does not commute with $\hat{A}$, whose spectrum is assumed discrete. Since $[\hat{A}, \hat{B}] \neq 0$, $|b_m\rangle$ is not an eigenstate of $\hat{A}$ and therefore the value $\langle b_m|\hat{A}|b_m\rangle$ now predicted for $\langle \hat{A}\rangle_\alpha$ can no longer be expressed as a finite sum of a_n's, as in Eq. (5.32). Indeed, using

$$\hat{I} = \sum_{n=1}^{\infty} |a_n\rangle\langle a_n| \tag{5.33}$$

as a resolution of the identity (see Postulate VI) and employing (5.33) in $\langle b_m|\hat{A}|b_m\rangle$, we find that

$$\langle \hat{A}\rangle_\alpha = \sum_{n=1}^{\infty} |\langle b_m|a_n\rangle|^2 a_n, \tag{5.34}$$

which is an infinite sum on the a_n's. In general, none of the coefficients $\langle b_m|a_n\rangle$ can be expected to be zero, leaving an awkward infinite sum to evaluate. This suggests attempting to determine $\langle b_m|\hat{A}|b_m\rangle$ directly. A possible means for doing so is to convert $\langle b_m|\hat{A}|b_m\rangle$ into an integral by introducing a representation. Let us assume that $\hat{A}$ is local in the coordinate representation. Its use leads to

$$\langle \hat{A}\rangle_\alpha = \langle b_m|\hat{A}|b_m\rangle = \int d^3 r\, \psi^*_{b_m}(\mathbf{r})\hat{A}(\mathbf{r})\psi_{b_m}(\mathbf{r}),$$

where $\hat{A}$ and $|b_m\rangle$ are presupposed to refer to a single-particle system. The preceding integral may well be easier to evaluate than the infinite sum in (5.34): for example, the integral might accurately be approximated numerically.

Further examples of the foregoing, for the quantal box and other systems, are discussed in the next chapter.

With these remarks concerning the connection with theoretical predictions, we turn to experimental aspects of Postulate III, in particular to measurements involving binding energies, decaying states, and collision phenomena.

Example: binding energy

Some experiments lead to the determination of more than one observable, others are unique in this regard. As an example of the latter, we consider the determination of the energy of a photon just sufficient to dissociate a deuteron – the stable nucleus consisting of a neutron and a proton bound together by the strong nuclear interaction – into a free (unbound) neutron and a free proton, each having zero kinetic energy in their center-of-mass coordinate system. To achieve this, the energy E_γ of the photon must be equal to the *binding energy* B_d of the deuteron. The goal of the measurement is to determine B_d.

The experiment may be thought of as the shining of photons of variable energy E_γ onto deuterium gas at room temperature; owing to the Boltzmann factor, the average kinetic energy of the deuterons is about 0.025 eV, a quantity small enough for our purposes to ignore.

When $E_\gamma < B_\mathrm{d}$, no protons and neutrons are produced, but when the threshold value $E_\gamma = B_\mathrm{d}$ is reached, the photon can be absorbed, dissociate the deuteron, and detectors that distinguish protons can then record their presence. The jth measurement of the threshold energy produces a value $B_\mathrm{d}^{(j)}$; their totality is the set $\{B_\mathrm{d}^{(j)}\}_{j=1}^{N}$.

The value for B_d that is extracted from the measured ones is, from (5.27a), the *average* or expected value, viz.,

$$B_\mathrm{d} = \sum_{j=1}^{N} P_\mathrm{d}^{(j)} B_\mathrm{d}^{(j)}, \tag{5.35}$$

where $P_\mathrm{d}^{(j)}$ is the probability that $B_\mathrm{d}^{(j)}$ is the outcome. In such experiments, it is assumed that each $B_\mathrm{d}^{(j)}$ is equally likely to occur, so that $P_j = 1/N$, with the result that[5]

$$B_\mathrm{d} = \frac{1}{N} \sum_{j=1}^{N} B_\mathrm{d}^{(j)}. \tag{5.36}$$

The experimental value of B_d is 2.2245 MeV; (5.36) might yield $B_\mathrm{d} = 2.23$ MeV.

The same kind of analysis would apply to the determination of, say, the minimum energy B_e needed to ionize an atom initially in its ground state, i.e., to remove one of its electrons from a state having negative energy to a state with zero energy.

Among the common ingredients in the preceding processes, viz.,

$$\gamma + \mathrm{d} \rightarrow \mathrm{n} + \mathrm{p}$$

[5] We need not address the question of assigning errors, determining a dispersion, etc.

and

$$\gamma + \mathrm{A} \rightarrow \mathrm{A}^{+} + \mathrm{e},$$

where A^{+} represents the singly ionized atom, is the fact that in all measurements for both cases, the target is always in its ground state. Hence, the measurement will always yield a value of B_{d} or B_{e}. That is, in order for the experiment to be repeatable, the systems on which the measurements are being carried out must each be in the same initial state, so that the measurement determines an energy relevant to the desired state. This condition is essential, and we henceforth assume it to hold even if no statement to that effect is made.

As a final point, we call the reader's attention to the fact that the LHS of (5.36) is a "call to arms": B_{d}, and eigenvalues in general, are not known in advance and need to be *calculated*. Very few physical systems are simple enough that the states $|a_n\rangle$ and/or their associated wave functions can be obtained exactly, textbook examples notwithstanding. Indeed, the soluble systems treated in textbooks tend to be the *only* ones for which exact solutions are available. Models and/or approximation methods, both of which will be considered in this book, are thus essential ingredients in analyses of real systems. Furthermore, the inability to solve dynamical equations exactly is often mirrored by an ignorance of some of the operators needed to describe one or another physical system, so that models and approximations occur here as well.

Example: decaying states/branching ratios

When the first excited state of an atom or particle-stable nucleus decays, only one final state in the atom or nucleus can be reached, viz., the ground state, in which case a photon of unique energy is emitted. However, for higher excited states, there is often a variety of final states that can be reached by photon emission. Figure 5.3 illustrates this situation using a Grotrian diagram and wavy lines for the photons. It shows a state of energy E_{e} that can decay via photon emission to one of three final states E_j, $j = 1, 2, 3$. The normalized probabilities P_j for the decay to occur via the "branch" $E_{\mathrm{e}} \rightarrow E_j$, $j = 1, 2, 3$, obey $\sum_j P_j = 1$. The ratio P_j/P_k is denoted the "branching" ratio for the decays $E_{\mathrm{e}} \rightarrow E_j$ and $E_{\mathrm{e}} \rightarrow E_k$. If N measurements are made on the decays from level E_{e}, then the number of decays N_j that proceed via branch j is $N_j = NP_j$. Hence, measurement of the relative numbers of photons corresponding to levels E_j and E_k, viz., N_j and N_k, yields the relative probabilities:

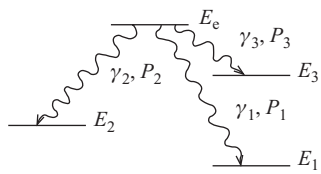

Fig. 5.3 An illustration of the different "branches" by which a hypothetical excited state of energy E_{e} can decay via photon emission to any one of three final states with energies $E_1 < E_2 < E_3$. The wavy lines represent the photons; the symbol γ_j denotes the photon in the transition $E_{\mathrm{e}} \rightarrow E_j$, while P_j is the probability that the decay will occur via branch j, $j = 1, 2, 3$.

$$\frac{N_j}{N_k} = \frac{P_j}{P_k}. \tag{5.37}$$

Each P_j, $j = 1, 2, 3$, is the absolute square of a quantal amplitude C_j and the task of theory is to determine these amplitudes, usually via models and approximation, and then to use the calculated values of P_j/P_k to compare with the LHS of (5.37) in an attempt to determine whether the model/approximation can be considered valid.

Branching ratios are not limited to photon emission: they occur when any unstable state can decay in more than one way. Examples are found in almost all areas of microphysics. One such concerns the short-lived, neutral K meson, denoted K^0_S. Its lifetime is 0.89×10^{-10} s and its primary decay modes are

$$\mathrm{K}^0_\mathrm{S} \to \pi^+ + \pi^- \tag{5.38}$$

and

$$\mathrm{K}^0_\mathrm{S} \to \pi^0 + \pi^0, \tag{5.39}$$

where π^0 and $\pi^\pm$ are the neutral, and the positively and negatively charged pi mesons or "pions." The branching ratio for the decays (5.38) and (5.39) is

$$\frac{\mathrm{K}^0_\mathrm{S} \to \pi^+ + \pi^-}{\mathrm{K}^0_\mathrm{S} \to \pi^0 + \pi^0} = \frac{69}{31}, \tag{5.40}$$

where the RHS of (5.40), the relative number of decays into the two branches, is experimentally determined. Note that the sum of the numerator plus the denominator in (5.40) adds up to 100, suggesting that only the two branches (5.38) and (5.39) can occur. In fact, other decay modes have been observed, but their occurrence is down by a factor of 10^3, so that, to an accuracy of better than within 1%, the ratio in (5.40) is valid. Correct prediction of the lifetime and the branching ratio (5.40) is a requirement of any theory of elementary particles claiming to be valid.

There is a long-lived partner to K^0_S, the symbol for which is K^0_L; its lifetime is 5.2×10^{-8} s. The K^0_S and K^0_L can be thought of as two manifestations of a single particle that can exist in one of only two states, denoted $|\mathrm{K}^0_\mathrm{S}\rangle$ and $|\mathrm{K}^0_\mathrm{L}\rangle$. We shall examine this situation in detail in the exercises to Chapter 13 (two-state systems).

Example: collision processes

A further instance in which a variety of final states can arise from a single initial state is afforded by collisions between a single-particle projectile and a structured target. Included here are electron–atom and electron–molecule scattering, and proton–nucleus collisions involving both scattering and reactions. If the energy E of the projectile is high enough for inelastic scattering to occur, assuming that the target has particle-stable excited states (with energies E^{ex}_j, $j = 1, 2, \ldots$), then inelastically scattered projectiles with final energies $E - E^{\mathrm{ex}}_j$ can be observed.

An inelastically scattered projectile with final energy $E - E^{\mathrm{ex}}_j$ corresponds to the target having been excited to a level with energy E^{ex}_j.[6] An analogous statement holds for a

[6] We assume for simplicity that negligible recoil energy is imparted to the target during the collision and that non-relativistic kinematics may be used. In addition, conservation of energy is taken for granted.

reaction, the only change being that $E - E_j^{\mathrm{ex}}$ is replaced by $E - E_j^{\mathrm{f}}$, the energy of the ejectile, where E_j^{f} is the energy of the jth excited state of the residual system f (e.g., a molecule or nucleus) reached via the reaction. Note that, in each case, the collision has "prepared" the final system in an excited state, the probability for which can be extracted from experiment, as described in the following.

After the collision – inelastic scattering or a reaction – the ejectile can be observed at an angle θ relative to the initial direction of the projectile and also with some final energy E_{f} (equal to $E - E_j^{\mathrm{ex}}$ in the case of inelastic scattering or to $E - E_j^{\mathrm{f}}$ in the case of a reaction). Either the final energy is fixed and the number $N(\theta)$ of ejectiles emitted at angle θ is measured, or θ is fixed and the number $N(E_{\mathrm{f}})$ of ejectiles emitted that leave the target or residual system in the jth excited level is measured.

An example of the latter situation is given by the proton-in, neutron-out nuclear reaction

$$\mathrm{p} + {}^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \mathrm{n}, \tag{5.41}$$

where C (N) is the chemical symbol for carbon (nitrogen) and the left-hand superscript 14 refers to the total number of neutrons plus protons in the nucleus. Once again, p (n) refers to the incident proton (ejected neutron). Shown in Fig. 5.4 is the number of ejected neutrons $N(E_{\mathrm{f}})$ observed at a scattering angle of 40° having energies E_{f} in the range of 26 MeV $\leqslant E_{\mathrm{f}} \leqslant$ 34 MeV. The neutrons are produced by protons of incident energy $E = 35$ MeV bombarding the ^{14}C target. Ten pronounced peaks are seen in this energy

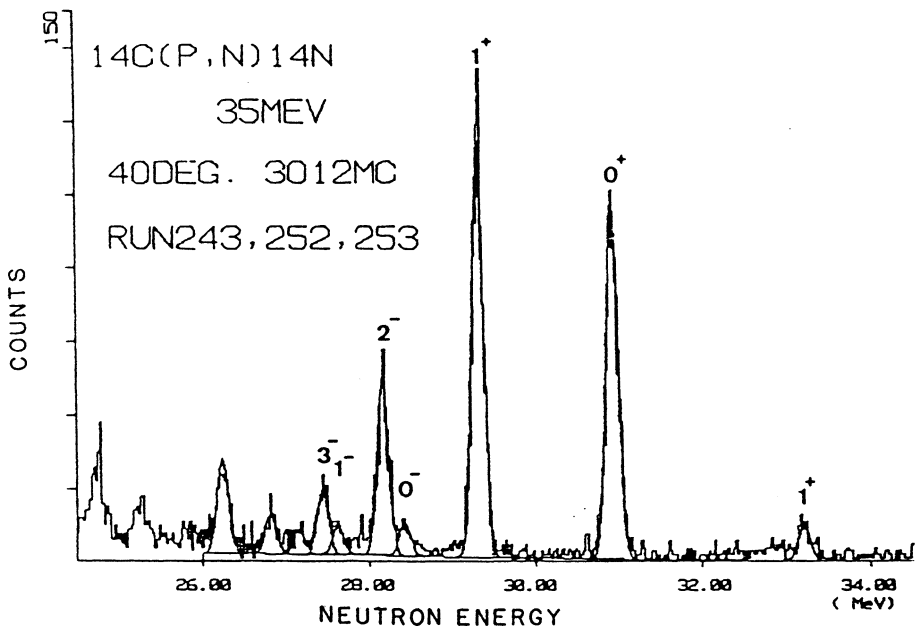

Fig. 5.4 A portion of the energy spectrum or "excitation function" of neutrons emerging from the reaction $\mathrm{p} + {}^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \mathrm{n}$. The energy of the incident protons was 35 MeV and the neutrons were detected at a scattering angle of 40° relative to the direction of incidence of the proton beam. (From Orihara *et al*. (1983).)

range. They correspond to the states in ^{14}N which the outgoing neutrons leave behind. That is, for each peak, ^{14}N is left in a discrete excited state whose energy is determined by conservation of energy. Since the neutron energy E_f increases to the right on the abscissa of Fig. 5.4, the excited-state energies increase to the left. Seven peaks are labeled by the value of the angular momentum and the value of a new quantum number denoted parity, which can be $+$ or $-$, and is discussed in Chapter 9.

The height h_j of the jth peak in Fig. 5.4 is proportional to the probability that this state is populated in the reaction when $\theta = 40°$. Thus, the 1^+ level corresponding to $E_f \cong 29.5$ MeV has the greatest probability of being excited, while the 1^-, the 0^-, and the other 1^+ levels have the least probability of being populated. Again, the aim of theory is to predict these results.

5.4. The coordinate representation for observables

Operators, along with states and their associated wave functions, are the means by which one can calculate the quantities that are measured in experiments. The determination of states/wave functions is thus a primary goal of quantum theory. To do this requires solving the relevant dynamical equations, viz., eigenvalue equations of the form (5.1) or the time-dependent Schrödinger equation, which is discussed in the next section.

These dynamical equations involve the operators that image physical observables. Since the operators are formulated as abstract entities in Hilbert space, some means for working directly with them is required. One procedure is to employ the commutation relations obeyed by the operators. This is relatively straightforward to do for simple systems like the harmonic oscillator and for the simplest model of the H-atom. It leads to the eigenstate representation, in which the operators are represented as infinite and, often, discrete matrices. We shall later treat the 1-D harmonic oscillator in this way.

While the commutation relation approach is useful, it tends to be limited to the simpler systems. Furthermore, if one needs the probability amplitudes that the system is at particular spatial points, then a coordinate representation must be introduced as well, in order to convert state vectors into wave functions. Coordinate-space wave functions are often utilized to help provide a physical feeling for the behavior and interpretation of quantal systems, an aspect of special importance when many degrees of freedom are involved.

Coordinate-space wave functions are usually obtained as the solutions of the coordinate-space forms of dynamical equations. Such equations must obviously contain quantal operators expressed in the coordinate representation. Examples are the momentum and energy (Hamiltonian) operators, which were informally introduced in Chapter 3 in connection with the quantal-box problem. Postulate IV formalizes and generalizes these definitions by stating the coordinate form of a number of (single-particle) quantal operators. From these one can then derive both the commutation relations obeyed by the operators and the momentum representation for the operators.

The single-particle operators whose coordinate representations are stated in Postulate IV are all local. Locality is discussed in Section 4.4, in particular via Eqs. (4.158)–(4.160). As an example of a relation involving local operators, consider the eigenvalue equation (5.1),

Table 5.2 *Some quantal operators and their (local) coordinate representations for a particle of mass m*

Operator	Coordinate representation
Position, $\hat{\mathbf{Q}}$	$\mathbf{r}$
Classical potential energy, $\hat{V}_{\rm cl}(\hat{\mathbf{Q}})$	$V_{\rm cl}(\mathbf{r})$
Linear momentum, $\hat{\mathbf{P}}$	$\hat{\mathbf{P}}(\mathbf{r}) = -i\hbar\,\nabla$
(Orbital) angular momentum, $\hat{\mathbf{L}}$	$\hat{\mathbf{L}}(\mathbf{r}) = -i\hbar\mathbf{r}\times\nabla$
Kinetic energy, $\hat{K}$	$\hat{K}(\mathbf{r}) = \hat{P}^2/(2m) = -[\hbar^2/(2m)]\,\nabla^2$
Energy, $\hat{H} = \hat{K} + \hat{V}$, $\hat{V} = \hat{V}_{\rm cl}(\hat{\mathbf{Q}})$	$\hat{H}(r) = -[\hbar^2/(2m)]\,\nabla^2 + V_{\rm cl}(\mathbf{r})$

$$\hat{A}|a_n\rangle = a_n|a_n\rangle,$$

where $\hat{A}$ and $|a_n\rangle$ now refer to a single particle in three dimensions. Locality of $\hat{A}$ means that the coordinate-space form of (5.1) becomes, in analogy to (4.159),

$$\hat{A}(\mathbf{r})\psi_n(\mathbf{r}) = a_n\psi_n(\mathbf{r}), \tag{5.42}$$

where $\mathbf{r}$ is the position of the particle and $\psi_n(\mathbf{r}) \equiv \langle\mathbf{r}|a_n\rangle$. In Eq. (5.42), $\hat{A}(\mathbf{r})$ stands for any of the operators in Tables 5.1 and 5.2, the latter of which is introduced in connection with Postulate IV.

In addition to their being local, operators discussed in this section are the quantum versions of classical quantities. The quantum operators such as spin and parity do not have coordinate representations, and are not included with those of Table 5.2.

POSTULATE IV.

The operators which are the quantal analogs of classical quantities are all local in the coordinate representation.

(a) The coordinate representation of the position operator $\hat{\mathbf{Q}}$ and of the operator $\hat{V}(\hat{\mathbf{Q}})$ corresponding to any classical potential energy or electromagnetic potential $V_{\rm cl}(\mathbf{r})$ are

$$\hat{\mathbf{Q}}(\mathbf{r}) = \mathbf{r} \tag{5.43}$$

and

$$\hat{V}(\hat{\mathbf{Q}}) = V_{\rm cl}(\mathbf{r}), \tag{5.44}$$

i.e., $\hat{\mathbf{Q}}$ becomes $\mathbf{r}$, and, for a classical potential, $\hat{V}(\hat{\mathbf{Q}})$ becomes $V_{\rm cl}(\mathbf{r})$. Examples are given below.

(b) The coordinate representation of the linear momentum operator $\hat{\mathbf{P}}$ is

$$\hat{\mathbf{P}}(\mathbf{r}) = -i\hbar\,\nabla, \tag{5.45}$$

where the derivatives in the gradient operator are taken with respect to the components of $\mathbf{r}$.

(c) The coordinate representations of the (orbital) angular-momentum operator $\hat{\mathbf{L}} = \hat{\mathbf{Q}} \times \hat{\mathbf{P}}$ and kinetic-energy operator $\hat{K} = \hat{\mathbf{P}} \cdot \hat{\mathbf{P}}/(2m)$ are

$$\hat{\mathbf{L}}(\mathbf{r}) = -i\hbar \mathbf{r} \times \nabla \tag{5.46}$$

and

$$\hat{K}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2. \tag{5.47}$$

(d) The Hamiltonian or energy operator, $\hat{H}$, is defined non-relativistically[7] as the sum of the kinetic- and potential-energy operators, $\hat{K}$ and $\hat{V}$, respectively:

$$\hat{H} = \hat{K} + \hat{V}. \tag{5.48}$$

For the case of a particle of mass m acted on by a classical potential $V_{\mathrm{cl}}(\mathbf{r})$, the coordinate representation of $\hat{H}$ is

$$\hat{H}(\mathbf{r}) = \hat{K}(\mathbf{r}) + V_{\mathrm{cl}}(\mathbf{r}) \tag{5.49a}$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + V_{cl}(\mathbf{r}). \tag{5.49b}$$

These statements are summarized in Table 5.2. Probably the most remarkable aspect of Postulate IV is given by Eq. (5.45), since it defines the coordinate representation of the momentum operator as being mass-independent. It is an unexpected contrast to the classical-physics situation, a contrast that would be maintained if one were to introduce $\hat{\mathbf{P}}/m$ as a velocity operator, since the coordinate representation of this operator, unlike the classical-physics analog, *is* mass-dependent.

The preceding statements concern a single particle in 3-D. If a 1-D situation is envisaged, then, e.g., $\mathbf{r} \to x$, $\hat{\mathbf{Q}}(\mathbf{r}) \to \hat{Q}_x(x) = x$, $\hat{\mathbf{P}}(\mathbf{r}) \to \hat{P}_x(x) = -i\hbar\, d/dx$, $\hat{\mathbf{L}}(\mathbf{r}) \to 0$, and $\hat{K}(\mathbf{r}) \to \hat{K}_x(x) = -[\hbar^2/(2m)]\, d^2/dx^2$, with corresponding changes in $V(\mathbf{r})$ and $\hat{H}(\mathbf{r})$. Furthermore, in a system containing N particles labeled 1, 2, ..., N, with coordinates $\mathbf{r}_1$, $\mathbf{r}_2$ ..., $\mathbf{r}_N$ and masses m_1, m_2, ..., m_N, one can introduce operators for position, potential, linear and angular momentum, kinetic energy, and total energy for each particle j, viz.,

$$\hat{\mathbf{Q}}_j,\ \hat{V}_j,\ \hat{\mathbf{P}}_j,\ \hat{\mathbf{L}}_j,\ \hat{K}_j,\ \hat{H}_j,$$

whose coordinate representations are as given in Postulate IV, the only change being the addition of the subscript j wherever an unsubscripted $\mathbf{r}$, ∇, or m appears. We shall consider these operators in the later sections of this book dealing with N-particle systems, $N \geqslant 2$.

Each of the coordinate representations of parts (b), (c), and (d) of Postulate IV allow one (at least in principle) to solve the eigenvalue problem typified by Eq. (5.1), thus yielding both eigenvalues and eigenfunctions. Much of this text is concerned with solution of the stationary-state equation

$$\hat{H}\psi = E\psi, \tag{5.50}$$

where the coordinate-dependence is suppressed to allow for the possibility of this

[7] Only non-relativistic quantum mechanics is considered in this book.