

Postulates and Theorems of Quantum Mechanics

6-1 Introduction

The first part of this book has treated a number of systems from a fairly physical viewpoint, using intuition as much as possible. Now, armed with the concepts already developed, the reader should be in a better position to understand the more formal foundation to be described in this chapter. This foundation is presented as a set of postulates. From these follow proofs of various theorems. The ultimate test of the validity of the postulates comes in comparing the theoretical predictions with experimental data. The extra effort required to master the postulates and theorems is repaid many times over when we seek to solve problems of chemical interest.

6-2 The Wavefunction Postulate

We have already described most of the requirements that a wavefunction must satisfy: ψ must be acceptable (i.e., single-valued, nowhere infinite, continuous, with a piecewise continuous first derivative). For bound states (i.e., states in which the particles lack the energy to achieve infinite separation classically) we require that ψ be square integrable. So far we have considered only cases where the state of the system does not vary with time. For much of quantum chemistry, these are the cases of interest, but, in general, a state may change with time, and ψ will be a function of t in order to follow the evolution of the system.

Gathering all this together, we arrive at

Postulate I *Any bound state of a dynamical system of n particles is described as completely as possible by an acceptable, square-integrable function $\Psi(q_1, q_2, \dots, q_{3n}, \omega_1, \omega_2, \dots, \omega_n, t)$, where the q 's are spatial coordinates, ω 's are spin coordinates, and t is the time coordinate. $\Psi^*\Psi d\tau$ is the probability that the space-spin coordinates lie in the volume element $d\tau (\equiv d\tau_1 d\tau_2 \cdots d\tau_n)$ at time t , if Ψ is normalized.*

For example, suppose we have a two-electron system in a time-dependent state described by the wavefunction $\Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, t)$. The spin coordinates ω would each be some combination of spin functions α and β . If we integrate $\Psi^*\Psi$ over the spin coordinates of both electrons, we are left with a spin-free density function. Call it $\rho(x_1, y_1, z_1, x_2, y_2, z_2, t) \equiv \rho(v_1, v_2, t)$. We interpret $\rho(v_1, v_2, t) dv_1 dv_2$ as

the probability that electron 1 is in dv_1 (i.e., between x_1 and $x_1 + dx$, y_1 and $y_1 + dy$, and z_1 and $z_1 + dz$) and electron two is in dv_2 at time t . If we now integrate over the coordinates of electron 2, we obtain a new density function, $\rho'(v_1, t)$, which describes the probability of finding electron 1 in various volume elements at various times regardless of the position of electron 2.

6-3 The Postulate for Constructing Operators

Much of the substance of the second postulate is already familiar. We earlier used arguments based on de Broglie waves to construct hamiltonian operators. We then noted that the kinetic energy part of the operators can be identified with a classical term like $p_x^2/2m$ through the relation $p_x \leftrightarrow (\hbar/i)\partial/\partial x$. The potential energy terms in the hamiltonian operators are completely classical, however. Thus, we could have constructed the quantum mechanical hamiltonians by writing down the *classical* energy expressions in terms of momenta and position, and then replacing every momentum term by the appropriate partial differential operator. This is an example of the use of part *c* of:

Postulate II *To every observable dynamical variable M there can be assigned a linear hermitian operator \hat{M} . One begins by writing the classical expression, as fully as possible in terms of momenta and positions. Then:*

- If M is q or t , \hat{M} is q or t . (q and t are space and time coordinates.)*
- If M is a momentum, p_j , for the j th particle, the operator is $(\hbar/i)\partial/\partial q_j$, where q_j is conjugate to p_j (e.g., x_j is conjugate to p_{xj}).*
- If M is expressible in terms of the q 's, p 's and t , \hat{M} is found by substituting the above operators in the expression for M in such a way that \hat{M} is hermitian.*

The reason for specifying that \hat{M} must be hermitian is that the eigenvalues of a hermitian operator must be real numbers.¹ We shall discuss this and other aspects of hermiticity (including its definition) later in this chapter.

As an explicit example of this procedure, we reconsider the hydrogen atom. Assuming a fixed nucleus (infinite inertia), the classical expression for the total energy of the system is

$$E_{\text{classical}} = (1/2m_e)(p_x^2 + p_y^2 + p_z^2) - e^2/[4\pi\epsilon_0(x^2 + y^2 + z^2)^{1/2}]$$

where the first term is just the kinetic energy of the electron and the second term is the electrostatic potential energy. The coordinate origin is on the nucleus. Application of postulate II retains the position variables x , y , and z of the potential term unchanged, but replaces p_x by $(\hbar/i)\partial/\partial x$, etc.:

$$\begin{aligned} \frac{1}{2m_e} (p_x^2 + p_y^2 + p_z^2) &\Rightarrow \frac{1}{2m_e} \left\{ \left(\frac{\hbar}{2\pi i} \frac{\partial}{\partial x} \right)^2 + \left(\frac{\hbar}{2\pi i} \frac{\partial}{\partial y} \right)^2 + \left(\frac{\hbar}{2\pi i} \frac{\partial}{\partial z} \right)^2 \right\} \\ &= \frac{-\hbar^2}{8\pi^2 m_e} \nabla^2 \end{aligned}$$

¹In this text (and in quantum chemistry in general) a caret indicates an operator and not a unit vector quantity as in classical physics.

Thus, we arrive at

$$\hat{H} = \frac{-\hbar^2}{8\pi^2 m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0(x^2 + y^2 + z^2)^{1/2}}$$

and we are now free to transform \hat{H} to other coordinate systems (such as r, θ, ϕ) if we wish.

6-4 The Time-Dependent Schrödinger Equation Postulate

We have discussed only cases where neither the hamiltonian \hat{H} nor ψ is time dependent. In those cases we required that ψ be an eigenfunction of \hat{H} . In the more general case in which Ψ and $\hat{\mathcal{H}}$ are time dependent,² a different requirement is imposed by

Postulate III *The state functions (or wavefunctions) satisfy the equation*

$$\hat{\mathcal{H}} \Psi(q, t) = \frac{-\hbar}{i} \frac{\partial}{\partial t} \Psi(q, t) \quad (6-1)$$

where $\hat{\mathcal{H}}$ is the hamiltonian operator for the system.

We should check to see if this is consistent with the time-independent Schrödinger equation we have been using. Suppose that the hamiltonian is time independent. Let us see if a solution to Eq. (6-1) exists when $\Psi(q, t)$ is separated into a product of space- and time-dependent functions: $\Psi(q, t) = \psi(q)f(t)$. Inserting this into Eq. (6-1) gives

$$\hat{H}\psi(q)f(t) = \frac{-\hbar}{i} \frac{\partial}{\partial t} \psi(q)f(t) \quad (6-2)$$

Dividing by $\psi(q)f(t)$ gives

$$\frac{\hat{H}\psi(q)}{\psi(q)} = \frac{(-\hbar/i)(\partial/\partial t)f(t)}{f(t)} \quad (6-3)$$

Since each side of Eq. (6-3) depends on a different variable, the two sides must equal the same constant, which we call E . This gives

$$\hat{H}\psi(q) = E\psi(q) \quad (6-4)$$

and

$$\frac{-\hbar}{i} \frac{d}{dt} f(t) = Ef(t) \quad (6-5)$$

The first of these equations is just the time-independent Schrödinger equation we have been using. The second equation has the solution $f(t) = A \exp(-iEt/\hbar)$. Hence, f^*f equals a constant, and so $\Psi^*\Psi = \psi^*\psi f^*f \propto \psi^*\psi$. Since f has no effect on energy or particle distribution, we can ignore it in dealing with stationary states. The situation is analogous to the case of standing waves discussed in Chapter 1.

² $\hat{\mathcal{H}}$ and Ψ symbolize time dependence; \hat{H} and ψ symbolize time independence.

Note that while we have shown that solutions may exist in which Ψ is separable, this does not mean that every solution of Eq. (6-1) with $\hat{\mathcal{H}} = \hat{H}$ is separable (i.e., stationary). We can imagine a situation where a system in a stationary state is suddenly perturbed to produce a new time-independent hamiltonian. Ψ will change as the system adjusts to this new situation, giving us a case where the hamiltonian is time-independent (after the perturbation, at least) but Ψ is not a stationary state function. The way in which Ψ evolves in time is governed by Eq. (6-1).

EXAMPLE 6-1 Show that the average energy for a nonstationary state of the hydrogen atom is conserved as the system evolves, if \hat{H} is not time-dependent.

SOLUTION ► We choose a simple example:

$$\psi = \frac{1}{\sqrt{2}}\{\psi_{1s} \exp(it/2\hbar) + \psi_{2s} \exp(it/8\hbar)\}$$

where each exponential equals $\exp(-iEt/\hbar)$. Then

$$\langle E \rangle = \int \psi^* \hat{H} \psi \, dv \, dt = \frac{1}{2} \int \psi_{1s}^* \exp(-it/2\hbar) \hat{H} \psi_{1s} \exp(it/2\hbar) \, dv \, dt$$

+ the analogous $2s2s$ term + $1s2s$ and $2s1s$ cross terms. Since \hat{H} does not operate on functions of t , the exponentials in each of the first two integrals can join together, giving $\exp(0) = 1$. So time-dependence disappears from the first two integrals, and they become respectively equal to $-\frac{1}{2}$ a.u., and $-\frac{1}{8}$ a.u. Dependence on time does not disappear from the cross-term integrals, but that doesn't matter because the integration over space gives zero in each case, due to orbital orthogonality. Thus, $\langle E \rangle = \frac{1}{2}(-\frac{1}{2} \text{ a.u.}) + \frac{1}{2}(-\frac{1}{8} \text{ a.u.}) = -\frac{5}{16}$ a.u., which has no time-dependence. ◀

6-5 The Postulate Relating Measured Values to Eigenvalues

The second postulate indicated that every observable variable of a system (such as position, momentum, velocity, energy, dipole moment) was associated with a hermitian operator. The connection between the observed value of a variable and the operator is given by

Postulate IV *Any result of a measurement of a dynamical variable is one of the eigenvalues of the corresponding operator.*

Any measurement always gives a real number, and so this postulate requires that eigenvalues of the appropriate operators be real. We will prove later that hermitian operators satisfy this requirement.

If we measured the electronic energy of a hydrogen atom (the negative of its ionization energy), we could get any of the allowed eigenvalues ($-1/2n^2$ a.u.) but no intermediate value. What if, instead, we measured the distance of the electron from the nucleus. By postulate II, the operator for this property is just the variable r itself. That is, $\hat{r} = r$. Hence, we need to consider the eigenvalues of r in the equation

$$r \delta(r, \theta, \phi) = \lambda \delta(r, \theta, \phi) \quad (6-6)$$

where δ is an eigenfunction and λ is a real number (corresponding to the distance of the electron from the nucleus). We can rewrite this equation as

$$(r - \lambda)\delta(r, \theta, \phi) = 0 \quad (6-7)$$

This form makes it more apparent that the function δ must vanish at all points in space except those where $r = \lambda$. But λ is an eigenvalue of r and hence is a possible result of a measurement. Thus, we see that postulate IV implies some connection between a measurement of, say, $r = 2$ a.u. and an eigenfunction of r that is finite only at $r = 2$ a.u. We symbolize this eigenfunction $\delta(r - 2 \text{ a.u.})$, this “delta function” being zero whenever the argument is *not* zero. If we measured the electron’s position to be at $r = 5.3$ a.u., the corresponding eigenfunction would be $\delta(r - 5.3 \text{ a.u.})$ —a function that is zero everywhere except in a shell of infinitesimal thickness at $r = 5.3$ a.u. If instead we measured the *point* in space of the electron, rather than just the distance from the nucleus, and found it to be r_0, θ_0, ϕ_0 , then the corresponding eigenfunction of the position operator would be $\delta(r - r_0)\delta(\theta - \theta_0)\delta(\phi - \phi_0)$. This function vanishes everywhere except at r_0, θ_0, ϕ_0 .

It is evident that any value of λ from zero to infinity in Eq. (6-7) may be chosen without spoiling the ability of δ to serve as an eigenfunction of r . This means that, unlike the energy measurement, the measurement of the distance of the electron from the nucleus can have any value.

The eigenfunctions of the position operator are called *Dirac delta functions*. They are “spike” functions having infinitesimal width. They are normalized through the equation

$$\int \delta(x - x_0) dx = 1 \quad (6-8)$$

where the integration range includes x_0 .³ On first acquaintance, these functions seem mathematically peculiar, but they make physical sense in the following way. One can interpret the actual measurement of position as a process that forces the particle to acquire a certain position at some instant. At that instant, ψ^2 for the system (now perturbed by the measuring process) ought to give unit probability for finding the particle at that point (where it definitely is) and zero probability elsewhere, and this is just what the Dirac delta function does.⁴

Postulate IV, then, is in accord with a picture wherein the process of measurement forces the measured system into an eigenstate for the appropriate operator, giving the corresponding eigenvalue as the measurement. This definition of “measurement” is somewhat restrictive and can be deceptive. Often scientists refer to measurements that are really measurements of average values rather than eigenvalues. This point is discussed further below.

³The reader should avoid confusing the Dirac delta function $\delta(x - x_0)$ with the Kronecker delta $\delta_{i,j}$ encountered earlier. They are similar in that both vanish unless $x = x_0$ in the former and $i = j$ in the latter. But they differ in that the *value* of $\delta_{i,j}$ is definite (unity) while the value of $\delta(x_0 - x_0)$ is not defined. The Dirac delta function has definite value only in integrated expressions like Eq. (6-8). The spin functions α and β may be thought of as Dirac delta functions in the spin “coordinate” ω . The Dirac delta function is admittedly unusual, and one tends to be uneasy with it at first. This function is important and useful in quantum mechanics. However, since we will make almost no use of it in this text, we will not develop the topic further.

⁴Notice that Eq. (6-8) does not involve $\delta^*\delta$, but merely δ . Because δ is nonzero only at one point, $\delta^*\delta$ is likewise nonzero only at the same point. δ and $\delta^*\delta$ are therefore not independent functions. It is convenient to view the δ function as both the eigenfunction for the position operator and also as the probability distribution function for the particle.

6-6 The Postulate for Average Values

Suppose that we had somehow prepared a large number of hydrogen atoms so that they were all in the same, known, stationary state. Then we could measure the distance of the electron from the nucleus once in each atom and average these measurements to obtain an average value. We have already indicated that this average would be given by the sum of all the r values, each multiplied by its frequency of occurrence, which is given by $\psi^2 dv$ if ψ is normalized. Since r is a continuous variable, the sum becomes an integral. This is the content of

Postulate V *When a large number of identical systems have the same state function ψ , the expected average of measurements on the variable M (one measurement per system) is given by*

$$M_{av} = \int \psi^* \hat{M} \psi d\tau / \int \psi^* \psi d\tau \quad (6-9)$$

The denominator is unity if ψ is normalized.

It is important to understand the distinction between average value and eigenvalue as they relate to measurements. A good example is the dipole moment. The dipole moment operator for a system of n charged particles is $\mu = \sum_{i=1}^n z_i \mathbf{r}_i$ where z_i is the charge on the i th particle and \mathbf{r}_i is its position vector with respect to an arbitrary origin. (We get this by writing the classical formula and observing that momentum terms do not appear. Hence, the quantum-mechanical operator is the same as the classical expression.) What will the eigenfunctions and eigenvalues of $\hat{\mu}$ be like?

The charge z_i is only a number, while \mathbf{r}_i is a position operator, which has Dirac delta functions as eigenfunctions. For a hydrogen atom, one eigenfunction of r_i would be a delta function at $r = 1$ a.u., $\theta = 0$, $\phi = 0$. The corresponding eigenvalue for $\hat{\mu}$ would be the dipole moment obtained when a proton and an electron are separated by 1 a.u., clearly a finite number. But “everybody knows” that an unperturbed atom in a stationary state has zero dipole moment. The difficulty is resolved when we recognize that measurement of a variable in postulates IV and V means measuring the value of a variable at a given instant. Hence, we must distinguish between the *instantaneous dipole moment* of an atom, which can have any value from among the eigenvalues of $\hat{\mu}$ and the *average dipole moment*, which is zero for the atom. In everyday scientific discussion, the term “dipole moment” is usually understood to refer to the *average dipole moment*. Indeed, the usual measurements of dipole moment are measurements that effectively average over many molecules or long times (in atomic terms) or both.

6-7 Hermitian Operators

Let ϕ and ψ be any square-integrable functions and \hat{A} be an operator, all having the same domain. \hat{A} is defined to be hermitian if

$$\int \psi^* \hat{A} \phi dv = \int \phi \hat{A}^* \psi^* dv \quad (6-10)$$

The integration is over the entire range of each spatial coordinate. Recall that the asterisk signifies reversal of the sign of i in a complex or imaginary term. The hermitian property has important consequences in quantum chemistry.

As an example of a test of an operator by Eq. (6-10), let us take the ψ and ϕ to be square-integrable functions of x and \hat{A} to be $i(d/dx)$. Then the left-hand side of Eq. (6-10) becomes, upon integration by parts,

$$\int_{-\infty}^{+\infty} \psi^*(i d\phi/dx) dx = \cancel{i\psi^*\phi} \Big|_{-\infty}^{+\infty} - i \int_{-\infty}^{+\infty} (d\psi^*/dx)\phi dx = -i \int_{-\infty}^{+\infty} \phi(d\psi^*/dx) dx \quad (6-11)$$

Since ψ and ϕ are square integrable, they (and their product) must vanish at infinity, giving the zero term in Eq. (6-11). We now write out the right-hand side of Eq. (6-10):

$$\int_{-\infty}^{+\infty} \phi(i d/dx)^* \psi^* dx = -i \int_{-\infty}^{+\infty} \phi(d\psi^*/dx) dx \quad (6-12)$$

where the minus sign comes from carrying out the operation indicated by the asterisk. Equation (6-12) is equal to Eq. (6-11), and so the operator $i(d/dx)$ is hermitian. Since the effect of i was to introduce a necessary sign reversal, it is apparent that the equality would not result for $\hat{A} = d/dx$. Clearly, any hermitian operator involving a first derivative in any Cartesian coordinate must contain the factor i . The operators for linear momenta (Chapter 2) are examples of this.

It is important to realize that Eq. (6-10) does not imply that $\psi^* \hat{A} \phi = \phi \hat{A}^* \psi^*$. A simple example will make this clearer. Let \hat{A} be the hydrogen atom hamiltonian, $\hat{H} = -\frac{1}{2}\nabla^2 - 1/r$, and let ϕ be the 1s eigenfunction: $\phi = (1/\sqrt{\pi}) \exp(-r)$. Also, let $\psi = \sqrt{8/\pi} \exp(-2r)$ which is not an eigenfunction of \hat{H} . Then, since $\hat{H}\phi = -\frac{1}{2}\phi$,

$$\psi^* \hat{H} \phi = -\frac{1}{2} \psi^* \phi \quad (6-13)$$

But

$$\phi \hat{H}^* \psi^* = \phi \left[-\frac{1}{2}(1/r^2)(d/dr)r^2(d/dr) - 1/r \right] \sqrt{8/\pi} \exp(-2r) \quad (6-14)$$

$$= \phi [(1/r) - 2] \sqrt{8/\pi} \exp(-2r) = [(1/r) - 2] \psi^* \phi \quad (6-15)$$

(Since ψ has no θ or ϕ dependence, the parts of \hat{H}^* that include $\partial/\partial\theta$ and $\partial/\partial\phi$ have been omitted in Eq. (6-14).) Here we have two functions, $-\frac{1}{2}\psi^*\phi$ and $[(1/r) - 2]\psi^*\phi$. They are obviously different. However, by Eq. (6-10), their integrals are equal since \hat{H} is hermitian.

6-8 Proof That Eigenvalues of Hermitian Operators Are Real

Let \hat{A} be a hermitian operator with a square-integrable eigenfunction ψ . Then

$$\hat{A}\psi = a\psi \quad (6-16)$$

Each side of Eq. (6-16) must be expressible as a real and an imaginary part. The real parts must be equal to each other and so must the imaginary parts. Taking the complex

conjugate of Eq. (6-16) causes the imaginary parts to reverse sign, but they remain equal. Therefore, we may write

$$\hat{A}^* \psi^* = a^* \psi^* \quad (6-17)$$

We multiply Eq. (6-16) from the left by ψ^* and integrate over all spatial variables:

$$\int \psi^* \hat{A} \psi \, dv = a \int \psi^* \psi \, dv \quad (6-18)$$

Similarly, we multiply Eq. (6-17) from the left by ψ and integrate:

$$\int \psi \hat{A}^* \psi^* \, dv = a^* \int \psi \psi^* \, dv \quad (6-19)$$

Since \hat{A} is hermitian, the left-hand sides of Eqs. (6-18) and (6-19) are equal by definition (Eq. 6-10). Therefore, the right-hand sides are equal, and their difference is zero:

$$(a - a^*) \int \psi^* \psi \, dv = 0 \quad (6-20)$$

Since ψ is square integrable the integral cannot be zero. Therefore, $a - a^*$ is zero, which requires that a be real.

6-9 Proof That Nondegenerate Eigenfunctions of a Hermitian Operator Form an Orthogonal Set

Let ψ and ϕ be two square-integrable eigenfunctions of the hermitian operator \hat{A} :

$$\hat{A} \psi = a_1 \psi \quad (6-21)$$

$$\hat{A}^* \phi^* = a_2 \phi^* \quad (6-22)$$

Multiplying Eq. (6-21) from the left by ϕ^* and Eq. (6-22) from the left by ψ , and integrating gives

$$\int \phi^* \hat{A} \psi \, dv = a_1 \int \phi^* \psi \, dv \quad (6-23)$$

$$\int \psi \hat{A}^* \phi^* \, dv = a_2 \int \psi \phi^* \, dv \quad (6-24)$$

The left sides of Eqs. (6-23) and (6-24) are equal by (6-10), and

$$(a_1 - a_2) \int \phi^* \psi \, dv = 0. \quad (6-25)$$

If $a_1 \neq a_2$, the integral vanishes. This proves that nondegenerate eigenfunctions are orthogonal.

EXAMPLE 6-2 It has been shown (Section 6-7) that $i(d/dx)$ is a hermitian operator. We know that it has eigenfunctions $\exp(\pm ikx)$ with eigenvalues $\pm k$, which are real. So far, so good. However, this operator also has eigenfunctions $\exp(\pm kx)$, with eigenvalues $\pm ik$, which are imaginary. This appears to violate the proof that eigenvalues of hermitian operators are real. Explain why neither of these eigenfunction sets is covered by the proof of section 6-8, and how one of them manages to obey the rule anyway.

SOLUTION ► The test for Hermiticity requires that $i\psi^*\phi|_{-\infty}^{+\infty} = 0$. If ϕ is ψ , and if ψ is square-integrable, this condition is satisfied, because $\psi^*\psi$ vanishes at $\pm\infty$, giving $0 - 0 = 0$. But neither of the exponential functions given above is square-integrable: They are both unequal to zero at $\pm\infty$, so they both fall outside of the proof as given. Despite this, $\exp(\pm ikx)$ does have real eigenvalues, leading us to look more closely. Is it the case that $i\psi^*\psi|_{-\infty}^{+\infty} = 0$ for this set of functions, even though they do not vanish at infinity? It is indeed, since $\psi^*\psi = 1$, giving $i - i = 0$ for this term. Thus we see that our requirement that ψ be square integrable is more restrictive than what is necessary, namely that $i\psi^*\psi|_{-\infty}^{+\infty} = 0$. Note that the other set of exponentials, $\exp(\pm kx)$, leads to $i\psi^*\psi = i\exp(\pm 2kx)$, which does not produce a value of zero when values at $x = \infty$ and $x = -\infty$ are subtracted. Note also that the functions $\exp(\pm ikx)$ are orthogonal for different values of k , whereas the functions $\exp(\pm kx)$ are not. ◀

The point of the above example is that all of our proofs about eigenvalues or eigenfunctions of hermitian operators refer to cases where the eigenfunctions satisfy the requirement that $i\psi^*\psi|_{-\infty}^{+\infty} = 0$. Square-integrability guarantees this, but some nonsquare-integrable sets of functions can satisfy it too. A hermitian operator can have eigenfunctions that are associated with complex or imaginary eigenvalues, but these must result from eigenfunctions that do not satisfy the requirement.

6-10 Demonstration That All Eigenfunctions of a Hermitian Operator May Be Expressed as an Orthonormal Set

If $a_1 = a_2$, Eq. (6-25) is satisfied even when the integral is finite. Therefore, degenerate eigenfunctions need not be orthogonal. But they must be linearly independent or else they are the self-same function (to within a multiplicative constant), and if they are linearly independent, they can be converted to an orthogonal pair. Hence, it is always possible to express the *degenerate* eigenfunctions of a hermitian operator as an orthogonal set (and, as we have just proved, it is *necessary* that *nondegenerate* eigenfunctions be orthogonal). Furthermore, the functions must be square integrable, hence normalizable. In general, then, we are able to assume that all of the eigenfunctions of a hermitian operator can be expressed as an orthonormal set.

One way to orthogonalize two nonorthogonal, linearly independent functions (which may or may not be eigenfunctions) will now be demonstrated. Let the functions be ψ and ϕ (assumed normalized) and the integral of their product have the value S :

$$\int \psi^*\phi dv = S \quad (6-26)$$

We keep one of the functions unchanged, say ψ , and let $\phi' \equiv \phi - S\psi$ be our new second function. ψ and ϕ' are orthogonal since

$$\int \psi^* \phi' dv = \int \psi^* (\phi - S\psi) dv = \underbrace{\int \psi^* \phi dv}_S - S \underbrace{\int \psi^* \psi dv}_1 = 0 \quad (6-27)$$

(The new function ϕ' needs to be renormalized.) This process, known as *Schmidt orthogonalization*, may be generalized and applied sequentially to any number of linearly independent functions.

EXAMPLE 6-3 Two normalized $1s$ AOs are located on nearby nuclei, A and B , and overlap each other enough so that $\int 1s_A 1s_B dv = 0.500$. Construct a function from these two that is orthogonal to $1s_A$ and is normalized.

SOLUTION ▶ $1s'_B = 1s_B - 0.5 \cdot 1s_A$ is orthogonal to $1s_A$. It is not yet normalized because

$$\begin{aligned} \int (1s'_B)^2 dv &= \int (1s_B^2 + 0.25 \cdot 1s_A^2 - 2 \cdot 0.5 \cdot 1s_A 1s_B) dv \\ &= 1 + 0.25 - 2 \cdot 0.5 \cdot 0.5 = 0.75 = \frac{3}{4}. \end{aligned}$$

So the normalized function we seek is $\frac{2}{\sqrt{3}}(1s_B - 0.5 \cdot 1s_A)$. ◀

6-11 Proof That Commuting Operators Have Simultaneous Eigenfunctions

\hat{A} and \hat{B} are commuting operators if, for the general square-integrable function f , $\hat{A}\hat{B}f = \hat{B}\hat{A}f$. This can be written $(\hat{A}\hat{B} - \hat{B}\hat{A})f = 0$, which requires that $\hat{A}\hat{B} - \hat{B}\hat{A} = \hat{O}$. (\hat{O} is called the null operator. It satisfies the equation, $\hat{O}f = 0$.) This difference of operator products is called the *commutator* of \hat{A} and \hat{B} and is usually symbolized⁵ by $[\hat{A}, \hat{B}]$. If the commutator $[\hat{A}, \hat{B}]$ vanishes, then \hat{A} and \hat{B} commute.

We will now prove an important property of commuting operators, namely, that they have “simultaneous” eigenfunctions (i.e., that a set of eigenfunctions can be found for one of the operators that is also an eigenfunction set for the other operator). Let β_i be the eigenfunctions for \hat{B} : $\hat{B}\beta_i = b_i\beta_i$. For the moment, assume all the numbers b_i are different (i.e., the eigenfunctions β_i are nondegenerate). Let $[\hat{A}, \hat{B}] = \hat{O}$. Then

$$\hat{B}(\hat{A}\beta_i) = \hat{A}\hat{B}\beta_i = \hat{A}b_i\beta_i = b_i(\hat{A}\beta_i) \quad (6-28)$$

The parentheses emphasize that the function obtained by operating on β_i with \hat{A} is an eigenfunction of \hat{B} with eigenvalue b_i . But that function can only be a constant times β_i itself. Hence, for nondegenerate β_i we have that $\hat{A}\beta_i = c\beta_i$, and so β_i is an eigenfunction of \hat{A} . This proves that the nondegenerate eigenfunctions for one operator will also be eigenfunctions for any other operators that commute with it.

⁵Other less common conventions are $[\hat{A}, \hat{B}]_-$ and (\hat{A}, \hat{B}) .

If β_i is degenerate with other functions $\beta_{i,k}$, then we can only go so far as to say that $\hat{A}\beta_i = \sum_k c_k \beta_{i,k}$, for this general linear combination is an eigenfunction of \hat{B} having eigenvalue b_i . But if this is so, then β_i is evidently not necessarily an eigenfunction of \hat{A} . We shall not prove it here, but it is possible to show that one can always find *some* linear combinations of $\beta_{i,k}$ to produce a set of new functions, β'_i , that *are* eigenfunctions of \hat{A} (and remain eigenfunctions of \hat{B} as well). Therefore we can state that, if \hat{A} and \hat{B} commute, there exists a set of functions that are eigenfunctions for \hat{A} and \hat{B} simultaneously.

An example of this property occurred in the particle-in-a-ring system described in Chapter 2. The hamiltonian and angular momentum operators commute for that system. There we found one set of functions, the trigonometric functions, that are eigenfunctions for \hat{H} but not for \hat{L}_z . But by mixing the energy-degenerate sines and cosines we produced exponential functions that are eigenfunctions for both of these operators.

Another example concerns the familiar symmetry operations for reflection, rotation, etc. If one of these operations, symbolized \hat{R} , commutes with the hamiltonian, then we should expect there to be a set of eigenfunctions for \hat{H} that are simultaneously eigenfunctions for \hat{R} . It was proved in Chapter 2 that this means that nondegenerate eigenfunctions must be symmetric or antisymmetric with respect to \hat{R} .

A symmetry operator that leaves \hat{H} unchanged can be shown to commute with \hat{H} . That is, if $\hat{R}\hat{H} = \hat{H}\hat{R}$, then $\hat{R}\hat{H}f = \hat{H}\hat{R}f$, where f is any function. To show this, let \hat{R} be, say, a reflection operator. Then \hat{R} operates on functions and operators to its right by reflecting the appropriate coordinates: $\hat{R}f(q) = f(Rq)$. If \hat{H} is invariant under reflection \hat{R} , then $H(q) = H(Rq)$, and it follows that $\hat{R}\hat{H}(q)f(q) = \hat{H}(Rq)f(Rq) = \hat{H}(q)f(Rq) = \hat{H}(q)\hat{R}f(q)$, and so $\hat{R}\hat{H}f = \hat{H}\hat{R}f$. We shall formally develop the ramifications of symmetry in quantum chemistry in Chapter 13.

The existence of simultaneous eigenfunctions for various operators has important ramifications for the measurement of a system's properties. This is discussed in Section 6-15.

6-12 Completeness of Eigenfunctions of a Hermitian Operator

In Chapter 3 we discussed the concept of completeness in connection with the power series expansion of a function. Briefly, a series of functions⁶ $\{\phi\}$ having certain restrictions (e.g., all derivatives vary smoothly) is said to be complete if an arbitrary function f having the same restrictions can be expressed in terms of the series⁷

$$f = \sum_i c_i \phi_i \quad (6-29)$$

Proofs exist that certain hermitian operators corresponding to observable properties have eigenfunctions forming a complete set in the space of well-behaved (continuous,

⁶A symbol in braces is frequently employed to represent an entire set of functions.

⁷Equation (6-29) is overly restrictive in that it requires that the function and the series have identical values at every point, whereas it is possible for them to disagree at points of zero measure. However, at the level of this book, we can ignore this distinction and use Eq. (6-29) without encountering difficulty.

single-valued, square-integrable) functions. These proofs are difficult and will not be given here.⁸ Instead we shall introduce

Postulate VI *The eigenfunctions for any quantum mechanical operator corresponding to an observable variable constitute a complete set. (Furthermore, we have seen in Section 6-10 that we can assume that this set has been made orthonormal.)*

We will now use this property to investigate further the nature of the average value of an operator. Let the system be in some state ψ (normalized), not an eigenfunction of \hat{M} . However, \hat{M} possesses eigenfunctions $\{\mu\}$ that must form a complete set. Therefore, we can express ψ in terms of μ 's:

$$\psi = \sum_i c_i \mu_i \quad (6-30)$$

Now we calculate the average value of M for the state ψ :

$$\begin{aligned} M_{\text{av}} &= \int \psi^* \hat{M} \psi dv = \int \sum_i c_i^* \mu_i^* \hat{M} \sum_j c_j \mu_j dv \\ &= \sum_i \sum_j c_i^* c_j \int \mu_i^* \hat{M} \mu_j dv \end{aligned} \quad (6-31)$$

But $\hat{M} \mu_i = m_i \mu_i$, and so

$$M_{\text{av}} = \sum_i \sum_j c_i^* c_j \int \mu_i^* m_j \mu_j dv = \sum_i \sum_j c_i^* c_j m_j \int \mu_i^* \mu_j dv \quad (6-32)$$

But we are assuming that $\{\mu\}$ is an orthonormal set, and so

$$M_{\text{av}} = \sum_i \sum_j c_i^* c_j m_j \delta_{ij} = \sum_i c_i^* c_i m_i \quad (6-33)$$

What does this expression mean? Each measurement of the property corresponding to \hat{M} must give one of the eigenvalues m_i (postulate IV) and the average of many such measurements must be M_{av} . Equation (6-33) states how the individual measurements must be weighted to give the average, so it follows that each $c_i^* c_i$ is a measure of the relative frequency for observing the corresponding m_i . Putting it another way, the absolute squares of the mixing coefficients in Eq. (6-30) give the probabilities that a measurement of the variable M will give the corresponding eigenvalue. For example, if ψ happens to be equal to $(1/\sqrt{2})\mu_1 + (1/\sqrt{2})\mu_3$, it follows that $M_{\text{av}} = (1/2)m_1 + (1/2)m_3$.

EXAMPLE 6-4 What is the average value for the z -component of orbital angular momentum for the normalized function $\phi = (1/\sqrt{5})(\psi_{2s} + 2 \cdot \psi_{2p_{+1}})$?

SOLUTION ► Since we know that the $2s$ and $2p_{+1}$ eigenfunctions have z -components of angular momentum of 0 and +1 respectively, we can say at once that $\bar{p}_z = \frac{1}{5} \cdot 0 + \frac{4}{5} \cdot 1 = 0.8$ a.u. ◀

⁸Sec. e.g., Kemble [1, Section 25].

6-13 The Variation Principle

Many of the calculations of quantum chemistry are based on the Rayleigh-Ritz variation principle which states: *For any normalized, acceptable function ϕ ,*

$$H_{\text{av}} \equiv \int \phi^* \hat{H} \phi d\tau \geq E_0 \quad (6-34)$$

where E_0 is the lowest eigenvalue of \hat{H} .

This statement is easily proved. We expand ϕ in terms of $\{\psi_i\}$, the complete, orthonormal set of eigenfunctions of \hat{H} :

$$\phi = \sum_i c_i \psi_i \quad (6-35)$$

As in the preceding section, this leads to

$$\int \phi^* \hat{H} \phi d\tau = \sum_i c_i^* c_i E_i \quad (6-36)$$

Now $c_i^* c_i$ is never negative, and so Eq. (6-36) is merely a weighted average of the eigenvalues E_i . Such an average can never be lower than the lowest contributing member and the principle is proved.

The variation principle is sometimes stated in an equivalent way by saying that the average value of \hat{H} over ϕ is an *upper bound* for the lowest eigenvalue of \hat{H} . Following the approach of the example at the end of the previous section, if ϕ for a hydrogen atom happens to be a function equal to $(1/\sqrt{2})\psi_{1s} + (1/\sqrt{2})\psi_{2s}$, the average energy for ϕ is $(1/2)E_{1s} + (1/2)E_{2s}$, which obviously lies above the lowest eigenvalue E_{1s} .

6-14 The Pauli Exclusion Principle

We have already discussed the Pauli exclusion principle in Chapter 5. In its most general form, this is:

Postulate VII ψ must be antisymmetric (symmetric) for the exchange of identical fermions (bosons).

6-15 Measurement, Commutators, and Uncertainty

If we measure the exact position of the electron in a hydrogen atom, we force it into a state having a Dirac delta function as its wavefunction. Since this function is also an eigenfunction for the dipole moment operator, it follows that we also know the (instantaneous) dipole moment for the atom at that instant. In effect, measuring position measures dipole moment too. But the delta function is *not* an eigenfunction for the hamiltonian operator of the atom, and so we have *not* simultaneously measured the electronic energy of the atom.

We have earlier seen that an eigenfunction for one operator can serve also as eigenfunction for another operator when the operators commute. In the above example, the

operators for position and dipole moment commute with each other but not with the hamiltonian operator. This leads us to recognize that we can simultaneously measure values for two variables only if their operators commute.

Let us consider this situation more deeply by imagining two successive measurements on a hydrogen atom, one immediately following the other. If we first measure position and find $r = 2.0$ a.u., and then measure dipole moment, we will get the value ($\mu = 2.0$ a.u.) corresponding to the electron being at $r = 2.0$ a.u. That is where we found it in the first measurement, and it has not had time to move elsewhere before the second measurement. If we immediately follow with yet another position measurement, the electron will still be found at $r = 2$ a.u. (We are imagining that no time elapses between measurements, which is a limit we cannot actually achieve. In the present case, though, since measurement of r is also a measure of μ , both measurements are done at once, so this is really not a problem.) Hence, it makes sense to say that we know these two values "simultaneously." However, if we first measure position and then measure energy, we find something very different. Suppose that we find $r = 2$ a.u. and then, in a subsequent measurement, $E = -1/2$ a.u. (E must, after all, be an eigenvalue of \hat{H} , according to postulate IV.) We know that the eigenfunction during the first measurement was $\delta(r - 2 \text{ a.u.})$, and that during the second measurement was a 1s AO. If we immediately do yet another position measurement, we can find any value of r (with probabilities given by $4\pi r^2 \psi_{1s}^2 dr$). The processes of measuring position and energy are incompatible in the sense that there is no single function that can describe the situation that exists during both measurements. The energy-measuring process can be pictured as forcing a reconstruction of the wavefunction in such a manner that it no longer corresponds to a particular position, while measurement of position forces a state function that does not correspond to a particular energy. (In this case, separate measurements would really be necessary, so the impossibility of doing a second measurement truly immediately after the first must be recognized. Indeed, one has to allow for the fact that finding an electron in one place and then at some other place must imply a lapse of time permitting the electron to travel.)

The reader may suspect that there is some connection between commutators and the uncertainty principle, and this is indeed the case. It can be shown⁹ that the product of widths of simultaneous measurements (i.e., the uncertainty in their values) of two variables satisfies the relation

$$\Delta a \cdot \Delta b \geq \frac{1}{2} \left| \int \psi^* [\hat{A}, \hat{B}] \psi d\tau \right| \quad (6-37)$$

where ψ is normalized, and the absolute value $|X|$ is defined as the positive square root of X^*X . If A and B are conjugate variables, such as position and momentum, Eq. (6-37) becomes $\Delta a \cdot \Delta b \geq \hbar/2$, which is Heisenberg's uncertainty relation. If \hat{A} and \hat{B} commute, the right-hand side of Eq. (6-37) vanishes, and the values of both variables may, in theory, be simultaneously known exactly.

Among the properties of greatest interest in molecular quantum mechanics are energy, symmetry, and electron orbital angular momentum because, for many molecules, some of these operators commute. Thus, if we know that an oxygen molecule is in a nondegenerate stationary electronic state, we know that it is possible to characterize that state by a definite value of the orbital angular momentum along

⁹See Merzbacher [2, Section 10-5].

the internuclear axis. Also, we know that the wavefunction must be symmetric or antisymmetric for inversion through the molecular midpoint.

6-16 Time-Dependent States

Much of quantum chemistry is concerned with *stationary* states, for which Ψ is a product of a space term ψ (an eigenfunction of \hat{H}) and a time-dependent factor $\exp(-iEt/\hbar)$, which we usually ignore because it has no effect on particle probability distribution. Sometimes, however, it becomes necessary to consider time-dependent states. In this section we illustrate how some of these may be treated.

There are two types of situation to distinguish. One is situations where the potential is changing as a function of time, and hence the hamiltonian operator is time dependent. An example is a molecule or atom in a time-varying electromagnetic field. The other is situations where the potential and hamiltonian operator do not change with time, but the particle is nonetheless in a nonstationary state. An example is a particle that is known to have been forced into a nonstationary state by a measurement of its position. We deal here with the second category.

As our first example, consider a particle in a one-dimensional box with infinite walls. Suppose that we measure the particle's position and find it in the left side of the box (i.e., between $x = 0$ and $L/2$; we will be more specific shortly) at some instant that we take to be $t = 0$. We are interested in knowing what this implies about a future measurement of the particle's position.

Our knowing that the particle is on the left side at $t = 0$ means that the wavefunction for this state is *not* one of the time-independent box eigenfunctions we saw in Chapter 2, because those all predict equal probabilities for finding the particle on the two sides of the box. If the state function is not stationary, it must be time dependent, and it must satisfy Schrödinger's time-dependent equation (6-1). We have, then, that the state function is time dependent, and that $\Psi^*\Psi \equiv |\Psi|^2$ is zero everywhere on the right side of the box when $t = 0$. (We have not yet been specific enough to describe $|\Psi|^2$ in detail on the left side of the box.)

Schrödinger's time-dependent equation (6-1) is not an eigenvalue equation. However, Eq. (6-2) shows that Schrödinger's time-dependent equation is satisfied by time-independent eigenfunctions of \hat{H} if they are multiplied by their time-dependent factors $f(t) = \exp(-iEt/\hbar)$. Furthermore, Eq. (6-2) continues to be satisfied if the term $\psi(q)f(t)$ is replaced by a sum of such terms. (See Problem 6-9.) This means that we can seek to express the time-dependent state function, $\Psi(x, t)$, as a sum of time-independent box eigenfunctions as long as each of these is accompanied by its time factor $f(t)$. When $t = 0$, all the factors $f(t)$ equal unity, so at that point in time Ψ becomes the same as the sum of box eigenfunctions without their time factors.

Our strategy, then, is to find a linear combination of time-independent box eigenfunctions, ψ_n , that describe Ψ when $t = 0$. This is easy to do because the time factors are all equal to unity. Once we have found the proper mixture of ψ_n , we multiply each by its time factor and then observe the behavior of $|\Psi|^2$ as t increases.

In the case of our particle-in-a-box example, we can start with a very simple approximation to ψ at $t = 0$ by taking a 50–50 mixture of ψ_1 and ψ_2 :

$$\Psi(x, t) = (1/\sqrt{2}) [\psi_1 \exp(-iE_1t/\hbar) + \psi_2 \exp(-iE_2t/\hbar)] \quad (6-38)$$

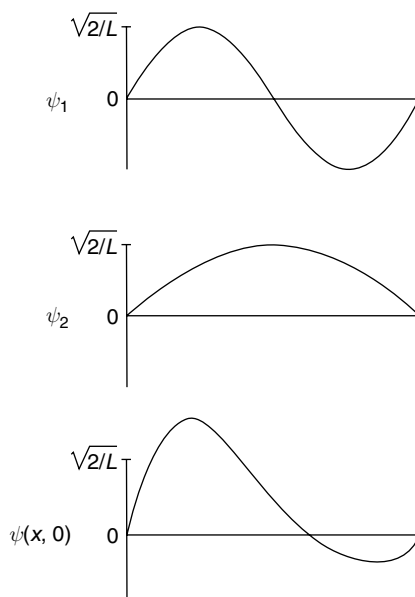


Figure 6-1 ▶ Stationary eigenfunctions ($n = 1, 2$) for the particle in a box and their normalized sum.

We have included the functions $f(t)$, even though they equal unity when $t = 0$, because they are needed to make $\Psi(x, t)$ a solution to Schrödinger's equation (6-1) and because they will inform us of the nature of Ψ at later times.

We choose this pair of functions because, when $t = 0$, both are positive on the left, but they differ in sign on the right, giving us some cancellation there. (See Fig. 6-1.) Obviously, we have not succeeded in describing a function that has no probability density on the right, but we already have a definite imbalance in that direction. (It is not difficult to see that some ψ_3 with a positive coefficient should help remove much of the remaining probability density on the right.)

Now we are in a position to examine this $|\Psi|^2$ as time progresses—the *time evolution of the square of a wavepacket* that describes the probability distribution for a particle that is known to have been in the left half of the box at $t = 0$. This is mathematically straightforward (Problem 6-20) and leads to the probability distributions sketched in Fig. 6-2 after time steps of Δt . The figure shows a changing distribution suggestive of the particle bouncing back and forth in the box with a cycle time of $8\Delta t$. It is not difficult to see why this happens. Ψ_1 and Ψ_2 have different “frequency factors” $\exp(-iE_n t/\hbar)$, so they behave like two waves oscillating at different frequencies. Since $E_2 = 4E_1$ (recall $E \propto n^2$ in the box), Ψ_2 oscillates four times faster than Ψ_1 . This means that, by the time Ψ_1 has made half a cycle (and is equal to -1 times its starting coordinates), Ψ_2 has made two cycles and is just as it was at $t = 0$. It is easy to see from Fig. 6-1 that this will give a Ψ that is skewed to the *right*, leading to the distribution shown in Fig. 6-2(e). (This allows us to conclude that $4\Delta t$ equals $1/2$ of the cycle time of Ψ_1 . See Problem 6-21.)

If we want a more accurate starting representation for the localized particle, we must mix together a larger number of stationary-state wavefunctions. In order to decide how much of each is needed, we must have a better-defined description of Ψ at $t = 0$.

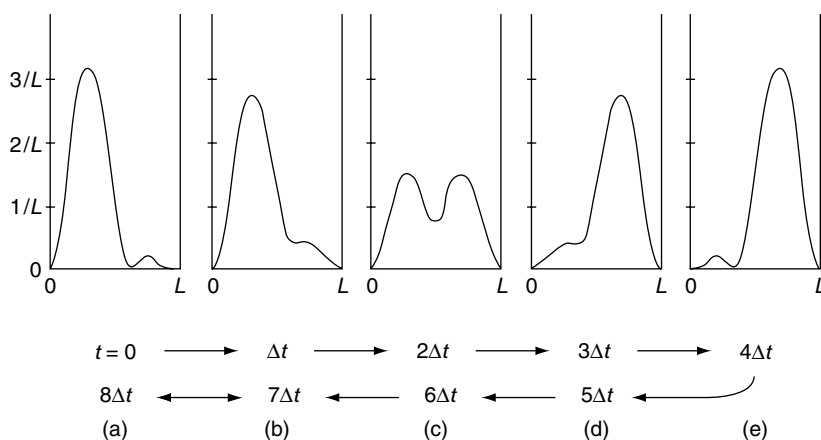


Figure 6-2 ▶ $|\Psi(x, t)|^2$ from Eq. (6-38) as it appears at various times.

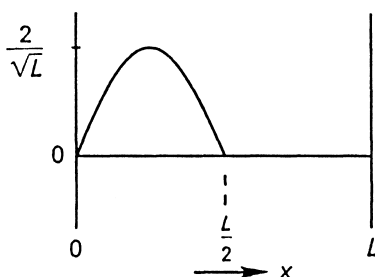


Figure 6-3 ▶ A normalized half sine wave in the left half of a “box.” The numbers at left are values of Ψ , not of E .

Suppose, for instance, we choose to describe the starting wavefunction $\Psi(x, 0)$ as a normalized half sine wave in the left side of the box and zero at the right (Fig. 6-3). Then we can calculate the amount (c_n) of each of the stationary-state functions ψ_n present in this function as follows:

$$c_n = \int_0^L \psi_n \Psi(x, 0) dx \quad (6-39)$$

This follows from the completeness¹⁰ and orthonormality of $\{\psi_n\}$. (See Problem 6-4.) Evaluation of Eq. (6-39) for the first few terms gives (Problem 6-22)

$$\Psi(x, t) = 0.600\psi_1 + 0.707\psi_2 + 0.360\psi_3 + 0.000\psi_4 + 0.086\psi_5 + \dots \quad (6-40)$$

This modifies slightly our earlier commonsense combination and also verifies our prediction that ψ_3 times a positive coefficient would be beneficial.

¹⁰Because $\Psi(x, 0)$ has a discontinuous derivative at the midpoint of the box, it falls outside the class for which $\{\psi_n\}$ is complete. However, because this problem is restricted to dx around one point, it should have little effect.

This example illustrates the basic approach to such problems:

1. Find a function that represents the initial particle distribution $\Psi(x, 0)$.
2. Expand that function as a series of eigenfunctions for the hamiltonian, and include the time-dependent factor for each term.
3. Evaluate the probability distribution at other times t by examining $|\Psi(x, t)|^2$.

As a second example, suppose one were considering the behavior of the electronic state immediately after a tritium atom emits a beta particle to become a helium ion: ${}^3_1\text{H} \rightarrow {}^3_2\text{He} + {}^0_{-1}e$. A crude analysis could be attempted by imagining that the nuclear charge suddenly changes from 1 to 2 a.u., and the orbiting electron (not the beta particle) suddenly finds itself in a state (the original 1s state) that is not an eigenfunction for the new hamiltonian. We would accordingly set $\Psi(t=0)$ to be the 1s AO of hydrogen and expand this in terms of He^+ eigenfunctions. Only s-type AOs could contribute because of symmetry. The coefficients are given by

$$c_n = \int^{\text{allspace}} \psi_{1s}(Z=1)\psi_{ns}(Z=2)dv \quad (6-41)$$

and the time-dependent wavefunction is (in a.u.)

$$\begin{aligned} \Psi(r, \theta, \phi, t) = & c_1 \psi_{1s}(Z=2) \exp(-2it) + c_2 \psi_{2s}(Z=2) \exp(-it/2) \\ & + c_3 \psi_{3s}(Z=2) \exp(-2it/9) + \dots \end{aligned} \quad (6-42)$$

This function could be evaluated at various times t and would be found to give an oscillating spherical distribution, as though the electron cloud were shrinking, then rebounding to its original distance, then shrinking again, etc.

Our next example is perhaps the most important: It is a particle initially localized in some region of space, say by measurement of its position, and free to move anywhere thereafter. Taking the one-dimensional case, we imagine that the particle has been detected around $x=0$ at $t=0$ (the measurement caused it to be “unfree” for an instant). We assume that the average momentum of the particle is zero. We seek to know how the probability distribution function for the particle will evolve in time.

As before, we need a functional description of the wavefunction at $t=0$, $\Psi(x, 0)$. We will then expand that in terms of eigenfunctions of the free-particle hamiltonian. As we have seen in Section 2-5, the free-particle eigenfunctions may be written $\exp(\pm i\sqrt{2mE}x/\hbar)$, where E is any nonnegative number. These are also eigenfunctions for the momentum operator, with eigenvalues $\sqrt{2mE}\hbar$.

The function usually selected to describe $\Psi(x, 0)$ is a gaussian function:

$$\Psi(x, 0) = \left(\frac{4\alpha/\pi}{\sqrt{2\alpha/\pi}}\right) \exp(-\alpha x^2) \quad (6-43)$$

The constant α affects the width of the gaussian and reflects our degree of certainty in our knowledge of position. Large α gives a tight function and small uncertainty Δx . The relationship between the gaussian function in x and the coefficients of the eigenfunctions as a function of $\sqrt{2mE}/\hbar$ is depicted in Fig. 6-4. Remarkably, the coefficient values are also described by a gaussian function (in $\sqrt{2mE}/\hbar$). Furthermore, the tighter the gaussian function is in x , the broader the corresponding gaussian function

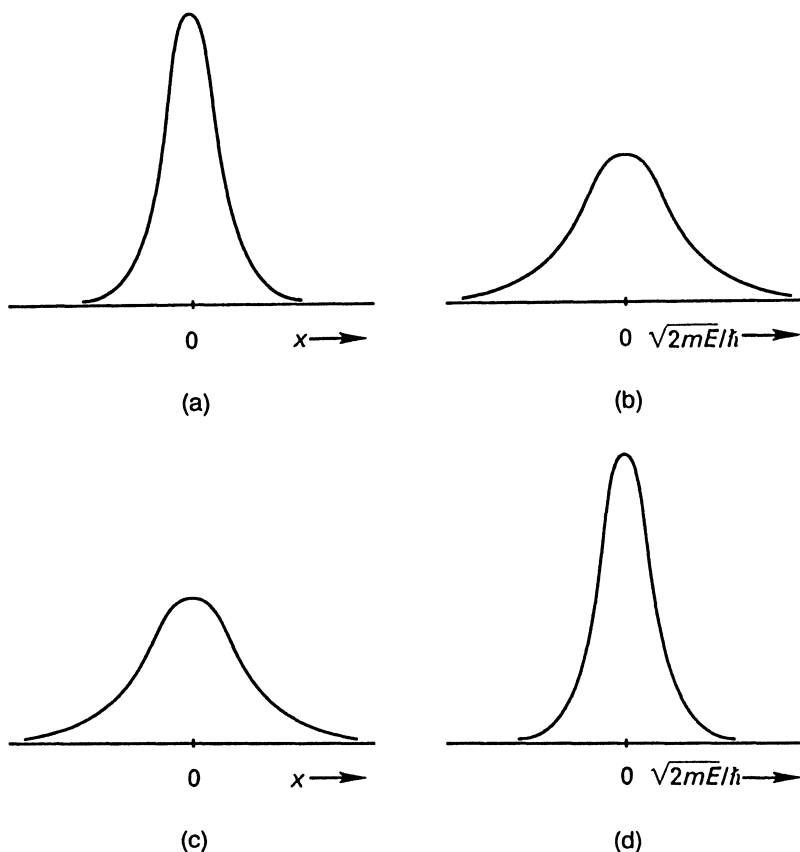


Figure 6-4 ▶ (a and c) Gaussian wave packets describing particles found to be at $x = 0$ with differing degrees of certainty. (b and d) Values of c_k (where $k = \sqrt{2mE}/\hbar$) for momentum eigenfunctions that combine to express the gaussian wave packets to their left. (a, b) corresponds to relatively certain position and relatively uncertain momentum, whereas (c, d) corresponds to the opposite situation.

is in $\sqrt{2mE}/\hbar$ (Problem 6-24). That is, we need to combine free-particle eigenfunction contributions from a wider range of momenta to create a tighter position function. This means that greater certainty in position goes with greater uncertainty in momentum, in accord with the uncertainty principle.

Once we have the appropriate mixture of momentum eigenfunctions, each with its time-dependent term, we can follow the time evolution of the particle wave packet. We find that the packet spreads out more and more about $x = 0$ as time passes, which means that our knowledge of position is decreasing as time passes. Even though the average position is not changing, the probability for finding the particle at a distance from $x = 0$ is increasing.

We can interpret this by remembering that the square of the wavefunction predicts the results of many experiments. In each of many position measurements finding the particle near $x = 0$, we impart some degree of momentum to the particle. Then, in a second measurement, we find that some of the particles have moved away from $x = 0$. The longer we wait before taking the second measurement, the greater this spread in x values. (Our assumption of zero *average* momentum amounts to saying that large deviations from zero momentum are equally likely for motion toward $x = +\infty$

and $-\infty$.) The more precise our first position measurement is, the greater the likelihood of introducing momenta quite different from zero and the more rapidly the wave packet spreads out as time passes.

In the first example, a packet located in half of a one-dimensional box, we saw $|\Psi|^2$ oscillate back and forth, changing shape in the process so that the motion cannot be described with a single frequency. A related important case is that of an oscillator moving in a harmonic potential. Let us assume the oscillator's position at $t = 0$ to be described by a gaussian wavefunction. If this function is *not* centered at the oscillator's equilibrium position, we have a time dependent situation analogous to the above particle-in-a-box case. For a harmonic potential, it can be shown¹¹ that $|\Psi|^2$ remains a gaussian function as time passes (i.e., does *not* change shape), and that the center of this gaussian oscillates back-and-forth about the equilibrium position with the classical frequency. This is a situation of interest to spectroscopists because it bears on the process of electronically exciting a sample of diatomic molecules. Suppose the molecules are initially in their ground electronic and ground vibrational states. Then their vibrational wavefunction is a simple gaussian function (the lowest-energy harmonic oscillator wavefunction) centered at R_e (i.e., *not* off-center). If the molecules are excited by a laser pulse to a new electronic state having an equilibrium internuclear distance of R'_e , the vibrational wavefunction at $t = 0$ is still the simple gaussian centered at R_e , which means that it is now off-center. As time passes, the center of this function oscillates back and forth about R'_e in a coherent manner (i.e., describable with a single frequency). Thus, we have gone from an initial state describing an ensemble of molecules vibrating about R_e with zero-point energy $h\nu/2$ and with *random* phases (i.e., a time-independent state wherein such measurable properties as average molecular dipole moment appear to be constant) to a final state where the molecules are vibrating *in phase* about R'_e (a time-dependent state, wherein one might expect to see time variation of such properties). If R_e were quite a bit smaller than R'_e , for instance, then almost all the molecules would find themselves to be "too short" at $t = 0$, "too long" a short time later, etc., as they swing in phase about R'_e . As a result of this simple behavior, it is possible to take advantage of it and time a second laser pulse to strike the molecules when they are almost all at their shortest, or all at their longest, extension. Of course, in real molecules the potential is not exactly harmonic. Furthermore, phase coherence is eventually lost due to collisions. So the second pulse must come very soon after the first one.

6-17 Summary

Some of the postulates and proofs described in this chapter are most important for what follows in this book, and we list these points here.

1. ψ describes a state as completely as possible and must meet certain mathematical requirements (single-valued, etc.). $\psi^*\psi$ is the probability density distribution function for the system.
2. For any observable variable, there is an operator (hermitian) which is constructed from the classical expression according to a simple recipe. (Operators related to

¹¹See Schiff [3, pp. 67, 68], and Tanner [4].

“spin” are the exception because the classical analog does not exist.) The eigenvalues for such an operator are the possible values we can measure for that quantity. The act of measuring the quantity forces the system into a state described by an eigenfunction of the operator. Once in that state, we may know exact values for other quantities only if their operators commute with the operator associated with our measurement.

3. If the hamiltonian operator for a system is time independent, stationary eigenfunctions exist of the form $\psi(q, \omega) \exp(-iEt/\hbar)$. The time-dependent exponential does not affect the measurable properties of a system in this state and is almost always completely ignored in any time-independent problem.
4. The formula for the quantum-mechanical average value [Eq. (6-9)] is equivalent to the arithmetic average of all the possible measured values of a property times their frequency of occurrence [Eq. (6-33)]. This means that it is impossible to devise a function that satisfies the general conditions on ψ and leads to an average energy lower than the lowest eigenvalue of \hat{H} .
5. The square-integrable eigenfunctions for an operator corresponding to an observable quantity form a complete set, which may be assumed orthonormal. The eigenvalues are all real.
6. Any operation that leaves \hat{H} unchanged also commutes with \hat{H} .
7. Wavefunctions describing time-dependent states are solutions to Schrödinger's time-dependent equation. The absolute square of such a wavefunction gives a particle distribution function that depends on time. The time evolution of this particle distribution function is the quantum-mechanical equivalent of the classical concept of a trajectory. It is often convenient to express the time-dependent wave packet as a linear combination of eigenfunctions of the time-independent hamiltonian multiplied by their time-dependent phase factors.

6-17.A Problems

- 6-1. Prove that d^2/dx^2 is hermitian.
- 6-2. Integrate the expressions in Eqs. (6-13) and (6-15) to show that their integrals are equal.
- 6-3. Prove that, if a normalized function is expanded in terms of an orthonormal set of functions, the sum of the absolute squares of the expansion coefficients is unity.
- 6-4. Show that a particular coefficient c_k in Eq. (6-30) is given by $c_k = \int \mu_k^* \psi dv$.
- 6-5. A particle in a ring is in a state with wavefunction $\psi = 1/\sqrt{\pi} \cos(2\phi)$.
 - a) Calculate the average value for the angular momentum by evaluating $\int \psi^* \hat{L}_z \psi d\phi$, where $\hat{L}_z = (\hbar/i) d/d\phi$. (Use symmetry arguments to evaluate the integral.)
 - b) Express ψ as a linear combination of exponentials and evaluate the average value of the angular momentum using the formula $L_{z,av} = \sum_i c_i^* c_i L_{zi}$ where L_{zi} is the eigenvalue for the i th exponential function.

- 6-6.** Using Eq. (6-37), show that $\Delta x \cdot \Delta p_x \geq \hbar/2$.
- 6-7.** What condition must the function ϕ satisfy for the *equality* part of \geq to hold in Eq. (6-34)?
- 6-8.** Suppose you had an operator and a set of eigenfunctions for it that were associated with real eigenvalues. Does it necessarily follow that the operator is hermitian as defined by Eq. (6-10)? [Hint: Consider d/dr and the set of all functions $\exp(-ar)$, where a is real and positive definite.]
- 6-9.** a) Show that the nonstationary state having wavefunction

$$\Psi = (1/\sqrt{2})\psi_{1s} \exp(it/2) + (1/\sqrt{2})\psi_{2p_0} \exp(it/8)$$

is a solution to Schrödinger's time-dependent equation when $\hat{\mathcal{H}}$ is the time-independent \hat{H} of the hydrogen atom. Use atomic units (i.e., $\hbar = 1$).

- b) This time-dependent state is dipolar and oscillates with a characteristic frequency ν . Show that ν satisfies the relation $E_2 - E_1 \equiv \Delta E = 2\pi\nu$ in a.u. (The dipole oscillates at the same frequency as that of light required to drive the $1s \longleftrightarrow 2p$ transition. This is central to the subject of spectroscopy.)
- 6-10.** From the definition that $\phi' = \phi - S\psi$ [see the discussion following Eq. (6-26)], evaluate the normalizing constant for ϕ' , assuming that ϕ and ψ are normalized.
- 6-11.** Given the two normalized *nonorthogonal* functions $(1/\sqrt{\pi})\exp(-r)$ and $\sqrt{1/3\pi}r\exp(-r)$, construct a new function ϕ that is orthogonal to the first function and lies within the function space spanned by these two functions, *and is normalized*.
- 6-12.** If the hydrogen atom $1s$ AO is expanded in terms of the He^+ AOs, what is the coefficient for (a) the He^+ $1s$ AO? (b) the He^+ $2p_0$ AO?
- 6-13.** The lowest-energy eigenfunction for the one-dimensional harmonic oscillator is $\psi_{n=0} = (\beta/\pi)^{1/4} \exp(-\beta x^2/2)$.
- a) Demonstrate whether or not momentum is a constant of motion (i.e., is a "sharp" quantity) for this state.
- b) Calculate the *average* momentum for this state.
- 6-14.** Demonstrate whether $x^2 d/dx$ and $x d^2/dx^2$ commute. What about $x d/dx$ and $x^2 d^2/dx^2$?
- 6-15.** Evaluate the following integrals over all space. In neither case should you need to do this by brute force.
- a) $\int (3d_{xy}) \hat{L}^2 (3d_{xy}) dv$
- b) $\int (3d_{xy}) \hat{L}_z (3d_{xy}) dv$

- 6-16.** The operators for energy and angular momentum for an electron constrained to move in a ring of constant potential are, respectively, in a.u. $-(1/2)d^2/d\phi^2$ and $(1/i)d/d\phi$.
- Discuss whether or not there should be a set of functions that are simultaneously eigenfunctions for both operators.
 - Discuss whether or not there is a set of functions that are eigenfunctions for one of these operators but not the other.
 - Discuss whether it is reasonable to expect these two physical quantities to be exactly knowable simultaneously or whether the uncertainty principle makes this impossible.
- 6-17.** Suppose a hydrogen atom state was approximated by the function $\phi = (1/\sqrt{3})1s + (1/\sqrt{3})2s + (1/\sqrt{3})3s$, where $1s$, $2s$, and $3s$ are normalized eigenfunctions for the hydrogen atom hamiltonian. What would be the average value of energy associated with this function, in a.u.?
- 6-18.** A function f is defined as follows: $f = 0.1 \cdot 1s + 0.2 \cdot 2p_1 + 0.3 \cdot 3d_2$, where $1s$ is the normalized eigenfunction for the $1s$ state of the hydrogen atom, etc. Evaluate the average value of the z component of angular momentum in a.u. for this function.
- 6-19.** Without looking back at the text, prove that (a) eigenvalues of hermitian operators are real, (b) nondegenerate eigenfunctions of hermitian operators are orthogonal, (c) nondegenerate eigenfunctions of \hat{A} must be eigenfunctions of \hat{B} if \hat{A} and \hat{B} commute.
- 6-20.** Using Eq. (6-38), obtain an expression for $|\Psi|^2$ as a function of x and t .
- 6-21.** Evaluate Δt of Fig. 6-2 in terms of m , h , and L .
- 6-22.** Verify the values of the coefficients in Eq. (6-40). How can you tell from simple inspection that (a) c_2 will be largest and positive, (b) c_4 will be zero, (c) c_i will tend toward small values at large i ?
- 6-23.** a) Evaluate the first *two* coefficients in Eq. (6-42).
b) What *qualitative* difference would you expect between Ψ of Eq. (6-42) and one that takes explicit account of the changing potential resulting as the beta particle travels away from the nucleus?
- 6-24.** Show by qualitative arguments based on mathematical functions why coefficients c_k should drop off more rapidly with k if the position wave packet is broader.
 $c_k = \int (\sqrt{2\alpha/\pi}) \exp(-\alpha x^2) \exp(ikx) dx$.
- 6-25.** a) Prove that, if V is real and $\Psi(x, y, z, t)$ satisfies Schrödinger's time-dependent equation, then $\Psi(x, y, z, -t)^*$ is also a solution. (This is called "invariance under time reversal.")
b) Show that, for *stationary* states, invariance under time reversal means that $\hat{H}\psi^* = E\psi^*$ if $\hat{H}\psi = E\psi$ and if V is real.
c) Show from (b) that nondegenerate eigenfunctions of \hat{H} (with real V) must be real.

- d) What becomes of the $2p_{-1}$ AO (with time dependence included) upon complex conjugation and time reversal? the $2p_0$ AO?
- e) Can the statement in (c) be reworded to say that all degenerate eigenfunctions of \hat{H} (with real V) must be complex?

Multiple Choice Questions

(Try to answer these without referring to the text.)

- Which one of the following statements about the eigenfunctions of a time-independent Hamiltonian operator is true?
 - Any linear combination of these eigenfunctions is also an eigenfunction for \hat{H} .
 - The state function for this system must be one of these eigenfunctions.
 - The eigenvalues associated with these eigenfunctions must all be real.
 - These eigenfunctions must all be orthogonal to one another.
 - These eigenfunctions have no time dependence.
- A hydrogen atom is in a nonstationary state having the wavefunction $\frac{1}{2}\{\psi_{1s} \exp(it/2\hbar) + \psi_{2s} \exp(it/8\hbar) + \psi_{2p_0} \exp(it/8\hbar) + \psi_{2p_{+1}} \exp(it/8\hbar)\}$. Which statement is true at any time t ?
 - A measurement of the energy has a 25% chance of giving -0.5 a.u.
 - The average value of the z component of angular momentum is 0.5 a.u.
 - The average energy is $-\frac{7}{8}$ a.u.
 - A measurement of the total angular momentum has a 75% chance of giving $\sqrt{2}$ a.u.
 - None of the above statements is true.
- The function $r \exp(-0.3r^2) \cos \theta$ is expanded in terms of hydrogen atom wavefunctions. This series may have finite contributions from bound-state eigenfunctions
 - of all types: s , p_x , p_y , p_z , d_{xy} , d_{yz} , etc.
 - of all types except s .
 - of types p_x , p_y , p_z only.
 - of type p_z only.
 - of types p_z and d_{z^2} only.

References

- [1] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics with Elementary Applications*. Dover, New York, 1958.
- [2] E. Merzbacher, *Quantum Mechanics*, 3rd ed. Wiley, New York, 1998.
- [3] L. I. Schiff, *Quantum Mechanics*, 3rd ed. McGraw-Hill, New York, 1968.
- [4] J. J. Tanner, *J. Chem. Ed.*, **67**, 917 (1990).