pretty much fill the box, so our knowledge of the electron’s position is of limited accuracy. If we write $\Delta x$ for the range of uncertainty in our knowledge of its position, then $\Delta x$ is roughly the same as the length of the box:

$$\Delta x \approx L$$

If we wish to know its position more accurately, we can certainly squeeze it into a smaller space by reducing $L$, but this has an unintended side-effect. A standing wave is really a superposition of two traveling waves going in opposite directions. The equation $p = h/\lambda$ really only gives the magnitude of the momentum vector, not its direction, so we should really interpret the wave as a 50/50 mixture of a right-going wave with momentum $p = h/\lambda$ and a left-going one with momentum $p = -h/\lambda$. The uncertainty in our knowledge of the electron’s momentum is $\Delta p = 2h/\lambda$, covering the range between these two values. Even if we make sure the electron is in the ground state, whose wavelength $\lambda = 2L$ is the longest possible, we have an uncertainty in momentum of $\Delta p = h/L$. In general, we find

$$\Delta p \gtrsim h/L,$$

with equality for the ground state and inequality for the higher-energy states. Thus if we reduce $L$ to improve our knowledge of the electron’s position, we do so at the cost of knowing less about its momentum. This trade-off is neatly summarized by multiplying the two equations to give

$$\Delta p \Delta x \gtrsim h.$$

Although we have derived this in the special case of a particle in a box, it is an example of a principle of more general validity:

**The Heisenberg uncertainty principle**

It is not possible, even in principle, to know the momentum and the position of a particle simultaneously and with perfect accuracy. The uncertainties in these two quantities are always such that $\Delta p \Delta x \gtrsim h$.

(This approximation can be made into a strict inequality, $\Delta p \Delta x > h/4\pi$, but only with more careful definitions, which we will not bother with.)

Note that although I encouraged you to think of this derivation in terms of a specific real-world system, the quantum dot, no reference was ever made to any specific laboratory equipment or procedures. The argument is simply that we cannot know the particle’s position very accurately unless it has a very well defined position, it cannot have a very well defined position unless its wave-pattern covers only a very small amount of space, and its wave-pattern cannot be thus compressed without giving it a short wavelength and a correspondingly uncertain momentum. The uncertainty principle is therefore a restriction on how much there is to know about
a particle, not just on what we can know about it with a certain technique.

An estimate for electrons in atoms

A typical energy for an electron in an atom is on the order of \((1\ \text{volt}) \cdot e\), which corresponds to a speed of about 1% of the speed of light. If a typical atom has a size on the order of 0.1 nm, how close are the electrons to the limit imposed by the uncertainty principle?

If we assume the electron moves in all directions with equal probability, the uncertainty in its momentum is roughly twice its typical momentum. This is only an order-of-magnitude estimate, so we take \(\Delta p\) to be the same as a typical momentum:

\[
\Delta p \Delta x = p_{\text{typical}} \Delta x = (m_{\text{electron}})(0.01c)(0.1 \times 10^{-9}\ \text{m}) = 3 \times 10^{-34}\ \text{J} \cdot\text{s}
\]

This is on the same order of magnitude as Planck’s constant, so evidently the electron is “right up against the wall.” (The fact that it is somewhat less than \(h\) is of no concern since this was only an estimate, and we have not stated the uncertainty principle in its most exact form.)

self-check F

If we were to apply the uncertainty principle to human-scale objects, what would be the significance of the small numerical value of Planck’s constant?

Discussion Questions

A Compare \(\Delta p\) and \(\Delta x\) for the two lowest energy levels of the one-dimensional particle in a box, and discuss how this relates to the uncertainty principle.

B On a graph of \(\Delta p\) versus \(\Delta x\), sketch the regions that are allowed and forbidden by the Heisenberg uncertainty principle. Interpret the graph: Where does an atom lie on it? An elephant? Can either \(p\) or \(x\) be measured with perfect accuracy if we don’t care about the other?

13.3.5 Electrons in electric fields

So far the only electron wave patterns we’ve considered have been simple sine waves, but whenever an electron finds itself in an electric field, it must have a more complicated wave pattern. Let’s consider the example of an electron being accelerated by the electron gun at the back of a TV tube. Newton’s laws are not useful, because they implicitly assume that the path taken by the particle is a meaningful concept. Conservation of energy is still valid in quantum physics, however. In terms of energy, the electron is moving from a region of low voltage into a region of higher voltage. Since
An electron in a gentle electric field gradually shortens its wavelength as it gains energy. (As discussed on p. 894, it is actually not quite correct to graph the wavefunction of an electron as a real number unless it is a standing wave, which isn’t the case here.)

The wavefunction as a whole does not have a single well-defined wavelength, but the wave changes so gradually that if you only look at a small part of it you can still pick out a wavelength and relate it to the momentum and energy. (The picture actually exaggerates by many orders of magnitude the rate at which the wavelength changes.)

But what if the electric field was stronger? The electric field in an old-fashioned vacuum tube TV screen is only \( \sim 10^5 \) N/C, but the electric field within an atom is more like \( 10^{12} \) N/C. In figure 1, the wavelength changes so rapidly that there is nothing that looks like a sine wave at all. We could get a rough idea of the wavelength in a given region by measuring the distance between two peaks, but that would only be a rough approximation. Suppose we want to know the wavelength at point \( P \). The trick is to construct a sine wave, like the one shown with the dashed line, which matches the curvature of the actual wavefunction as closely as possible near \( P \). The sine wave that matches as well as possible is called the “osculating” curve, from a Latin word meaning “to kiss.” The wavelength of the osculating curve is the wavelength that will relate correctly to conservation of energy.

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Tunneling

We implicitly assumed that the particle-in-a-box wavefunction would cut off abruptly at the sides of the box, k/1, but that would be unphysical. A kink has infinite curvature, and curvature is related to energy, so it can’t be infinite. A physically realistic wavefunction must always “tail off” gradually, k/2. In classical physics, a particle can never enter a region in which its interaction energy \( U \) would be greater than the amount of energy it has available. But in quantum
physics the wavefunction will always have a tail that reaches into the classically forbidden region. If it was not for this effect, called tunneling, the fusion reactions that power the sun would not occur due to the high electrical energy nuclei need in order to get close together! Tunneling is discussed in more detail in the following subsection.

13.3.6 The Schrödinger equation

In subsection 13.3.5 we were able to apply conservation of energy to an electron’s wavefunction, but only by using the clumsy graphical technique of osculating sine waves as a measure of the wave’s curvature. You have learned a more convenient measure of curvature in calculus: the second derivative. To relate the two approaches, we take the second derivative of a sine wave:

\[
\frac{d^2}{dx^2} \sin(\frac{2\pi x}{\lambda}) = \frac{d}{dx} \left( \frac{2\pi}{\lambda} \cos \left( \frac{2\pi x}{\lambda} \right) \right) = - \left( \frac{2\pi}{\lambda} \right)^2 \sin \left( \frac{2\pi x}{\lambda} \right)
\]

Taking the second derivative gives us back the same function, but with a minus sign and a constant out in front that is related to the wavelength. We can thus relate the second derivative to the osculating wavelength:

\[
\frac{d^2}{dx^2} \Psi = - \left( \frac{2\pi}{\lambda} \right)^2 \Psi
\]

This could be solved for \( \lambda \) in terms of \( \Psi \), but it will turn out below to be more convenient to leave it in this form.

Applying this to conservation of energy, we have

\[
E = K + U = \frac{p^2}{2m} + U = \frac{(h/\lambda)^2}{2m} + U
\]

Note that both equation [1] and equation [2] have \( \lambda^2 \) in the denominator. We can simplify our algebra by multiplying both sides of equation [2] by \( \Psi \) to make it look more like equation [1]:
Further simplification is achieved by using the symbol $\hbar$ ($\hbar$ with a slash through it, read “h-bar”) as an abbreviation for $\hbar/2\pi$. We then have the important result known as the **Schrödinger equation**:  

$$E \cdot \Psi = -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + U \cdot \Psi$$

(Actually this is a simplified version of the Schrödinger equation, applying only to standing waves in one dimension.) Physically it is a statement of conservation of energy. The total energy $E$ must be constant, so the equation tells us that a change in interaction energy $U$ must be accompanied by a change in the curvature of the wavefunction. This change in curvature relates to a change in wavelength, which corresponds to a change in momentum and kinetic energy.

**Self-check G**

Considering the assumptions that were made in deriving the Schrödinger equation, would it be correct to apply it to a photon? To an electron moving at relativistic speeds?  

$\triangleright$ Answer, p. 1063

Usually we know right off the bat how $U$ depends on $x$, so the basic mathematical problem of quantum physics is to find a function $\Psi(x)$ that satisfies the Schrödinger equation for a given interaction-energy function $U(x)$. An equation, such as the Schrödinger equation, that specifies a relationship between a function and its derivatives is known as a differential equation.

The detailed study of the solution of the Schrödinger equation is beyond the scope of this book, but we can gain some important insights by considering the easiest version of the Schrödinger equation, in which the interaction energy $U$ is constant. We can then rearrange the Schrödinger equation as follows:

$$\frac{d^2 \Psi}{dx^2} = \frac{2m(U - E)}{\hbar^2} \Psi,$$

which boils down to

$$\frac{d^2 \Psi}{dx^2} = a \Psi,$$
where, according to our assumptions, \( a \) is independent of \( x \). We need to find a function whose second derivative is the same as the original function except for a multiplicative constant. The only functions with this property are sine waves and exponentials:

\[
\frac{d^2}{dx^2} [ q \sin(rx + s) ] = -qr^2 \sin(rx + s)
\]

\[
\frac{d^2}{dx^2} [ q e^{rx+s} ] = qr^2 e^{rx+s}
\]

The sine wave gives negative values of \( a \), \( a = -r^2 \), and the exponential gives positive ones, \( a = r^2 \). The former applies to the classically allowed region with \( U < E \).

This leads us to a quantitative calculation of the tunneling effect discussed briefly in the preceding subsection. The wavefunction evidently tails off exponentially in the classically forbidden region. Suppose, as shown in figure m, a wave-particle traveling to the right encounters a barrier that it is classically forbidden to enter. Although the form of the Schrödinger equation we’re using technically does not apply to traveling waves (because it makes no reference to time), it turns out that we can still use it to make a reasonable calculation of the probability that the particle will make it through the barrier. If we let the barrier’s width be \( w \), then the ratio of the wavefunction on the left side of the barrier to the wavefunction on the right is

\[
\frac{qe^{rx+s}}{qe^{r(x+w)+s}} = e^{-rw}.
\]

Probabilities are proportional to the squares of wavefunctions, so
the probability of making it through the barrier is

\[ P = e^{-2rw} \]

\[ = \exp \left( -\frac{2w}{\hbar} \sqrt{2m(U - E)} \right). \]

**Self-check H**

If we were to apply this equation to find the probability that a person can walk through a wall, what would the small value of Planck’s constant imply?

---

**Tunneling in alpha decay**  
*Example 17*

Naively, we would expect alpha decay to be a very fast process. The typical speeds of neutrons and protons inside a nucleus are extremely high (see problem 20). If we imagine an alpha particle coalescing out of neutrons and protons inside the nucleus, then at the typical speeds we’re talking about, it takes a ridiculously small amount of time for them to reach the surface and try to escape. Clattering back and forth inside the nucleus, we could imagine them making a vast number of these “escape attempts” every second.

Consider figure n, however, which shows the interaction energy for an alpha particle escaping from a nucleus. The electrical energy is \( kq_1q_2/r \) when the alpha is outside the nucleus, while its variation inside the nucleus has the shape of a parabola, as a consequence of the shell theorem. The nuclear energy is constant when the alpha is inside the nucleus, because the forces from all the neighboring neutrons and protons cancel out; it rises sharply near the surface, and flattens out to zero over a distance of \( \sim 1 \text{ fm} \), which is the maximum distance scale at which the strong force can operate. There is a classically forbidden region immediately outside the nucleus, so the alpha particle can only escape by quantum mechanical tunneling. (It’s true, but somewhat counterintuitive, that a repulsive electrical force can make it more difficult for the alpha to get out.)

In reality, alpha-decay half-lives are often extremely long — sometimes billions of years — because the tunneling probability is so small. Although the shape of the barrier is not a rectangle, the equation for the tunneling probability on page 907 can still be used as a rough guide to our thinking. Essentially the tunneling probability is so small because \( U - E \) is fairly big, typically about 30 MeV at the peak of the barrier.

---

**The correspondence principle for \( E > U \)**  
*Example 18*

The correspondence principle demands that in the classical limit \( \hbar \to 0 \), we recover the correct result for a particle encountering a barrier \( U \), for both \( E < U \) and \( E > U \). The \( E < U \) case was analyzed in self-check H on p. 907. In the remainder of this example, we analyze \( E > U \), which turns out to be a little trickier.
A particle encounters a step of height $U < E$ in the interaction energy. Both sides are classically allowed. A reflected wave exists, but is not shown in the figure.

The marble has zero probability of being reflected from the edge of the table. (This example has $U < 0$, not $U > 0$ as in figures o and q).

We can simplify things a little by letting the width $w$ of the barrier go to infinity. Classically, after all, there is no possibility that the particle will turn around, no matter how wide the barrier. We then have the situation shown in figure o.\(^6\)

The analysis is similar to that for any other wave being partially reflected at the boundary between two regions where its velocity differs, and the result is the same as the one found on p. 381. (There are some technical differences, which don’t turn out to matter. This is discussed in more detail on p. 970.) The ratio of the amplitude of the reflected wave to that of the incident wave is $R = (v_2 - v_1)/(v_2 + v_1)$. The probability of reflection is $R^2$.

(Counterintuitively, $R^2$ is nonzero even if $U < 0$, i.e., $v_2 > v_1$.)

This seems to violate the correspondence principle. There is no $m$ or $h$ anywhere in the result, so we seem to have the result that, even classically, the marble in figure p can be reflected!

The solution to this paradox is that the step in figure o was taken to be completely abrupt — an idealized mathematical discontinuity. Suppose we make the transition a little more gradual, as in figure q. As shown in problem 17 on p. 395, this reduces the amplitude with which a wave is reflected. By smoothing out the step more and more, we continue to reduce the probability of reflection, until finally we arrive at a barrier shaped like a smooth ramp. More detailed calculations show that this results in zero reflection in the limit where the width of the ramp is large compared to the wavelength.

Beta decay: a push or pull on the way out the door example 19

The nucleus $^{64}$Cu undergoes $\beta^+$ and $\beta^-$ decay with similar probabilities and energies. Each of these decays releases a fixed amount of energy $Q$ due to the difference in mass between the parent nucleus and the decay products. This energy is shared randomly between the beta and the neutrino. In experiments, the beta’s energy is easily measured, while the neutrino flies off without interacting. Figure r shows the energy spectrum of the $\beta^+$ and

---

\(^6\)As in several previous examples, we cheat by representing a traveling wave as a real-valued function. See pp. 894 and 970.
There is a relatively high probability for the beta and neutrino each to carry off roughly half the kinetic energy, the reason being identical to the kind of phase-space argument discussed in sec. 5.4.2, p. 328. Therefore in each case we get a bell-shaped curve stretching from 0 up to the energy $Q$, with $Q$ being slightly different in the two cases.

So we expect the two bell curves to look almost the same except for a slight rescaling of the horizontal axis. Yes — but we also see markedly different behavior at low energies. At very low energies, there is almost no chance to see a $\beta^+$ with very low energy, but quite a high probability for a $\beta^-$. We could try to explain this difference in terms of the release of electrical energy. The $\beta^+$ is repelled by the nucleus, so it gets an extra push on the way out the door. A $\beta^-$ should be held back as it exits, and so should lose some energy. The bell curves should be shifted up and down in energy relative to one another, as observed.

But if we try to estimate this energy shift using classical physics, we come out with a wildly incorrect answer. This would be a process in which the beta and neutrino are released in a point-like event inside the nucleus. The radius $r$ of the $^{64}$Cu nucleus is on the order of 4 fm ($1 \text{ fm} = 10^{-15} \text{ m}$). Therefore the energy lost or gained by the $\beta^+$ or $\beta^-$ on the way out would be $U \sim kZe^2/r \sim 10 \text{ MeV}$. The actual shift is much smaller.

To understand what’s really going on, we need quantum mechanics. A beta in the observed energy range has a wavelength of about 2000 fm, which is hundreds of times greater than the size of the nucleus. Therefore the beta cannot be much better localized than that when it is emitted. This means that we should really use something more like $r \sim 500 \text{ fm}$ (a quarter of a wavelength) in our calculation of the electrical energy. This gives $U \sim 0.08 \text{ MeV}$, which is about the right order of magnitude compared to observation.

A byproduct of this analysis is that a $\beta^+$ is always emitted within the classically forbidden region, and then has to tunnel out through the barrier. As in example 17, we have the counterintuitive fact about quantum mechanics that a repulsive force can hinder the escape of a particle.

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7Redrawn from Cook and Langer, 1948.
Three dimensions

For simplicity, we’ve been considering the Schrödinger equation in one dimension, so that \( \Psi \) is only a function of \( x \), and has units of \( m^{-1/2} \) rather than \( m^{-3/2} \). Since the Schrödinger equation is a statement of conservation of energy, and energy is a scalar, the generalization to three dimensions isn’t particularly complicated. The total energy term \( E \cdot \Psi \) and the interaction energy term \( U \cdot \Psi \) involve nothing but scalars, and don’t need to be changed at all. In the kinetic energy term, however, we’re essentially basing our computation of the kinetic energy on the squared magnitude of the momentum, \( p_x^2 \), and in three dimensions this would clearly have to be generalized to \( p_x^2 + p_y^2 + p_z^2 \). The obvious way to achieve this is to replace the second derivative \( \frac{d^2 \Psi}{dx^2} \) with the sum \( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \). Here the partial derivative symbol \( \partial \), introduced on page 220, indicates that when differentiating with respect to a particular variable, the other variables are to be considered as constants. This operation on the function \( \Psi \) is notated \( \nabla^2 \Psi \), and the derivative-like operator \( \nabla^2 = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \) is called the Laplacian, and was introduced briefly on p. 655. It occurs elsewhere in physics. For example, in classical electrostatics, the voltage in a region of vacuum must be a solution of the equation \( \nabla^2 V = 0 \). Like the second derivative, the Laplacian is essentially a measure of curvature. Or, as shown in figure s, we can think of it as a measure of how much the value of a function at a certain point differs from the average of its value on nearby points.

Examples of the Laplacian in two dimensions

\( \nabla^2 A > 0 \)

A. Compute the Laplacians of the following functions in two dimensions, and interpret them: \( A = x^2 + y^2 \), \( B = -x^2 - y^2 \), \( C = x^2 - y^2 \).

The first derivative of function \( A \) with respect to \( x \) is \( \frac{\partial A}{\partial x} = 2x \). Since \( y \) is treated as a constant in the computation of the partial derivative \( \partial / \partial x \), the second term goes away. The second derivative of \( A \) with respect to \( x \) is \( \frac{\partial^2 A}{\partial x^2} = 2 \). Similarly we have \( \frac{\partial^2 A}{\partial y^2} = 2 \), so \( \nabla^2 A = 4 \).

All derivative operators, including \( \nabla^2 \), have the linear property that multiplying the input function by a constant just multiplies the output function by the same constant. Since \( B = -A \), and we have \( \nabla^2 B = -4 \).

For function \( C \), the \( x \) term contributes a second derivative of 2, but the \( y \) term contributes \( -2 \), so \( \nabla^2 C = 0 \).

The interpretation of the positive sign in \( \nabla^2 A = 4 \) is that \( A \)'s graph is shaped like a trophy cup, and the cup is concave up. \( \nabla^2 B = -4 \) is because \( B \) is concave down. Function \( C \) is shaped like a saddle. Since its curvature along one axis is concave up, but the curvature along the other is down and equal in magnitude, the
function is considered to have zero concavity over all.

**A classically allowed region with constant \( U \) example 21**

In a classically allowed region with constant \( U \), we expect the solutions to the Schrödinger equation to be sine waves. A sine wave in three dimensions has the form

\[
Ψ = \sin (k_x x + k_y y + k_z z).
\]

When we compute \( \partial^2 Ψ / \partial x^2 \), double differentiation of \( \sin \) gives \( -\sin \), and the chain rule brings out a factor of \( k^2 \). Applying all three second derivative operators, we get

\[
\nabla^2 Ψ = \left( -k_x^2 - k_y^2 - k_z^2 \right) \sin (k_x x + k_y y + k_z z)
= - \left( k_x^2 + k_y^2 + k_z^2 \right) Ψ.
\]

The Schrödinger equation gives

\[
E \cdot Ψ = -\frac{ℏ^2}{2m} \nabla^2 Ψ + U \cdot Ψ
= -\frac{ℏ^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right) Ψ + U \cdot Ψ
\]

\[
E - U = \frac{ℏ^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right)
\]

which can be satisfied since we’re in a classically allowed region with \( E - U > 0 \), and the right-hand side is manifestly positive.

**Use of complex numbers**

In a classically forbidden region, a particle’s total energy, \( U + K \), is less than its \( U \), so its \( K \) must be negative. If we want to keep believing in the equation \( K = p^2 / 2m \), then apparently the momentum of the particle is the square root of a negative number. This is a symptom of the fact that the Schrödinger equation fails to describe all of nature unless the wavefunction and various other quantities are allowed to be complex numbers. In particular it is not possible to describe traveling waves correctly without using complex wavefunctions. Complex numbers were reviewed in subsection 10.5.5, p. 625.

This may seem like nonsense, since real numbers are the only ones that are, well, real! Quantum mechanics can always be related to the real world, however, because its structure is such that the results of measurements always come out to be real numbers. For example, we may describe an electron as having non-real momentum in classically forbidden regions, but its average momentum will always come out to be real (the imaginary parts average out to zero), and it can never transfer a non-real quantity of momentum to another particle.
1. Oscillations can go back and forth, but it’s also possible for them to move along a path that bites its own tail, like a circle. Photons act like one, electrons like the other.

2. Back-and-forth oscillations can naturally be described by a segment taken from the real number line, and we visualize the corresponding type of wave as a sine wave. Oscillations around a closed path relate more naturally to the complex number system. The complex number system has rotation built into its structure, e.g., the sequence 1, \(i\), \(i^2\), \(i^3\), \ldots\) rotates around the unit circle in 90-degree increments.

3. The double slit experiment embodies the one and only mystery of quantum physics. Either type of wave can undergo double-slit interference.

A complete investigation of these issues is beyond the scope of this book, and this is why we have normally limited ourselves to standing waves, which can be described with real-valued wavefunctions. Figure t gives a visual depiction of the difference between real and complex wavefunctions. The following remarks may also be helpful.

Neither of the graphs in t/2 should be interpreted as a path traveled by something. This isn’t anything mystical about quantum physics. It’s just an ordinary fact about waves, which we first encountered in subsection 6.1.1, p. 354, where we saw the distinction between the motion of a wave and the motion of a wave pattern. In both examples in t/2, the wave pattern is moving in a straight line to the right.

The helical graph in t/2 shows a complex wavefunction whose value rotates around a circle in the complex plane with a frequency \(f\) related to its energy by \(E = hf\). As it does so, its squared magnitude \(|\Psi|^2\) stays the same, so the corresponding probability stays constant. Which direction does it rotate? This direction is purely a matter of convention, since the distinction between the symbols \(i\) and \(-i\) is arbitrary — both are equally valid as square roots of \(-1\). We can,
for example, arbitrarily say that electrons with positive energies have wavefunctions whose phases rotate counterclockwise, and as long as we follow that rule consistently within a given calculation, everything will work. Note that it is not possible to define anything like a right-hand rule here, because the complex plane shown in the right-hand side of t/2 doesn’t represent two dimensions of physical space; unlike a screw going into a piece of wood, an electron doesn’t have a direction of rotation that depends on its direction of travel.

Superposition of complex wavefunctions example 22

The right side of figure t/3 is a cartoonish representation of double-slit interference; it depicts the situation at the center, where symmetry guarantees that the interference is constructive. Suppose that at some off-center point, the two wavefunctions being superposed are $\Psi_1 = b$ and $\Psi_2 = bi$, where $b$ is a real number with units. Compare the probability of finding the electron at this position with what it would have been if the superposition had been purely constructive, $b + b = 2b$.

The probability per unit volume is proportional to the square of the magnitude of the total wavefunction, so we have

$$\frac{P_{\text{off center}}}{P_{\text{center}}} = \frac{|b + bi|^2}{|b + b|^2} = \frac{1^2 + 1^2}{2^2 + 0^2} = \frac{1}{2}.$$

Figure u shows a method for visualizing complex wavefunctions. The idea is to use colors to represent complex numbers, according to the arbitrary convention defined in figure u/1. Brightness indicates magnitude, and the rainbow hue shows the argument. Because this representation can’t be understood in a black and white printed book, the figure is also reproduced on the back cover of printed copies. To avoid any confusion, note that the use of rainbow colors does not mean that we are representing actual visible light. In fact, we will be using these visual conventions to represent the wavefunctions of a material particle such as an electron. It is arbitrary that we use red for positive real numbers and blue-green for negative numbers, and that we pick a handedness for the diagram such that going from red toward yellow means going counterclockwise. Although physically the rainbow is a linear spectrum, we are not representing physical colors here, and we are exploiting the fact that the human brain tends to perceive color as a circle rather than a line, with violet and red being perceptually similar. One of the limitations of this representation is that brightness is limited, so we can’t represent complex numbers with arbitrarily large magnitudes.

Figure u/2 shows a traveling wave as it propagates to the right. The standard convention in physics is that for a wave moving in a certain direction, the phase in the forward direction is farther counterclockwise in the complex plane, and you can verify for yourself
1. A representation of complex numbers using color and brightness. 2. A wave traveling toward the right. 3. A wave traveling toward the left. 4. A standing wave formed by superposition of waves 2 and 3. 5. A two-dimensional standing wave. 6. A double-slit diffraction pattern.

that this is the case by comparing with the convention defined by u/1. The function being plotted here is $\Psi = e^{ikx}$, where $k = \frac{2\pi}{\lambda}$ is the spatial analog of frequency, with an extra factor of $2\pi$ for convenience. For the use of the complex exponential, see sec. 10.5.6, p.627; it simply represents a point on the unit circle in the complex plane. The wavelength $\lambda$ is a constant and can be measured, for example, from one yellow point to the next. The wavelength is not different at different points on the figure, because we are using the colors merely as a visual encoding of the complex numbers — so, for example, a red point on the figure is not a point where the wave has a longer wavelength than it does at a blue point.

Figure u/3 represents a wave traveling to the left.

Figure u/4 shows a standing wave created by superimposing the traveling waves from u/2 and u/3, $\Psi_4 = (\Psi_2 + \Psi_3)/2$. (The reason for the factor of 2 is simply that otherwise some portions of $\Psi_4$ would have magnitudes too great to be represented using the available range of brightness.) All points on this wave have real values, represented by red and blue-green. We made the superposition real by an appropriate choice of the phases of $\Psi_2$ and $\Psi_3$. This is always possible to do when we have a standing wave, but it is only possible for a standing wave, and this is the reason for all of the disclaimers in the captions of previous figures in which I took the liberty of representing a traveling wave as a sine-wave graph.

Figure u/5 shows a two-dimensional standing wave of a particle in a box, and u/6 shows a double-slit interference pattern. (In the latter, I’ve cheated by making the amplitude of the wave on the
right-hand half of the picture much greater than it would actually be.)

\begin{flushleft}
A paradox resolved example 23
\end{flushleft}

Consider the following paradox. Suppose we have an electron that is traveling wave, and its wavefunction looks like a wave-train consisting of 5 cycles of a sine wave. Call the distance between the leading and trailing edges of the wave-train \( L \), so that \( \lambda = \frac{L}{5} \). By sketching the wave, you can easily check that there are 11 points where its value equals zero. Therefore at a particular moment in time, there are 11 points where a detector has zero probability of detecting the electron.

But now consider how this would look in a frame of reference where the electron is moving more slowly, at one fifth of the speed we saw in the original frame. In this frame, \( L \) is the same, but \( \lambda \) is five times greater, because \( \lambda = \frac{\hbar}{p} \). Therefore in this frame we see only one cycle in the wave-train. Now there are only 3 points where the probability of detection is zero. But how can this be? All observers, regardless of their frames of reference, should agree on whether a particular detector detects the electron.

The resolution to this paradox is that it starts from the assumption that we can depict a traveling wave as a real-valued sine wave, which is zero in certain places. Actually, we can’t. It has to be a complex number with a rotating phase angle in the complex plane, as in figure u/2, and a constant magnitude.

\textit{Linearity of the Schrödinger equation}

Some mathematical relationships and operations are \textit{linear}, and some are not. For example, \( 2 \times (3+2) \) is the same as \( 2 \times 3 + 2 \times 2 \), but \( \sqrt{1 + 1} \neq \sqrt{1} + \sqrt{1} \). Differentiation is a linear operation, \( (f + g)' = f' + g' \). The Schrödinger equation is built out of derivatives, so it is linear as well. That is, if \( \Psi_1 \) and \( \Psi_2 \) are both solutions of the Schrödinger equation, then so is \( \Psi_1 + \Psi_2 \). Linearity normally implies linearity with respect both to addition and to multiplication by a scalar. For example, if \( \Psi \) is a solution, then so is \( \Psi + \Psi + \Psi \), which is the same as \( 3\Psi \).

Linearity guarantees that the phase of a wavefunction makes no difference as to its validity as a solution to the Schrödinger equation. If \( \sin kx \) is a solution, then so is the sine wave \( -\sin kx \) with the opposite phase. This fact is logically interdependent with the fact that, as discussed on p. 894, the phase of a wavefunction is unobservable. For measuring devices and humans are material objects that can be described by wavefunctions. So suppose, for example, that we flip the phase of all the particles inside the entire laboratory. By linearity, the evolution of this measurement process is still a valid solution of the Schrödinger equation.

The Schrödinger equation is a wave equation, and its linearity
implies that the waves obey the principle of superposition. In most cases in nature, we find that the principle of superposition for waves is at best an approximation. For example, if the amplitude of a tsunami is so huge that the trough of the wave reaches all the way down to the ocean floor, exposing the rocks and sand as it passes overhead, then clearly there is no way to double the amplitude of the wave and still get something that obeys the laws of physics. Even at less extreme amplitudes, superposition is only an approximation for water waves, and so for example it is only approximately true that when two sets of ripples intersect on the surface of a pond, they pass through without “seeing” each other.

It is therefore natural to ask whether the apparent linearity of the Schrödinger equation is only an approximation to some more precise, nonlinear theory. This is not currently believed to be the case. If we are to make sense of Schrödinger’s cat (sec. 13.2.4, p. 885), then the experimenter who sees a live cat and the one who sees a dead cat must remain oblivious to their other selves, like the ripples on the pond that intersect without “seeing” each other. Attempts to create slightly nonlinear versions of standard quantum mechanics have been shown to have implausible physical properties, such as allowing the propagation of signals faster than $c$. (This is known as Gisin’s theorem. The original paper, “Weinberg’s non-linear quantum mechanics and supraluminal communications,” is surprisingly readable and nonmathematical.)

If you have had a course in linear algebra, then it is worth noting that the linearity of the Schrödinger equation allows us to talk about its solutions as vectors in a vector space. For example, if $\Psi_1$ represents an unstable nucleus that has not yet gamma decayed, and $\Psi_2$ is its state after the decay, then any superposition $\alpha \Psi_1 + \beta \Psi_2$, with real or complex coefficients $\alpha$ and $\beta$, is a possible wavefunction, and we can notate this as a vector, $\langle \alpha, \beta \rangle$, in a two-dimensional vector space.

**Discussion Questions**

A The zero level of interaction energy $U$ is arbitrary, e.g., it’s equally valid to pick the zero of gravitational energy to be on the floor of your lab or at the ceiling. Suppose we’re doing the double-slit experiment, t/3, with electrons. We define the zero-level of $U$ so that the total energy $E = U + K$ of each electron is positive. and we observe a certain interference pattern like the one in figure i on p. 878. What happens if we then redefine the zero-level of $U$ so that the electrons have $E < 0$?
The top panel of the figure shows a series of snapshots in the motion of two pulses on a coil spring, one negative and one positive, as they move toward one another and superpose. The final image is very close to the moment at which the two pulses cancel completely. The following discussion is simpler if we consider infinite sine waves rather than pulses. How can the cancellation of two such mechanical waves be reconciled with conservation of energy? What about the case of colliding electromagnetic waves?

Quantum-mechanically, the issue isn’t conservation of energy, it’s conservation of probability, i.e., if there’s initially a 100% probability that a particle exists somewhere, we don’t want the probability to be more than or less than 100% at some later time. What happens when the colliding waves have real-valued wavefunctions $\Psi$? Now consider the sketches of complex-valued wave pulses shown in the bottom panel of the figure as they are getting ready to collide.

The figure shows a skateboarder tipping over into a swimming pool with zero initial kinetic energy. There is no friction, the corners are smooth enough to allow the skater to pass over the smoothly, and the vertical distances are small enough so that negligible time is required for the vertical parts of the motion. The pool is divided into a deep end and a shallow end. Their widths are equal. The deep end is four times deeper. (1) Classically, compare the skater’s velocity in the left and right regions, and infer the probability of finding the skater in either of the two halves if an observer peeks at a random moment. (2) Quantum-mechanically, this could be a one-dimensional model of an electron shared between two atoms in a diatomic molecule. Compare the electron’s kinetic energies, momenta, and wavelengths in the two sides. For simplicity, let’s assume that there is no tunneling into the classically forbidden regions. What is the simplest standing-wave pattern that you can draw, and what are the probabilities of finding the electron in one side or the other? Does this obey the correspondence principle?
13.4 The atom

You can learn a lot by taking a car engine apart, but you will have learned a lot more if you can put it all back together again and make it run. Half the job of reductionism is to break nature down into its smallest parts and understand the rules those parts obey. The second half is to show how those parts go together, and that is our goal in this chapter. We have seen how certain features of all atoms can be explained on a generic basis in terms of the properties of bound states, but this kind of argument clearly cannot tell us any details of the behavior of an atom or explain why one atom acts differently from another.

The biggest embarrassment for reductionists is that the job of putting things back together job is usually much harder than the taking them apart. Seventy years after the fundamentals of atomic physics were solved, it is only beginning to be possible to calculate accurately the properties of atoms that have many electrons. Systems consisting of many atoms are even harder. Supercomputer manufacturers point to the folding of large protein molecules as a process whose calculation is just barely feasible with their fastest machines. The goal of this chapter is to give a gentle and visually oriented guide to some of the simpler results about atoms.

13.4.1 Classifying states

We’ll focus our attention first on the simplest atom, hydrogen, with one proton and one electron. We know in advance a little of what we should expect for the structure of this atom. Since the electron is bound to the proton by electrical forces, it should display a set of discrete energy states, each corresponding to a certain standing wave pattern. We need to understand what states there are and what their properties are.
What properties should we use to classify the states? The most sensible approach is to use conserved quantities. Energy is one conserved quantity, and we already know to expect each state to have a specific energy. It turns out, however, that energy alone is not sufficient. Different standing wave patterns of the atom can have the same energy.

Momentum is also a conserved quantity, but it is not particularly appropriate for classifying the states of the electron in a hydrogen atom. The reason is that the force between the electron and the proton results in the continual exchange of momentum between them. (Why wasn’t this a problem for energy as well? Kinetic energy and momentum are related by $K = p^2/2m$, so the much more massive proton never has very much kinetic energy. We are making an approximation by assuming all the kinetic energy is in the electron, but it is quite a good approximation.)

Angular momentum does help with classification. There is no transfer of angular momentum between the proton and the electron, since the force between them is a center-to-center force, producing no torque.

Like energy, angular momentum is quantized in quantum physics. As an example, consider a quantum wave-particle confined to a circle, like a wave in a circular moat surrounding a castle. A sine wave in such a “quantum moat” cannot have any old wavelength, because an integer number of wavelengths must fit around the circumference, $C$, of the moat. The larger this integer is, the shorter the wavelength, and a shorter wavelength relates to greater momentum and angular momentum. Since this integer is related to angular momentum, we use the symbol $\ell$ for it:

$$\lambda = C/\ell$$

The angular momentum is

$$L = rp.$$ 

Here, $r = C/2\pi$, and $p = h/\lambda = h\ell/C$, so

$$L = \frac{C}{2\pi} \cdot \frac{h\ell}{C} = \frac{h\ell}{2\pi}.$$ 

In the example of the quantum moat, angular momentum is quantized in units of $h/2\pi$. This makes $h/2\pi$ a pretty important number, so we define the abbreviation $\hbar = h/2\pi$. This symbol is read “h-bar.”

In fact, this is a completely general fact in quantum physics, not just a fact about the quantum moat:
Quantization of angular momentum

The angular momentum of a particle due to its motion through space is quantized in units of $\hbar$.

**self-check I**

What is the angular momentum of the wavefunction shown at the beginning of the section?  

**Degeneracy**

Comparing the oversimplified figure a/1 with the more realistic depiction in a/2 using complex numbers, we see that there is a direction of rotation, which was drawn as counterclockwise in the figure. As in figures u/2 and u/3 on p. 914, we could have drawn the clockwise version by putting the rainbow colors in the opposite order, i.e., by letting the phase spin in the opposite direction in the complex plane. This feature was hidden in a/1, where in order to get a depiction using real numbers, we had to use a standing wave. A standing wave, however, can be constructed as a superposition of two traveling waves, so the issue was still there, just hidden. We really have *two* quantum-mechanical states here, regardless of whether we use standing waves or traveling waves. If we use standing waves, they are of the form $\sin 8\theta$ and $\cos 8\theta$, while in terms of the traveling waves we have $e^{8i\theta}$ and $e^{-8i\theta}$. By Euler’s formula (sec. 10.5.6, p. 627), either traveling wave can be expressed as a superposition of the two standing waves, and vice versa. (Physically, there are not four different states here but two. The situation is a bit like choosing a Cartesian coordinate system in the plane, where we could choose one coordinate system $(x, y)$, or some other coordinates system $(x', y')$ rotated with respect to the first one; but this does not mean there are four coordinates needed to describe a plane.)

These two states are simplified models of states in an atom, so it’s worth thinking about how we could tell, for a real atom, whether the electron had angular momentum in one direction or the other. One technique would be to look at absorption or emission spectra of thin gases, as in example 13 on p. 898. But this only distinguishes states according to their energies, and since these two states have the same kinetic energy, that would not necessarily help. In quantum mechanics, when we have more than one state with the same energy, they are said to be degenerate. In our example, the degeneracy of the $\ell = 8$ state is 2. This degeneracy arises from the symmetry of space, which does not distinguish one direction from another. Degeneracies often, but not always, arise from symmetries. (Cf. p. 927.)

If we wanted to distinguish these two degenerate states observationally, one way to do it would be to “lift” the degeneracy by
applying an external magnetic field. Since an electron has an electric charge, it acts like a current loop, and the two states behave like oppositely oriented magnetic dipoles with an additional potential energy $-m \cdot B$, which lowers the energy of one state and raises the energy of the other. The existence of the magnetic field breaks the symmetry, which was the reason for the degeneracy.

13.4.2 Three dimensions

Our discussion of quantum-mechanical angular momentum has so far been limited to rotation in a plane, for which we can simply use positive and negative signs to indicate clockwise and counterclockwise directions of rotation. A hydrogen atom, however, is unavoidably three-dimensional. The classical treatment of angular momentum in three-dimensions has been presented in section 4.3; in general, the angular momentum of a particle is defined as the vector cross product $\mathbf{r} \times \mathbf{p}$.

There is a basic problem here: the angular momentum of the electron in a hydrogen atom depends on both its distance $r$ from the proton and its momentum $\mathbf{p}$, so in order to know its angular momentum precisely it would seem we would need to know both its position and its momentum simultaneously with good accuracy. This, however, seems forbidden by the Heisenberg uncertainty principle.

Actually the uncertainty principle does place limits on what can be known about a particle’s angular momentum vector, but it does not prevent us from knowing its magnitude as an exact integer multiple of $\hbar$. The reason is that in three dimensions, there are really three separate uncertainty principles:

$$\Delta p_x \Delta x \gtrsim \hbar$$
$$\Delta p_y \Delta y \gtrsim \hbar$$
$$\Delta p_z \Delta z \gtrsim \hbar$$

Now consider a particle, $b/1$, that is moving along the $x$ axis at position $x$ and with momentum $p_x$. We may not be able to know both $x$ and $p_x$ with unlimited accuracy, but we can still know the particle’s angular momentum about the origin exactly: it is zero, because the particle is moving directly away from the origin.

Suppose, on the other hand, a particle finds itself, $b/2$, at a position $x$ along the $x$ axis, and it is moving parallel to the $y$ axis with momentum $p_y$. It has angular momentum $x p_y$ about the $z$ axis, and again we can know its angular momentum with unlimited accuracy, because the uncertainty principle only relates $x$ to $p_x$ and $y$ to $p_y$. It does not relate $x$ to $p_y$.

As shown by these examples, the uncertainty principle does not restrict the accuracy of our knowledge of angular momenta as severely as might be imagined. However, it does prevent us from
knowing all three components of an angular momentum vector simultaneously. The most general statement about this is the following theorem:

**The angular momentum vector in quantum physics**

The most that can be known about a (nonzero) orbital angular momentum vector is its magnitude and one of its three vector components. Both are quantized in units of $\hbar$.

To see why this is true, consider the example wavefunction shown in figure c. This is the like the quantum moat of figure a, p. 919, but extended to one more dimension. If we slice the sphere in any plane perpendicular to the $z$ axis, we get an 8-cycle circular rainbow exactly like figure a. This is required because $L_z = 8 \hbar$. But if we take a slice perpendicular to some other axis, such as the $y$ axis, we don’t get a circular rainbow as we would for a state with a definite value of $L_y$. It is obviously not possible to get circular rainbows for slices perpendicular to more than one axis.

For those with a taste for rigor, here is a complete argument:

Theorem: On the sphere, if a wavefunction has definite values of both $L_z$ and $L_x$, then it is a wavefunction that is constant everywhere, so $L = 0$.

Lemma 1: If the component of $\ell_A$ along a certain axis $A$ has a definite value and is nonzero, then (a) $\Psi = 0$ at the poles, and (b) $\Psi$ is of the form $A e^{i \ell_A \phi}$ on any circle in a plane perpendicular to the axis. Part a holds because $L = 0$ if $r_\perp = 0$. For b, see p. 919.

Lemma 2: If the component of $L$ along a certain axis has a definite value and is zero, then $\Psi$ is constant in any plane perpendicular to that axis. This follows from lemma 1 in the case where $\ell_A = 0$.

Case I: $\ell_z$ and $\ell_x$ are both nonzero. We have $\Psi = 0$ at the poles along both the $x$ axis and the $z$ axis. The $z$-axis pole is a point on the great circle perpendicular to the $x$ axis, and vice versa, so applying 1b, $A = 0$ and $\Psi$ vanishes on both of these great circles. But now if we apply 1b along any slice perpendicular to either axis, we get $\Psi = 0$ everywhere on that slice, so $\Psi = 0$ everywhere.

Case II: $\ell_z$ and $\ell_x$ are both zero. By lemma 2, $\Psi$ is a constant everywhere.

Case III: One component is zero and the other nonzero. Let $\ell_z$ be the one that is zero. By 1a, $\Psi = 0$ at the $x$-axis pole, so by 2, $\Psi = 0$ on the great circle perpendicular to $z$. But then 1b tells us that $\Psi = 0$ everywhere.
13.4.3 Quantum numbers

Completeness

For a given $\ell$, consider the set of states with all the possible values of the angular momentum’s component along some fixed axis. This set of states is complete, meaning that they encompass all the possible states with this $\ell$.

For example, figure d shows wavefunctions with $\ell = 1$ that are solutions of the Schrödinger equation for a particle that is confined to the surface of a sphere. Although the formulae for these wavefunctions are not particularly complicated,\(^8\) they are not our main focus here, so to help with getting a feel for the idea of completeness, I have simply selected three points on the sphere at which to give numerical samples of the value of the wavefunction. These are the top (where the sphere is intersected by the positive $z$ axis), left ($x$), and front ($y$). (Although the wavefunctions are shown using the color conventions defined in figure u, p. 914, these numerical samples should make the example understandable if you’re looking at a black and white copy of the book.)

Suppose we arbitrarily choose the $z$ axis as the one along which to quantize the component of the angular momentum. With this choice, we have three possible values for $\ell_z$: $-1$, 0, and 1. These three states are shown in the three boxes surrounded by the black rectangle. This set of three states is complete.

Consider, for example, the fourth state, shown on the right outside the box. This state is clearly identifiable as a copy of the $\ell_z = 0$ state, rotated by 90 degrees counterclockwise, so it is the $\ell_x = 0$ state. We might imagine that this would be an entirely new prize to be added to our stamp collection. But it is actually not a state that we didn’t possess before. We can obtain it as the sum of the $\ell_z = -1$ and $\ell_z = 1$ states, divided by an appropriate normalization factor. Although I’m avoiding making this example an exercise in

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\(^8\)They are $\Psi_{1,-1} = \sin \theta e^{-i\phi}$, $\Psi_{10} = \sqrt{2} \cos \theta$, and $\Psi_{11} = \sin \theta e^{i\phi}$, where $\theta$ is the angle measured down from the $z$ axis, and $\phi$ is the angle running counterclockwise around the $z$ axis. These functions are called spherical harmonics.
manipulating formulae, it is easy to check that the sum does work out properly at the three sample points.

Sets of compatible quantum numbers

Figure e shows some examples in which we can completely describe a wavefunction by giving a few numbers. These are referred to as “quantum numbers.” It is important that the quantum numbers we use in describing a state be compatible. By analogy, “Bond, James, 007” would be a clear and consistent definition of the famous fictional spy, but in general this identification scheme would not work, because although almost everyone has a first and last name, most people do not have a license to kill with a corresponding double-oh number.

The laser beam in the figure is a state described according to its definite values \( p_x \) and \( y \), so we have the vanishing uncertainties \( \Delta p_x = 0 \) and \( \Delta y = 0 \). Since the Heisenberg uncertainty principle doesn’t talk about an \( x \) momentum in relation to a \( y \) position, this is OK. If we had been in doubt about whether this violated the uncertainty principle, we would have been reassured by our ability to draw the picture.

It is also possible to have \emph{incompatible} quantum numbers. The combination of \( p_x \) with \( x \) would be an incompatible set of quantum numbers, because a state can’t have a definite \( p_x \) and also a definite...
$x$. If we try to draw such a wave, we fail. $L_x$ and $L_z$ would also be an incompatible set.

**Complete and compatible sets of quantum numbers**

Let’s summarize. Just as we expect everyone to have a first and last name, we expect there to be a complete and compatible set of quantum numbers for any given quantum-mechanical system. Completeness means that we have enough quantum numbers to uniquely describe every possible state of the system, although we may need to describe a state as a superposition, as with the state $\ell_x = 0$ in figure d on p. 923. Compatibility means that when we specify a set of quantum numbers, we aren’t making a set of demands that can’t be met. These ideas are revisited in a slightly fancier mathematical way on p. 987.

**13.4.4 The hydrogen atom**

![A cross-section of a hydrogen wavefunction.](image)

13.4.4 The hydrogen atom

Deriving all the wavefunctions of the states of the hydrogen atom from first principles would be mathematically too complex for this book. (The ground state is not too hard, and we analyze it on p. 931.). But it’s not hard to understand the logic behind the wavefunctions in visual terms. Consider the wavefunction from the beginning of the section, which is reproduced in figure f. Although the graph looks three-dimensional, it is really only a representation of the part of the wavefunction lying within a two-dimensional plane. The third (up-down) dimension of the plot represents the value of the wavefunction at a given point, not the third dimension of space. The plane chosen for the graph is the one perpendicular to the angular momentum vector.
The energy of a state in the hydrogen atom depends only on its \( n \) quantum number. Each ring of peaks and valleys has eight wavelengths going around in a circle, so this state has \( L = 8\hbar \), i.e., we label it \( \ell = 8 \). The wavelength is shorter near the center, and this makes sense because when the electron is close to the nucleus it has a lower electrical energy, a higher kinetic energy, and a higher momentum.

Between each ring of peaks in this wavefunction is a nodal circle, i.e., a circle on which the wavefunction is zero. The full three-dimensional wavefunction has nodal spheres: a series of nested spherical surfaces on which it is zero. The number of radii at which nodes occur, including \( r = \infty \), is called \( n \), and \( n \) turns out to be closely related to energy. The ground state has \( n = 1 \) (a single node only at \( r = \infty \)), and higher-energy states have higher \( n \) values. There is a simple equation relating \( n \) to energy, which we will discuss in subsection 13.4.5.

The numbers \( n \) and \( \ell \), which identify the state, are called its quantum numbers. A state of a given \( n \) and \( \ell \) can be oriented in a variety of directions in space. We might try to indicate the orientation using the three quantum numbers \( \ell_x = L_x/\hbar \), \( \ell_y = L_y/\hbar \), and \( \ell_z = L_z/\hbar \). But we have already seen that it is impossible to know all three of these simultaneously. To give the most complete possible description of a state, we choose an arbitrary axis, say the \( z \) axis, and label the state according to \( n \), \( \ell \), and \( \ell_z \).

Angular momentum requires motion, and motion implies kinetic energy. Thus it is not possible to have a given amount of angular momentum without having a certain amount of kinetic energy as well. Since energy relates to the \( n \) quantum number, this means that for a given \( n \) value there will be a maximum possible \( \ell \). It turns out that this maximum value of equals \( n - 1 \).

In general, we can list the possible combinations of quantum numbers as follows:

- \( n \) can equal 1, 2, 3, ...
- \( \ell \) can range from 0 to \( n - 1 \), in steps of 1
- \( \ell_z \) can range from \( -\ell \) to \( \ell \), in steps of 1

Applying these rules, we have the following list of states:

\[
\begin{array}{ccc}
n = 1, & \ell = 0, & \ell_z = 0 \\
n = 2, & \ell = 0, & \ell_z = 0 \\
n = 2, & \ell = 1, & \ell_z = -1, 0, \text{ or } 1 \\
\ldots \\
\end{array}
\]

\textit{self-check J}

Continue the list for \( n = 3 \). \( \triangleright \) Answer, p. 1063

Because the energy only depends on \( n \), we have degeneracies. For example, the \( n = 2 \) energy level is 4-fold degenerate (and in fact

\[\text{See page 936 for a note about the two different systems of notations that are used for quantum numbers.}\]
this degeneracy will be doubled to 8 when we take into account the
intrinsic spin of the electron, sec. 13.4.6, p. 934). The degeneracy
of the different $\ell_z$ states follows from symmetry, as in our original
element of degeneracy on p. 920, and is therefore exact. The de-
generacy with respect to different values of $\ell$ for the same $n$ is not
at all obvious, and is in fact not exact when effects such as rela-
tivity are taken into account. We refer to this as an “accidental”
degeneracy. The very high level of degeneracy in the hydrogen atom
means that when you observe it the hydrogen spectrum in your lab
course, there is a great deal of structure that is effectively hidden
from you. Historically, physicists were fooled by the apparent sim-
plicity of the spectrum, and more than 70 years passed between the
measurement of the spectrum and the time when the degeneracies
were fully recognized and understood.

Figure h on page 928 shows the lowest-energy states of the hy-
drogen atom. The left-hand column of graphs displays the wave-
functions in the $x−y$ plane, and the right-hand column shows the
probability distribution in a three-dimensional representation.

Discussion Questions

A  The quantum number $n$ is defined as the number of radii at which
the wavefunction is zero, including $r = \infty$. Relate this to the features of
figure h.

B  Based on the definition of $n$, why can’t there be any such thing as
an $n = 0$ state?

C  Relate the features of the wavefunction plots in figure h to the
the corresponding features of the probability distribution pictures.

D  How can you tell from the wavefunction plots in figure h which ones
have which angular momenta?

E  Criticize the following incorrect statement: “The $\ell = 8$ wavefunction
in figure f has a shorter wavelength in the center because in the center
the electron is in a higher energy level.”

F  Discuss the implications of the fact that the probability cloud in of the
$n = 2, \ell = 1$ state is split into two parts.

13.4.5 Energies of states in hydrogen

History

The experimental technique for measuring the energy levels of
an atom accurately is spectroscopy: the study of the spectrum of
light emitted (or absorbed) by the atom. Only photons with certain
energies can be emitted or absorbed by a hydrogen atom, for ex-
ample, since the amount of energy gained or lost by the atom must
equal the difference in energy between the atom’s initial and final
states. Spectroscopy had become a highly developed art several
decades before Einstein even proposed the photon, and the Swiss
The three states of the hydrogen atom having the lowest energies.

spectroscopist Johann Balmer determined in 1885 that there was a simple equation that gave all the wavelengths emitted by hydrogen. In modern terms, we think of the photon wavelengths merely as indirect evidence about the underlying energy levels of the atom, and we rework Balmer’s result into an equation for these atomic energy levels:

$$E_n = -\frac{2.2 \times 10^{-18}}{n^2} \text{ J},$$

This energy includes both the kinetic energy of the electron and the electrical energy. The zero-level of the electrical energy scale is chosen to be the energy of an electron and a proton that are
Where does the mysterious numerical factor of $2.2 \times 10^{-18}$ J come from? In 1913 the Danish theorist Niels Bohr realized that it was exactly numerically equal to a certain combination of fundamental physical constants:

$$E_n = -\frac{mk^2e^4}{2\hbar^2} \cdot \frac{1}{n^2},$$

where $m$ is the mass of the electron, and $k$ is the Coulomb force constant for electric forces.

Bohr was able to cook up a derivation of this equation based on the incomplete version of quantum physics that had been developed by that time, but his derivation is today mainly of historical interest. It assumes that the electron follows a circular path, whereas the whole concept of a path for a particle is considered meaningless in our more complete modern version of quantum physics. Although Bohr was able to produce the right equation for the energy levels, his model also gave various wrong results, such as predicting that the atom would be flat, and that the ground state would have $\ell = 1$ rather than the correct $\ell = 0$.

**Approximate treatment**

Rather than leaping straight into a full mathematical treatment, we’ll start by looking for some physical insight, which will lead to an approximate argument that correctly reproduces the form of the Bohr equation.

A typical standing-wave pattern for the electron consists of a central oscillating area surrounded by a region in which the wavefunction tails off. As discussed in subsection 13.3.6, the oscillating type of pattern is typically encountered in the classically allowed region, while the tailing off occurs in the classically forbidden region where the electron has insufficient kinetic energy to penetrate according to classical physics. We use the symbol $r$ for the radius of the spherical boundary between the classically allowed and classically forbidden regions. Classically, $r$ would be the distance from the proton at which the electron would have to stop, turn around, and head back in.

If $r$ had the same value for every standing-wave pattern, then we’d essentially be solving the particle-in-a-box problem in three dimensions, with the box being a spherical cavity. Consider the energy levels of the particle in a box compared to those of the hydrogen atom, i. They’re qualitatively different. The energy levels of the particle in a box get farther and farther apart as we go higher in energy, and this feature doesn’t even depend on the details of whether the box is two-dimensional or three-dimensional, or its exact shape. The reason for the spreading is that the box is taken to
be completely impenetrable, so its size, \( r \), is fixed. A wave pattern with \( n \) humps has a wavelength proportional to \( r/n \), and therefore a momentum proportional to \( n \), and an energy proportional to \( n^2 \). In the hydrogen atom, however, the force keeping the electron bound isn’t an infinite force encountered when it bounces off of a wall, it’s the attractive electrical force from the nucleus. If we put more energy into the electron, it’s like throwing a ball upward with a higher energy — it will get farther out before coming back down. This means that in the hydrogen atom, we expect \( r \) to increase as we go to states of higher energy. This tends to keep the wavelengths of the high energy states from getting too short, reducing their kinetic energy. The closer and closer crowding of the energy levels in hydrogen also makes sense because we know that there is a certain energy that would be enough to make the electron escape completely, and therefore the sequence of bound states cannot extend above that energy.

When the electron is at the maximum classically allowed distance \( r \) from the proton, it has zero kinetic energy. Thus when the electron is at distance \( r \), its energy is purely electrical:

\[
E = -\frac{k e^2}{r}
\]

Now comes the approximation. In reality, the electron’s wavelength cannot be constant in the classically allowed region, but we pretend that it is. Since \( n \) is the number of nodes in the wavefunction, we can interpret it approximately as the number of wavelengths that fit across the diameter \( 2r \). We are not even attempting a derivation that would produce all the correct numerical factors like 2 and \( \pi \) and so on, so we simply make the approximation

\[
\lambda \sim \frac{r}{n}.
\]

Finally we assume that the typical kinetic energy of the electron is on the same order of magnitude as the absolute value of its total energy. (This is true to within a factor of two for a typical classical system like a planet in a circular orbit around the sun.) We then have

\[
\text{absolute value of total energy} = \frac{k e^2}{r} \\
\sim K \\
= \frac{p^2}{2m} \\
= \frac{(\hbar/\lambda)^2}{2m} \\
\sim \frac{\hbar^2 n^2}{2mr^2}
\]
We now solve the equation $ke^2/r \sim h^2 n^2 / 2 m r^2$ for $r$ and throw away numerical factors we can’t hope to have gotten right, yielding

$$r \sim \frac{h^2 n^2}{mke^2}.$$  

Plugging $n = 1$ into this equation gives $r = 2$ nm, which is indeed on the right order of magnitude. Finally we combine equations [4] and [1] to find

$$E \sim -\frac{mk^2 e^4}{h^2 n^2},$$

which is correct except for the numerical factors we never aimed to find.

**Exact treatment of the ground state**

The general proof of the Bohr equation for all values of $n$ is beyond the mathematical scope of this book, but it’s fairly straightforward to verify it for a particular $n$, especially given a lucky guess as to what functional form to try for the wavefunction. The form that works for the ground state is

$$\Psi = u e^{-r/a},$$

where $r = \sqrt{x^2 + y^2 + z^2}$ is the electron’s distance from the proton, and $u$ provides for normalization. In the following, the result $\partial r/\partial x = x/r$ comes in handy. Computing the partial derivatives that occur in the Laplacian, we obtain for the $x$ term

$$\frac{\partial \Psi}{\partial x} = \frac{\partial \Psi}{\partial r} \frac{\partial r}{\partial x} = -\frac{x}{ar} \Psi,$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{1}{ar} \Psi - \frac{x}{a} \left( \frac{\partial}{\partial x} \frac{1}{r} \right) \Psi + \left( \frac{x}{ar} \right)^2 \Psi$$

$$= -\frac{1}{ar} \Psi + \frac{x^2}{ar^3} \Psi + \left( \frac{x}{ar} \right)^2 \Psi,$$

so

$$\nabla^2 \Psi = \left( -\frac{2}{ar} + \frac{1}{a^2} \right) \Psi.$$  

The Schrödinger equation gives

$$E \cdot \Psi = -\frac{h^2}{2m} \nabla^2 \Psi + U \cdot \Psi$$

$$= \frac{h^2}{2m} \left( \frac{2}{ar} - \frac{1}{a^2} \right) \Psi - \frac{ke^2}{r} \cdot \Psi.$$  

If we require this equation to hold for all $r$, then we must have equality for both the terms of the form $(\text{constant}) \times \Psi$ and for those
of the form \((constant/r) \times \Psi\). That means

\[ E = -\frac{\hbar^2}{2ma^2} \]

and

\[ 0 = \frac{\hbar^2}{mar} - \frac{ke^2}{r}. \]

These two equations can be solved for the unknowns \(a\) and \(E\), giving

\[ a = \frac{\hbar^2}{mke^2} \]

and

\[ E = -\frac{mk^2e^4}{2\hbar^2}, \]

where the result for the energy agrees with the Bohr equation for \(n = 1\). The calculation of the normalization constant \(u\) is relegated to homework problem 36.

**self-check K**

We’ve verified that the function \(\Psi = he^{-r/a}\) is a solution to the Schrödinger equation, and yet it has a kink in it at \(r = 0\). What’s going on here? Didn’t I argue before that kinks are unphysical?

---

**Wave phases in the hydrogen molecule**

Example 24

In example 15 on page 899, I argued that the existence of the \(H_2\) molecule could essentially be explained by a particle-in-a-box argument: the molecule is a bigger box than an individual atom, so each electron’s wavelength can be longer, its kinetic energy lower. Now that we’re in possession of a mathematical expression for the wavefunction of the hydrogen atom in its ground state, we can make this argument a little more rigorous and detailed. Suppose that two hydrogen atoms are in a relatively cool sample of monoatomic hydrogen gas. Because the gas is cool, we can assume that the atoms are in their ground states. Now suppose that the two atoms approach one another. Making use again of the assumption that the gas is cool, it is reasonable to imagine that the atoms approach one another slowly. Now the atoms come a little closer, but still far enough apart that the region between them is classically forbidden. Each electron can tunnel through this classically forbidden region, but the tunneling probability is small. Each one is now found with, say, 99% probability in its original home, but with 1% probability in the other nucleus. Each electron is now in a state consisting of a superposition of the ground state of its own atom with the ground state of the other atom. There are two peaks in the superposed wavefunction, but one is a much bigger peak than the other.
An interesting question now arises. What are the relative phases of the two electrons? As discussed on page 893, the absolute phase of an electron’s wavefunction is not really a meaningful concept. Suppose atom A contains electron Alice, and B electron Bob. Just before the collision, Alice may have wondered, “Is my phase positive right now, or is it negative? But of course I shouldn’t ask myself such silly questions,” she adds sheepishly.

Example 24. But relative phases are well defined. As the two atoms draw closer and closer together, the tunneling probability rises, and eventually gets so high that each electron is spending essentially 50% of its time in each atom. It’s now reasonable to imagine that either one of two possibilities could obtain. Alice’s wavefunction could either look like $j/1$, with the two peaks in phase with one another, or it could look like $j/2$, with opposite phases. Because relative phases of wavefunctions are well defined, states 1 and 2 are physically distinguishable. In particular, the kinetic energy of state 2 is much higher; roughly speaking, it is like the two-hump wave pattern of the particle in a box, as opposed to 1, which looks roughly like the one-hump pattern with a much longer wavelength. Not only that, but an electron in state 1 has a large probability of being found in the central region, where it has a large negative electrical energy due to its interaction with both protons. State 2, on the other hand, has a low probability of existing in that region. Thus state 1 represents the true ground-state wavefunction of the $H_2$ molecule, and putting both Alice and Bob in that state results in a lower energy than their total energy when separated, so the molecule is bound, and will not fly apart spontaneously.

The reader who has studied chemistry may find it helpful to make contact with the terminology and notation used by chemists. The state represented by pictures 1 and 4 is known as a $\sigma$ orbital, which is a type of “bonding orbital.” The state in 2 and 3 is a $\sigma^*$, a kind of “antibonding orbital.” Note that although we will not discuss electron spin or the Pauli exclusion principle until sec. 13.4.6, p. 934, those considerations have no effect on this example, since the two electrons can have opposite spins.
The top has angular momentum both because of the motion of its center of mass through space and due to its internal rotation. Electron spin is roughly analogous to the intrinsic spin of the top.

State \( j/3 \), on the other hand, is not physically distinguishable from \( j/2 \), nor is \( j/4 \) from \( j/1 \). Alice may say to Bob, “Isn’t it wonderful that we’re in state 1 or 4? I love being stable like this.” But she knows it’s not meaningful to ask herself at a given moment which state she’s in, 1 or 4.

**Discussion Questions**

A. States of hydrogen with \( n \) greater than about 10 are never observed in the sun. Why might this be?

B. Sketch graphs of \( r \) and \( E \) versus \( n \) for the hydrogen, and compare with analogous graphs for the one-dimensional particle in a box.

13.4.6 Electron spin

It’s disconcerting to the novice ping-pong player to encounter for the first time a more skilled player who can put spin on the ball. Even though you can’t see that the ball is spinning, you can tell something is going on by the way it interacts with other objects in its environment. In the same way, we can tell from the way electrons interact with other things that they have an intrinsic spin of their own. Experiments show that even when an electron is not moving through space, it still has angular momentum amounting to \( \hbar/2 \).

An important historical experiment of this type, the Stern-Gerlach experiment, is described in detail in section 14.1.

This may seem paradoxical because the quantum moat, for instance, gave only angular momenta that were integer multiples of \( \hbar \), not half-units, and I claimed that angular momentum was always quantized in units of \( \hbar \), not just in the case of the quantum moat. That whole discussion, however, assumed that the angular momentum would come from the motion of a particle through space. The \( \hbar/2 \) angular momentum of the electron is simply a property of the particle, like its charge or its mass. It has nothing to do with whether the electron is moving or not, and it does not come from any internal motion within the electron. Nobody has ever succeeded in finding any internal structure inside the electron, and even if there was internal structure, it would be mathematically impossible for it to result in a half-unit of angular momentum.

We simply have to accept this \( \hbar/2 \) angular momentum, called the “spin” of the electron — Mother Nature rubs our noses in it as an observed fact. Protons and neutrons have the same \( \hbar/2 \) spin, while photons have an intrinsic spin of \( \hbar \). In general, half-integer spins are typical of material particles. Integral values are found for the particles that carry forces: photons, which embody the electric and magnetic fields of force, as well as the more exotic messengers of the nuclear and gravitational forces. The photon is particularly important: it has spin 1.

As was the case with ordinary angular momentum, we can describe spin angular momentum in terms of its magnitude, and its
component along a given axis. We write \( s \) and \( s_z \) for these quantities, expressed in units of \( \hbar \), so an electron has \( s = 1/2 \) and \( s_z = +1/2 \) or \(-1/2\).

**Adds and evens, and how they add up**

From grade-school arithmetic, we have the rules

\[
\text{even} + \text{even} = \text{even} \\
\text{odd} + \text{even} = \text{odd} \\
\text{odd} + \text{odd} = \text{even}.
\]

Thus we know that \( 123456789 + 987654321 \) is even, without having to actually compute the result. Dividing by two gives similar relationships for integer and half-integer angular momenta. For example, a half-integer plus an integer gives a half-integer, and therefore when we add the intrinsic spin \( 1/2 \) of an electron to any additional, integer spin that the electron has from its motion through space, we get a half-integer angular momentum. That is, the total angular momentum of an electron will always be a half-integer. Similarly, when we add the intrinsic spin \( 1 \) of a photon to its angular momentum due to its integral motion through space, we will always get an integer. Thus the integer or half-integer character of any particle’s total angular momentum (spin + motion) is determined entirely by the particle’s spin.

These relationships tell us things about the spins we can make by putting together different particles to make bigger particles, and they also tell us things about decay processes.

---

### Spin of the helium atom example 25

A helium-4 atom consists of two protons, two neutrons, and two electrons. A proton, a neutron, and an electron each have spin \( 1/2 \). Since the atom is a composite of six particles, each of which has half-integer spin, the atom as a whole has an integer angular momentum.

### Emission of a photon from an atom example 26

An atom can emit light,

\[ \text{atom} \rightarrow \text{atom} + \text{photon}. \]

This works in terms of angular momentum because the photon’s spin \( 1 \) is an integer. Thus, regardless of whether the atom’s angular momentum is an integer or a half-integer, the process is allowed by conservation of angular momentum. If the atom’s angular momentum is an integer, then we have integer = integer + 1, and if it’s a half-integer, half-integer = half-integer + 1; either of these is possible. If not for this logic, it would be impossible for matter to emit light. In general, if we want a particle such as a photon to pop into existence like this, it must have an integer spin.
Beta decay example 27

When a free neutron undergoes beta decay, we have

\[ n \rightarrow p + e^- + \bar{\nu}. \]

All four of these particles have spin 1/2, so the angular momenta go like

\[ \text{half-integer} \rightarrow \text{half-integer} + \text{half-integer} + \text{half-integer}, \]

which is possible, e.g., \( 1/2 = 3/2 - 5/2 + 3/2 \). Because the neutrino has almost no interaction with normal matter, it normally flies off undetected, and the reaction was originally thought to be

\[ n \rightarrow p + e. \]

With hindsight, this is impossible, because we can never have

\[ \text{half-integer} \rightarrow \text{half-integer} + \text{half-integer}. \]

The reasoning holds not just for the beta decay of a free neutron, but for any beta decay: a neutrino or antineutrino must be emitted in order to conserve angular momentum. But historically, this was not understood at first, and when Enrico Fermi proposed the existence of the neutrino in 1934, the journal to which he first submitted his paper rejected it as “too remote from reality.”

States in hydrogen, with spin

Taking electron spin into account, we need a total of four quantum numbers to label a state of an electron in the hydrogen atom: \( n, \ell, \ell_z, \) and \( s_z \). (We omit \( s \) because it always has the same value.) The symbols \( \ell \) and \( \ell_z \) include only the angular momentum the electron has because it is moving through space, not its spin angular momentum. The availability of two possible spin states of the electron leads to a doubling of the numbers of states:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \ell )</th>
<th>( \ell_z )</th>
<th>( s_z )</th>
<th>Number of States</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>( \pm 1/2 )</td>
<td>two states</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>( \pm 1/2 )</td>
<td>two states</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1, 0, 1</td>
<td>( \pm 1/2 ) or ( \pm 1/2 )</td>
<td>six states</td>
</tr>
</tbody>
</table>

...  

A note about notation

There are unfortunately two inconsistent systems of notation for the quantum numbers we’ve been discussing. The notation I’ve been using is the one that is used in nuclear physics, but there is a different one that is used in atomic physics.
The nuclear physics notation is more logical (not giving special status to the \( z \) axis) and more memorable (\( \ell_z \) rather than the obscure \( m \)), which is why I use it consistently in this book, even though nearly all the applications we’ll consider are atomic ones.

We are further encumbered with the following historically derived letter labels, which deserve to be eliminated in favor of the simpler numerical ones:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \ell )</th>
<th>( \ell_x )</th>
<th>( \ell_y )</th>
<th>( \ell_z )</th>
<th>( s = 1/2 )</th>
<th>( s_x )</th>
<th>( s_y )</th>
<th>( s_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>same</td>
<td>same</td>
<td>no notation</td>
<td>no notation</td>
<td>( m )</td>
<td>no notation (sometimes ( \sigma ))</td>
<td>no notation</td>
<td>no notation</td>
<td>( s )</td>
</tr>
</tbody>
</table>

The spdf labels are used in both nuclear\(^{11}\) and atomic physics, while the KLMNOPQ letters are used only to refer to states of electrons.

And finally, there is a piece of notation that is good and useful, but which I simply haven’t mentioned yet. The vector \( \mathbf{j} = \ell + s \) stands for the total angular momentum of a particle in units of \( \hbar \), including both orbital and spin parts. This quantum number turns out to be very useful in nuclear physics, because nuclear forces tend to exchange orbital and spin angular momentum, so a given energy level often contains a mixture of \( \ell \) and \( s \) values, while remaining fairly pure in terms of \( j \).

13.4.7 **Atoms with more than one electron**

What about other atoms besides hydrogen? It would seem that things would get much more complex with the addition of a second electron. A hydrogen atom only has one particle that moves around much, since the nucleus is so heavy and nearly immobile. Helium, with two, would be a mess. Instead of a wavefunction whose square tells us the probability of finding a single electron at any given location in space, a helium atom would need to have a wavefunction whose square would tell us the probability of finding two electrons at any given combination of points. Ouch! In addition, we would

---

\(^{11}\)After \( f \), the series continues in alphabetical order. In nuclei that are spinning rapidly enough that they are almost breaking apart, individual protons and neutrons can be stirred up to \( \ell \) values as high as 7, which is \( j \).
have the extra complication of the electrical interaction between the
two electrons, rather than being able to imagine everything in terms
of an electron moving in a static field of force created by the nucleus
alone.

Despite all this, it turns out that we can get a surprisingly good
description of many-electron atoms simply by assuming the elec-
trons can occupy the same standing-wave patterns that exist in a
hydrogen atom. The ground state of helium, for example, would
have both electrons in states that are very similar to the \( n = 1 \)
states of hydrogen. The second-lowest-energy state of helium would
have one electron in an \( n = 1 \) state, and the other in an \( n = 2 \) states.
The relatively complex spectra of elements heavier than hydrogen
can be understood as arising from the great number of possible com-
binations of states for the electrons.

A surprising thing happens, however, with lithium, the three-
electron atom. We would expect the ground state of this atom to
be one in which all three electrons settle down into \( n = 1 \) states.
What really happens is that two electrons go into \( n = 1 \) states, but
the third stays up in an \( n = 2 \) state. This is a consequence of a new
principle of physics:

**The Pauli Exclusion Principle**

Two electrons can never occupy the same state.

There are two \( n = 1 \) states, one with \( s_z = +1/2 \) and one with
\( s_z = -1/2 \), but there is no third \( n = 1 \) state for lithium's third
electron to occupy, so it is forced to go into an \( n = 2 \) state.

It can be proved mathematically that the Pauli exclusion prin-
ciple applies to any type of particle that has half-integer spin. Thus
two neutrons can never occupy the same state, and likewise for two
protons. Photons, however, are immune to the exclusion principle
because their spin is an integer.

**Deriving the periodic table**

We can now account for the structure of the periodic table, which
seemed so mysterious even to its inventor Mendeleev. The first row
consists of atoms with electrons only in the \( n = 1 \) states:

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1 electron in an ( n = 1 ) state</td>
</tr>
<tr>
<td>He</td>
<td>2 electrons in the two ( n = 1 ) states</td>
</tr>
<tr>
<td>Li</td>
<td>2 electrons in ( n = 1 ) states, 1 electron in an ( n = 2 ) state</td>
</tr>
<tr>
<td>Be</td>
<td>2 electrons in ( n = 1 ) states, 2 electrons in ( n = 2 ) states</td>
</tr>
<tr>
<td>...</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2 electrons in ( n = 1 ) states, 6 electrons in ( n = 2 ) states</td>
</tr>
<tr>
<td>F</td>
<td>2 electrons in ( n = 1 ) states, 7 electrons in ( n = 2 ) states</td>
</tr>
<tr>
<td>Ne</td>
<td>2 electrons in ( n = 1 ) states, 8 electrons in ( n = 2 ) states</td>
</tr>
</tbody>
</table>
In the third row we start in on the \( n = 3 \) levels:

Na 2 electrons in \( n = 1 \) states, 8 electrons in \( n = 2 \) states, 1 electron in an \( n = 3 \) state

...

We can now see a logical link between the filling of the energy levels and the structure of the periodic table. Column 0, for example, consists of atoms with the right number of electrons to fill all the available states up to a certain value of \( n \). Column I contains atoms like lithium that have just one electron more than that.

This shows that the columns relate to the filling of energy levels, but why does that have anything to do with chemistry? Why, for example, are the elements in columns I and VII dangerously reactive? Consider, for example, the element sodium (Na), which is so reactive that it may burst into flames when exposed to air. The electron in the \( n = 3 \) state has an unusually high energy. If we let a sodium atom come in contact with an oxygen atom, energy can be released by transferring the \( n = 3 \) electron from the sodium to one of the vacant lower-energy \( n = 2 \) states in the oxygen. This energy is transformed into heat. Any atom in column I is highly reactive for the same reason: it can release energy by giving away the electron that has an unusually high energy.

Column VII is spectacularly reactive for the opposite reason: these atoms have a single vacancy in a low-energy state, so energy is released when these atoms steal an electron from another atom.

It might seem as though these arguments would only explain reactions of atoms that are in different rows of the periodic table, because only in these reactions can a transferred electron move from a higher-\( n \) state to a lower-\( n \) state. This is incorrect. An \( n = 2 \) electron in fluorine (F), for example, would have a different energy than an \( n = 2 \) electron in lithium (Li), due to the different number of protons and electrons with which it is interacting. Roughly speaking, the \( n = 2 \) electron in fluorine is more tightly bound (lower in energy) because of the larger number of protons attracting it. The effect of the increased number of attracting protons is only partly counteracted by the increase in the number of repelling electrons, because the forces exerted on an electron by the other electrons are in many different directions and cancel out partially.
Problems

The symbols √, □, etc. are explained on page 951.

1. If a radioactive substance has a half-life of one year, does this mean that it will be completely decayed after two years? Explain.

2. What is the probability of rolling a pair of dice and getting “snake eyes,” i.e., both dice come up with ones?

3. Problem 3 has been deleted.

4. Problem 4 has been deleted.

5. Refer to the probability distribution for people’s heights in figure f on page 862.
   (a) Show that the graph is properly normalized.
   (b) Estimate the fraction of the population having heights between 140 and 150 cm.

6. (a) A nuclear physicist is studying a nuclear reaction caused in an accelerator experiment, with a beam of ions from the accelerator striking a thin metal foil and causing nuclear reactions when a nucleus from one of the beam ions happens to hit one of the nuclei in the target. After the experiment has been running for a few hours, a few billion radioactive atoms have been produced, embedded in the target. She does not know what nuclei are being produced, but she suspects they are an isotope of some heavy element such as Pb, Bi, Fr or U. Following one such experiment, she takes the target foil out of the accelerator, sticks it in front of a detector, measures the activity every 5 min, and makes a graph (figure). The isotopes she thinks may have been produced are:

   \[
   \begin{array}{|c|c|}
   \hline
   \text{isotope} & \text{half-life (minutes)} \\
   \hline
   ^{211}\text{Pb} & 36.1 \\
   ^{214}\text{Pb} & 26.8 \\
   ^{214}\text{Bi} & 19.7 \\
   ^{223}\text{Fr} & 21.8 \\
   ^{239}\text{U} & 23.5 \\
   \hline
   \end{array}
   \]

   Which one is it?

   (b) Having decided that the original experimental conditions produced one specific isotope, she now tries using beams of ions traveling at several different speeds, which may cause different reactions. The following table gives the activity of the target 10, 20 and 30 minutes after the end of the experiment, for three different ion speeds.

<table>
<thead>
<tr>
<th>activity (millions of decays/s) after...</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>first ion speed</td>
<td>1.933</td>
<td>0.832</td>
<td>0.382</td>
</tr>
<tr>
<td>second ion speed</td>
<td>1.200</td>
<td>0.545</td>
<td>0.248</td>
</tr>
<tr>
<td>third ion speed</td>
<td>7.211</td>
<td>1.296</td>
<td>0.248</td>
</tr>
</tbody>
</table>

   Since such a large number of decays is being counted, assume that
the data are only inaccurate due to rounding off when writing down the table. Which are consistent with the production of a single isotope, and which imply that more than one isotope was being created?

7 Devise a method for testing experimentally the hypothesis that a gambler’s chance of winning at craps is independent of her previous record of wins and losses. If you don’t invoke the mathematical definition of statistical independence, then you haven’t proposed a test. This has nothing to do with the details of the rules of craps, or with the fact that it’s a game played using dice.

8 A blindfolded person fires a gun at a circular target of radius $b$, and is allowed to continue firing until a shot actually hits it. Any part of the target is equally likely to get hit. We measure the random distance $r$ from the center of the circle to where the bullet went in.

(a) Show that the probability distribution of $r$ must be of the form $D(r) = kr$, where $k$ is some constant. (Of course we have $D(r) = 0$ for $r > b$.)

(b) Determine $k$ by requiring $D$ to be properly normalized.

(c) Find the average value of $r$.

(d) Interpreting your result from part c, how does it compare with $b/2$? Does this make sense? Explain.

9 We are given some atoms of a certain radioactive isotope, with half-life $t_{1/2}$. We pick one atom at random, and observe it for one half-life, starting at time zero. If it decays during that one-half-life period, we record the time $t$ at which the decay occurred. If it doesn’t, we reset our clock to zero and keep trying until we get an atom that cooperates. The final result is a time $0 \leq t \leq t_{1/2}$, with a distribution that looks like the usual exponential decay curve, but with its tail chopped off.

(a) Find the distribution $D(t)$, with the proper normalization.

(b) Find the average value of $t$.

(c) Interpreting your result from part b, how does it compare with $t_{1/2}/2$? Does this make sense? Explain.

10 The speed, $v$, of an atom in an ideal gas has a probability distribution of the form $D(v) = bve^{-cv^2}$, where $0 \leq v < \infty$, $c$ relates to the temperature, and $b$ is determined by normalization.

(a) Sketch the distribution.

(b) Find $b$ in terms of $c$.

(c) Find the average speed in terms of $c$, eliminating $b$. (Don’t try to do the indefinite integral, because it can’t be done in closed form. The relevant definite integral can be found in tables or done with computer software.)
All helium on earth is from the decay of naturally occurring heavy radioactive elements such as uranium. Each alpha particle that is emitted ends up claiming two electrons, which makes it a helium atom. If the original $^{238}\text{U}$ atom is in solid rock (as opposed to the earth’s molten regions), the He atoms are unable to diffuse out of the rock. This problem involves dating a rock using the known decay properties of uranium 238. Suppose a geologist finds a sample of hardened lava, melts it in a furnace, and finds that it contains 1230 mg of uranium and 2.3 mg of helium. $^{238}\text{U}$ decays by alpha emission, with a half-life of $4.5 \times 10^9$ years. The subsequent chain of alpha and electron (beta) decays involves much shorter half-lives, and terminates in the stable nucleus $^{206}\text{Pb}$. Almost all natural uranium is $^{238}\text{U}$, and the chemical composition of this rock indicates that there were no decay chains involved other than that of $^{238}\text{U}$.

(a) How many alphas are emitted per decay chain? [Hint: Use conservation of mass.]
(b) How many electrons are emitted per decay chain? [Hint: Use conservation of charge.]
(c) How long has it been since the lava originally hardened?  

When light is reflected from a mirror, perhaps only 80% of the energy comes back. One could try to explain this in two different ways: (1) 80% of the photons are reflected, or (2) all the photons are reflected, but each loses 20% of its energy. Based on your everyday knowledge about mirrors, how can you tell which interpretation is correct? [Based on a problem from PSSC Physics.]

Suppose we want to build an electronic light sensor using an apparatus like the one described in subsection 13.2.2 on p. 873. How would its ability to detect different parts of the spectrum depend on the type of metal used in the capacitor plates?

The photoelectric effect can occur not just for metal cathodes but for any substance, including living tissue. Ionization of DNA molecules can cause cancer or birth defects. If the energy required to ionize DNA is on the same order of magnitude as the energy required to produce the photoelectric effect in a metal, which of the following types of electromagnetic waves might pose such a hazard? Explain.

- 60 Hz waves from power lines
- 100 MHz FM radio
- microwaves from a microwave oven
- visible light
- ultraviolet light
- x-rays
(a) Rank-order the photons according to their wavelengths, frequencies, and energies. If two are equal, say so. Explain all your answers.

(b) Photon 3 was emitted by a xenon atom going from its second-lowest-energy state to its lowest-energy state. Which of photons 1, 2, and 4 are capable of exciting a xenon atom from its lowest-energy state to its second-lowest-energy state? Explain.

The figures show the wavefunction of an electron as a function of position. Which one could represent an electron speeding up as it moves to the right? Explain.

The beam of a 100 W overhead projector covers an area of 1 m × 1 m when it hits the screen 3 m away. Estimate the number of photons that are in flight at any given time. (Since this is only an estimate, we can ignore the fact that the beam is not parallel.)

In the photoelectric effect, electrons are observed with virtually no time delay (~ 10 ns), even when the light source is very weak. (A weak light source does however only produce a small number of ejected electrons.) The purpose of this problem is to show that the lack of a significant time delay contradicted the classical wave theory of light, so throughout this problem you should put yourself in the shoes of a classical physicist and pretend you don’t know about photons at all. At that time, it was thought that the electron might have a radius on the order of 10⁻¹⁵ m. (Recent experiments have shown that if the electron has any finite size at all, it is far smaller.)

(a) Estimate the power that would be soaked up by a single electron in a beam of light with an intensity of 1 mW/m².

(b) The energy, $E_s$, required for the electron to escape through the surface of the cathode is on the order of 10⁻¹⁹ J. Find how long it would take the electron to absorb this amount of energy, and explain why your result constitutes strong evidence that there is something wrong with the classical theory.
In a television, suppose the electrons are accelerated from rest through a voltage difference of $10^4$ V. What is their final wavelength?

Use the Heisenberg uncertainty principle to estimate the minimum velocity of a proton or neutron in a $^{208}$Pb nucleus, which has a diameter of about 13 fm (1 fm=10$^{-15}$ m). Assume that the speed is nonrelativistic, and then check at the end whether this assumption was warranted.

Find the energy of a particle in a one-dimensional box of length $L$, expressing your result in terms of $L$, the particle’s mass $m$, the number of peaks and valleys $n$ in the wavefunction, and fundamental constants.

A free electron that contributes to the current in an ohmic material typically has a speed of $10^5$ m/s (much greater than the drift velocity).

(a) Estimate its de Broglie wavelength, in nm.

(b) If a computer memory chip contains $10^8$ electric circuits in a 1 cm$^2$ area, estimate the linear size, in nm, of one such circuit.

(c) Based on your answers from parts a and b, does an electrical engineer designing such a chip need to worry about wave effects such as diffraction?

(d) Estimate the maximum number of electric circuits that can fit on a 1 cm$^2$ computer chip before quantum-mechanical effects become important.

In classical mechanics, an interaction energy of the form $U(x) = \frac{1}{2}kx^2$ gives a harmonic oscillator: the particle moves back and forth at a frequency $\omega = \sqrt{k/m}$. This form for $U(x)$ is often a good approximation for an individual atom in a solid, which can vibrate around its equilibrium position at $x = 0$. (For simplicity, we restrict our treatment to one dimension, and we treat the atom as a single particle rather than as a nucleus surrounded by electrons).

The atom, however, should be treated quantum-mechanically, not classically. It will have a wave function. We expect this wave function to have one or more peaks in the classically allowed region, and we expect it to tail off in the classically forbidden regions to the right and left. Since the shape of $U(x)$ is a parabola, not a series of flat steps as in figure m on page 906, the wavy part in the middle will not be a sine wave, and the tails will not be exponentials.

(a) Show that there is a solution to the Schrödinger equation of the form

$$\Psi(x) = e^{-bx^2},$$

and relate $b$ to $k$, $m$, and $\hbar$. To do this, calculate the second derivative, plug the result into the Schrödinger equation, and then find what value of $b$ would make the equation valid for all values of $x$. This wavefunction turns out to be the ground state. Note that this wavefunction is not properly normalized — don’t worry about that.
(b) Sketch a graph showing what this wavefunction looks like.
(c) Let’s interpret $b$. If you changed $b$, how would the wavefunction look different? Demonstrate by sketching two graphs, one for a smaller value of $b$, and one for a larger value.
(d) Making $k$ greater means making the atom more tightly bound. Mathematically, what happens to the value of $b$ in your result from part a if you make $k$ greater? Does this make sense physically when you compare with part c?

24  (a) A distance scale is shown below the wavefunctions and probability densities illustrated in figure h on page 928. Compare this with the order-of-magnitude estimate derived in subsection 13.4.5 for the radius $r$ at which the wavefunction begins tailing off. Was the estimate on the right order of magnitude?
(b) Although we normally say the moon orbits the earth, actually they both orbit around their common center of mass, which is below the earth’s surface but not at its center. The same is true of the hydrogen atom. Does the center of mass lie inside the proton, or outside it?

25  The figure shows eight of the possible ways in which an electron in a hydrogen atom could drop from a higher energy state to a state of lower energy, releasing the difference in energy as a photon. Of these eight transitions, only D, E, and F produce photons with wavelengths in the visible spectrum.
(a) Which of the visible transitions would be closest to the violet end of the spectrum, and which would be closest to the red end? Explain.
(b) In what part of the electromagnetic spectrum would the photons from transitions A, B, and C lie? What about G and H? Explain.
(c) Is there an upper limit to the wavelengths that could be emitted by a hydrogen atom going from one bound state to another bound state? Is there a lower limit? Explain.

26  Find an equation for the wavelength of the photon emitted when the electron in a hydrogen atom makes a transition from energy level $n_1$ to level $n_2$.

27  Estimate the angular momentum of a spinning basketball, in units of $\hbar$. Explain how this result relates to the correspondence principle.

28  Assume that the kinetic energy of an electron in the $n = 1$ state of a hydrogen atom is on the same order of magnitude as the absolute value of its total energy, and estimate a typical speed at which it would be moving. (It cannot really have a single, definite speed, because its kinetic and interaction energy trade off at different distances from the proton, but this is just a rough estimate of a typical speed.) Based on this speed, were we justified in assuming that the electron could be described nonrelativistically?
29 Before the quantum theory, experimentalists noted that in many cases, they would find three lines in the spectrum of the same atom that satisfied the following mysterious rule: $1/\lambda_1 = 1/\lambda_2 + 1/\lambda_3$. Explain why this would occur. Do not use reasoning that only works for hydrogen — such combinations occur in the spectra of all elements. [Hint: Restate the equation in terms of the energies of photons.]

30 The wavefunction of the electron in the ground state of a hydrogen atom, shown in the top left of figure h on p. 928, is

$$\Psi = \pi^{-1/2}a^{-3/2}e^{-r/a},$$

where $r$ is the distance from the proton, and $a = \hbar^2/kme^2 = 5.3 \times 10^{-11}$ m is a constant that sets the size of the wave. The figure doesn’t show the proton; let’s take the proton to be a sphere with a radius of $b = 0.5$ fm.

(a) Reproduce figure h in a rough sketch, and indicate, relative to the size of your sketch, some idea of how big $a$ and $b$ are.

(b) Calculate symbolically, without plugging in numbers, the probability that at any moment, the electron is inside the proton. [Hint: Does it matter if you plug in $r = 0$ or $r = b$ in the equation for the wavefunction?]

(c) Calculate the probability numerically.

(d) Based on the equation for the wavefunction, is it valid to think of a hydrogen atom as having a finite size? Can $a$ be interpreted as the size of the atom, beyond which there is nothing? Or is there any limit on how far the electron can be from the proton?

31 Use physical reasoning to explain how the equation for the energy levels of hydrogen,

$$E_n = -\frac{mk^2e^4}{2\hbar^2} \cdot \frac{1}{n^2},$$

should be generalized to the case of an atom with atomic number $Z$ that has had all its electrons removed except for one.

32 A muon is a subatomic particle that acts exactly like an electron except that its mass is 207 times greater. Muons can be created by cosmic rays, and it can happen that one of an atom’s electrons is displaced by a muon, forming a muonic atom. If this happens to a hydrogen atom, the resulting system consists simply of a proton plus a muon.

(a) Based on the results of section 13.4.5, how would the size of a muonic hydrogen atom in its ground state compare with the size of the normal atom?

(b) If you were searching for muonic atoms in the sun or in the earth’s atmosphere by spectroscopy, in what part of the electromagnetic spectrum would you expect to find the absorption lines?
33 An electron is initially at rest. A photon collides with the electron and rebounds from the collision at 180 degrees, i.e., going back along the path on which it came. The rebounding photon has a different energy, and therefore a different frequency and wavelength. Show that, based on conservation of energy and momentum, the difference between the photon’s initial and final wavelengths must be $2\hbar/mc$, where $m$ is the mass of the electron. The experimental verification of this type of “pool-ball” behavior by Arthur Compton in 1923 was taken as definitive proof of the particle nature of light. Note that we’re not making any nonrelativistic approximations. To keep the algebra simple, you should use natural units — in fact, it’s a good idea to use even-more-natural-than-natural units, in which we have not just $c = 1$ but also $\hbar = 1$, and $m = 1$ for the mass of the electron. You’ll also probably want to use the relativistic relationship $E^2 - p^2 = m^2$, which becomes $E^2 - p^2 = 1$ for the energy and momentum of the electron in these units.

34 Generalize the result of problem 33 to the case where the photon bounces off at an angle other than 180° with respect to its initial direction of motion.

35 On page 906 we derived an expression for the probability that a particle would tunnel through a rectangular barrier, i.e., a region in which the interaction energy $U(x)$ has a graph that looks like a rectangle. Generalize this to a barrier of any shape. [Hints: First try generalizing to two rectangular barriers in a row, and then use a series of rectangular barriers to approximate the actual curve of an arbitrary function $U(x)$. Note that the width and height of the barrier in the original equation occur in such a way that all that matters is the area under the $U$-versus-$x$ curve. Show that this is still true for a series of rectangular barriers, and generalize using an integral.] If you had done this calculation in the 1930’s you could have become a famous physicist.

36 Show that the wavefunction given in problem 30 is properly normalized.

37 Show that a wavefunction of the form $\Psi = e^{by} \sin ax$ is a possible solution of the Schrödinger equation in two dimensions, with a constant potential $U$. Can we tell whether it would apply to a classically allowed region, or a classically forbidden one?

38 This problem generalizes the one-dimensional result from problem 21.
Find the energy levels of a particle in a three-dimensional rectangular box with sides of length $a$, $b$, and $c$. \[\checkmark\]
39 Americium-241 is an artificial isotope used in smoke detectors. It undergoes alpha decay, with a half-life of 432 years. As discussed in example 17 on page 907, alpha decay can be understood as a tunneling process, and although the barrier is not rectangular in shape, the equation for the tunneling probability on page 907 can still be used as a rough guide to our thinking. For americium-241, the tunneling probability is about $1 \times 10^{-29}$. Suppose that this nucleus were to decay by emitting a tritium (helium-3) nucleus instead of an alpha particle (helium-4). Estimate the relevant tunneling probability, assuming that the total energy $E$ remains the same. This higher probability is contrary to the empirical observation that this nucleus is not observed to decay by tritium emission with any significant probability, and in general tritium emission is almost unknown in nature; this is mainly because the tritium nucleus is far less stable than the helium-4 nucleus, and the difference in binding energy reduces the energy available for the decay.

40 As far as we know, the mass of the photon is zero. However, it’s not possible to prove by experiments that anything is zero; all we can do is put an upper limit on the number. As of 2008, the best experimental upper limit on the mass of the photon is about $1 \times 10^{-52}$ kg. Suppose that the photon’s mass really isn’t zero, and that the value is at the top of the range that is consistent with the present experimental evidence. In this case, the $c$ occurring in relativity would no longer be interpreted as the speed of light. As with material particles, the speed $v$ of a photon would depend on its energy, and could never be as great as $c$. Estimate the relative size $(c - v)/c$ of the discrepancy in speed, in the case of a photon of visible light.

\[\text{Answer, p. 1065}\]

41 Hydrogen is the only element whose energy levels can be expressed exactly in an equation. Calculate the ratio $\lambda_E/\lambda_F$ of the wavelengths of the transitions labeled E and F in problem 25 on p. 945. Express your answer as an exact fraction, not a decimal approximation. In an experiment in which atomic wavelengths are being measured, this ratio provides a natural, stringent check on the precision of the results.

\[\sqrt{\text{42}}\]

42 Give a numerical comparison of the number of photons per second emitted by a hundred-watt FM radio transmitter and a hundred-watt lightbulb.
On pp. 929-931 of subsection 13.4.5, we used simple algebra to derive an approximate expression for the energies of states in hydrogen, without having to explicitly solve the Schrödinger equation. As input to the calculation, we used the proportionality $U \propto r^{-1}$, which is a characteristic of the electrical interaction. The result for the energy of the $n$th standing wave pattern was $E_n \propto n^{-2}$.

There are other systems of physical interest in which we have $U \propto r^k$ for values of $k$ besides $-1$. Problem 23 discusses the ground state of the harmonic oscillator, with $k = 2$ (and a positive constant of proportionality). In particle physics, systems called charmonium and bottomonium are made out of pairs of subatomic particles called quarks, which interact according to $k = 1$, i.e., a force that is independent of distance. (Here we have a positive constant of proportionality, and $r > 0$ by definition. The motion turns out not to be too relativistic, so the Schrödinger equation is a reasonable approximation.) The figure shows actual energy levels for these three systems, drawn with different energy scales so that they can all be shown side by side. The sequence of energies in hydrogen approaches a limit, which is the energy required to ionize the atom. In charmonium, only the first three levels are known.\footnote{See Barnes et al., “The XYZs of Charmonium at BES,” \texttt{arxiv.org/abs/hep-ph/0608103}. To avoid complication, the levels shown are only those in the group known for historical reasons as the $\Psi$ and $J/\Psi$.}

Generalize the method used for $k = -1$ to any value of $k$, and find the exponent $j$ in the resulting proportionality $E_n \propto n^j$. Compare the theoretical calculation with the behavior of the actual energies shown in the figure. Comment on the limit $k \to \infty$.

The electron, proton, and neutron were discovered, respectively, in 1897, 1919, and 1932. The neutron was late to the party, and some physicists felt that it was unnecessary to consider it as fundamental. Maybe it could be explained as simply a proton with an electron trapped inside it. The charges would cancel out, giving the composite particle the correct neutral charge, and the masses at least approximately made sense (a neutron is heavier than a proton). (a) Given that the diameter of a proton is on the order of $10^{-15}$ m, use the Heisenberg uncertainty principle to estimate the trapped electron’s minimum momentum. \footnote{See Barnes et al., “The XYZs of Charmonium at BES,” \texttt{arxiv.org/abs/hep-ph/0608103}. To avoid complication, the levels shown are only those in the group known for historical reasons as the $\Psi$ and $J/\Psi$.}

(b) Find the electron’s minimum kinetic energy.

(c) Show via $E = mc^2$ that the proposed explanation fails, because the contribution to the neutron’s mass from the electron’s kinetic energy would be many orders of magnitude too large.
Suppose that an electron, in one dimension, is confined to a certain region of space so that its wavefunction is given by

\[ \Psi = \begin{cases} 
0 & \text{if } x < 0 \\
A \sin(2\pi x/L) & \text{if } 0 \leq x \leq L \\
0 & \text{if } x > L 
\end{cases} \]

Determine the constant \( A \) from normalization.

In the following, \( x \) and \( y \) are variables, while \( u \) and \( v \) are constants. Compute (a) \( \partial(ux \ln(vy))/\partial x \), (b) \( \partial(ux \ln(vy))/\partial y \).

(a) A radio transmitter radiates power \( P \) in all directions, so that the energy spreads out spherically. Find the energy density at a distance \( r \).

(b) Let the wavelength be \( \lambda \). As described in example 8 on p. 876, find the number of photons in a volume \( \lambda^3 \) at this distance \( r \).

(c) For a 1000 kHz AM radio transmitting station, assuming reasonable values of \( P \) and \( r \), verify, as claimed in the example, that the result from part b is very large.

The wavefunction \( \Psi \) of an electron is a complex number. Make up an example of a value for the wavefunction that is not a real number, and consider the following expressions: \( \Psi^2 \), \( |\Psi|^2 \), \( |\Psi|^2 \).

Which of these would it make sense to interpret as a probability density? All of them? Some? Only one?

(a) Consider the function defined by \( f(x,y) = (x - y)^2 \). Visualize the graph of this function as a surface. (This is a simple enough example that you should not have to resort to computer software.) Use this visualization to determine the behavior of the sign of the Laplacian, as in example 20 on p. 910.

(b) Consider the following incorrect calculation of this Laplacian. We take the first derivatives and find

\[ \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y} = 0. \]

Next we take the second derivatives, but those are zero as well, so the Laplacian is zero. Critique this calculation in two ways: (1) by comparing with part a; (2) by comparing with a correct calculation.

(c) In general, if we have a function \( f \) of two variables, the quantity \( Q = \partial f/\partial x + \partial f/\partial y \) can never be of physical interest, because it is not rotationally invariant (sec. 3.4.2, p. 195). Prove this by showing that by rotating your coordinate system, you can get a completely different answer than the one calculated in part b.