been expected in classical physics. To preserve the correspondence between classical and quantum physics, the amount of energy deposited in a given region of the picture over the long run must be proportional to the square of the wave’s amplitude. The amount of energy deposited in a certain area depends on the number of photons picked up, which is proportional to the probability of finding any given photon there.

A microwave oven example 10

The figure shows two-dimensional (top) and one-dimensional (bottom) representations of the standing wave inside a microwave oven. Gray represents zero field, and white and black signify the strongest fields, with white being a field that is in the opposite direction compared to black. Compare the probabilities of detecting a microwave photon at points A, B, and C.

A and C are both extremes of the wave, so the probabilities of detecting a photon at A and C are equal. It doesn’t matter that we have represented C as negative and A as positive, because it is the square of the amplitude that is relevant. The amplitude at B is about 1/2 as much as the others, so the probability of detecting a photon there is about 1/4 as much.

The probability interpretation was disturbing to physicists who had spent their previous careers working in the deterministic world of classical physics, and ironically the most strenuous objections against it were raised by Einstein, who had invented the photon concept in the first place. The probability interpretation has nevertheless passed every experimental test, and is now as well established as any part of physics.

An aspect of the probability interpretation that has made many people uneasy is that the process of detecting and recording the photon’s position seems to have a magical ability to get rid of the wavelike side of the photon’s personality and force it to decide for once and for all where it really wants to be. But detection or measurement is after all only a physical process like any other, governed by the same laws of physics. We will postpone a detailed discussion of this issue until p. 868, since a measuring device like a digital camera is made of matter, but we have so far only discussed how quantum mechanics relates to light.

What is the proportionality constant? example 11

What is the proportionality constant that would make an actual equation out of (probability distribution) \( \propto (\text{amplitude})^2 \)?

The probability that the photon is in a certain small region of volume \( v \) should equal the fraction of the wave’s energy that is within that volume. For a sinusoidal wave, which has a single,
well-defined frequency \( f \), this gives

\[
P = \frac{\text{energy in volume } v}{\text{energy of photon}} = \frac{\text{energy in volume } v}{hf}.
\]

We assume \( v \) is small enough so that the electric and magnetic fields are nearly constant throughout it. We then have

\[
P = \frac{\left( \frac{1}{8\pi k} |E|^2 + \frac{c^2}{8\pi k} |B|^2 \right) v}{hf}.
\]

We can simplify this formidable looking expression by recognizing that in a plane wave, \( |E| \) and \( |B| \) are related by \( |E| = c|B| \). This implies (problem 40, p. 729), that the electric and magnetic fields each contribute half the total energy, so we can simplify the result to

\[
P = 2 \left( \frac{1}{8\pi k} |E|^2 \right) \frac{v}{hf} = \frac{v}{4\pi khf} |E|^2.
\]

The probability is proportional to the square of the wave’s amplitude, as advertised.\(^3\)

\(^3\)But note that along the way, we had to make two crucial assumptions: that the wave was sinusoidal, and that it was a plane wave. These assumptions will not prevent us from describing examples such as double-slit diffraction, in which the wave is approximately sinusoidal within some sufficiently small region such as one pixel of a camera’s imaging chip. Nevertheless, these issues turn out to be symptoms of deeper problems, beyond the scope of this book, involving the way in which relativity and quantum mechanics should be combined. As a taste of the ideas involved, consider what happens when a photon is reflected from a conducting surface, as in example 23 on p. 703, so that the electric field at the surface is zero, but the magnetic field isn’t. The superposition is a standing wave, not a plane wave, so \( |E| = c|B| \) need not hold, and doesn’t. A detector’s probability of detecting a photon near the surface could be zero if the detector sensed electric fields, but nonzero if it sensed magnetism. It doesn’t make sense to say that either of these is the probability that the photon “was really there.”
Discussion Questions

A Referring back to the example of the carrot in the microwave oven, show that it would be nonsensical to have probability be proportional to the field itself, rather than the square of the field.

B Einstein did not try to reconcile the wave and particle theories of light, and did not say much about their apparent inconsistency. Einstein basically visualized a beam of light as a stream of bullets coming from a machine gun. In the photoelectric effect, a photon “bullet” would only hit one atom, just as a real bullet would only hit one person. Suppose someone reading his 1905 paper wanted to interpret it by saying that Einstein’s so-called particles of light are simply short wave-trains that only occupy a small region of space. Comparing the wavelength of visible light (a few hundred nm) to the size of an atom (on the order of 0.1 nm), explain why this poses a difficulty for reconciling the particle and wave theories.

C Can a white photon exist?

D In double-slit diffraction of photons, would you get the same pattern of dots on the digital camera image if you covered one slit? Why should it matter whether you give the photon two choices or only one?

13.2.4 Photons in three dimensions

Up until now I’ve been sneaky and avoided a full discussion of the three-dimensional aspects of the probability interpretation. The example of the carrot in the microwave oven, for example, reduced to a one-dimensional situation because we were considering three points along the same line and because we were only comparing ratios of probabilities. The purpose of bringing it up now is to head off any feeling that you’ve been cheated conceptually rather than to prepare you for mathematical problem solving in three dimensions, which would not be appropriate for the level of this course.

A typical example of a probability distribution in section 13.1 was the distribution of heights of human beings. The thing that varied randomly, height, \( h \), had units of meters, and the probability distribution was a graph of a function \( D(h) \). The units of the probability distribution had to be \( m^{-1} \) (inverse meters) so that areas under the curve, interpreted as probabilities, would be unitless: (area) = (height)(width) = \( m^{-1} \cdot m \).

Now suppose we have a two-dimensional problem, e.g., the probability distribution for the place on the surface of a digital camera chip where a photon will be detected. The point where it is detected would be described with two variables, \( x \) and \( y \), each having units of meters. The probability distribution will be a function of both variables, \( D(x, y) \). A probability is now visualized as the volume under the surface described by the function \( D(x, y) \), as shown in figure n. The units of \( D \) must be \( m^{-2} \) so that probabilities will be unitless: (probability) = (depth)(length)(width) = \( m^{-2} \cdot m \cdot m \). In terms of calculus, we have \( P = \int D \, dx \, dy \).

Generalizing finally to three dimensions, we find by analogy that

\[ n \quad \text{Probability is the volume under a surface defined by} \quad D(x, y). \]
the probability distribution will be a function of all three coordinates, $D(x, y, z)$, and will have units of $m^{-3}$. It is unfortunately impossible to visualize the graph unless you are a mutant with a natural feel for life in four dimensions. If the probability distribution is nearly constant within a certain volume of space $v$, the probability that the photon is in that volume is simply $vD$. If not, then we can use an integral, $P = \int D \, dx \, dy \, dz$. 
13.3 Matter As a Wave

[In] a few minutes I shall be all melted... I have been wicked in my
day, but I never thought a little girl like you would ever be able to
melt me and end my wicked deeds. Look out — here I go!

_The Wicked Witch of the West_

As the Wicked Witch learned the hard way, losing molecular
cohesion can be unpleasant. That’s why we should be very grate-
ful that the concepts of quantum physics apply to matter as well
as light. If matter obeyed the laws of classical physics, molecules
wouldn’t exist.

Consider, for example, the simplest atom, hydrogen. Why does
one hydrogen atom form a chemical bond with another hydrogen
atom? Roughly speaking, we’d expect a neighboring pair of hy-
drogen atoms, A and B, to exert no force on each other at all,
attractive or repulsive: there are two repulsive interactions (proton
A with proton B and electron A with electron B) and two attractive
interactions (proton A with electron B and electron A with proton
B). Thinking a little more precisely, we should even expect that once
the two atoms got close enough, the interaction would be repulsive.
For instance, if you squeezed them so close together that the two
protons were almost on top of each other, there would be a tremen-
dously strong repulsion between them due to the $1/r^2$ nature of the
electrical force. The repulsion between the electrons would not be
as strong, because each electron ranges over a large area, and is not
likely to be found right on top of the other electron. Thus hydrogen
molecules should not exist according to classical physics.

Quantum physics to the rescue! As we’ll see shortly, the whole
problem is solved by applying the same quantum concepts to elec-
Electrons as waves

We started our journey into quantum physics by studying the random behavior of matter in radioactive decay, and then asked how randomness could be linked to the basic laws of nature governing light. The probability interpretation of wave-particle duality was strange and hard to accept, but it provided such a link. It is now natural to ask whether the same explanation could be applied to matter. If the fundamental building block of light, the photon, is a particle as well as a wave, is it possible that the basic units of matter, such as electrons, are waves as well as particles?

A young French aristocrat studying physics, Louis de Broglie (pronounced “broylee”), made exactly this suggestion in his 1923 Ph.D. thesis. His idea had seemed so farfetched that there was serious doubt about whether to grant him the degree. Einstein was asked for his opinion, and with his strong support, de Broglie got his degree.

Only two years later, American physicists C.J. Davisson and L. Germer confirmed de Broglie’s idea by accident. They had been studying the scattering of electrons from the surface of a sample of nickel, made of many small crystals. (One can often see such a crystalline pattern on a brass doorknob that has been polished by repeated handling.) An accidental explosion occurred, and when they put their apparatus back together they observed something entirely different: the scattered electrons were now creating an interference pattern! This dramatic proof of the wave nature of matter came about because the nickel sample had been melted by the explosion and then resolidified as a single crystal. The nickel atoms, now nicely arranged in the regular rows and columns of a crystalline lattice, were acting as the lines of a diffraction grating. The new crystal was analogous to the type of ordinary diffraction grating in which the lines are etched on the surface of a mirror (a reflection grating) rather than the kind in which the light passes through the transparent gaps between the lines (a transmission grating).

Although we will concentrate on the wave-particle duality of electrons because it is important in chemistry and the physics of atoms, all the other “particles” of matter you’ve learned about show wave properties as well. Figure a, for instance, shows a wave interference pattern of neutrons.

It might seem as though all our work was already done for us, and there would be nothing new to understand about electrons: they have the same kind of funny wave-particle duality as photons. That’s almost true, but not quite. There are some important ways in which electrons differ significantly from photons:
1. Electrons have mass, and photons don’t.

2. Photons always move at the speed of light, but electrons can move at any speed less than $c$.

3. Photons don’t have electric charge, but electrons do, so electric forces can act on them. The most important example is the atom, in which the electrons are held by the electric force of the nucleus.

4. Electrons cannot be absorbed or emitted as photons are. Destroying an electron or creating one out of nothing would violate conservation of charge.

(In section 13.4 we will learn of one more fundamental way in which electrons differ from photons, for a total of five.)

Because electrons are different from photons, it is not immediately obvious which of the photon equations from chapter 11 can be applied to electrons as well. A particle property, the energy of one photon, is related to its wave properties via $E = hf$ or, equivalently, $E = hc/\lambda$. The momentum of a photon was given by $p = hf/c$ or $p = h/\lambda$. Ultimately it was a matter of experiment to determine which of these equations, if any, would work for electrons, but we can make a quick and dirty guess simply by noting that some of the equations involve $c$, the speed of light, and some do not. Since $c$ is irrelevant in the case of an electron, we might guess that the
equations of general validity are those that do not have $c$ in them:

$$E = hf$$
$$p = h/\lambda$$

This is essentially the reasoning that de Broglie went through, and experiments have confirmed these two equations for all the fundamental building blocks of light and matter, not just for photons and electrons.

The second equation, which I soft-pedaled in the previous chapter, takes on a greater important for electrons. This is first of all because the momentum of matter is more likely to be significant than the momentum of light under ordinary conditions, and also because force is the transfer of momentum, and electrons are affected by electrical forces.

**The wavelength of an elephant**  
**example 12**

What is the wavelength of a trotting elephant?

One may doubt whether the equation should be applied to an elephant, which is not just a single particle but a rather large collection of them. Throwing caution to the wind, however, we estimate the elephant’s mass at $10^3$ kg and its trotting speed at 10 m/s. Its wavelength is therefore roughly

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(10^3 \text{ kg})(10 \text{ m/s})} = 10^{-37} \text{ m}$$

The wavelength found in this example is so fantastically small that we can be sure we will never observe any measurable wave phenomena with elephants or any other human-scale objects. The result is numerically small because Planck’s constant is so small, and as in some examples encountered previously, this smallness is in accord with the correspondence principle.

Although a smaller mass in the equation $\lambda = h/mv$ does result in a longer wavelength, the wavelength is still quite short even for individual electrons under typical conditions, as shown in the following example.

**The typical wavelength of an electron**  
**example 13**

Electrons in circuits and in atoms are typically moving through
These two electron waves are not distinguishable by any measuring device.

voltage differences on the order of 1 V, so that a typical energy is \((e)(1 \text{ V})\), which is on the order of \(10^{-19} \text{ J}\). What is the wavelength of an electron with this amount of kinetic energy?

\[ E = (e)(1 \text{ V}) = 10^{-19} \text{ J}. \]

This energy is nonrelativistic, since it is much less than \(mc^2\). Momentum and energy are therefore related by the nonrelativistic equation \(K = p^2/2m\). Solving for \(p\) and substituting in to the equation for the wavelength, we find

\[ \lambda = \frac{h}{\sqrt{2mK}} = 1.6 \times 10^{-9} \text{ m}. \]

This is on the same order of magnitude as the size of an atom, which is no accident: as we will discuss in the next chapter in more detail, an electron in an atom can be interpreted as a standing wave. The smallness of the wavelength of a typical electron also helps to explain why the wave nature of electrons wasn’t discovered until a hundred years after the wave nature of light. To scale the usual wave-optics devices such as diffraction gratings down to the size needed to work with electrons at ordinary energies, we need to make them so small that their parts are comparable in size to individual atoms. This is essentially what Davisson and Germer did with their nickel crystal.

**self-check E**

These remarks about the inconvenient smallness of electron wavelengths apply only under the assumption that the electrons have typical energies. What kind of energy would an electron have to have in order to have a longer wavelength that might be more convenient to work with?

\[ \text{Answer, p. 933} \]

**What kind of wave is it?**

If a sound wave is a vibration of matter, and a photon is a vibration of electric and magnetic fields, what kind of a wave is an electron made of? The disconcerting answer is that there is no experimental “observable,” i.e., directly measurable quantity, to correspond to the electron wave itself. In other words, there are devices like microphones that detect the oscillations of air pressure in a sound wave, and devices such as radio receivers that measure the oscillation of the electric and magnetic fields in a light wave, but nobody has ever found any way to measure the electron wave directly.

We can of course detect the energy (or momentum) possessed by an electron just as we could detect the energy of a photon using a digital camera. (In fact I’d imagine that an unmodified digital camera chip placed in a vacuum chamber would detect electrons just as handily as photons.) But this only allows us to determine where the

\[ b/ \text{These two electron waves are not distinguishable by any measuring device.} \]
wave carries high probability and where it carries low probability. Probability is proportional to the square of the wave’s amplitude, but measuring its square is not the same as measuring the wave itself. In particular, we get the same result by squaring either a positive number or its negative, so there is no way to determine the positive or negative sign of an electron wave.

Most physicists tend toward the school of philosophy known as operationalism, which says that a concept is only meaningful if we can define some set of operations for observing, measuring, or testing it. According to a strict operationalist, then, the electron wave itself is a meaningless concept. Nevertheless, it turns out to be one of those concepts like love or humor that is impossible to measure and yet very useful to have around. We therefore give it a symbol, \( \Psi \) (the capital Greek letter psi), and a special name, the electron wavefunction (because it is a function of the coordinates \( x, y, \) and \( z \) that specify where you are in space). It would be impossible, for example, to calculate the shape of the electron wave in a hydrogen atom without having some symbol for the wave. But when the calculation produces a result that can be compared directly to experiment, the final algebraic result will turn out to involve only \( \Psi^2 \), which is what is observable, not \( \Psi \) itself.

Since \( \Psi \), unlike \( E \) and \( B \), is not directly measurable, we are free to make the probability equations have a simple form: instead of having the probability density equal to some funny constant multiplied by \( \Psi^2 \), we simply define \( \Psi \) so that the constant of proportionality is one:

\[
\text{(probability distribution)} = \Psi^2.
\]

Since the probability distribution has units of \( m^{-3} \), the units of \( \Psi \) must be \( m^{-3/2} \).

Discussion Question

A. Frequency is oscillations per second, whereas wavelength is meters per oscillation. How could the equations \( E = hf \) and \( p = h/\lambda \) be made to look more alike by using quantities that were more closely analogous? (This more symmetric treatment makes it easier to incorporate relativity into quantum mechanics, since relativity says that space and time are not entirely separate.)

13.3.2 Dispersive waves

A colleague of mine who teaches chemistry loves to tell the story about an exceptionally bright student who, when told of the equation \( p = h/\lambda \), protested, “But when I derived it, it had a factor of 2!” The issue that’s involved is a real one, albeit one that could be glossed over (and is, in most textbooks) without raising any alarms in the mind of the average student. The present optional section addresses this point; it is intended for the student who wishes to delve a little deeper.
Here's how the now-legendary student was presumably reasoning. We start with the equation $v = f\lambda$, which is valid for any sine wave, whether it's quantum or classical. Let's assume we already know $E = hf$, and are trying to derive the relationship between wavelength and momentum:

$$\lambda = \frac{v}{f} = \frac{vh}{E} = \frac{vh}{\frac{1}{2}mv^2} = \frac{2h}{mv} = \frac{2h}{p}.$$ 

The reasoning seems valid, but the result does contradict the accepted one, which is after all solidly based on experiment.

The mistaken assumption is that we can figure everything out in terms of pure sine waves. Mathematically, the only wave that has a perfectly well defined wavelength and frequency is a sine wave, and not just any sine wave but an infinitely long sine wave, c. The unphysical thing about such a wave is that it has no leading or trailing edge, so it can never be said to enter or leave any particular region of space. Our derivation made use of the velocity, $v$, and if velocity is to be a meaningful concept, it must tell us how quickly stuff (mass, energy, momentum, ...) is transported from one region of space to another. Since an infinitely long sine wave doesn’t remove any stuff from one region and take it to another, the “velocity of its stuff” is not a well defined concept.

Of course the individual wave peaks do travel through space, and one might think that it would make sense to associate their speed with the “speed of stuff,” but as we will see, the two velocities are in general unequal when a wave’s velocity depends on wavelength. Such a wave is called a dispersive wave, because a wave pulse consisting of a superposition of waves of different wavelengths will separate (disperse) into its separate wavelengths as the waves move through space at different speeds. Nearly all the waves we have encountered have been nondispersive. For instance, sound waves and light waves (in a vacuum) have speeds independent of wavelength. A water wave is one good example of a dispersive wave. Long-wavelength water waves travel faster, so a ship at sea that encounters a storm typically sees the long-wavelength parts of the wave first. When dealing with dispersive waves, we need symbols and words to distinguish the two speeds. The speed at which wave peaks move is called the phase velocity, $v_p$, and the speed at which “stuff” moves is called the group velocity, $v_g$. 
An infinite sine wave can only tell us about the phase velocity, not the group velocity, which is really what we would be talking about when we refer to the speed of an electron. If an infinite sine wave is the simplest possible wave, what’s the next best thing? We might think the runner up in simplicity would be a wave train consisting of a chopped-off segment of a sine wave, d. However, this kind of wave has kinks in it at the end. A simple wave should be one that we can build by superposing a small number of infinite sine waves, but a kink can never be produced by superposing any number of infinitely long sine waves.

Actually the simplest wave that transports stuff from place to place is the pattern shown in figure e. Called a beat pattern, it is formed by superposing two sine waves whose wavelengths are similar but not quite the same. If you have ever heard the pulsating howling sound of musicians in the process of tuning their instruments to each other, you have heard a beat pattern. The beat pattern gets stronger and weaker as the two sine waves go in and out of phase with each other. The beat pattern has more “stuff” (energy, for example) in the areas where constructive interference occurs, and less in the regions of cancellation. As the whole pattern moves through space, stuff is transported from some regions and into other ones.

If the frequency of the two sine waves differs by 10%, for instance, then ten periods will be occur between times when they are in phase. Another way of saying it is that the sinusoidal “envelope” (the dashed lines in figure e) has a frequency equal to the difference in frequency between the two waves. For instance, if the waves had frequencies of 100 Hz and 110 Hz, the frequency of the envelope would be 10 Hz.

To apply similar reasoning to the wavelength, we must define a quantity \( z = 1/\lambda \) that relates to wavelength in the same way that frequency relates to period. In terms of this new variable, the \( z \) of the envelope equals the difference between the \( z' \)'s of the two sine waves.

The group velocity is the speed at which the envelope moves through space. Let \( \Delta f \) and \( \Delta z \) be the differences between the frequencies and \( z' \)'s of the two sine waves, which means that they equal the frequency and \( z \) of the envelope. The group velocity is \( v_g = f_{envelope}/\lambda_{envelope} = \Delta f/\Delta z \). If \( \Delta f \) and \( \Delta z \) are sufficiently small, we can approximate this expression as a derivative, \( v_g = \frac{df}{dz} \).

This expression is usually taken as the definition of the group velocity for wave patterns that consist of a superposition of sine waves having a narrow range of frequencies and wavelengths. In quantum mechanics, with \( f = E/h \) and \( z = p/h \), we have \( v_g = \frac{dE}{dp} \). In the case of a nonrelativistic electron the relationship between
energy and momentum is $E = p^2 / 2m$, so the group velocity is $dE / dp = p/m = v$, exactly what it should be. It is only the phase velocity that differs by a factor of two from what we would have expected, but the phase velocity is not the physically important thing.

13.3.3 **Bound states**

Electrons are at their most interesting when they’re in atoms, that is, when they are bound within a small region of space. We can understand a great deal about atoms and molecules based on simple arguments about such bound states, without going into any of the realistic details of atom. The simplest model of a bound state is known as the particle in a box: like a ball on a pool table, the electron feels zero force while in the interior, but when it reaches an edge it encounters a wall that pushes back inward on it with a large force. In particle language, we would describe the electron as bouncing off of the wall, but this incorrectly assumes that the electron has a certain path through space. It is more correct to describe the electron as a wave that undergoes 100% reflection at the boundaries of the box.

Like a generation of physics students before me, I rolled my eyes when initially introduced to the unrealistic idea of putting a particle in a box. It seemed completely impractical, an artificial textbook invention. Today, however, it has become routine to study electrons in rectangular boxes in actual laboratory experiments. The “box” is actually just an empty cavity within a solid piece of silicon, amounting in volume to a few hundred atoms. The methods for creating these electron-in-a-box setups (known as “quantum dots”) were a by-product of the development of technologies for fabricating computer chips.

For simplicity let’s imagine a one-dimensional electron in a box, i.e., we assume that the electron is only free to move along a line. The resulting standing wave patterns, of which the first three are shown in the figure, are just like some of the patterns we encountered with sound waves in musical instruments. The wave patterns must be zero at the ends of the box, because we are assuming the walls are impenetrable, and there should therefore be zero probability of finding the electron outside the box. Each wave pattern is labeled according to $n$, the number of peaks and valleys it has. In quantum physics, these wave patterns are referred to as “states” of the particle-in-the-box system.

The following seemingly innocuous observations about the particle in the box lead us directly to the solutions to some of the most vexing failures of classical physics:

*The particle’s energy is quantized (can only have certain values).* Each wavelength corresponds to a certain momentum, and a given
momentum implies a definite kinetic energy, \( E = \frac{p^2}{2m} \). (This is the second type of energy quantization we have encountered. The type we studied previously had to do with restricting the number of particles to a whole number, while assuming some specific wavelength and energy for each particle. This type of quantization refers to the energies that a single particle can have. Both photons and matter particles demonstrate both types of quantization under the appropriate circumstances.)

The particle has a minimum kinetic energy. Long wavelengths correspond to low momenta and low energies. There can be no state with an energy lower than that of the \( n = 1 \) state, called the ground state.

The smaller the space in which the particle is confined, the higher its kinetic energy must be. Again, this is because long wavelengths give lower energies.

<table>
<thead>
<tr>
<th>Spectra of thin gases</th>
<th>example 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>A fact that was inexplicable by classical physics was that thin gases absorb and emit light only at certain wavelengths. This was observed both in earthbound laboratories and in the spectra of stars. The figure on the left shows the example of the spectrum of the star Sirius, in which there are “gap teeth” at certain wavelengths. Taking this spectrum as an example, we can give a straightforward explanation using quantum physics.</td>
<td></td>
</tr>
</tbody>
</table>

Energy is released in the dense interior of the star, but the outer layers of the star are thin, so the atoms are far apart and electrons are confined within individual atoms. Although their standing-wave patterns are not as simple as those of the particle in the box, their energies are quantized.

When a photon is on its way out through the outer layers, it can be absorbed by an electron in an atom, but only if the amount of energy it carries happens to be the right amount to kick the electron from one of the allowed energy levels to one of the higher levels. The photon energies that are missing from the spectrum are the ones that equal the difference in energy between two electron energy levels. (The most prominent of the absorption lines in Sirius’s spectrum are absorption lines of the hydrogen atom.)

<table>
<thead>
<tr>
<th>The stability of atoms</th>
<th>example 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>In many Star Trek episodes the Enterprise, in orbit around a planet, suddenly lost engine power and began spiraling down toward the planet’s surface. This was utter nonsense, of course, due to conservation of energy: the ship had no way of getting rid of energy, so it did not need the engines to replenish it.</td>
<td></td>
</tr>
</tbody>
</table>

Consider, however, the electron in an atom as it orbits the nucleus. The electron does have a way to release energy: it has an acceleration due to its continuously changing direction of motion,
and according to classical physics, any accelerating charged particle emits electromagnetic waves. According to classical physics, atoms should collapse!

The solution lies in the observation that a bound state has a minimum energy. An electron in one of the higher-energy atomic states can and does emit photons and hop down step by step in energy. But once it is in the ground state, it cannot emit a photon because there is no lower-energy state for it to go to.

I began this section with a classical argument that chemical bonds, as in an H₂ molecule, should not exist. Quantum physics explains why this type of bonding does in fact occur. When the atoms are next to each other, the electrons are shared between them. The “box” is about twice as wide, and a larger box allows a smaller energy. Energy is required in order to separate the atoms. (A qualitatively different type of bonding is discussed on page 895. Example 23 on page 891 revisits the H₂ bond in more detail.)

Discussion Questions

A Neutrons attract each other via the strong nuclear force, so according to classical physics it should be possible to form nuclei out of clusters of two or more neutrons, with no protons at all. Experimental searches, however, have failed to turn up evidence of a stable two-neutron system (dineutron) or larger stable clusters. These systems are apparently not just unstable in the sense of being able to beta decay but unstable in the sense that they don’t hold together at all. Explain based on quantum physics why a dineutron might spontaneously fly apart.

B The following table shows the energy gap between the ground state and the first excited state for four nuclei, in units of picojoules. (The nuclei were chosen to be ones that have similar structures, e.g., they are all spherical in shape.)

<table>
<thead>
<tr>
<th>nucleus</th>
<th>energy gap (picojoules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴He</td>
<td>3.234</td>
</tr>
<tr>
<td>¹⁶O</td>
<td>0.968</td>
</tr>
<tr>
<td>⁴⁰Ca</td>
<td>0.536</td>
</tr>
<tr>
<td>²⁰⁸Pb</td>
<td>0.418</td>
</tr>
</tbody>
</table>

Explain the trend in the data.

13.3.4 The uncertainty principle and measurement

Eliminating randomness through measurement?

A common reaction to quantum physics, among both early-twentieth-century physicists and modern students, is that we should be able to get rid of randomness through accurate measurement. If I say, for example, that it is meaningless to discuss the path of a photon or an electron, one might suggest that we simply measure the particle’s position and velocity many times in a row. This series
Werner Heisenberg (1901-1976). Heisenberg helped to develop the foundations of quantum mechanics, including the Heisenberg uncertainty principle. He was the scientific leader of the Nazi atomic-bomb program up until its cancellation in 1942, when the military decided that it was too ambitious a project to undertake in wartime, and too unlikely to produce results.

A practical objection to this plan is that the process of measurement will have an effect on the thing we are trying to measure. This may not be of much concern, for example, when a traffic cop measures your car’s motion with a radar gun, because the energy and momentum of the radar pulses are insufficient to change the car’s motion significantly. But on the subatomic scale it is a very real problem. Making a videotape through a microscope of an electron orbiting a nucleus is not just difficult, it is theoretically impossible. The video camera makes pictures of things using light that has bounced off them and come into the camera. If even a single photon of visible light was to bounce off of the electron we were trying to study, the electron’s recoil would be enough to change its behavior significantly.

The Heisenberg uncertainty principle

This insight, that measurement changes the thing being measured, is the kind of idea that clove-cigarette-smoking intellectuals outside of the physical sciences like to claim they knew all along. If only, they say, the physicists had made more of a habit of reading literary journals, they could have saved a lot of work. The anthropologist Margaret Mead has recently been accused of inadvertently encouraging her teenaged Samoan informants to exaggerate the freedom of youthful sexual experimentation in their society. If this is considered a damning critique of her work, it is because she could have done better: other anthropologists claim to have been able to eliminate the observer-as-participant problem and collect untainted data.

The German physicist Werner Heisenberg, however, showed that in quantum physics, any measuring technique runs into a brick wall when we try to improve its accuracy beyond a certain point. Heisenberg showed that the limitation is a question of what there is to be known, even in principle, about the system itself, not of the ability or inability of a specific measuring device to ferret out information that is knowable but not previously hidden.

Suppose, for example, that we have constructed an electron in a box (quantum dot) setup in our laboratory, and we are able to adjust the length $L$ of the box as desired. All the standing wave patterns 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.

---

*Example 17*

> 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 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?

$\Delta \text{Answer, p. 933}$

**Measurement and Schrödinger’s cat**

On p. 851 I briefly mentioned an issue concerning measurement that we are now ready to address carefully. If you hang around a laboratory where quantum-physics experiments are being done and secretly record the physicists’ conversations, you’ll hear them say many things that assume the probability interpretation of quantum mechanics. Usually they will speak as though the randomness of quantum mechanics enters the picture when something is measured. In the digital camera experiments of section 13.2, for example, they would casually describe the detection of a photon at one of the pixels as if the moment of detection was when the photon was forced to “make up its mind.” Although this mental cartoon usually works fairly well as a description of things they experience in the lab, it cannot ultimately be correct, because it attributes a special role to measurement, which is really just a physical process like all other physical processes.\(^4\)

If we are to find an interpretation that avoids giving any special role to measurement processes, then we must think of the entire laboratory, including the measuring devices and the physicists themselves, as one big quantum-mechanical system made out of protons, neutrons, electrons, and photons. In other words, we should take quantum physics seriously as a description not just of microscopic

\(^4\)This interpretation of quantum mechanics is called the Copenhagen interpretation, because it was originally developed by a school of physicists centered in Copenhagen and led by Niels Bohr.
objects like atoms but of human-scale ("macroscopic") things like the apparatus, the furniture, and the people.

The most celebrated example is called the Schrödinger’s cat experiment. Luckily for the cat, there probably was no actual experiment — it was simply a “thought experiment” that the German theorist Schrödinger discussed with his colleagues. Schrödinger wrote:

One can even construct quite burlesque cases. A cat is shut up in a steel container, together with the following diabolical apparatus (which one must keep out of the direct clutches of the cat): In a Geiger tube [radiation detector] there is a tiny mass of radioactive substance, so little that in the course of an hour perhaps one atom of it disintegrates, but also with equal probability not even one; if it does happen, the counter [detector] responds and ... activates a hammer that shatters a little flask of prussic acid [filling the chamber with poison gas]. If one has left this entire system to itself for an hour, then one will say to himself that the cat is still living, if in that time no atom has disintegrated. The first atomic disintegration would have poisoned it.

Now comes the strange part. Quantum mechanics describes the particles the cat is made of as having wave properties, including the property of superposition. Schrödinger describes the wavefunction of the box’s contents at the end of the hour:

The wavefunction of the entire system would express this situation by having the living and the dead cat mixed ... in equal parts [50/50 proportions]. The uncertainty originally restricted to the atomic domain has been transformed into a macroscopic uncertainty...

At first Schrödinger’s description seems like nonsense. When you opened the box, would you see two ghostlike cats, as in a doubly exposed photograph, one dead and one alive? Obviously not. You would have a single, fully material cat, which would either be dead or very, very upset. But Schrödinger has an equally strange and logical answer for that objection. In the same way that the quantum randomness of the radioactive atom spread to the cat and made its wavefunction a random mixture of life and death, the randomness spreads wider once you open the box, and your own wavefunction becomes a mixture of a person who has just killed a cat and a person who hasn’t.5

Discussion Questions

A Compare \(\Delta p\) and \(\Delta x\) for the two lowest energy levels of the one-

5This interpretation, known as the many-worlds interpretation, was developed by Hugh Everett in 1957.
An electron in a gentle electric field gradually shortens its wavelength as it gains energy.

The wavefunction’s tails go where classical physics says they shouldn’t.

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 its charge is negative, it loses electrical energy by moving to a higher voltage, so its kinetic energy increases. As its electrical energy goes down, its kinetic energy goes up by an equal amount, keeping the total energy constant. Increasing kinetic energy implies a growing momentum, and therefore a shortening wavelength.

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 a TV 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.

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:

$$\frac{d^2}{dx^2} \sin(2\pi x/\lambda) = \frac{d}{dx} \left( \frac{2\pi}{\lambda} \cos \frac{2\pi x}{\lambda} \right)$$

$$= - \left( \frac{2\pi}{\lambda} \right)^2 \sin \frac{2\pi x}{\lambda}$$

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:

$$\frac{1}{\lambda} \frac{d^2}{dx^2} \Psi = - \left( \frac{2\pi}{\lambda} \right)^2 \Psi$$

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]:

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

\[ = \frac{1}{2m} \left( \frac{h}{2\pi} \right)^2 \left( \frac{2\pi}{\lambda} \right)^2 \Psi + U \cdot \Psi \]

\[ = -\frac{1}{2m} \left( \frac{h}{2\pi} \right)^2 \frac{d^2 \Psi}{dx^2} + U \cdot \Psi \]

Further simplification is achieved by using the symbol \( \hbar \) (\( h \) with a slash through it, read “h-bar”) as an abbreviation for \( h/2\pi \). 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?

▷ Answer, p. 933

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:

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?  

\( \triangleright \) Answer, p. 933

**Tunneling in alpha decay example 18**

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 874 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 $E > U$

The correspondence principle demands that in the classical limit $h \to 0$, 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. 874. In the remainder of this example, we analyze $E > U$, which turns out to be a little trickier.

The particle has enough energy to get over the barrier, and the classical result is that it continues forward at a different speed (a reduced speed if $U > 0$, or an increased one if $U < 0$), then regains its original speed as it emerges from the other side. What happens quantum-mechanically in this case? We would like to get a "tunneling" probability of 1 in the classical limit. The expression derived on p. 874, however, doesn't apply here, because it was derived under the assumption that the wavefunction inside the barrier was an exponential; in the classically allowed case, the barrier isn't classically forbidden, and the wavefunction inside it is a sine wave.

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. The analysis is the same as 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. 367. 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. 380, 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.
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 \( \frac{\partial^2 \Psi}{\partial x^2} \) 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 216, 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 \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \) is called the Laplacian. 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 1, 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

> 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 \( \frac{\partial}{\partial x} \), 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. \( \nabla^2 B < 0 \) 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.
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

$$\Psi = \sin \left( k_x x + k_y y + k_z z \right).$$

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

$$\nabla^2 \Psi = \left( -k_x^2 - k_y^2 - k_z^2 \right) \sin \left( k_x x + k_y y + k_z z \right)$$

$$= -\left( k_x^2 + k_y^2 + k_z^2 \right) \Psi.$$

The Schrödinger equation gives

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

$$= \frac{\hbar^2}{2m} \cdot -\left( k_x^2 + k_y^2 + k_z^2 \right) \Psi + U \cdot \Psi$$

$$E - U = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right),$$

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. 607.

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 5 gives a visual depiction of the difference between real and complex wavefunctions. The following remarks may also be helpful.

Neither of the graphs in 6/2 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. 340, where we saw the distinction between the motion of a wave and the motion of a wave pattern. In both examples in 6/2, the wave pattern is moving in a straight line to the right.

The helical graph in 6/2 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 s/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 s/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

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

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, s/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. 848. What happens if we then redefine the zero-level of \( U \) so that the electrons have \( E < 0 \)?

B 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 \( \Psi \)? Complex ones? What happens with standing waves?
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

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

$$= \frac{h}{2\pi \ell}$$

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 1**

What is the angular momentum of the wavefunction shown at the beginning of the section?  
Answer, p. 933

### 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 $p$, 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 accurately, 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 $xp_y$ 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 $p_y$. 

---

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1

2

b / Reconciling the uncertainty principle with the definition of angular momentum.
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, which we present without proof:

**The angular momentum vector in quantum physics**

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

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

**13.4.3 The hydrogen atom**

Deriving the wavefunctions of the states of the hydrogen atom from first principles would be mathematically too complex for this book, but it’s not hard to understand the logic behind such a wavefunction in visual terms. Consider the wavefunction from the beginning of the section, which is reproduced in figure c. 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.

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 13.4.4.

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 \( \ell_x = L_x/h \), \( \ell_y = L_y/h \), and \( \ell_z = L_z/h \). 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 \( \ell_z \).\(^6\)

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. 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:

- \( n = 1 \), \( \ell = 0 \), \( \ell_z = 0 \) one state
- \( n = 2 \), \( \ell = 0 \), \( \ell_z = 0 \) one state
- \( n = 2 \), \( \ell = 1 \), \( \ell_z = -1 \), 0, or 1 three states
- \( \ldots \)

**Self-check J**

Continue the list for \( n = 3 \).

\(^6\)See page 893 for a note about the two different systems of notations that are used for quantum numbers.
The three states of the hydrogen atom having the lowest energies.

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 e.

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 e to the corresponding features of the probability distribution pictures.

D  How can you tell from the wavefunction plots in figure e which ones have which angular momenta?
E Criticize the following incorrect statement: “The $\ell = 8$ wavefunction in figure c 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.

13.4.4 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 example, 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 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:

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

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 infinitely far apart. With this choice, negative energies correspond to bound states and positive energies to unbound ones.

Where does the mysterious numerical factor of $2.2 \times 10^{-18} \text{ J}$ 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, $f$. 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:

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

1 The energy levels of a particle in a box, contrasted with those of the hydrogen atom.
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

\[
\text{absolute value of total energy} = \frac{ke^2}{r} \sim K = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} \sim \frac{h^2n^2}{2mr^2}.
\]

We now solve the equation \( ke^2/r \sim \frac{h^2n^2}{2mr^2} \) for \( r \) and throw away numerical factors we can’t hope to have gotten right, yielding

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

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

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

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

\[
\Psi = ue^{-r/\alpha},
\]

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
\( \frac{\partial r}{\partial x} = \frac{x}{r} \) comes in handy. Computing the partial derivatives that occur in the Laplacian, we obtain for the \( x \) term

\[
\begin{align*}
\frac{\partial \Psi}{\partial x} &= \frac{\partial \Psi}{\partial r} \frac{\partial r}{\partial x} \\
&= -\frac{x}{ar} \Psi
\end{align*}
\]

\[
\begin{align*}
\frac{\partial^2 \Psi}{\partial x^2} &= -\frac{1}{ar} \Psi - \frac{x}{a} \left( \frac{\partial}{\partial x} \frac{1}{r} \right) \Psi + \left( \frac{x}{ar} \right)^2 \Psi \\
&= -\frac{1}{ar} \Psi + \frac{x^2}{ar^3} \Psi + \left( \frac{x}{ar} \right)^2 \Psi
\end{align*}
\]

so

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

The Schrödinger equation gives

\[
E \cdot \Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U \cdot \Psi
\]

\[
= \frac{\hbar^2}{2m} \left( \frac{2}{ar} - \frac{1}{a^2} \right) \Psi - \frac{k e^2}{r} \cdot \Psi
\]

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 \((\text{constant}/r) \times \Psi\). That means

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

and

\[
0 = \frac{\hbar^2}{mar} - \frac{k e^2}{r}
\]

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

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

and

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

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 \( \Psi = \hbar e^{-r/a} \) 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?

\( \triangleright \) Answer, p. 933
In example 16 on page 865, 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 859, 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.

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
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.

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 g/1, with the two peaks in phase with one another, or it could look like g/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\textsubscript{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.

State g/3, on the other hand, is not physically distinguishable from g/2, nor is g/4 from g/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.

13.4.5 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 \( \hbar/2 \).

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.

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 $-1/2$.

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 and 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>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>$\pm 1/2$</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.

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

The nuclear physics notation is more logical (not giving special sta-
tus 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:

\[
\begin{array}{cccc}
\ell = 0 & \ell = 1 & \ell = 2 & \ell = 3 \\
\text{s} & \text{p} & \text{d} & \text{f}
\end{array}
\]

\[
\begin{array}{ccccccccc}
n = 1 & n = 2 & n = 3 & n = 4 & n = 5 & n = 6 & n = 7 \\
\text{K} & \text{L} & \text{M} & \text{N} & \text{O} & \text{P} & \text{Q}
\end{array}
\]

The spdf labels are used in both nuclear 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 $j$.

### 13.4.6 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 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 electrons 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 $n = 2$ state.

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7After $f$, 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 $j$. 

The relatively complex spectra of elements heavier than hydrogen can be understood as arising from the great number of possible combinations 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**

Only one electron can ever occupy a given 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 principle 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:

- **H** 1 electron in an \( n = 1 \) state
- **He** 2 electrons in the two \( n = 1 \) states

The next row is built by filling the \( n = 2 \) energy levels:

- **Li** 2 electrons in \( n = 1 \) states, 1 electron in an \( n = 2 \) state
- **Be** 2 electrons in \( n = 1 \) states, 2 electrons in \( n = 2 \) states

...  

- **O** 2 electrons in \( n = 1 \) states, 6 electrons in \( n = 2 \) states
- **F** 2 electrons in \( n = 1 \) states, 7 electrons in \( n = 2 \) states
- **Ne** 2 electrons in \( n = 1 \) states, 8 electrons in \( n = 2 \) states

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 √, II, etc. are explained on page 907.

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 832.
   (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:

<table>
<thead>
<tr>
<th>isotope</th>
<th>half-life (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>211Pb</td>
<td>36.1</td>
</tr>
<tr>
<td>214Pb</td>
<td>26.8</td>
</tr>
<tr>
<td>214Bi</td>
<td>19.7</td>
</tr>
<tr>
<td>223Fr</td>
<td>21.8</td>
</tr>
<tr>
<td>239U</td>
<td>23.5</td>
</tr>
</tbody>
</table>

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>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
</tr>
<tr>
<td>first ion speed</td>
</tr>
<tr>
<td>second ion speed</td>
</tr>
<tr>
<td>third ion speed</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.

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.)
11 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? $\sqrt{12}$

12 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.]

13 Suppose we want to build an electronic light sensor using an apparatus like the one described in subsection 13.2.2 on p. 842. 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.

Which figure could be an electron speeding up as it moves to the right? Explain.

The beam of a 100-W overhead projector covers an area of $1 \text{ m} \times 1 \text{ m}$ 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 ($\sim 10 \text{ ns}$), 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 $10^{-15} \text{ m}$. (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 $1 \text{ mW/m}^2$.

(b) The energy, $E_s$, required for the electron to escape through the surface of the cathode is on the order of $10^{-19} \text{ J}$. 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.