Let $\Psi = e^{2x+y}$. Compute $\nabla^2 \Psi$.  

Key to symbols:

- easy
- typical
- challenging
- difficult
- very difficult

✓ An answer check is available at www.lightandmatter.com.
Exercises

Exercise 13A: Quantum Versus Classical Randomness

1. Imagine the classical version of the particle in a one-dimensional box. Suppose you insert the particle in the box and give it a known, predetermined energy, but a random initial position and a random direction of motion. You then pick a random later moment in time to see where it is. Sketch the resulting probability distribution by shading on top of a line segment. Does the probability distribution depend on energy?

2. Do similar sketches for the first few energy levels of the quantum mechanical particle in a box, and compare with 1.

3. Do the same thing as in 1, but for a classical hydrogen atom in two dimensions, which acts just like a miniature solar system. Assume you’re always starting out with the same fixed values of energy and angular momentum, but a position and direction of motion that are otherwise random. Do this for \( L = 0 \), and compare with a real \( L = 0 \) probability distribution for the hydrogen atom.

4. Repeat 3 for a nonzero value of \( L \), say \( L = \hbar \).

5. Summarize: Are the classical probability distributions accurate? What qualitative features are possessed by the classical diagrams but not by the quantum mechanical ones, or vice-versa?
Exercise 13B: Choice of quantum numbers

We could choose to identify a human by their first and last names, or by their social security number. We’re free to choose any set of labels, as long as they’re compatible.

1. Warm-up, nothing to do with quantum mechanics:

Express the $x', y'$ coordinates in terms of the $x, y$ coordinates:

$$x' = x + y$$
$$y' = x + y$$

2. Consider these four $\ell = 1$ wavefunctions on the “quantum moat:”

$$\Psi_{\bigcirc} = e^{i\theta} \quad \Psi_{\bigcirc} = e^{-i\theta}$$
$$\Psi_s = \sin \theta \quad \Psi_c = \cos \theta$$

Determine the normalization factor for your group’s wave.

3. We now want to discuss the standing waves in terms of the traveling waves:

$$\Psi_c = \Psi_{\bigcirc} + \Psi_{\bigcirc}$$
$$\Psi_s = \Psi_{\bigcirc} + \Psi_{\bigcirc}$$

Determine the coefficients assigned to your group, and check your equation at the value of $\theta$ assigned to your group: $\theta = 0, \pi/2, \pi, \text{ or } 3\pi/2$.

4. An electron is initially in state $\Psi_c$, and Jane then measures its angular momentum. Discuss what happens to the electron’s wavefunction and to Jane’s, as in sec. 13.2.4, p. 885, on entanglement.

5. Discuss the probability interpretation and normalization.
Exercise 13C: Rotation around different axes

This exercise refers to the example at the beginning of section 13.4.3 on p. 923, which analyzes the figure below:

To simplify the writing:

- $\Psi_{-1}$ means the state with $\ell_z = -1$, $\Psi_0$ has $\ell_z = 0$, etc.
- States with definite values of $\ell_x$ are notated as $\Psi_{\ell_x=0}$, etc.

1. The wavefunctions are shown with values of the wavefunction written at the north pole and at two points on the equator. Fill in the south poles. Why do the results make sense physically for the $\ell_z = 1$ and $-1$ wavefunctions?

2. By rotating the pictures 90 degrees counterclockwise, we can make states of definite $\ell_x$. We now want to express the states of definite $\ell_x$ in terms of the states of definite $\ell_z$.

\[
\Psi_{\ell_x=0} = \frac{1}{\sqrt{2}} \Psi_{-1} + 0 \Psi_0 + \frac{1}{\sqrt{2}} \Psi_1
\]

Done on p. 923.

\[
\Psi_{\ell_x=1} = \Psi_{-1} + \Psi_0 + \Psi_1
\]

Demonstrated by the instructor.

\[
\Psi_{\ell_x=-1} = \Psi_{-1} + \Psi_0 + \Psi_1
\]

Done by the students.

3. Fred takes a molecule known to have $\ell = 1$, and measures its $\ell_x$. (This can be done by passing it through a magnetic field, as described in more detail in section 14.1.) If the molecule is not prepared in any particular orientation, then the result is random, and can be $\ell_x = -1$, 0, or 1. (The probabilities are all 1/3, although this is not obvious.) Suppose he measures $\ell_x = 0$, so that after measurement, he is sure that the wavefunction is $\Psi_{\ell_x=0}$. (Fred may now be superimposed with other versions of himself who saw $\ell_x = -1$ or 1, but we stop keeping track of them now.)

Now suppose that Fred follows up with a second measurement, on the same molecule, but this time he orients the magnetic field so that he’s measuring $\ell_z$. What are the probabilities of the three possible results? Check normalization.
Exercise 13D: The Einstein-Podolsky-Rosen paradox

A nucleus having zero angular momentum undergoes symmetric fission into two fragments, each with \( \ell = 1 \). By conservation of momentum, they fly off back to back, and by conservation of angular momentum their angular momenta are also opposite. Let’s say that except for this correlation, the two angular momentum vectors are randomly oriented.

1. Warm-up: Suppose Alice measures the \( \ell_x \) of particle A, and Bob measures \( \ell_x \) of fragment B. Make a table of the probabilities of the outcomes.

<table>
<thead>
<tr>
<th>particle A (( \ell_x ))</th>
<th>particle B (( \ell_x ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ell_x = -1 )</td>
<td>( \ell_x = -1 )</td>
</tr>
<tr>
<td>( \ell_x = 0 )</td>
<td>( \ell_x = 0 )</td>
</tr>
<tr>
<td>( \ell_x = 1 )</td>
<td>( \ell_x = 1 )</td>
</tr>
</tbody>
</table>

2. In a 1935 paper that ended up being one of the most frequently cited physics papers of all time, Einstein and his collaborators considered a scenario similar to the following. Suppose now that Alice measures \( \ell_x \), but Bob measures \( \ell_z \). It shouldn’t matter who goes first, but let’s say that Alice does. Using the results of exercise C, compute the probabilities in the row assigned to your group. Take into account the factor of 1/3, because in this table, as in the first one, we’re talking about the probability of a certain result for A and a certain result for B.

<table>
<thead>
<tr>
<th>Bob’s probabilities (( \ell_z ))</th>
<th>( \ell_z = -1 )</th>
<th>( \ell_z = 0 )</th>
<th>( \ell_z = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3 of the time, Alice gets ( \ell_x = -1 )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
</tr>
<tr>
<td>1/3 of the time, Alice gets ( \ell_x = 0 )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
</tr>
<tr>
<td>1/3 of the time, Alice gets ( \ell_x = 1 )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
<td>( \Rightarrow )</td>
</tr>
<tr>
<td>total probabilities for Bob</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Can Alice send information to Bob by deciding whether or not to measure her particle’s \( \ell_x \)?
14.1 The Stern-Gerlach experiment

In 1921, Otto Stern proposed an experiment about angular momentum, shown in figure a on p. 958, that his boss at the University of Frankfurt and many of his colleagues were certain wouldn’t work. At this time, quantization of angular momentum had been proposed by Niels Bohr, but most physicists, if they had heard of it at all, thought of the idea as a philosophical metaphor or a mathematical trick that just happened to give correct results. World War I was over, hyperinflation was getting under way in Germany (a paper mark was worth a few percent of its prewar value), and the Nazi coup was still in the future, so that Stern, a Jew, had not yet been forced to flee to America. Because of the difficult economic situation, Stern and his colleague Walther Gerlach scraped up some of the funds to carry out the experiment from US banker Henry Goldman, cofounder of the investment house Goldman-Sachs.
The entire apparatus was sealed inside a vacuum chamber with the best vacuum obtainable at the time. A sample of silver was heated to 1000°C, evaporating it. The atoms leaving the oven encountered two narrow slits, so that what emerged was a beam with a width of only 0.03 mm, or about a third of the width of a human hair. The atoms then encountered a magnetic field. Because the atoms were electrically neutral, we would normally expect them to be unaffected by a magnetic field. But in the planetary model of the atom, we imagine the electrons as orbiting in circles like little current loops, which would give the atom a magnetic dipole moment \( \mathbf{m} \). Even if we are sophisticated enough about quantum mechanics not to believe in the circular orbits, it is reasonable to imagine that such a dipole moment would exist. When a dipole encounters a nonuniform field, it experiences a force (example 7, p. 589). In this example, the forces in the \( x \) and \( z \) directions would be \( F_x = \mathbf{m} \cdot (\partial \mathbf{B}/\partial x) \) and \( F_z = \mathbf{m} \cdot (\partial \mathbf{B}/\partial z) \). (Because of Gauss’s law for magnetism, these two derivatives are not independent — we have \( \partial B_x/\partial x + \partial B_z/\partial z = 0 \).) The rapidly varying magnetic field for this experiment was provided by a pair of specially shaped magnet poles, described in example 27, p. 743.

Because electrons have charge, we expect the motion of an electron to give it a magnetic dipole moment \( \mathbf{m} \). But they also have mass, so for exactly the same reasons, we expect there to be some angular momentum \( \mathbf{L} \) as well. The analogy is in fact mathematically exact, as discussed in sec. 11.2.4, p. 695. Therefore this experiment with dipoles and magnetic fields is actually a probe of the behavior of angular momentum at the atomic level.

Luckily for Stern and Gerlach, who had no modern knowledge of atomic structure, the silver atoms that they chose to use do happen to have nonzero total \( \mathbf{L} \), and therefore nonzero \( \mathbf{m} \). The atoms come out of the oven with random orientations.

Classically, we would expect the following. Each atom has an energy \( \mathbf{m} \cdot \mathbf{B} \) due to its interaction with the magnetic field, and this energy is conserved, so that the component \( m_x \) stays constant. However, there is a torque \( \mathbf{m} \times \mathbf{B} \), and this causes the direction of the atom’s angular momentum to precess, i.e., wobble like a top, with its angular momentum forming a cone centered on the \( x \) axis (example 25, p. 289). This precession is extremely fast, carrying out about \( 10^{10} \) wobbles per second, so that the atom precesses about \( 10^6 \) times while traveling the 3.5 cm length of the spectrometer. So even though the forces \( F_x \) and \( F_z \) are typically about the same size, the rapid precession causes \( F_z \) to average out to nearly zero, and only a deflection in the \( x \) direction is expected. Because the orientations of the atoms are random as they enter the magnetic field, they will have every possible value of \( L_x \) ranging from \(-|\mathbf{L}|\) to \(+|\mathbf{L}|\), and therefore we expect that when the magnetic field is turned on, the effect should be to smear out the image on the glass plate from a
vertical line to a somewhat wider oval. The atoms are dispersed from left to right along a certain scale of measurement according to their random value of $L_x$. The spectrometer is a device for determining $L_x$, a continuously varying number.

But that’s all the classical theory. Quantum mechanically, $L_x$ is quantized, so that only certain very specific values of $F_x$ can occur. Although the discussion of precession above is really classical rather than quantum-mechanical, the result of $F_x$ averaging out to zero turns out to be approximately right if the field is strong. Therefore we expect to see well separated vertical bands on the glass plate corresponding to the quantized values of $L_x$. This is approximately what is seen in figure a, although the field rapidly weakens outside the $x$-$y$ plane, so we get the slightly more complicated pattern like a sideways lipstick kiss. Since we observe two values of $L_x$ (the two “lips”), we conclude from these results that a silver atom has spin $1/2$, so that $L_x$ takes on the values $-\hbar/2$ and $+\hbar/2$. Although it took about five years for the experiment to be interpreted completely correctly, we now understand the Stern-Gerlach experiment to be not just a confirmation of the quantization of angular momentum along any given axis but also the first experimental evidence that the electron has an intrinsic spin of $1/2$.

**Discussion Questions**

A  Could the Stern-Gerlach experiment be carried out with a beam of electrons?

B  A few weeks after the Stern-Gerlach experiment’s results became public, Einstein and Ehrenfest carried out the following reasoning, which seemed to them to make the results inexplicable. Before a particular silver atom enters the magnetic field, its magnetic moment $m$ is randomly oriented. Once it enters the magnetic field, it has an energy $m \cdot B$. Unless there is a mechanism for the transfer of energy in or out of the atom, this energy can’t change, and therefore the magnetic moment can only precess about the $B$ vector, but the angle between $m$ and $B$ must remain the same. Therefore the atom cannot align itself with the field. (They considered various mechanisms of energy loss, such as collisions and radiation, and concluded that all of them were too slow by orders of magnitude to have an effect during the atom’s time of flight.) It seemed to them that as soon as the atom left the oven, it was somehow required to have anticipated the direction of the field and picked one of two orientations with respect to it. How can this paradox be resolved?

C  Suppose we send a beam of oxygen molecules, with $L = \hbar$, through a Stern-Gerlach spectrometer, throwing away the emerging parts with $\ell_x = -1$ and $+1$ to make a beam of the pure $\ell_x = 0$ state. Now we let this beam pass through a second spectrometer that is identical but oriented along the $z$ axis. Can we produce a beam in which every molecule has both $\ell_x = 0$ and $\ell_z = +1$? Hint: See the example in fig. d, p. 923.
14.2 Rotation and vibration

14.2.1 Types of excitations

Figure a shows the visible-light spectrum of the molecule N\(_2\). Because this particular chemical bond is unusually strong, the molecule does not break apart, even at the high temperature of a gas discharge tube, so we see the spectrum of the molecule, not of monoatomic nitrogen. This spectrum is more complex than the spectrum of the hydrogen atom, and that’s not surprising, because the number of different states grows exponentially with the number of particles (here, 14 electrons plus 2 nuclei).

What is more surprising is that there are some clear, simple patterns in this spectrum — patterns simpler than any that we would see in the spectrum of a monoatomic gas with the same number of particles. To start to understand this, we note that N\(_2\) lacks the spherical symmetry of an individual atom, but it does have an axis of symmetry, b/1. These properties are also possessed by many nuclei, e.g., b/2. We now consider three different ways in which an excited energy state could occur in N\(_2\):

- Individual *particles* (electrons) can be raised to a higher energy level.
- The molecule can *vibrate* along its long axis, so that the nuclei (which have nearly all the inertia) move back and forth, elongating and compressing the system.
- The molecule can *rotate*.

14.2.2 Vibration

Particle excitations would produce the type of very complex, disorganized spectrum that we normally see in atoms that have many electrons, so that isn’t what we’re seeing in figure a. What about vibrations? For a classical harmonic oscillator, we know that the frequency of vibration is independent of the amplitude. If a classical oscillator contains electric charge, it will emit electromagnetic radiation at this frequency, smoothly and continuously draining itself of energy. As the energy is lost, the frequency stays the same.
By the correspondence principle, we expect that when the quantum mechanical version of such a system is highly excited, it should emit a large number of photons of this frequency \( f \), so that the discrete quantum jumps are undetectable and the radiation appears as a classical wave. We can thus infer that for a quantum vibrator, the excited states should show an \textit{evenly spaced} ladder of energy levels.

Figure c shows how the series of red lines in figure a arises. For an excitation consisting only of vibrational motion, we expect based on the correspondence principle to see the evenly spaced ladder of states shown in a stack built above the ground state, with all of the photons having the same energy. These states and transitions do exist, but the light lies in the infrared spectrum and so is not seen in figure a. The red visible-light lines arise as shown in the second box, from states that involve both a certain particle excitation and some vibration. Because the spacing of the two ladders is slightly unequal, the red lines all have slightly different wavelengths.

### 14.2.3 Rotation

What about rotation? An interesting thing happens here due to the structure of quantum mechanics. Quantum mechanics can describe motion only as a wave, with the value of the wave oscillating from one place to another. But this implies that according to quantum mechanics, no object can rotate about one of its axes of symmetry, for the rotated version of a state would then be the same state. This is why rotational excitations are never seen in individual atoms, or in nuclei that have spherical shapes. In examples like the ones in figure b, which have a single axis of symmetry, we can therefore have end-over-end rotation, but never rotation about the symmetry axis. Such end-over-end rotational states are observed in \( \text{N}_2 \), for example, but because this involves large motions by the high-mass nuclei, the moment of inertia \( I \) is quite large, and therefore the rotational energies — classically, \( K = L^2/2I \) — are very small, and infrared rather than visible photons are emitted. If rotation about the symmetry axis were possible, then the moment of inertia would be thousands of times smaller, because in such a rotation the nuclei would not move. The energies involved would be thousands of times higher, and the photons would lie approximately in the visible region of the spectrum. No such visible lines are actually observed.

Perhaps more vivid evidence for the nonexistence of rotation about a symmetry axis is shown in figure d. The states involving end-over-end rotation of the nucleus as a whole (“collective” rotation) are approximately a parabola on this graph, which is reasonable given the classical relation \( K = L^2/2I \). But angular momentum cannot be generated along the symmetry axis through collective rotation. Instead, we see an irregular set of energy levels in which first one particle (for \( L \leq 8\hbar \)) and then two (14 and 16\( \hbar \)) are excited.
Note that only even multiples of $\hbar$ are observed in collective rotation in figure d. This is because the nucleus’s shape has an additional mirror symmetry, so that it is unaffected by a 180-degree rotation. This means that the wavefunction describing the collective rotation must oscillate twice as we pass through a full rotation.

### 14.2.4 Corrections to semiclassical energies

So far we’ve been using the correspondence principle to make educated guesses about quantum-mechanical expressions for the energies of vibrators and rotors. This style of reasoning is called semiclassical, because it combines ideas from classical and quantum physics. These expressions are guaranteed to be good approximations in the classical limit obtained when the quantum numbers are large, but figure e shows that the approximations can be poorer when the quantum numbers are small.

![Quantum-mechanical corrections to the semiclassical results for the energy of a vibrator and a rotor. The rotational levels are shown for the case of a rotor with mirror symmetry, so that only even values of $\ell$ occur.](image)

In the case of the $n$th excited state of a vibrator, the energy is $(n + 1/2)\hbar\omega$, where the $+1/2$ term represents a quantum correction to the semiclassical approximation. This shifts the entire ladder upward in energy by half a step. In particular, the energy of the ground state is not zero but rather $(1/2)\hbar\omega$. This can be verified quantitatively by calculating the energy for the solution to the Schrödinger discussed using the guess-and-check method in problem 23, p. 944. It is easy to see why the answer cannot be zero, for if it were, then the particle in the ground state would have zero kinetic energy and zero potential energy. To have zero kinetic energy, it would have to have a momentum of exactly zero, so $\Delta p = 0$, but to have zero potential energy it would also have to sit still at exactly the equi-
librium position, so $\Delta x = 0$. But this would violate the Heisenberg uncertainty principle and so is impossible.

The inevitable motion that is present even in the ground state is known as zero-point motion, and its energy is the zero-point energy. Relativity tells us that $E = mc^2$, so the zero-point energy of particles is equivalent to a certain amount of mass. In fact, nearly all the mass of ordinary matter arises from the zero-point energy of the quarks inside the neutrons and protons. Another interesting application is to spontaneous nuclear fission, which is the basis for nuclear energy, providing the kick-off for a chain reaction. Spontaneous fission requires that a nucleus become more and more elongated until it breaks apart into two pieces. The very elongated shapes have a high potential energy, so that spontaneous fission requires quantum-mechanical tunneling. If it were not for the zero-point vibrational energy associated with this motion, the tunneling probability for uranium and plutonium isotopes would be extremely small. These isotopes would decay only by alpha emission, and nuclear reactors and bombs would not work.

Figure f shows visually the reason for the correction of $\ell^2$ to $\ell(\ell + 1)$. Each of these standing waves has $|\ell_z| = 16$, where $z$ is the vertical axis. But only $f/2$ is a solution of the Schrödinger equation for a state of definite $\ell$. To be a solution of the Schrödinger equation, such a wave must have the same kinetic energy everywhere. Each of these three has the same kinetic energy associated with its wavelength in the “east-west,” or azimuthal, direction. Wave $f/1$ is not a solution, because near the equator, it has an extremely short wavelength in the “north-south,” or longitudinal, direction, and this gives it a greater kinetic energy near the equator than elsewhere. The opposite problem occurs in $f/3$, where the wave is constant in the longitudinal direction; at the poles, the wavefunction varies infinitely rapidly, and therefore the kinetic energy blows up to infinity there. The only valid solution is $f/2$, which has a Goldilocks-style just-right wavelength in the longitudinal direction. The kinetic energy associated with this wavelength is the difference between the semiclassical $\ell^2$ and the correct quantum mechanical $\ell(\ell + 1)$.

A different example that is particularly easy to reason about is
the wavefunction $\Psi_{10}$ shown in figure d on p. 923, for $\ell = 1$ and $\ell_z = 0$. (The odd value of $\ell$ is possible for a rotor that doesn’t have mirror symmetry, e.g., the carbon monoxide molecule CO.) The ratio of the correct quantum mechanical energy to the semiclassical one is $\ell(\ell + 1)/\ell^2 = 2$, and the factor of two makes sense because at the poles, the wave has equal contributions to its kinetic energy due to oscillations in the two perpendicular directions that occur in the Laplacian $\partial^2/\partial x^2 + \partial^2/\partial y^2$.

**Discussion Question**

A The correction of the semiclassical proportionality for the energy of a rotor from $\ell^2$ to $\ell(\ell + 1)$ is effectively the addition of a correction equal to $\ell$. What if someone tells you that there is an additional correction term that depends only on $\ell_z$ (for a fixed $\ell$)? Is this plausible?

B Can the correction $\ell^2 \rightarrow \ell(\ell + 1)$ be tested experimentally by measuring the energy of a spinning steel ring in the laboratory? Can the correction $n \rightarrow n + 1/2$ be tested using a cart on an air track that vibrates back and forth between two springs?

### 14.3 A tiny bit of linear algebra

This optional section is a self-contained presentation of a very small amount of linear algebra. None of the later physics requires this material, but reading it may be helpful as review for the reader who has already had an entire linear algebra course, or to help make connections for the one who is taking such a course concurrently or will take it in the future.

A vector space is a set of objects, which we refer to as vectors, along with operations of addition and scalar multiplication defined on the vectors. The scalars may be the real numbers or the complex numbers. We require that the addition and scalar multiplication operations have the properties that addition is commutative ($u + v = v + u$), that we have an additive identity 0 and additive inverses ($v + (-v) = 0$), and that both operations are associative and distributive in the ways that we would expect from the notation. The prototypical example of a vector space is vectors in three-dimensional space, with the scalars being the real numbers.

Consider the set of all polynomials. If we define addition of polynomials and multiplication of a polynomial by a real number in the obvious ways, then these functions are a vector space. Note that there is no well-defined division operation, since dividing a polynomial by a polynomial typically does not give a polynomial.

In quantum mechanics, we are interested in the vector space of wavefunctions, with the scalars being the complex numbers.

A set of vectors is said to be linearly independent if it is not possible to form the zero vector as a linear combination of them.
For vectors in three-dimensional space, a set of three vectors is not linearly independent if they lie in the same plane. The set of polynomials \(\{1, x\}\) is linearly independent, but the set \(\{P, Q, R\}\), where \(P = 1, Q = 1 - x,\) and \(R = 1 + x,\) is not, because \(-2P + Q + R = 0.\)

A basis for a vector space is a linearly independent set of vectors, called basis vectors, such that any vector can be formed as a linear combination of basis vectors. The standard basis for vectors in two-dimensional space is \(\{\hat{x}, \hat{y}\}\), while a possible basis for the polynomials is the infinite set \(\{1, x, x^2, x^3, \ldots\}\). A basis exists for any vector space, and in fact there are normally many different bases to choose from, with none being preferred. In the plane, for example, we can choose to rotate the standard \(\{\hat{x}, \hat{y}\}\) basis by any angle we like. Every basis for a given vector space has the same number of elements, and this number is called the dimension of the vector space. The plane is a two-dimensional vector space. The polynomials are an infinite-dimensional vector space.

A linear operator is a function \(O\) that takes a vector as an input and gives a vector as an output, with the properties \(O(u + v) = O(u) + O(v)\) and \(O(\alpha u) = \alpha O(u)\). A rotation in the plane is a linear operator.

\[\text{Differentiation as a linear operator example 2}\]

Consider the set of all differentiable functions, taken as a vector space over either the real numbers or the complex numbers. Then the derivative is a linear operator, as is the second derivative. The kinetic energy term in the Schrödinger equation is built out of second derivatives, so it is a linear operator.

For vectors in three-dimensional space, we have a dot product, which is a function that takes two vectors as inputs and gives a scalar as its output. A vector space may or may not come equipped with such an operation. If it does, we call the operation an inner product. The inner product on wavefunctions is introduced in section 14.6.2, p. 980. In quantum mechanics, the inner product is a basic tool used to define probabilities, and for example normalization becomes the requirement that a wavefunction have an inner product with itself that equals 1. That is, a normalized wavefunction is a kind of unit vector.

When a vector space is finite-dimensional and a basis has been chosen, then if we wish we can represent vectors in column vector notation. For example, in the space of first-order polynomials with the basis \(\{1, x\}\), the polynomial \(3 + 5x\) can be represented by \((3, 5)\). Linear operators can similarly be represented by matrices, but we will seldom find this possible or useful in this book. For example, we can’t represent the derivative as a matrix, because the vector space is infinite-dimensional.
Unobservability of phase and normalization

When we say that phase and normalization don’t count as knowledge of a system, we’re saying something very mathematically specific: that $\Psi$ and $c\Psi$ represent the same state, where $c \neq 0$ is a complex number; the magnitude of $c$ would only affect the normalization, and its argument would only affect the phase. We do not mean, for example, that wavefunctions like $\sin x$ and $\cos x$ are indistinguishable. The sine and cosine give different probability distributions, so they are distinguishable. For example, the $\sin x$ wavefunction gives zero probability of detection at $x = 0$. See also problem 17, p. 1012 and example 8, p. 978.

Linear algebra application

Wavefunctions can be described by vectors in a vector space (p. 964). A state is a one-dimensional subspace of the vector space, i.e., the set of all wavefunctions of the form $c\Psi$ for some fixed $\Psi$.

14.4 The underlying structure of quantum mechanics, part 1

So far we have been building up the structure of quantum mechanics by casually laying one brick on top of another, but at this point it will be advantageous to pause and consider the broader blueprint.

14.4.1 The time-dependent Schrödinger equation

For simplicity, our discussion of the Schrödinger equation in section 13.3.6, p. 905, was limited to standing waves, allowing us to avoid explicitly discussing how the wavefunction changed with passing time. Let’s consider the generalization to the full time-dependent case.

Classically, suppose I show you a picture of a baseball next to a tree, and I ask you how long it will take to hit the ground. You can’t tell, because you also need information about the ball’s initial velocity. That is, the future time-evolution of the system $x(t)$ depends not just on the initial position $x(0)$ but also on its initial time derivative $x'(0)$.

But if I show you a uranium atom in its lowest energy state, you don’t need to know any other information to predict everything that can be predicted about its future decay. Whereas the baseball could be thrown downward in order to make it reach the ground more quickly, nobody knows of any way to prepare the uranium nucleus in such a way that it is any more likely to decay sooner. Knowing the initial wavefunction $\Psi(0)$ to be that of the ground state lets us say as much as can be said about the future time-evolution $\Psi(t)$, and it’s neither necessary nor helpful to know the time derivative $\Psi'(t)$.

This is an example of a more general idea about the interpretation of quantum mechanics, which is that the wavefunction is a complete description of any system. There isn’t more information that can be known about the system. This principle seems to be widely agreed upon by physicists, but doesn’t seem to have a standard name. (The phase and normalization of the wavefunction are not considered to give any information, since the phase is unobservable, and the normalization can be standardized so that the total probability is 1. See the sidebar for more detail.)

Wavefunction fundamentalism

All knowable information about a system is encoded in its wavefunction (ignoring phase and normalization).

An example of an idea that would violate this principle is the pilot wave theory proposed by de Broglie around 1927, and improved by Bohm in the 1950’s. In this theory, an electron-particle is a separate object from an electron-wave, with the particle surfing the
wave along a deterministic trajectory.

Another example that shows the contrast with the classical description is that if I show you a snapshot of a wave on a string, you can’t tell which direction it’s going — as with the baseball, you need to know its initial velocity in addition. But if I show you a snapshot of a quantum-mechanical traveling wave, you can tell which direction it’s going, because of the complex phase, as shown in figures u/2 and u/3 on page 914. Note that this mechanism wouldn’t work if wavefunctions were always real numbers, so wavefunction fundamentalism implies complex wavefunctions.

Given the wavefunction at some initial time, we can predict its evolution into the future by making use of the principle that \( E = hf \). Suppose for example that we have a sinusoidal plane wave traveling to the right. Then we expect the value of the wavefunction at a particular point in space to rotate clockwise about the origin in the complex plane at the appropriate frequency \( f \), showing a time dependence \( e^{-i\omega t} \) (where, as usual, \( \omega = 2\pi f \)). Thus the time derivative of the wavefunction is \( \Psi' = -i\omega \Psi = -i(E/h)\Psi \), so that \( E\Psi = i\hbar\Psi' \). Then to generalize the time-independent Schrödinger equation to its time-dependent version, the most obvious thing to try is simply to substitute \( i\hbar \partial \Psi / \partial t \) for \( E\Psi \), which gives

\[
i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U\Psi.
\]

(In section 14.6.4, p. 988, we will generalize this to cases where the wavefunction is not expressed in terms of the spatial coordinates \( x, y, \) and \( z \).) Unlike Newton’s laws of motion, which refer to a second derivative with respect to time, the Schrödinger equation involves only a first time derivative. This is why we don’t need initial data on \( \partial \Psi / \partial t \), but only \( \Psi \); if we know \( \Psi \), then the right-hand side of the Schrödinger equation is what gives us \( \partial \Psi / \partial t \). But the Schrödinger equation has some other properties that match up with those of Newton’s laws.

---

A plane wave example 3

Consider a free particle of mass \( m \) in one dimension, with the wavefunction

\[
\Psi = e^{i(kx - \omega t)},
\]

where \( k = 2\pi / \lambda = p / \hbar \) is called the wavenumber. If \( k \) and \( \omega \) are both positive, we can tell that the particle is moving to the right, because the signs inside the exponential are such that \( x \) could increase as \( t \) increases while keeping the phase the same. This would happen for \( k\Delta x - \omega \Delta t = 0 \), or \( v = \omega / k \), which is the phase velocity (not the same as the group velocity, sec. 13.3.2, p. 894).

Suppose that the particle is in free space, so that \( U \) is constant, and for convenience take \( U = 0 \). Application of the Schrödinger equation, \( i\hbar \partial \Psi / \partial t = -(\hbar^2 / 2m)\partial^2 \Psi / \partial x^2 \), gives \( \hbar \omega e^{(-...)} = \frac{\hbar^2 k^2}{2m} e^{(-...)} \).
and if this is to hold true for all values of \( x \) and \( t \), then we must have \( \hbar \omega = \frac{\hbar^2 k^2}{2m} \), which is simply an expression of the Newtonian relation \( K = p^2/2m \), since \( k\lambda = 2\pi \) and \( p = \hbar/\lambda \). Flipping the sign of \( k \) results in an equally valid solution, and a negative \( k \) is how we would represent a wave traveling to the left.

We have two solutions to the Schrödinger equation corresponding to the two signs of \( k \), and because the Schrödinger equation is linear, it follows that we can make a more general solution of the form

\[
A e^{i(kx - \omega t)} + B e^{-i(kx - \omega t)},
\]

where \( A \) and \( B \) are any two complex numbers. (We could also try to elaborate on this theme by allowing for an arbitrary phase angle \( \delta \) inside the complex exponentials, e.g., changing the argument of the first exponential to \( i(kx - \omega t + \delta) \). However, this would be equivalent to changing \( A \) to \( Ae^{i\delta} \), which is just a change in \( A \)'s phase angle, not a new solution.)

\[\text{Dispersion of a wave packet example 4}\]

An annoying feature of example 3 is that the wavefunction cannot be normalized because it extends in all directions to infinity. This type of infinite plane wave is at best an idealization of the wavefunction for a realistic example such an electron launched by a cathode ray tube, or an alpha particle emitted by a nucleus. As a more realistic example, we might try something like a wave packet, such as a pulse with a certain shape, traveling in a certain direction. This works for waves on a string or for electromagnetic waves: the pulse or packet simply glides along while rigidly maintaining its shape. To investigate this idea using the time-dependent Schrödinger equation, it will be convenient to adopt the frame of reference in which the particle is at rest. In this frame, we would expect the wave to look frozen, just as an ocean wave looks frozen in place to a surfer who is riding it. It must therefore be of the form

\[
\Psi = e^{-i\omega tf}(x),
\]

where \( f \) is some function specifying the shape of the wave packet. But this \( \Psi \) is not a solution to the Schrödinger equation. On the left-hand side of the Schrödinger equation, evaluating the time derivative gives \( i\hbar \omega \Psi \), which is just the original wavefunction multiplied by a constant. If we are to satisfy the Schrödinger equation, then the right-hand side, which is the second derivative with respect to \( x \), must also be equal to the original wavefunction multiplied by a constant. But the only functions for which \( (d^2 / dx^2)(\ldots) = (\text{constant})(\ldots) \) are exponentials and sine waves. An exponential shape obviously isn’t a physical realization of a wave packet. A sine wave works, but it just describes an infinite plane wave like the one in example 3, not a wave packet that can be localized and normalized.
The underlying reason for this result is that the Schrödinger equation is dispersive: waves with different wavelengths travel at different speeds (because they correspond to different momenta). Suppose a pulse has the shape \( f(x) \) at \( t = 0 \). Since a pulse is not a sine wave, it doesn’t have a single well-defined wavelength, and therefore it doesn’t have a definite momentum or velocity. In fact, the spread in momentum must be at least a certain size due to the Heisenberg uncertainty principle \( \Delta p \Delta x \gtrsim h \). This causes the pulse to spread out over time.

This leads to a strange thought experiment. Suppose that a uranium atom in the Andromeda galaxy emits an alpha particle, which then travels thousands of light years and eventually flies past the earth. Its wave packet may initially have been as narrow as the diameter of an atomic nucleus, \( \sim 10^{-15} \) m, but by the time it arrives perhaps it is the size of an aircraft carrier. Will an observer see a gigantic alpha particle flying by? No, because observing it constitutes a measurement of its position, and by the probability interpretation of the wavefunction this measurement simply has a certain probability of giving a result that is anywhere within some region the size of an aircraft carrier.

14.4.2 Unitarity

The Schrödinger equation is completely deterministic, so that if we know \( \Psi \) initially, we can always predict it in the future. We can also “predict” backward in time, so that the system’s history can always be recovered from knowledge of its present state. Thus there is never any loss of information over time. Furthermore, it can be shown that probability is always conserved, in the sense that if the wavefunction is initially normalized, it will also be normalized at all later times.

Unitary evolution of the wavefunction
The wavefunction evolves over time, according to the Schrödinger equation, in a deterministic and unitary manner, meaning that probability is conserved and information is never lost.

(Unitarity is defined more rigorously on p. 984.)

Since we think of quantum mechanics as being all about randomness, this determinism may seem surprising. But determinism in the time-evolution of the wavefunction isn’t the same as determinism in the results of experiments as perceived and recorded by a human brain. Suppose that you prepare a uranium atom in its ground state, then wait one half-life and observe whether or not it has decayed, as in the thought experiment of Schrödinger’s cat (p. 885). There is no uncertainty or randomness about the wavefunction of the whole system (atom plus you) at the end. We know for sure what it looks like. It consists of an equal superposition of...
two states, one in which the atom has decayed and your brain has observed that fact, and one in which the atom has not yet decayed and that fact is instead recorded in your brain.

To get more of a feeling for what is meant by unitarity, it may be helpful to consider some examples of how it could be violated. One is the mythical “collapse” of the wavefunction in naïve interpretations of the Copenhagen approximation (p. 887). Another example of nonunitarity is given in example 14 on p. 989.

A more exotic example is the disappearance of matter into a black hole. If I throw my secret teenage diary into a black hole, then it contributes a little bit to the black hole’s mass, but the embarrassing information on the pages is lost forever. This loss of information seems to imply nonunitarity. This is one of several arguments suggesting that quantum mechanics cannot fully handle the gravitational force. Thus although physicists currently seem to possess a completely successful theory of gravity (Einstein’s theory of general relativity) and a completely successful theory of the microscopic world (quantum mechanics), the two theories are irreconcilable, and we can only make educated guesses, for example, about the behavior of a hypothetical microscopic black hole.

14.5 Methods for solving the Schrödinger equation

14.5.1 Cut-and-paste solutions

Quite a few of the interesting phenomena of quantum mechanics can be demonstrated by finding solutions to the one-dimensional Schrödinger equation using the following “cut and paste” method. We break up the $x$ axis into pieces, where the potential $U(x)$ does different things, and such that we already know the solutions of the Schrödinger equation for each piece. We then splice together the different parts of the solution, requiring that no discontinuities occur in the wavefunction $\Psi$ or its derivative $\partial \Psi / \partial x$. (If the momentum and kinetic energy are to be finite, and $U$ is finite, then we need all derivatives up to the second to be defined.)

Partial reflection at a step

The simplest example of this kind is a potential step,

$$U(x) = \begin{cases} U_1, & x < 0 \\ U_2, & x > 0, \end{cases}$$

where $U_1$ and $U_2$ are constants, and the energy of the particle is such that both sides are classically allowed. We have discussed this example 18 on p. 907, where we cheated by drawing real-valued wavefunctions, and simply assumed that we could still use our previous results for classical wave reflection (p. 381). It is not actually
An incident wave is partially reflected and partially transmitted at a step in the potential $U$. The complex wavefunctions are represented using a complex plane perpendicular to the direction of propagation, so that they look like corkscrews. The incident and reflected wavefunctions actually superposed, but are drawn as separate entities and offset for purposes of visualization.

To sidestep the problem of dispersion, we will carry out our analysis using an infinitely long wave-train with a definite wavelength. Let the incident wave have unit amplitude and travel to the right,

$$\Psi_I = e^{i(kx - \omega t)} \quad (x < 0),$$

as in example 3, p. 967. Recall that the wavenumber $k$ is basically just momentum, $p = \hbar k$.

For the reflected and transmitted parts of the wave, we take

$$\Psi_R = Re^{i(-kx - \omega t)} \quad (x < 0),$$

and

$$\Psi_T = Te^{i(k'x - \omega t)} \quad (x > 0),$$

where the reflected and transmitted amplitudes $R$ and $T$ are unknown, and our goal is to find them. The different sign inside the exponential for $\Psi_R$ corresponds to the opposite direction of motion at the same speed $v$, while in the expression for $\Psi_T$ we have motion to the right, but with a different momentum $p' = \hbar k'$ as required by conservation of energy.

Demanding continuity of $\Psi$ gives

$$1 + R = T.$$

The derivatives are $\partial \Psi_I / \partial x = ik \Psi_I$, $\partial \Psi_R / \partial x = -ik \Psi_R$, and $\partial \Psi_T / \partial x = ik' \Psi_T$, and evaluating these at $x = 0$, $t = 0$ gives $ik$, $-ikR$, and $ik'T$. If the derivative is to be the same for $x \to 0^-$ and for $x \to 0^+$, we need to have $ik - R i k = i T k'$, or

$$1 - R = \frac{k'}{k} T,$$

But these two equations are exactly the same as the ones found on p. 381 for a classical, nondispersive wave, the only difference being the replacement of $v/v'$ with $k'/k$. To keep the writing simple, let $\alpha = k'/k$. With this replacement, the solutions are the same as before, $R = (1 - \alpha)/(1 + \alpha)$ and $T = 2/(1 + \alpha)$. For a particle of energy $E$, we can find the momentum ratio $\alpha$ using conservation of energy, $\alpha = \sqrt{(E - U_2)/(E - U_1)}$. There is partial reflection not just in the case of a sudden rise in the potential, but also at a sudden drop ($U_2 < U_1$), which is surprising and seems to violate the correspondence principle, but actually does not, as discussed in example 18 on p. 907.

Section 14.5   Methods for solving the Schrödinger equation   971
One of our principles of quantum mechanics is unitarity (p. 969), which says, in part, that probability is conserved. Normally we would interpret this to mean that a wavefunction stays normalized if it was originally normalized. In this example, the wavefunctions are not normalizable, but we still expect the fluxes of particles balance out. We have

\[
\text{flux} = \text{(probability density)} \times \text{(group velocity)}
\]

\[
= \psi^2 \times \frac{p}{m}
\]

\[
= \frac{\hbar}{m} k \psi^2,
\]

so that if we want the total incident flux to equal the total outgoing flux, we need

\[
k = kR^2 + k'T^2,
\]

which is straightforward to verify.

**Infinite potential well**

In sec. 13.3.3, p. 897, we analyzed the one-dimensional particle in a box. There was nothing wrong with those results, but it is of interest to see how they fit into the framework of the time-dependent Schrödinger equation. If we want the walls of the box to be completely impenetrable, then we should describe it using a potential such as

\[
U(x) = \begin{cases} 
\infty, & x < 0 \\
0, & 0 < x < L \\
\infty, & x > L
\end{cases}
\]

shown in figure b/1. Because the potential is infinite outside the box, we expect that there is no tunneling, and zero probability of finding the particle outside.

In general when we do the cut-and-paste technique, we expect both the wavefunction and its first derivative to be continuous where the pieces are joined together. But because we have already solved this problem by more elementary methods, we know that there will be kinks in the wavefunction at the walls of the box, \(x = 0\) and \(L\). The kink is a point where the second derivative \(\partial^2 \psi / \partial x^2\) is undefined, and it’s undefined because it’s infinite. The second derivative is essentially the kinetic energy operator, and normally it would not be possible to have the kinetic energy be \(\pm \infty\). But in this problem, it is reasonable to have a kinetic energy of \(-\infty\), because the potential energy is \(+\infty\).

Within the box, for a fixed energy \(E = \hbar \omega\), the possible wavefunctions will be those of a free particle, which we have already found. There are two possibilities, of the form

\[
\Psi_1 = e^{i(kx - \omega t)} \\
\Psi_2 = e^{i(-kx - \omega t)}
\]
figure b/2, where \( k \) is a positive real number satisfying \( k = p/h = \sqrt{2mE}/h \). \( \Psi_1 \) is a wave traveling to the right, and \( \Psi_2 \) is a wave traveling to the left. The most general solution will be a superposition of these,

\[
\Psi = A\Psi_1 + B\Psi_2.
\]

Because the wavefunction has to be continuous at \( x = 0 \), where \( \Psi_1 = \Psi_2 \), we must have \( A + B = 0 \). Since \( e^{iz} - e^{-iz} = 2\sin z \), we end up with

\[
\Psi = 2A\sin kxe^{-i\omega t}.
\]

Throwing out the time-dependent phase, we get the sinusoidal solutions to the time-independent Schrödinger equation that we have already found, e.g., figure b/3. Imposing the additional constraint that \( \Psi \) be continuous at \( x = L \), we get the condition \( kL = n\pi \), where \( n \) is an integer, and this makes the energies quantized, as we found before.

### 14.5.2 Separability

When we first generalized the Schrödinger equations from one dimension to two and three dimensions, a trick for finding solutions was to take solutions to the one-dimensional equation and multiply them. For example, we knew that in the case of a constant potential (a free particle), the one-dimensional time-independent equation had solutions of the form \( \sin ax \) and \( e^{ax} \). We then saw in problem 37, p. 947, that \( e^{by}\sin ax \) was a solution to the two-dimensional equation. This is because the two-dimensional time-independent Schrödinger equation for a free particle, which has the form

\[
\nabla^2 \Psi = c\Psi,
\]

has a property called separability. What this means is that if functions \( X \) and \( Y \) are both solutions of the one-dimensional version of the equation, then \( \Psi(x, y) = X(x)Y(y) \) is a solution of the two-dimensional one. To see this, we calculate

\[
\nabla^2 \Psi = \nabla^2[X(x)Y(y)] = [X(x)Y''(y)] + [X''(x)Y(y)] = Y''(y)X(x) + X''(x)Y(y).
\]

We’re looking for functions \( X \) and \( Y \) such that this is a solution to the two-dimensional equation, so that

\[
Y''(y)X(x) + X''(x)Y(y) = cX(x)Y(y).
\]

Dividing both sides by \( X(x)Y(y) \) simplifies this equation to

\[
\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} = c.
\]
But if $X$ and $Y$ are solutions of the one-dimensional equation, then both terms on the left are constants, so we have a valid solution to the two-dimensional equation.

As an example, we know that $\sin kx$ is a solution to the one-dimensional Schrödinger equation, so the function $\sin kx \sin ky$ is also a solution. The result, shown in figure c, can be chopped off and made into a solution of the two-dimensional particle in a box. Solutions similar to this one are found in real-life examples such as microwave photons in a microwave oven. For more about separability, and how it compares with entanglement, see sec. 14.11, p. 1004.

14.6 The underlying structure of quantum mechanics, part 2

14.6.1 Observables

By the time my first-year mechanics students have been in class for a week, they know how to answer when I ask them the velocity of the tape dispenser at the front of the classroom: “We don’t know, it depends on your frame of reference.” The absolute velocity of an object is a meaningless concept, part of the mythical dungeons-and-dragons cosmology of Aristotelian physics. Quantum mechanics is as great a break from Newton as Newton was from Aristotle, and similar care is required in redefining what concepts are observables — meaningful things to talk about measuring.

Classically, we describe the state of the system as a point in phase space (sec. 5.4.2, p. 328) — which is just a fancy way of saying that we specify all the positions and momenta of its particles — and an observable is defined as a function that takes that point as an input and produces a real number as an output. (By the way, the word “phase” in “phase space” doesn’t refer directly to the phase of a wave, which we’ll also be discussing below.) For example, kinetic energy is a classical observable, and $K(\Theta) = 0$, where the picture represents a tennis ball at rest. For a moving tennis ball with one unit of energy, $K(\Theta) = 1$. For a vibrating violin string, we could have $U(\Theta) = 1$, and $U(\Theta) = 4$ (where doubling the amplitude gives four times the energy).

Quantum-mechanically, the Heisenberg uncertainty principle tells us that we can’t independently dial in the desired values of a particle’s position and momentum. They aren’t two variables that are independent of one another. Therefore we don’t have a phase space, so an observable has to be represented by a function whose input is a wavefunction. Furthermore, we expect that:

- The output shouldn’t depend on the phase\(^1\) of the wavefunc-

\(^1\)“Phase” as in the phase of a wave, not as in “phase space.”
• The output shouldn’t depend on amplitude (because a different amplitude might just mean an incorrectly normalized state).

• The output should be well defined when we superpose any two states.

These requirements are hard to reconcile with the idea that the output of the observable is just a real number representing the result of the measurement. We could decree that the input wavefunction is just required to be have the standard normalization, but there’s no obvious way to define a standardization of phase. And suppose we have a particle in a one-dimensional box, with the two lowest energies being $E(\uparrow) = 1$ and $E(\downarrow) = 4$. Then what should we define for the superposition $E(\uparrow + \downarrow)$? We could define it to be the average, 2.5, but that isn’t even a possible value of the measurement; in reality, the result of the measurement would be either 1 or 4, with equal probability.

For a clue as to a better way to proceed, note the structure of the time-independent Schrödinger equation for a free particle, omitting all constant factors like $m$, 2, and $\hbar$. It isn’t $(d^2/dx^2)\Psi = E$, it’s $(d^2/dx^2)\Psi = E\Psi$. This fixes all the problems. For example, if we change the phase of the wavefunction by flipping its sign, the equation still holds with the same value of $E$. This equation is a specific example of a more general type of equation that looks like

$$\text{operator(input)} = \text{number} \times \text{input}.$$  

Another, simpler example is $(d/dx)f = 3f$, which is satisfied if $f = Ae^{3x}$, where $A$ is any constant. Such an equation says that applying the operator to the input just gives back the input itself, multiplied by some constant. For this reason, this type of equation is called an eigenvalue equation, because “eigen” is the German word for “self.” We say that 3 is the eigenvalue of the eigenvalue equation $(d/dx)f = 3f$. In the time-independent Schrödinger equation, the eigenvalue is the energy, and a solution $\Psi$ is called a state of definite energy (or “eigenstate”).

All observables in quantum mechanics are described by operators such as derivatives. The second derivative (with the appropriate factor of $-\hbar^2/2m$) is the kinetic energy operator in quantum mechanics. Given an operator $\mathcal{O}$ that describes a certain observable, a state $\Psi$ with a definite value $c$ of that observable is one for which $\mathcal{O}(\Psi) = c\Psi$. Although it’s common to use parentheses when notating functions, as in $\cos(\pi) = -1$, they are optional, and we can write $\cos \pi = -1$, so we will often use notations like $\mathcal{O}\Psi$ instead of $\mathcal{O}(\Psi)$, but keep in mind that this not multiplication, just as $\cos \pi$ doesn’t mean multiplying $\cos$ by $\pi$. 

Section 14.6  The underlying structure of quantum mechanics, part 2  975
When we carried over the classical kinetic energy observable to quantum mechanics, we weren’t going blind. For example, the factor of $-\hbar^2/2m$ in front is tightly constrained by requirements like units and the need for a traveling sine wave to have positive energy. But for the superposition of two states, classical mechanics will never give us any guidance. For example, what is the body temperature of Schrödinger’s cat? For the energy operators appearing in the Schrödinger equation, we used linear operators. The result was that our law of physics was perfectly linear, and this is a hard requirement, for the reasons described on p. 915. It therefore seems natural to require that all observables be represented by linear operators,

$$\mathcal{O}(\Psi_1 + \Psi_2) = \mathcal{O}\Psi_1 + \mathcal{O}\Psi_2.$$ 

Indeed, if they were not linear, then quantum mechanics would lack self-consistency, for the act of measurement can be described by applying the Schrödinger equation to a big system consisting of the system being observed interacting with the measuring device.

Finally, we have one more requirement, which is that the linear operator representing an observable should have eigenvalues that are real. This isn’t because the results of a measurement must logically be real — e.g., we can measure complex impedances. But in any real-world application of the complex number system, we must always choose some arbitrary phase conventions, such as that an inductor has a positive imaginary impedance to represent the fact that the voltage leads the current by 90 degrees. (Such phase conventions are always arbitrary because we define $i$ as $\sqrt{-1}$, but this doesn’t distinguish $i$ from $-i$.) These phase conventions are all independent of one another, and the classical ones are independent of the convention used for wavefunctions in quantum mechanics, which is that a state with positive energy twirls clockwise in the complex plane. (See also example 14, p. 989.)

**Observables**

Observables are represented a linear operators (p. 965). We also require that this operator have real eigenvalues.

Some important examples of observables are momentum (example 5 below), position (example 7), energy, and angular momentum. These are represented by linear operators $\mathcal{O}_x$, $\mathcal{O}_p$, $\mathcal{O}_E$, and $\mathcal{O}_L$, respectively.

**The momentum operator**

Quantum mechanics represents motion as a dependence of the wavefunction on position, so that a constant wavefunction has no motion. This suggests defining the momentum operator as the derivative with respect to position. This almost works, but needs to be tweaked a little. We expect that a state of definite
momentum is a sine wave of the form \( \psi = e^{ikx} \). We have \( k\lambda = 2\pi \) and \( p = h/\lambda = \hbar k \), and the sign is a matter of convention. Taking the derivative of \( \psi \) gives an eigenvalue \( ik \), which has the wrong units (easily fixed by tacking on a factor of \( \hbar \)), but more importantly is not real. This suggests defining the momentum operator as
\[
\hat{O}_p = -i\hbar \frac{d}{dx}.
\]

A further note about the momentum operator is example 13 on p. 985.

\textbf{A nonexample} \textbf{example 6}

Consider the one-dimensional particle in a box, and restrict our attention to the two lowest-energy states and their superpositions. Define an operator \( \hat{O} \) by the rule
\[
\hat{O}(\bigwedge) = \bigvee
\]
\[
\hat{O}(\bigvee) = -(\bigwedge).
\]

Since \( \hat{O} \) is linear, defining its action on \( \bigwedge \) and \( \bigvee \) suffices to define its action on the superpositions of these states as well. This operator has eigenvalues, one of which is \( i \), corresponding to the state \( \bigwedge - i\bigvee \). (It also has a second eigenvalue, which is imaginary as well.) Because this operator doesn’t have real eigenvalues, it is not a valid observable.

Note that in examples 5 and 6, it doesn’t matter whether the operator is \textit{defined} using complex numbers. Our definition of the momentum operator was stated using an equation that had an \( i \) in it, but its eigenvalues are real, so that’s OK. The operator \( \hat{O} \) in example 6 was defined using only real numbers, but its eigenvalues are not real.

\textbf{Position is an observable} \textbf{example 7}

If we have a wavefunction \( \psi(x) \) expressed as a function of position \( x \), then we simply take the operator for position \( \hat{O}_x \) to be multiplication by the number \( x \),
\[
\hat{O}_x(\psi) = x\psi.
\]

For example, if \( \psi = e^{ix} \) (ignoring units), then \( \hat{O}_x(\psi) = xe^{ix} \). This operator is definitely linear, because multiplication by a number is linear, e.g., \( 7(a + b) = 7a + 7b \). The only question is whether it has eigenvalues, and whether those are real. A state of definite \( x \), say a state with \( x = 0 \), would have to be represented by a wavefunction \( \psi(x) \) for which there was zero probability of having \( x \neq 0 \), and this requires us to have \( \psi(0) = 0 \) for nonzero \( x \). But what would be the value of \( \psi(0) \)? It has to be \textit{infinite} if \( \psi \) is to be properly normalized. With this motivation, the physicist P.A.M. Dirac defined the Dirac delta function,
\[
\delta(x) = \begin{cases} 
0 & \text{for } x \neq 0 \\
+\infty & \text{for } x = 0 
\end{cases}
\]
Its graph is an infinitely narrow, infinitely tall spike at \( x = 0 \), and it has \( \int_{-\infty}^{+\infty} \delta(x) \, dx = 1 \). Mathematicians will shake their heads and say that this is not a definition of a function, but it’s very useful to pretend that it is, and the delta “function” is widely used in a variety of fields such as electrical engineering. Because it was useful, mathematicians felt obliged to define a theory in which functions are generalized to things called distributions or generalized functions.

Because we represent an observable as an operator that changes a wavefunction into a new wavefunction, a common misconception is that this change represents the effect of measurement on the system. Although it is often true that microscopic systems are delicate, so that the act of measurement may have a significant effect on them, that action of the operator on the wavefunction does not represent that effect. For example, the position operator \( \hat{O}_x \) from example 7 consists simply of multiplication of the wavefunction by \( x \). Suppose we have a particle in a box with a wavefunction given by \( \Psi = \sin x \), where we ignore units and normalization, and the box is defined by \( 0 \leq x \leq \pi \). Then \( \hat{O}_x \Psi \) eats the input wavefunction \( \sin x \) and poops out the new function \( x \sin x \). But the act of measuring the particle’s position clearly can’t do anything like this — for one thing, the function \( x \sin x \) has larger values on the right side of the box than on the left, but there is nothing to create such an asymmetry in either the original state or the measuring process. The real-world effect of the measurement would probably be to knock the particle out of the box completely, since a high-resolution measurement will have a small uncertainty \( \Delta x \), which by the Heisenberg uncertainty principle means creating a large \( \Delta p \).

Nor is it always true that measuring a system disturbs it. For example, suppose that we prepare a beam of silver atoms, as in the Stern-Gerlach experiment, in such a way that every atom is guaranteed to be in either a state of definite \( L_x = +1/2 \) or \( L_x = -1/2 \). That is, the beam may be a mixture of both of these possibilities, but each atom is guaranteed have its spin either exactly aligned with the magnetic field or exactly antiparallel to it. Then the effect of the magnetic field is simply to sort out the two types of atoms according to spin, without having the slightest effect on those spins.

\[ \text{Phase is not an observable} \]

On p. 974 we listed three criteria for implementing the concept of an observable in quantum mechanics, and one of these was that since wavefunctions that differ only by a phase describe the same state, the result of an observation should not depend on phase. For this reason, it should not be a surprise that the mathematical definition of an observable that we came up with does not allow for the creation of an observable to describe measurement of a phase.
By way of rigorous proof, suppose to the contrary that we did have such an observable $\mathcal{O}_{\text{ph}}$. By our definition of an observable, it would have to have some set of eigenvalues that were real numbers. Consider such an eigenvalue $\varphi$, which might perhaps be the argument of the wavefunction in the complex plane, although we will not need to assume that. Let $\Psi$ be the state of definite phase having the phase $\varphi$, so that

$$\mathcal{O}_{\text{ph}} \Psi = \varphi \Psi. \tag{1}$$

We can change the phase of $\Psi$ to create a new wavefunction. Let's retard its phase by 90 degrees, creating $i \Psi$. Since $\Psi$ was a state of definite phase, clearly $i \Psi$ is as well, and it must have some different eigenvalue $\varphi'$. Perhaps $\varphi' = \varphi + \pi/2$, but in any case we must have $\varphi' \neq \varphi$. Then

$$\mathcal{O}_{\text{ph}} (i \Psi) = \varphi' (i \Psi). \tag{2}$$

But by linearity equation [2] is equivalent to $i \mathcal{O}_{\text{ph}} \Psi = i \varphi' \Psi$, or $\mathcal{O}_{\text{ph}} \Psi = \varphi' \Psi$, and therefore by comparison with equation [1], $\varphi = \varphi'$, which is a contradiction, so we conclude that there cannot be an observable representing phase.

The result of example 8 was a bit of a foregone conclusion, since we specifically designed our notion of an observable to be insensitive to phase. Therefore this argument is subject to the objection that perhaps there is some way to measure a quantum-mechanical phase, but our definition of an observable is just too restrictive to describe it. However, we will see on p. 998 that there are more concrete reasons why phase cannot be measured.

\textit{Time is not an observable \textsuperscript{example 9}}

We do not expect to have a time operator in quantum mechanics. This follows simply because an operator is supposed to be a function that takes a wavefunction as an input, but we typically can't tell what time it is by looking at the wavefunction. For example, if the electron in a hydrogen atom is in its ground state, then we could say its energy is zero, so its frequency is zero, the period is infinite, and the wavefunction doesn't vary at all with time. (We can choose our reference level for the electrical energy $U_{\text{elec}}$ to be anything we like. Even if we choose it such that the energy of the ground state is nonzero, the only change in the electron's wavefunction over time will be a phase rotation, which by example 8 is not observable.)

Of course this doesn't mean that quantum mechanics forbids us from building clocks. It just tells us that many quantum mechanical systems are too simple to function as clocks. In particular, we would be misled if we pictured a hydrogen atom classically in terms of an electron traveling in a circular orbit around a proton, in which case it really could act like the hand on a tiny clock. For further discussion of this idea, see p. 997
Since you’ve already studied relativity, you’ve had carefully inculcated in you the idea that space and time are to be treated symmetrically, as parts of a more general thing called spacetime. The differing results of examples 7 and 9 are clearly not consistent with relativity. This is to be expected because the Schrödinger equation is nonrelativistic (cf. self-check G, p. 905), and the principles laid out in this section are the principles of nonrelativistic quantum mechanics.

**Parity example 10**

In freshman calculus you will have encountered the notion of even and odd functions. In quantum mechanics, we can have even and odd wavefunctions, and they can be distinguished from one another using the parity operator $\mathcal{P}$. If $\Psi(x)$ is a wavefunction, then $\mathcal{P}\Psi$ is a new wavefunction, call it $\Psi'$, such that $\Psi'(x) = \Psi(-x)$. In other words, the parity operator flips the wavefunction across the origin. (In three dimensions, we negate all three coordinates.) States of definite parity are represented by wavefunctions that are even (eigenvalue +1) or odd (−1).

**States of definite angular momentum example 11**

In section 14.2.4, p. 962, we saw that the kinetic energy of a quantum mechanical rotor is proportional not to $\ell^2$ but instead to $\ell(\ell + 1)$. This was justified qualitatively in terms of the solutions of the Schrödinger equation for a particle on a sphere, but in fact there is a deeper reason, which is that the eigenvalues of the orbital angular momentum operator turn out to be $\ell(\ell + 1)$. The parity of such a state is $(-1)^\ell$, which can be seen in figure h on p. 928.

If we have two observables, it may or may not be possible to measure them both on the same state and get exact and meaningful results. Position and momentum $p$ and $x$ are incompatible observables, as expressed by the Heisenberg uncertainty principle. No state is simultaneously a state of definite $p$ and of definite $x$. The magnitude of an angular momentum $L$ and its component along some axis $L_z$ are compatible. It is common to have a state that is simultaneously a state of definite $L$ and of definite $L_z$. Another example of incompatible observables is $L_z$ and $L_x$, as proved on p. 922.

**14.6.2 The inner product**

We’ve defined the normalization of a wavefunction as the requirement $\int_{-\infty}^{+\infty} \Psi^*\Psi \, dx = 1$, which means that the total probability that the particle is somewhere equals 1. (Another way of writing $\Psi^*\Psi$ would be $|\Psi|^2$.) This assumes that the wavefunction is written as a function of the position $x$. But it is also possible to have a wavefunction that depends on some other variable, such as spin or momentum, or on some combination of variables, e.g., both the spin $s$ and the position $x$ of an electron, $\Psi(x,s)$. We can also use a wavefunction to describe a correlation between multiple particles,
in which case the wavefunction might look like \( \Psi(x_1, x_2) \). The variables that the wavefunction depends on may be either continuous, like position and momentum, or discrete, like spin or angular momentum. Given all of these possibilities, we need to figure out an appropriate generalization of the integral over \( x \) that we originally used to define our normalization condition. To provide for flexibility and generality, we will start by simply defining a new notation that looks like this:

\[
\langle \Psi | \Psi \rangle = 1.
\]

In the case where \( \Psi \) is a function of \( x \) alone, the angle brackets \( \langle \ldots | \ldots \rangle \) basically mean just an integral over \( x \), and we think of the \( \langle \ldots | \rangle \) part as automatically implying the complex conjugation of the thing inside it. The operation \( \langle \ldots | \ldots \rangle \) is called the inner product.

Because negative probabilities don’t make sense, we require that the inner product of a wavefunction with itself always be positive,

\[
\langle u|u \rangle \geq 0.
\]

This makes it similar to the dot product used with vectors in Euclidean geometry.

In the case of Euclidean geometry, the ability to add vectors and measure their lengths automatically gives us a way to judge the similarity of two vectors. For example, if \( |u| = 1, |v| = 1, \) and \( |u+v| = 2 \), then we conclude that \( u \) and \( v \) are in the same direction. On the other hand, if \( |u| = 1, |v| = 1, \) and \( |u+v| = \sqrt{2} \), then we can tell that \( u \) and \( v \) are perpendicular, which makes them as different as two unit-length vectors can be. More generally, \( (u+v) \cdot (u+v) = |u|^2 + |v|^2 + 2u \cdot v \), because the dot product is linear, so we can see that the information about how similar \( u \) and \( v \) are is all contained in their dot product \( u \cdot v \). Making the analogy with quantum mechanics, we expect that since we can define normalization of wavefunctions, we should automatically get, “for free,” a way of measuring how similar two states are.

With this motivation, we assume that there is an inner product on wavefunctions that has properties analogous to those of the dot product. We assume linearity, so that if \( u, v, \) and \( w \) are wavefunctions, then

\[
\langle u|\alpha v + \beta w \rangle = \alpha \langle u|v \rangle + \beta \langle u|w \rangle
\]

and

\[
\langle \alpha u + \beta v|w \rangle = \alpha^* \langle u|w \rangle + \beta^* \langle v|w \rangle.
\]

In the second equation, we need to take the complex conjugates \( \alpha^* \) and \( \beta^* \), for if we omitted the conjugation, then when \( \langle u|u \rangle = 1 \) we would have \( \langle iu|iu \rangle = -1 \), describing a negative probability. For similar reasons, we require that

\[
\langle u|v \rangle = \langle v|u \rangle^*
\]
Linear algebra application
The properties listed here for inner products in quantum mechanics are just standard rules for inner products in linear algebra.

Inner product
Wavefunctions come equipped with an inner product that has the properties described above.

If we’re dealing with wavefunctions that are expressed as functions of position, then it’s pretty clear how to define an appropriate inner product: \( \langle u|v \rangle = \int u^* v \, dx \). The inner product axiom stated above then requires that this (possibly improper) integral converge in all cases, which means, for example, that we have to exclude infinite plane waves from consideration. However, because it’s so convenient sometimes to talk about plane waves, we may break this rule when nobody is looking. Note the similarity between the expression \( \int u^* v \, dx \) and the expression \( u_x v_x + u_y v_y + u_z v_z \) for a dot product: the integral is a continuous sum, and the dot product is a discrete sum.

Two wavefunctions have a zero inner product if and only if they are completely distinguishable from each other by the measurement of some observable. By analogy with vectors in Euclidean space, we say that the two wavefunctions are orthogonal. For example, \( \langle u|v \rangle = 0 \), as can be verified from the integral \( \int_0^\pi \sin x \sin 2x \, dx = 0 \). These states are also distinguishable by measuring either their momentum or their energy.

Let’s consider more carefully the general justification for this assertion that perfect distinguishability is logically equivalent to a zero inner product. We have described valid observables in quantum mechanics as being represented by operators that have real eigenvalues. An alternative description of such an operator \( \Theta \), called a hermitian operator after Charles Hermite, is that it is one such that for any \( u \) and \( v \), the equation \( \langle \Theta u|v \rangle = \langle u|\Theta v \rangle \) holds.\(^3\) Being hermitian is, for an operator, analogous to being real for a number. (Cf. problem 8, p. 1009.) Just as a randomly chosen complex number is unlikely to be real, a randomly chosen linear operator will almost never be hermitian. Like love, patriotism, or beauty, a nonhermitian operator fails to translate into anything a physicist can measure.

Using this alternative characterization of what makes a valid wavefunction, we can state the correspondence principle as follows: if we are dealing with a classical system and if we believe that the corresponding quantum system must be described by some state \( \psi \), then we must have \( \langle \psi|\psi \rangle = 1 \). For any \( \psi \) other \( \psi \), we must have \( \langle \psi|\psi \rangle < 1 \). This follows from the fact that a classical system is distinguished from any other by measuring just one observable.

\(^2\)The mathematician’s standard definition of a hermitian operator adds an additional technical condition, which is that all of the operator’s eigenvalues should have magnitudes below a certain fixed bound. This is much too restrictive for our purposes, since, for example, an alpha particle in free space can have an arbitrarily large kinetic energy. In fact, nothing really bad happens if we relax our requirement for quantum-mechanical operators to be that they merely need a property called being normal.

\(^3\)Proof that a hermitian operator has real eigenvalues: Let \( e \) be an eigenvalue, \( \Theta u = eu \) for \( u \neq 0 \). Then \( \langle \Theta u|u \rangle = \langle u|\Theta u \rangle \), so \( \langle eu|u \rangle = \langle u|eu \rangle \), and \( e^* \langle u|u \rangle = e \langle u|u \rangle \), so \( e^* = e \), meaning that \( e \) is real.
observable, we can prove, as claimed above, that if two states are
distinguishable because they have definite, different values of some
observable, then they are orthogonal.4

| $\langle \bigwedge | \bigwedge \rangle = 1$ | The wave $\bigwedge$ is
properly normalized. |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \bigwedge</td>
<td>\bigwedge \rangle = 0$</td>
</tr>
</tbody>
</table>
| $\langle \bigwedge | \bigwedge \rangle = -0.81$ | The wave $\bigwedge$ can be expressed as $-0.81 \sqrt{\bigwedge}$ plus distinguishable waves.
Or: measurements have probability $(-0.81)^2 \approx 0.66$ of saying one of these waves is the same as the other. |
| $\langle \bigwedge | \mathcal{O} x \bigwedge \rangle = \frac{L}{2}$ | The wave $\bigwedge$ has an average position $L/2$. |
| $\langle \bigwedge | U \bigwedge \rangle$ | Measures the ability of an externally applied potential $U$ to cause a jump from $\bigwedge$ to $\bigwedge$. The square is the transition rate per second. |

Suppose that $u$ and $v$ are both properly normalized wavefunctions. If $|\langle u|v \rangle| = 1$, then the states are identical.5 If $\langle u|v \rangle = 0$, then $u$ and $v$ are completely distinguishable from one another. There is also the intermediate case where $\langle u|v \rangle$ has a magnitude greater than 0 but less than 1. In this case, we could say that $u$ is a mixture of $v$ plus some other state $w$ that is distinguishable from $v$, i.e., that

$$|u\rangle = \alpha|v\rangle + \beta|w\rangle.$$ 

where $\langle v|w \rangle = 0$. We then have

$$\langle u|v \rangle = (\alpha \langle v | + \beta \langle w |) \vert v \rangle = \alpha.$$ 

Now suppose that we make measurements capable of determining whether or not the system is in the state $v$. If the system is prepared in state $u$, and we make these measurements on it, then by

4Proof: Consider states $u$ and $v$ with $\mathcal{O}u = e_1 u$ and $\mathcal{O}v = e_2 v$. If $\mathcal{O}$ is Hermitian, we have $\langle \mathcal{O} u | v \rangle = \langle u | \mathcal{O} v \rangle$, so $e_1 \langle u | v \rangle = e_2 \langle u | v \rangle$. But since $e_1$ and $e_2$ are real and unequal, we must have $\langle u | v \rangle = 0$.

5If the inner product is, for example, $-1$, then the wavefunctions differ only by an unobservable difference in phase, so they really describe the same state.
the linearity of the Schrödinger equation, the result is that the measuring apparatus or observer ends up in a Schrödinger’s-cat state that looks like

\[ \alpha|\text{observed } v\rangle + \beta|\text{observed } w\rangle. \]

We interpret squares of amplitudes as probabilities, so

\[ P = |\alpha|^2 = |\langle u|v\rangle|^2 \]

gives us the probability that we will have observed the state to be \( v \). This final leap in the logic, to a probability interpretation, has felt mysterious to several generations of physicists, but recent work has clarified the situation somewhat.

On p. 938 we stated the Pauli exclusion principle by saying that two particles with half-integer spins could never occupy the same state. This was not a completely rigorous definition of the principle, since we didn’t really define “same state.” A more mathematically precise statement is that if one electron’s wavefunction is \( u \) and another’s is \( v \), then \( \langle u|v\rangle = 0 \). In other words, we are ruling out not just the case where \( u \) and \( v \) are the same wavefunction, \( \langle u|v\rangle = 1 \), but also the intermediate case where \( \langle u|v\rangle \) is greater than 0 but less than 1.

A unitary transformation is one that preserves inner products. That is, \( \langle Ou|Ov\rangle = \langle u|v\rangle \). This is similar to the way in which rotations preserve dot products in Euclidean geometry. This provides a more rigorous definition of what we meant by postulating the unitary evolution of the wavefunction (p. 969). It can be shown that if the Hamiltonian is hermitian, then the evolution of the wavefunction over time is a unitary operation. This protects us from bad scenarios like the one described in example 14, p. 989.

### Traveling waves in the quantum moat example 12

On p. 920 we discussed the “quantum moat,” in which a particle is constrained to a circle like the moat around a castle. For the \( \ell = 1 \) state, the two degenerate traveling wave solutions to the Schrödinger equation are (ignoring normalization) the counterclockwise \( |\text{ccw}\rangle = e^{i\theta} \) and the clockwise \( |\text{cw}\rangle = e^{-i\theta} \). These states are distinguishable by their angular momenta \( \ell_z = \pm 1 \), so we expect them to be orthogonal. Let’s check that directly.

\[
\langle \text{ccw}|\text{cw}\rangle = \int_0^{2\pi} [(e^{i\theta})^*] e^{-i\theta} d\theta \\
= \int_0^{2\pi} e^{-i\theta} e^{-i\theta} d\theta \\
= \int_0^{2\pi} e^{-2i\theta} d\theta
\]
This is easily seen to be zero without an explicit calculation, because when we take the antiderivative of $e^{-2i\theta}$, we will get the same type of exponential, whose values when we plug in the upper and lower limits of integration will cancel each other out.

---

**Imaginary momentum?**

Here’s a paradox. If we take a wavefunction $e^{rx}$, where $r$ is a constant, then applying the momentum operator $\hat{p} = -i\frac{d}{dx}$ (example 5, p. 976) gives

$$\hat{p}e^{rx} = -ire^{rx}.$$  

For a state of definite momentum, we normally have in mind, as in examples 5 and 12, an oscillating wave where $r = ik$ is purely imaginary. But what if $r$ is real, say $r = 1$ (ignoring units)? Then our wavefunction is $e^{x}$, and it’s a state of definite momentum — *imaginary* momentum. Oh no, what’s going on? Nice polite observables like momentum aren’t supposed to have imaginary eigenvalues.

The resolution to this paradox lies in the fundamental principles of quantum mechanics that we’ve learned. Wavefunctions are supposed to belong to a vector space in which we have a well-defined inner product. A wavefunction like $\Psi = e^{x}$ is ruled out by this requirement, because $\langle \Psi | \Psi \rangle$ is infinite, and therefore undefined.

Of course we could raise the same objection to a wavefunction like $\Phi = e^{ikx}$ defined for all real values of $x$. But when we work with wavefunctions like $\Phi$, we usually just have in mind a computational shortcut, with the actual wavefunction being some kind of wavepacket or wave train consisting of a finite number of wavelengths. (Or we could be talking about rotation, as in the quantum moat of example 12. Note that in such an example, oscillating functions can be made to join smoothly to themselves as they wrap around, but this doesn’t work with functions like $e^{x}$.)

---

**Averages**

The average family lives down the street from me. Their family income in 2014 was $72,641, and they have 2.5 kids. This joke depends on the fact that you can’t superpose families to make a single family — but we can do this for wavefunctions. Suppose that the particle-in-a-box wavefunction $\psi$ has a definite energy of 1 unit, $\hat{E}\psi = 1\psi$. This says that $\psi$ is a state of definite energy 1, so that when we act on it with the energy operator $\hat{E}$, the result is just to multiply the wave by 1 (the eigenvalue).

If this is true, then shortening the wavelength by a factor of 2 means increasing the momentum by a factor of 2, and increasing the energy by a factor of 4. Therefore the wavefunction $\psi$ has 4 units of energy $\hat{E}\psi = 4\psi$.

Now there is nothing wrong with mixing these together to get a
state $\Psi = c \cdot + c' \cdot$. If both $c$ and $c'$ are nonzero, then we expect to get a state with properties in between those of $\cdot$ and $\cdot$. If we measure the energy of such a state, then our wavefunction becomes entangled with that of the particle, and we look like this:

\[
\begin{array}{c}
\boxed{\text{We measured the}} \\
\text{energy to be 1.} \\
\end{array} + \begin{array}{c}
\boxed{\text{We measured the}} \\
\text{energy to be 4.}
\end{array}
\]

Suppose we make the mixture an equal one, $c = c'$. Then the average should be $(1 + 4)/2 = 2.5$. This turns out to be easily expressible using an inner product:

\[
\langle \Psi | \Omega E \Psi \rangle = 2.5.
\]

It’s a good exercise to work this out for yourself (problem 20, p. 1013). The key point is that $\Psi$ can be expressed as a superposition of states of definite energy $\Psi = c \cdot + c' \cdot$, and when the operator $\Omega E$ works on $\Psi$, it gives $\Omega E \Psi = c \cdot + 4c' \cdot$. (And remember that by normalization, $|c| = |c'| = 1/\sqrt{2}$.)

This is a general rule for calculating averages: for a state $\Psi$, the average value for an observable $\Omega$ is $\langle \Psi | \Omega \Psi \rangle$. Because observables are hermitian, this is the same as $\langle \Omega \Psi | \Psi \rangle$.

**Discussion Questions**

**A** Suppose that by rotating vectors we could change the results of dot products. Explain why this would be very naughty, first by using an example in which $u \cdot u = 1$, and then, just to make it naughtier, one where $u \cdot v = 0$.

**B** Suppose that as a system evolved over time, inner products of wavefunctions could change. As in discussion question A, give shockingly naughty examples where initially we have $\langle \Psi | \Psi \rangle = 1$ and $\langle \Psi | \Phi \rangle = 0$, but later these inner products change.

**14.6.3 Completeness**

We have used math to back up our claim that distinguishable states are orthogonal. Going in the opposite direction, suppose that $\langle u | v \rangle = 0$. How can we then conclude that there exists some observable $\Omega$ that can distinguish them? There is no straightforward mathematical reason why this must be true, but it would not make sense physically to talk about two states that were utterly distinct and yet indistinguishable by any experiment. We therefore take this as a postulate.$^6$

$^6$ Our statement of the completeness principle refers to taking a sum of wavefunctions. Because the physical motivation for the completeness postulate is so appealing, physicists are willing to stretch the definition of the word “sum” in order to make it true. The sum can be an infinite sum, and in certain cases we may even need to make it an integral, which is a kind of continuous sum. For example, consider a one-dimensional particle in a box. A complete set of observables for this system can be found by picking the energy operator alone. Now suppose we throw a particle in the box, in such a way that its position is...
Completeness
For any system of interest, there exists a set of compatible observables, called a complete set, such that any state of the system can be expressed as a sum of wavefunctions having definite values of these observables.

The completeness postulate was discussed at a more elementary level in section 13.4.3, p. 923.

The set of wavefunctions referred to above is called a basis. (The terminology comes from linear algebra.) If we require normalization and ignore the undetectable phase, then choosing a complete set of observables is equivalent to choosing a basis. Therefore “choice of basis” and “choice of a complete set of observables” are nearly synonyms, so we will usually use the shorter phrase. Normally there is more than one possible choice of basis. The choice from among these possibilities is arbitrary, and nature doesn’t care which one we pick. That is, there is no preferred basis. An example of this principle is the fact that we habitually talk about “up” and “down” for the spin of an electron, which we are free to do, although it would be equally permissible to talk about left and right. Another good example is the discussion of the double degeneracy of the quantum moat on p. 920, where we were free to talk about a basis consisting of either two standing waves or two traveling waves.

As an example of the completeness principle, we have seen in the example in fig. d, p. 923, that for a rotor, the state with \( \ell = 1 \) and \( \ell_x = 0 \) can be written as a sum of the states with \( \ell_z = -1 \) and \( \ell_z = 1 \). In the language of the completeness postulate, we can express this as follows. Let our system be the set of possible states of a rotor. The observables \( L \) and \( L_z \) are compatible, and they turn out (although we will not prove it here) to be a complete set of observables for this system. The completeness postulate is satisfied in this example because the state with \( \ell_x = 0 \) can be expressed as \( |\ell_z = -1\rangle/\sqrt{2} + |\ell_z = 1\rangle/\sqrt{2} \).

Translating this scenario into a hypothetical real-world experiment, suppose that, as in figure b, we pass a beam of randomly oriented oxygen molecules (referred to as an unpolarized beam) through a Stern-Gerlach spectrometer that disperses them into beams with \( \ell_x = -1, 0, \) and \( +1 \). All three states are present, and in fact the beam is split into three beams of equal intensity, 1/3 that of the original beam. Then we throw away all but the molecules having \( \ell_x = 0 \), and pass these through a second spectrometer, this one select-
ing states according to their $\ell_z$. You can simulate experiments like this using an app at physics.weber.edu/schroeder/software/Spins.html. We have already found that the wavefunction of the intermediate beam is equal to the sum $|\ell_z = -1\rangle/\sqrt{2} + |\ell_z = 1\rangle/\sqrt{2}$, so interpreting squares of amplitudes as probabilities we predict a probability $(1/\sqrt{2})^2 = 1/2$ that each particle will be measured to have $\ell_z = -1$, the same probability for $-1$, and zero probability for 0. As explored in discussion question C on p. 959, this does not mean that the two beams that emerge from the second spectrometer have definite values of both $\ell_x$ and $\ell_z$; those two observables are not compatible.

In most of the examples we’ve encountered so far, it has been possible to think of the “wavefunction” as exactly what the word implies: a mathematical function of $x$ (and possibly also of $y$, and $z$), whose shape we visualize as a wave. The completeness principle, however, does not assign any special role to the position operator, nor does quantum mechanics in general. And there are cases where we do not even have the option of resorting to the picture of a wave that exists in space. For example, the intrinsic angular momentum $\hbar/2$ of an electron is not a possible amount of angular momentum for a particle to generate by moving through space. In section 14.7.1, p. 990, we will discuss a very simple quantum-mechanical system consisting of an electron, at rest, surrounded by a uniform magnetic field. In this example, the motion of the electron through space is not even of interest, and a complete set of observables simply consists of $L$ and $L_z$ (or $s$ and $s_z$, in notation that emphasizes that we’re talking about intrinsic spin).

### 14.6.4 The Schrödinger equation in general

This raises the question of what we mean by “the Schrödinger equation” in cases where nothing is being expressed as a function of $x$. The basic idea of the Schrödinger equation is that a particle’s energy is related to its frequency by $E = hf$, or $E = \hbar \omega$. In the form of the time-dependent Schrödinger equation that we have discussed on p. 967, $i\hbar \frac{\partial \Psi}{\partial t} = -\left(\frac{\hbar^2}{2m}\right) \nabla^2 \Psi + U \Psi$, the quantity on the right-hand side of the equation is just the energy operator acting on the wavefunction. So to generalize this to cases where the wavefunction isn’t expressed in terms of $x$, we just make that substitution:

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{O}_E \Psi.$$

This is as good a point as any to introduce a not-very-memorable piece of terminology, which is that the energy operator in quantum mechanics is called the **Hamiltonian**, after W.R. Hamilton. There is a classical version of the Hamiltonian, which is usually a synonym for the energy of a system, although it turns out that there comes more plausible if you consider the randomness of the unpolarized beam as being defined by its having maximum entropy.
are cases where it is not the same, e.g., when we adopt a rotating frame of reference. In both classical and quantum mechanics, the Hamiltonian is what determines the time-evolution of a system; in quantum mechanics, this is because it is the Hamiltonian that occurs in the Schrödinger equation. Because the Hamiltonian occurs so frequently, we will notate it as $\hat{H}$ rather than the more cumbersome $\Theta_E$, where the hat is to remind us that it is an operator. A similar notation can be used for other operators when it is easier to write, e.g., $\hat{s}_z$ rather than the clumsy $\Theta_{s_z}$. In the hat notation, the time-dependent Schrödinger equation looks like this:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi.$$

### An illegal energy operator example 14

We have pointed out on p. 976 some reasons to think that it would be bad to have a quantum-mechanical observable whose eigenvalues were not real, i.e., one represented by a non-hermitian operator (p. 982). Even worse things happen if we try to use a non-hermitian operator for our energy operator, the Hamiltonian. As the simplest possible example, consider a system consisting of a particle at rest, and the Hamiltonian defined by

$$\hat{H}\Psi = ik\Psi,$$

where $k$ is a nonzero real constant with units of energy. That is, the energy of the system is a constant value, which is the imaginary number $ik$. This operator has a single eigenvalue, $ik$, which is not real. The fact that it has a non-real eigenvalue is equivalent to a statement that it is non-hermitian (problem 8, p. 1009). If we plug this in to the Schrödinger equation, we get

$$i\hbar \frac{\partial \Psi}{\partial t} = ik\Psi,$$

or

$$\frac{\partial \Psi}{\partial t} = \frac{k}{\hbar}\Psi.$$

This differential equation is not hard to solve by the guess-and-check method. A function whose derivative is itself (except for a multiplicative constant) is an exponential. The solution is

$$\Psi = A e^{(k/\hbar)t},$$

where $A$ is a constant. This is bad. Very bad. If $\Psi$ is properly normalized at $t = 0$, then it will not be normalized at other times. If $k$ is positive, then the total probability will become greater than 1 for $t > 0$, which we could perhaps interpret as meaning that the particle is spawning more copies of itself. Almost as bad is the case of $k < 0$, for which the particle exponentially vanishes into nothingness like the Cheshire cat. Either behavior would violate the principle of the unitary evolution of the wavefunction (p. 969).
14.6.5 Summary of the structure of quantum mechanics

We can now summarize the logical structure of quantum mechanics using the following five principles.

1. **Wavefunction fundamentalism:** All knowable information about a system is encoded in its wavefunction (ignoring phase and normalization).

2. **Inner product:** Wavefunctions come equipped with an inner product that has the properties $\langle u|\alpha v + \beta w \rangle = \alpha \langle u|v \rangle + \beta \langle u|w \rangle$ and $\langle u|v \rangle = \langle v|u \rangle^*$. 

3. **Observables:** In quantum mechanics, any observable is represented by a linear operator $\Theta$ that takes a wavefunction as an input and is hermitian, $\langle \Theta u|v \rangle = \langle u|\Theta v \rangle$.

4. **Unitary evolution of the wavefunction:** The wavefunction evolves over time, according to the Schrödinger equation $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$, in a deterministic manner. Because $\hat{H}$ is an observable, the Schrödinger equation is linear and also unitary. Unitarity means that $\langle u(t)|v(t) \rangle = \langle u(t')|v(t') \rangle$, so that probability is conserved and information is never lost.

5. **Completeness:** For any system of interest, there exists a set of compatible observables, called a complete set, such that any state of the system can be expressed as a sum of wavefunctions having definite values of these observables.

14.7 Applications to the two-state system

14.7.1 A proton in a magnetic field

As an application of the ideas discussed in section 14.6, let us consider the example of a proton at rest in a uniform magnetic field. We will find that this very simple example has surprising properties, and also that it throws light on much more general ideas than would be expected, given how specific the situation is. We discuss the proton because the physics is then the physics of nuclear magnetic resonance (NMR), which is the technology used for, among other things, medical MRI scans.

Classically, the proton feels no magnetic force because it is at rest, and also because the field is uniform (unlike the one in the Stern-Gerlach experiment). Therefore we expect it to stay at rest. Its energy is $-m \cdot B$, and for the reasons discussed in sec. 11.2.4, p. 695, the magnetic dipole moment $m$ is proportional to the spin angular momentum vector $s$, so that the energy can be broken up into a sum of three terms as $ks_x B_x + ks_y B_y + ks_z B_z$, where $k$ is $-1/g$ times the proton’s charge-to-mass ratio.
Quantum-mechanically, the components of the magnetic field will act like ordinary numbers (since the field is static, and we aren’t trying to describe its dynamics quantum-mechanically), but the components of the angular momentum are observable properties of the proton, to be represented by operators. There is not always a foolproof procedure for translating a classical expression into something quantum-mechanical, but in this example it seems sensible to imagine that the classical expression for the energy can be made into a quantum-mechanical energy operator that is obtained simply by substituting the components of the angular momentum operator into the expression.

What we have determined so far is that the Hamiltonian \( \hat{H} \) will simply be a weighted sum of \( \hat{s}_x \), \( \hat{s}_y \), and \( \hat{s}_z \), with the weighting determined by the components of the magnetic field.

From our previous study of angular momentum in quantum mechanics, we know that a full description of our proton’s angular momentum can be given by specifying the magnitude of the angular momentum, which is a fixed \( \hbar/2 \), and its component along some arbitrarily chosen axis, say \( z \). We have a state \( | \uparrow \rangle \) which has eigenvalue \( s_z = +\hbar/2 \), and a \( | \downarrow \rangle \) with \( -\hbar/2 \). If the magnetic field is parallel to the \( z \) axis, then the action of the Hamiltonian is easy to define in terms of these two states,

\[
\hat{H} | \uparrow \rangle = \varepsilon | \uparrow \rangle \quad \text{and} \quad \hat{H} | \downarrow \rangle = -\varepsilon | \downarrow \rangle,
\]

where to keep the notation compact we write \( \varepsilon = k \hbar/2 \), which is an energy. The interpretation is that if there is no external magnetic field \( k = 0 \), then the energies of these two states are the same (and set to zero because we choose that as an arbitrary definition), while in the presence of a \( B_z \) the two energies become unequal. The pair of states is “split” in energy by the field. Note that the above two equations are sufficient to define the Hamiltonian for all states, not just for states in which \( s_z \) has a definite value. This follows from the completeness principle — a state having a definite value of, say, \( s_x \) can be written as some kind of linear combination of the form \( \alpha | \uparrow \rangle + \beta | \downarrow \rangle \), and we then have \( \hat{H} = \alpha \varepsilon | \uparrow \rangle - \beta \varepsilon | \downarrow \rangle \).

Now suppose that the magnetic field is not parallel to the \( z \) axis. One way to handle this situation would be simply to redefine the coordinate system so that the \( z \) axis was back in alignment with the direction of the field. But suppose that’s not convenient. Then the Hamiltonian will have a different form. But because the Hamiltonian must be Hermitian (see p. 982), there is not much freedom in choosing this form. It must look something like this:

\[
\hat{H} | \uparrow \rangle = \varepsilon | \uparrow \rangle + f | \downarrow \rangle \\
\hat{H} | \downarrow \rangle = f^* | \uparrow \rangle - \varepsilon | \downarrow \rangle.
\]

**Application to MRI scans**

In nuclear magnetic resonance (NMR), which is the technological basis for medical MRI scans, a very large DC magnetic field, \( \sim 3 \text{T} \), is applied to the sample using a superconducting magnet. Protons in hydrogen atoms have their spin states split in energy by \( \Delta E = 2\varepsilon = k\hbar \). After \( \sim 1 \text{s} \), the protons reach a new thermal equilibrium state in which the probability of \( | \downarrow \rangle \) and \( | \uparrow \rangle \) differ by \( \sim 10^{-5} \).

A brief radio-frequency pulse is then applied at the frequency \( \omega \) such that \( \Delta E = \hbar \omega \), so that a radio photon has the correct energy to cause a transition between the two spin states. Since there is a large number of protons, and they interact with one another, their response can be described semiclassically. The magnetization vector of the sample precesses in a complicated manner, which can be affected by the polarization and duration of the pulse.

After the radio pulse has stopped, the protons return to equilibrium again, and this changing magnetic field causes induced electric fields in a coil, which picks up a signal at the frequency \( \omega \). Spatial resolution for imaging is accomplished by adding a gradient to the magnetic field, amounting to a few percent over a distance of one meter, so that \( \omega \) has different values for different points in space.
Here the constant $f$ is a complex number with units of energy. The interpretation is that $\varepsilon$ tells us how much energy splitting we would have had if the magnetic field had not had any $x$ or $y$ components, while $f$ brings in the effect of those components. We could go ahead and work out the eigenvalues of this operator by writing down the eigenvalue equation and solving it by brute force, but the result is likely to seem less mysterious if we instead apply the following physical argument.

Although $f$ lies at some point in the complex plane with some phase angle $\text{arg} \ f$, such phase angles in quantum mechanics are not directly observable. Since energies are observable, it follows that the two eigenvalues of energy can only depend on the magnitude of $f$, not on its phase. By rotational invariance (sec. 3.4.2, p. 195), we also know that these energies can only depend on $|B| = \sqrt{B_x^2 + B_y^2 + B_z^2}$, and in fact when the direction of the field is fixed they must be proportional to $|B|$ (not to, e.g., the cube of the field). We have already interpreted $\varepsilon$ as being essentially $B_z$, except for a constant of proportionality, so it follows from units that the energies must be of the form $E = \pm \sqrt{\varepsilon^2 + (\ldots)|f|^2} = \pm \sqrt{\varepsilon^2 + (\ldots)f^*f}$, where $(\ldots)$ represents a universal unitless constant, which turns out to be 1. We therefore have for the energies the result

$$E = \pm \sqrt{\varepsilon^2 + f^*f}.$$  

Note that our earlier result of $E = \pm \varepsilon$ is recovered when $f = 0$.

14.7.2 The ammonia molecule

I chose the example of the proton in a magnetic field in the preceding section for ease of computation, but the treatment of the general case where $f \neq 0$ may not have seemed especially compelling, since we would always have the freedom to align our $z$ axis with the field, giving $f = 0$. But our results from that analysis are of much greater generality. They do not depend on any facts about the system other than the fact that it is a system with two states. To see the full power and generality of this approach, we will apply it to the ammonia molecule, NH$_3$, shown in figure a.

At ordinary temperatures, this molecule is likely to be rotating, and its angular momentum will have some component about its symmetry axis (the left-right axis in the diagram). Let’s say, for example, that the angular momentum vector points to the right, which we’ll say is the positive $x$ direction. Then the two orientations of the molecule shown in figure a are distinguishable. In one, the electric dipole vector (example 6, p. 586) points in the same direction as the angular momentum vector, and in the other they point in opposite directions. For a fixed angular momentum, we have a two-state system, as in section 14.7.1.

\footnote{This argument shows that when $L_z \neq 0$ we have two distinguishable states, but it does not necessarily tell us anything about the converse. When $L_z = 0$,}
Classically, the molecule’s moment of inertia is the same for orientations \( a/1 \) and \( a/2 \), so we would expect there to be two states with the same energy. We can always add an arbitrary constant to the energies, so if they’re the same, we can just say they’re both zero. Does this mean that quantum-mechanically, we simply have \( \hat{H} = 0 \)? That would be boring. But this cannot be true, for the following reason. According to the Schrödinger equation, a state of definite energy is a state that has a definite frequency, so it lasts forever, just twirling its phase angle around in the complex plane at a rate \( \omega = E/\hbar \). So if state 1 were a state of definite energy, then according to the Schrödinger equation if we initially put the molecule in state 1 it would stay in that state forever. But this cannot be the case, because we know it is possible for the molecule to switch from state 1 to state 2 by turning itself inside out like an umbrella caught by a gust of wind. The possibility of this type of inversion is not just an optional thing. Vibrations that flex the shape will exist due to zero-point motion (p. 963). Even if inversion requires a lot of energy, and the molecule doesn’t have that much energy, there is at least some probability of having quantum-mechanical tunneling from 1 to 2. If we prepare the molecule in state 1, and then observe it at some later time, there is some nonzero probability of finding it in state 2. This is a contradiction, so our assumption of \( \hat{H} = 0 \) must have been false.

So the Hamiltonian is not zero, but we already know the full variety of forms that the Hamiltonian of a two-state system can have. We only have a couple of parameters to play with, the numbers \( \varepsilon \) and \( f \). We have \( \varepsilon = 0 \) by symmetry, so the only possible form for the Hamiltonian is this:

\[
\hat{H}|1\rangle = f|2\rangle \\
\hat{H}|2\rangle = f^*|1\rangle.
\]

Because we can define the states \( |1\rangle \) and \( |2\rangle \) with any phases we like, we are free to take \( f \) to be real, \( f^* = f \), although this implies a certain relationship between the phases of \( |1\rangle \) and \( |2\rangle \). If we visualize these states as bell-shaped functions of an \( x \) coordinate describing the position of the nitrogen relative to the plane of the hydrogens, then it would be nice to have a phase convention such that where the tails of the wavefunctions overlap, inside the barrier, they have the same phase. This turns out to be the case when \( f \) is real and negative, so we will assume that from now on. Recycling our previous result for the energies, we have \( E = \pm \sqrt{\varepsilon^2 + f^2} = \pm f \). If the tunneling probability approaches zero, then we expect \( f \) to go to zero, and the energy splitting approaches zero, as we had expected classically.

---

Section 14.7  Applications to the two-state system  993

are there two states, or only one? The analysis in this case is rather intricate, and depends on the Pauli exclusion principle and the fact that the hydrogen atoms are all identical, that there are three of them, and that their nuclei are fermions. See Townes and Schawlow, Microwave Spectroscopy, 1955, pp. 69-71.
Experimentally, we do observe these two states in ammonia. The difference in energy is extremely small — e.g., for the state with angular momentum $1\hbar$ it is about $9.8 \times 10^{-5} \text{ eV}$, so that if a photon is emitted or absorbed in a transition between the states, it lies in the microwave spectrum. This energy difference equals $2|f|$, and its smallness indicates that the tunneling probability is small.

Let’s find the states of definite energy for this system. For the ground state, whose energy is $-|f|$, we need to look for a state of the form $|\text{g.s.}\rangle = (\ldots)|1\rangle + (\ldots)|2\rangle$ such that $\hat{H}|\text{g.s.}\rangle = -|f||\text{g.s.}\rangle = f|\text{g.s.}\rangle$. If we don’t worry about normalization or an over-all phase, we are free to take the first $(\ldots)$ equal to 1, so that $|\text{g.s.}\rangle = |1\rangle + \alpha|2\rangle$, for some complex number $\alpha$. We then have

$$\hat{H}|\text{g.s.}\rangle = \hat{H}(|1\rangle + \alpha|2\rangle) = f|2\rangle + \alpha f|1\rangle,$$

and setting this equal to $f|\text{g.s.}\rangle$ gives $\alpha = 1$, so that $|\text{g.s.}\rangle = |1\rangle + |2\rangle$.

The coefficients $(\ldots)$ that we set out to find are both equal to $+1$. Their equal magnitudes tell us that the ground state is one in which the molecule has an equal probability of existing in either inversion. Since the two coefficients are both positive, and we have defined $|1\rangle$ and $|2\rangle$ such that their phases agree when they overlap inside the barrier, this is a state of positive parity. The determination of the excited state is left as an exercise, problem 10 on p. 1010.

From a classical point of view, we would think of the set of states

$$\{ |1\rangle, |2\rangle \}$$

as the natural way of describing the possible states of the system. These two states are the ones that we can draw pictures of, $a/1$ and $a/2$. But part of the structure of quantum mechanics is that there is no preferred basis (p. 987), and there is nothing wrong with using the ground state and first excited state to form the basis

$$\{ |\text{g.s.}\rangle, |\text{ex.s.}\rangle \}$$

instead. In the language of the completeness principle (p. 987), one possible choice of a complete set of compatible observables for this molecule is the set consisting of a single observable, the energy. The $\{\text{ground-state,excited-state}\}$ basis just happens to be the one associated with this particular observable. If the ammonia molecule had just broken off from some larger molecule, then it would be oriented in a specific direction, and we would probably find it more convenient to describe it in the $\{1,2\}$ basis.
14.8 Energy-time uncertainty

14.8.1 Classical uncertainty relations

Consider the following classical system of analogies.

\[
\begin{array}{cccc}
\text{space} & x & k & \Delta x \Delta k \gtrsim 1 \\
\text{time} & t & \omega & \Delta t \Delta \omega \gtrsim 1 \\
\end{array}
\]

Here the quantity \( k = \frac{2\pi}{\lambda} \) is called the wavenumber. The inequality \( \Delta x \Delta k \gtrsim 1 \) is a kind of classical uncertainty relation that is closely related to the Heisenberg uncertainty principle. Its classical nature is immediately apparent because it doesn’t involve Planck’s constant. If you look back at the argument given on p. 901 to justify the Heisenberg uncertainty principle, you will see that it carries through equally well if we simply omit the quantum-mechanical ingredients and use it to put a bound on \( \Delta x \Delta k \) instead of \( \Delta x \Delta p \).

Once we’ve established the bound on \( \Delta x \Delta k \), the one on \( \Delta x \Delta p \) follows immediately because \( p = \frac{h}{\lambda} = \hbar k \).

The second line of the table is in strict analogy to the first line. A good practical example is the high-speed transmission of digital data over transmission lines such as fiber-optic cables. Suppose that we wish to send a string of 0’s and 1’s, and a 1 is to be represented by a square pulse. If we want to transmit the data at high speed, then we need the duration \( \Delta t \) of this pulse to be short, perhaps in the microsecond or even nanosecond range. This cannot be done if the signal consists only of a single frequency. A signal that only contains a single, pure frequency is just a sinusoidal wave that has existed infinitely far back in the past and will exist infinitely far into the future. Such a wave carries no information at all. Out frequency-time uncertainty relation tells us that if the duration of a pulse is to be, say, a microsecond, then the signal’s spread in frequency much be at least on the order of 1 MHz. This is why we use the term “bandwidth” to describe the speed of a communication channel.

14.8.2 Energy-time uncertainty

In a quantum-mechanical context, we have \( E = h\omega \), so there is an energy-time uncertainty relation,

\[ \Delta E \Delta t \gtrsim h. \]

As with the Heisenberg uncertainty principle for momentum and position, the symbol \( \gtrsim \) means that we leave out a numerical factor, which can only be precisely defined if we fix some specific statistical definition of \( \Delta \), e.g., a standard deviation.

The interpretation of the energy-time uncertainty relation is a little tricky, because although the classical analogy between space and time is exact, the quantum-mechanical analogy breaks down. This is because time in nonrelativistic quantum mechanics, unlike position, is not an observable (example 9). Time in this theory
is just a universal parameter. The physicist Lev Landau liked to
tell his students that there was no energy-time uncertainty relation,
because “I can measure the energy, and look at my watch; then I
know both energy and time!” One good way of interpreting it is that
if there is a transfer of energy between two systems, then it relates
the uncertainty $\Delta E$ in the amount of energy transferred during the
duration $\Delta t$ of the interaction.

For example, suppose we wish to bounce a photon off of a hydro-
gen atom in order to determine whether the atom is in its ground
state. This is not necessarily an easy thing to do by extracting what-
ever information we get from the reflected photon, but the ground
state is orthogonal to the other states, so we are at least encour-
gaged to believe that it is not theoretically impossible. But there is a
hard theoretical limit on how *quickly* we can make such a determi-
nation. The difference in energy between the ground state and the
first excited state is $1.6 \times 10^{-18}$ J, so we must use a photon with
an energy less than this amount, or else the act of observing the
atom may in fact destroy the property we were hoping to measure.
By the energy-time uncertainty relation, this implies that the mea-
surement process cannot be done in less than about $10^{-15}$ seconds.
This example may seem impractical, but in fact computer memories
are starting to reach the level of speed and miniaturization at which
such fundamental constraints become relevant.

1*Mortality for hydrogen*  
Example 15

In atomic physics, when a photon is emitted or absorbed it is al-
most always in a wave pattern with angular momentum $1$ (i.e., $1\hbar$)
and negative parity (example 10). Classically, this is the type of
radiation pattern that we would get from an electric dipole spin-
ing end over end, so we call it an electric dipole transition. Be-
cause the electromagnetic interaction has a symmetry between
left- and right-handedness (section 11.1.5, p. 685), this means
that an electric dipole transition can never cause a transition from
one state of an atom to another state with the same parity.

Now the ground state of the hydrogen atom has $\ell = 0$ and is
therefore a state of positive parity. One of the first excited states,
referred to as the 2s state, also has these properties, and there-
fore it is impossible for the 2s state to decay to the ground state
by emitting an electric dipole photon. The happy atom proba-
bly believes that once it’s in the exalted 2s state, it can stay that
way forever. One way for it to be cheated of immortality is if it
undergoes a collision with another atom, but in some so-called
planetary nebulae (hot clouds of gas cast off by dying stars), the
density can be so low that collisions are very infrequent. In this
situation, the dominant process for decay of the 2s state can be
the simultaneous emission of two photons. An exact and rigorous
calculation of the rate of decay for this process is quite technical,
but a fairly reasonable estimate can be obtained by the following
semiclassical argument based on the energy-time uncertainty relation.

The typical rate of emission for a photon, when not forbidden by parity, is \( R \sim 10^9 \text{ s}^{-1} \), i.e., it takes about a nanosecond. We can think of the two-photon decay as an energy-nonconserving jump up to some higher-energy state, with the emission of a photon, followed by the emission of a second photon leading down to the ground state. The first jump can happen because of the energy-time uncertainty relation, which allows the electron to stay in the intermediate state for a time \( t \sim \frac{\hbar}{E} \), which is on the order of \( 10^{-15} \text{ s} \). The probability for the second photon to be emitted within this time is \( Rt \), so the rate for the whole two-photon process is \( R^2 t \sim 10 \text{ s}^{-1} \). Considering the extremely crude nature of this calculation, the result is in good agreement with the observed rate of about \( 0.1 \text{ s}^{-1} \). The process is actually observed, and contributes a continuous background spectrum in addition to the discrete line spectrum when such nebulae are observed with a spectrometer through a telescope.

A fundamental application of the energy-time uncertainty relation is to the explication of what it means to measure time in quantum mechanics. In example 9 on p. 979 we argued that time is not an observable in quantum mechanics because time cannot in general be measured by looking at a quantum-mechanical system: many quantum-mechanical systems are too simple to function as clocks. We can now see in more detail what “too simple” might mean here. Microscopic systems, unlike macroscopic ones, are often encountered in a definite state of energy, such as the ground state. Such a state has \( \Delta E = 0 \) and therefore by the energy-time uncertainty relation it has \( \Delta t = \infty \). In other words, the only time evolution in such a system consists of the system’s over-all phase twirling in the complex plane at a steady rate, but phase isn’t measurable, so we can’t use this rotation like the hand on a clock. To make a clock, we need, at a bare minimum, a system that is in a superposition of two different energy levels. We then have two independent phases. Although absolute phases are not measurable, relative ones are, and for example when we measure a double-slit interference pattern, that is exactly what we are doing: observing (statistically) the difference between two phases. As a loose conceptual analogy, this is like the idea that a figure-eight Lissajous pattern has an identifiable feature where it crosses itself, the crossing being like the tick of a clock.

14.9 Randomization of phase
14.9.1 Randomization of phase in a measurement

The energy-time uncertainty relation can help us to understand one of the most puzzling issues in quantum mechanics, which is the problem of measurement. What happens when we use a macroscopic measuring device, which is well described by classical physics, to observe a microscopic system, which is quantum-mechanical? How do we reconcile these two seemingly incompatible descriptions of reality when both appear to be in play simultaneously?

Consider an electron passing through a double-slit apparatus. We have already considered the possibility of covering one slit (discussion question D, p. 881). Suppose instead that we carefully watch one slit through a microscope, and see whether or not the electron passed through it. If we could perform this observation without disturbing the electron, then a paradox would arise. For if we haven’t disturbed the electron, then there should still be a double-slit interference pattern. But if we watch one slit, then half of the time we should see that the electron did not go through it, and therefore the slit’s existence is of no importance, and we can’t possibly get a double-slit interference pattern.

To avoid this contradiction, it appears that nature must conspire against us in such a way that observing the slit inevitably does disturb the electron. The energy-time uncertainty relation explains why this is so. Our observation of the electron is an interaction between the electron and our macroscopic measuring device. This interaction will presumably transfer some amount of energy $E$ into or out of the electron, and if our goal was to avoid disturbing the electron, we would imagine that it would be best to make $E$ very small. But the energy-time uncertainty $\Delta E \Delta t \geq \hbar$ relation tells us that if this energy is to have a value that is confined to some small range $\Delta E$, then the time $\Delta t$ it takes for the interaction to occur must be at least $\sim \hbar/\Delta E$. While the electron is being subjected to this interaction, its phase is rotating around the complex plane like $e^{i\omega t} = e^{iEt/\hbar}$. The total change in the phase angle $\phi = E\Delta t/\hbar$ is uncertain because $E$ is uncertain, so our observation will inevitably change the phase by some random amount, which is uncertain by an amount $\Delta \phi = \Delta E \Delta t/\hbar$, so $\Delta \phi \gtrsim 1$.

Thus is won’t actually help us if we make the interaction very gentle, because the lengthening of the time has a compensating effect. Any slight alteration in the frequency will have more time to accumulate into a big phase difference, and we still end up with a phase uncertainty that is at least on the order of 1. Although we haven’t stated our uncertainty relations with enough mathematical precision to state this lower bound with all the right factors of 2 and $\pi$, it turns out that $\Delta \phi \geq 2\pi$. That is, any such observation will have the effect of completely randomizing the phase of the thing being observed. In fact, macroscopic measuring devices nor-
nally exceed the bounds set by the uncertainty relations by many orders of magnitude, so there will typically be a vast amount of overkill in this randomization. This is a general rule for reasoning about quantum-mechanical measurements: they always completely randomize the quantum-mechanical phase of the thing being measured. This provides a more physical justification for our more abstract mathematical proof in example 8 on p. 978 that phase is not an observable.

In our example of the double slit, what will be the effect of this randomization of the electron’s phase? In our usual description of the double slit, we assume that the circular waves emerging from one slit are in phase with those that come out through the other one, so that the double-slit interference pattern has a maximum in the center. But if, for example, one of the waves has its phase inverted, then all the maxima of our interference pattern will become minima and vice versa. If the phase is randomized, then the positions of the maxima and minima are randomized as well, and thus if we try to collect data on enough electrons to see an interference pattern, we will not see maxima and minima at all.

One subtle question about this description is the following. The randomization of the phase by the measurement appears to have erased the information about the phase relationship between the parts of the wave in the two slits. But how can this be, since one of our principles of quantum mechanics (p. 990) is that time evolution is always unitary, so no information is ever supposed to be lost? The resolution of this paradox is that the phase information still exists, but it has been taken away from the electron and flowed out into the observer and the environment. This is similar to the classical paradox of what happens to the (classical) information written on a piece of paper when we burn the paper: the information still exists, and could in principle be reconstructed by observing all the molecules and tracing their trajectories back in time using Newton’s laws.

14.9.2 Decoherence

Starting around 1970, physicists began to realize that ideas involving a loss of coherence, or “decoherence,” could help to explain some things about quantum mechanics that had previously seemed mysterious. The classical notions of coherence and coherence length were described in sec. 12.5.8, p. 823, and quantum-mechanical decoherence was briefly introduced on p. 885.

One mystery was the fact that it is difficult to demonstrate wave interference effects with large objects. This is partly because the wavelength \( \lambda = h/p = h/mv \) tends to be small for an object with a large mass. But even taking this into account, we do not seem to have much luck observing, for example, double-slit diffraction of very large molecules, even when we use slits with appropriate
dimensions and a detector with a good enough angular resolution.

In the early days of quantum mechanics, people like Bohr and Heisenberg imagined that there was simply a clear division between the macroscopic and microscopic worlds. Big things and small things just had different rules: Newton’s laws in one case, quantum mechanics in the other. But this is no longer a tenable position, because we now know that there is no limit on the distance scales over which quantum-mechanical behavior can occur. For example, a communication satellite carried out a demonstration in 2017 in which a coherence length of 1200 km was demonstrated using photons.\textsuperscript{9}

The insight about decoherence was the following. Consider the most massive material object that has so far been successfully diffracted through a grating, which was a molecule consisting of about 810 atoms in an experiment by Eibenberger \textit{et al.} in 2013.\textsuperscript{10} While this molecule was propagating through the apparatus as a wave, the experimenters needed to keep it from simply being stopped by a collision with an air molecule. For this reason, they had to do the experiment inside a vacuum chamber, with an extremely good vacuum. But even then, the molecule was being bombarded by photons of infrared light emitted from the walls of the chamber. The effect of this bombardment is to disrupt the molecule’s wavefunction and reduce its coherence length (p. 824).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{A large molecule such as the one in the Eibenberger experiment is represented by its wavepacket. As the molecule starts out, its coherence length, shown by the arrows, is quite long. As it flies to the right, it is bombarded by infrared photons, which randomize its phase, causing its coherence length to shorten exponentially: by a factor of two in the second panel, and by a further factor of two in the final one. When the packet enters the double slit, its coherence length is on the same order of magnitude as the slits’ spacing $d$, which will worsen but not entirely eliminate the observability of interference fringes. (This is only a schematic representation, with the wavepacket shown as being many orders of magnitude bigger than its actual size in relation to the vacuum chamber. Also, the real experiment used a reflecting grating, not a transmitting double slit.)}
\end{figure}

This causes an effect similar to the one in the situation illustrated in figure a, where we spy on one slit of a double-slit apparatus. The microscope would operate by bouncing photons off of the electron, and the result is to disrupt the coherence of the electron’s wavefunction, so that the coherence length is no longer as large as the distance between the slits. The infrared photons in the Eibenberger experiment were not introduced intentionally, but

\textsuperscript{9}Yin \textit{et al.}, arxiv.org/abs/1707.01339
\textsuperscript{10}arxiv.org/abs/1310.8343

1000 Chapter 14 Additional Topics in Quantum Physics