5. The Schrödinger Equations

The energy eigenfunctions for the infinite square well are simple and easy to guess—but they're the exception, not the rule. For a more general (and more realistic) potential energy function $V(x)$ the energy eigenfunctions will be more complicated, and simply guessing them isn't an option. We need a more systematic method. Unfortunately, there's no general formula for the energy eigenfunctions themselves. But there *is* a general way of writing down the differential equation of which these functions are the solutions.

The time-independent Schrödinger equation

To see where this differential equation comes from, consider again the sinusoidal waves that are energy eigenfunctions for a free particle, or inside an infinite square well, or (it turns out) in any region where $V(x) = 0$. Whether the sinusoidal function is e^{ikx} or $\sin(kx)$ or $\cos(kx)$, its second derivative equals $-k^2$ times itself:

$$\frac{d^2}{dx^2}\psi(x) = -k^2\psi(x) \qquad \text{for energy eigenfunctions where } V(x) = 0. \qquad (1)$$

Here the wavenumber k is, as usual, $p/\hbar$, and we don't have to worry about whether p is positive or negative because it's squared.

From here on, unless I say otherwise, I will assume that the particle in question is nonrelativistic. Then $p^2 = 2mK$, where K is the kinetic energy, so

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2mK}{\hbar^2}\psi(x) \qquad \text{for energy eigenfunctions where } V(x) = 0. \qquad (2)$$

Of course, for a free particle, we could just as well write E (total energy) instead of K (kinetic energy). But now think about what should happen where $V(x) \neq 0$. The second derivative of the wavefunction, or its curvature, is what determines its wavelength: the distance that it takes the wave to loop around and back to make a full cycle. The wavelength is directly related to the momentum, which determines the *kinetic* energy, so adding in some potential energy, while keeping K fixed, shouldn't affect the second derivative or the relationship expressed in equation 2. Therefore, even where $V(x)$ is nonzero, we can substitute $E - V(x)$ for K in equation 2 to obtain

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2m}{\hbar^2}\big(E - V(x)\big)\psi(x) \qquad \text{for } any \text{ energy eigenfunction.} \qquad (3)$$

This is the famous *time-independent Schrödinger equation*, or TISE for short. It is the differential equation that is satisfied by the energy eigenfunctions for a quantum

particle in one dimension, and it is the equation that we must solve in order to find those eigenfunctions for an arbitrary potential energy $V(x)$. It's really a *different* differential equation for every new $V(x)$, and its solutions are different as well, so solving the TISE for the myriad possible $V(x)$ functions can be a never-ending task. We'll solve it repeatedly, in particular cases, during the next few weeks. First, though, I'd like to digress into a more abstract interpretation of the TISE.

Operators and eigenvalues

With a simple algebraic rearrangement, we can instead write the TISE as

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x). \tag{4}$$

I'll now "factor" out the $\psi(x)$ on the left-hand side to obtain

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x), \tag{5}$$

where the quantity in brackets is what we call an *operator*, which acts on the function $\psi(x)$. In general, an operator is basically a "machine" that converts a function into some other function. Examples of operators would include d/dx ("take the derivative"), x ("multiply the function by x"), and $-\hbar^2/2m$ ("multiply the function by the constant $-\hbar^2/2m$"). The operator in the brackets of equation 5 says, "Take the function's second derivative, multiply the result by the constant $-\hbar^2/2m$, then add that onto what you get when you multiply the function by $V(x)$." This rather intricate operator is called the *Hamiltonian* operator and is often abbreviated H:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x). \tag{6}$$

Using this handy abbreviation, we can write the TISE as simply

$$H\psi = E\psi, \tag{7}$$

where here it is understood that ψ is a function of x.

Equation 7 has the form of an *eigenvalue* equation: It says that the solutions to the TISE are precisely those functions that, when acted upon by the Hamiltonian operator, are left unchanged except for multiplication by a constant E (the so-called *eigenvalue*). This is why those solutions are called energy *eigen*functions.

You've probably heard of eigenvalues before, in the context of matrices and eigen*vectors*. Later I'll show you how to rewrite equation 7 in vector-matrix form—although the matrix H and vectors ψ turn out to be infinite-dimensional. For now, just rest assured that the "eigen" terminology is entirely consistent with what you learned in linear algebra.

To provide more context for these ideas, let me digress even further to discuss some other operators and their eigenfunctions. The *momentum operator* is $-i\hbar d/dx$, because the momentum eigenfunctions, $e^{ip_x x/\hbar}$, are eigenfunctions of this operator with eigenvalues p_x:

$$\left[-i\hbar\frac{d}{dx}\right]\psi(x) = p_x\psi(x), \qquad \text{for } \psi(x) = e^{ip_x x/\hbar}. \tag{8}$$

From the momentum operator we can construct the *kinetic energy operator* using the formula $p_x^2/2m$; that is, apply the momentum operator twice, then divide by the constant $2m$. The result is just the first term in the Hamiltonian operator, equation 6.

The *position operator*, meanwhile, is simply x, that is, "multiply by a factor of x." The eigenfunctions of this operator are Dirac delta functions, because the eigenvalue equation

$$x\psi(x) = x_0\psi(x) \tag{9}$$

(where x_0 is a constant) is satisfied by the delta function $\delta(x - x_0)$. (The equation must be satisfied for *all* x, but it is: check it separately for $x = x_0$ and $x \neq x_0$.) The operator for any function of x is simply (to multiply by) that function; in particular, the potential energy operator is simply (to multiply by) $V(x)$.

Equation 6, therefore, simply says that the Hamiltonian operator is the sum of the kinetic energy and potential energy operators: it is the *total energy* operator, and that's why its eigenvalues are the energy values E that correspond to its eigenfunctions. (The reason it's called the Hamiltonian and not just the energy operator has to do with the Hamiltonian formulation of classical mechanics, which you may or may not have studied in another course.)

In the linear algebra of finite vector spaces, a matrix has only a finite number of eigenvalues and eigenvectors. Here we're working in an infinite-dimensional vector space (the space of all normalizable functions $\psi(x)$), and most operators have an infinite number of eigenvalues and eigenvectors. In fact, *every* real number x_0 is an eigenvalue of the position operator, and *every* real number p_x is an eigenvalue of the momentum operator. But *not* every real number E need be an eigenvalue of the Hamiltonian operator, at least when we restrict the eigenfunctions $\psi(x)$ to those that are normalizable (that is, those for which $\int |\psi(x)|^2 dx$ is finite). In fact, the eigenvalues are often limited to a discrete (but still infinite) set of real numbers, as we saw in the previous lesson for the infinite square well. In general, "solving the time-independent Schrödinger equation" means finding both the eigenfunctions $\psi(x)$ and the corresponding eigenvalues E.

At the end of Lesson 3 I asserted that the energy eigenfunctions for any $V(x)$ always form a complete basis: any *other* function can be written as a linear combination of them. Actually, this statement is also true for the momentum eigenfunctions, and for the position eigenfunctions, and for the eigenfunctions of any other operator that corresponds to an observable quantity in quantum mechanics. To make the

3

statement precise, I would need to digress into some assumptions about the convergence of infinite sums, and explain how to handle continuous eigenvalues in terms of integrals instead of sums. But intuitively, the statement just says that you can think of any wavefunction as a *mixture* of wavefunctions for which $\mathcal{O}$ is well defined, where $\mathcal{O}$ can be position, momentum, energy, or any other observable quantity.

The time-dependent Schrödinger equation

Among all the observable quantities, however, energy is special because it is closely tied to time evolution. Recall from Lesson 3 that an energy eigenstate evolves in time with a simple wiggle factor,

$$\psi(t) = \psi(0)e^{-iEt/\hbar}, \tag{10}$$

implementing the Einstein relation $E = \hbar\omega$. If we act on this function with the Hamiltonian operator H, the wiggle factor simply factors out and we obtain the same factor of E as in equation 7:

$$H\psi(t) = H\psi(0)e^{-iEt/\hbar} = \big(H\psi(0)\big)e^{-iEt/\hbar} = E\psi(0)e^{-iEt/\hbar} = E\psi(t). \tag{11}$$

But now notice that we can obtain almost the same expression by instead taking the time derivative:

$$\frac{\partial}{\partial t}\psi(t) = \frac{\partial}{\partial t}\big(\psi(0)e^{-iEt/\hbar}\big) = (-iE/\hbar)\psi(0)e^{-iEt/\hbar} = (-iE/\hbar)\psi(t). \tag{12}$$

(It's a partial derivative because $\psi(t)$ is also a function of x.) Multiplying both sides by $+i\hbar$ and comparing to the previous equation, we have

$$H\psi(t) = i\hbar\frac{\partial\psi}{\partial t}. \tag{13}$$

This result would be of little use if it applied only to energy eigenfunctions, for which we already have the more explicit formula 10. But amazingly, equation 13 applies to *any* wavefunction, because any wavefunction can be written as a sum of energy eigenfunctions, each of which oscillates in time according to its own wiggle factor. The explicit formula is

$$\psi(t) = \sum_n c_n\psi_n e^{-iE_n t/\hbar}, \tag{14}$$

for some collection of complex coefficients c_n, where the sum runs over all energy eigenfunctions ψ_n (and the sum should be replaced by an integral when the eigenvalues E_n are continuous instead of discrete). The calculations of equations 11 and 12 work the same as before, for each term in this sum. Each term has its own E_n, but everything still matches up, with the same extra factor of $-i/\hbar$, resulting in equation 13.

Equation 13 is a first-order differential equation that tells us how *any* wavefunction evolves in time. Although we've already written out its explicit solution in equation 14, that solution can be extremely cumbersome because it entails an infinite sum and requires that we first find all the energy eigenfunctions and eigenvalues. Sometimes it's simpler just to work with the differential equation directly—not that that's always easy either.

If we write out the Hamiltonian operator explicitly, then equation 13 takes the form

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t) = i\hbar\frac{\partial\psi}{\partial t}. \tag{15}$$

As you can see, this is actually a *partial* differential equation. Given any initial wavefunction $\psi(x,0)$, we can in principle use this equation to predict the wavefunction at all future times. Thus, this equation plays the same logical role in quantum mechanics that Newton's second law, $F = m(d^2x/dt^2)$, plays in classical mechanics.

Equation 15 (or 13) is called the *time-dependent Schrödinger equation*, or the TDSE for short. As you can see, it looks an awful lot like the time-*in*dependent Schrödinger equation (equation 3 or 7), because both involve the same Hamiltonian operator. But the logical roles of the two Schrödinger equations are *completely different*: The TISE is the equation that we must solve to find the energy eigenfunctions and their corresponding eigenvalues, while the TDSE is the equation that governs the time evolution of any wavefunction whatsoever.