Question (2) — Problem 2.1(a)
(3) — 2.1 (b)
(4) — 2.4
(5)(6) — 2.5

CHAPTER 2

TIME-INDEPENDENT SCHRÖDINGER EQUATION

2.1 STATIONARY STATES

In Chapter 1 we talked a lot about the wave function, and how you use it to calculate various quantities of interest. The time has come to stop procrastinating, and confront what is, logically, the prior question: How do you *get* $\Psi(x, t)$ in the *first* place? We need to solve the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi, \qquad [2.1]$$

for a specified potential[1] $V(x, t)$. In this chapter (and most of this book) I shall assume that V is *independent of* t. In that case the Schrödinger equation can be solved by the method of **separation of variables** (the physicist's first line of attack on any partial differential equation): We look for solutions that are simple *products*,

$$\Psi(x, t) = \psi(x)\,\varphi(t), \qquad [2.2]$$

where ψ (*lower*-case) is a function of x alone, and φ is a function of t alone. On its face, this is an absurd restriction, and we cannot hope to get more than a tiny

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[1] It is tiresome to keep saying "potential energy function," so most people just call V the "potential," even though this invites occasional confusion with *electric* potential, which is actually potential energy *per unit charge*.

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subset of all solutions in this way. But hang on, because the solutions we *do* obtain turn out to be of great interest. Moreover (as is typically the case with separation of variables) we will be able at the end to patch together the separable solutions in such a way as to *construct* the most general solution.

For separable solutions we have

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\varphi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}\varphi$$

(*ordinary* derivatives, now), and the Schrödinger equation reads

$$i\hbar\psi \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\varphi + V\psi\varphi.$$

Or, dividing through by $\psi\varphi$:

$$i\hbar \frac{1}{\varphi}\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V. \qquad [2.3]$$

Now, the left side is a function of t alone, and the right side is a function of x alone.[2] The only way this can possibly be true is if both sides are in fact *constant*—otherwise, by varying t, I could change the left side without touching the right side, and the two would no longer be equal. (That's a subtle but crucial argument, so if it's new to you, be sure to pause and think it through.) For reasons that will appear in a moment, we shall call the separation constant E. Then

$$i\hbar \frac{1}{\varphi}\frac{d\varphi}{dt} = E,$$

or

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi, \qquad [2.4]$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V = E,$$

or

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi.} \qquad [2.5]$$

Separation of variables has turned a *partial* differential equation into two *ordinary* differential equations (Equations 2.4 and 2.5). The first of these (Equation 2.4)

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[2] Note that this would *not* be true if V were a function of t as well as x.

is easy to solve (just multiply through by dt and integrate); the general solution is $C\exp(-iEt/\hbar)$, but we might as well absorb the constant C into ψ (since the quantity of interest is the product $\psi\varphi$). Then

$$\varphi(t) = e^{-iEt/\hbar}. \qquad [2.6]$$

The second (Equation 2.5) is called the **time-independent Schrödinger equation**; we can go no further with it until the potential $V(x)$ is specified.

The rest of this chapter will be devoted to solving the time-independent Schrödinger equation, for a variety of simple potentials. But before I get to that you have every right to ask: *What's so great about separable solutions?* After all, *most* solutions to the (time *de*pendent) Schrödinger equation do *not* take the form $\psi(x)\varphi(t)$. I offer three answers—two of them physical, and one mathematical:

1. They are **stationary states**. Although the wave function itself,

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}, \qquad [2.7]$$

does (obviously) depend on t, the *probability density*,

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2, \qquad [2.8]$$

does *not*—the time-dependence cancels out.[3] The same thing happens in calculating the expectation value of any dynamical variable; Equation 1.36 reduces to

$$\langle Q(x,p)\rangle = \int \psi^* Q\left(x, \frac{\hbar}{i}\frac{d}{dx}\right)\psi\, dx. \qquad [2.9]$$

Every expectation value is constant in time; we might as well drop the factor $\varphi(t)$ altogether, and simply use ψ in place of Ψ. (Indeed, it is common to refer to ψ as "the wave function," but this is sloppy language that can be dangerous, and it is important to remember that the *true* wave function always carries that exponential time-dependent factor.) In particular, $\langle x\rangle$ is constant, and hence (Equation 1.33) $\langle p\rangle = 0$. Nothing ever *happens* in a stationary state.

2. They are states of *definite total energy*. In classical mechanics, the total energy (kinetic plus potential) is called the **Hamiltonian**:

$$H(x,p) = \frac{p^2}{2m} + V(x). \qquad [2.10]$$

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[3] For normalizable solutions, E must be *real* (see Problem 2.1(a)).

The corresponding Hamiltonian *operator*, obtained by the canonical substitution $p \rightarrow (\hbar/i)(\partial/\partial x)$, is therefore[4]

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \qquad [2.11]$$

Thus the time-independent Schrödinger equation (Equation 2.5) can be written

$$\hat{H}\psi = E\psi, \qquad [2.12]$$

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi \, dx = E \int |\psi|^2 \, dx = E \int |\Psi|^2 \, dx = E. \qquad [2.13]$$

(Notice that the normalization of Ψ entails the normalization of ψ.) Moreover,

$$\hat{H}^2\psi = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2\psi,$$

and hence

$$\langle H^2 \rangle = \int \psi^* \hat{H}^2 \psi \, dx = E^2 \int |\psi|^2 \, dx = E^2.$$

So the variance of H is

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0. \qquad [2.14]$$

But remember, if $\sigma = 0$, then every member of the sample must share the same value (the distribution has zero spread). *Conclusion:* A separable solution has the property that *every measurement of the total energy is certain to return the value* E. (That's why I chose that letter for the separation constant.)

3. The general solution is a **linear combination** of separable solutions. As we're about to discover, the time-independent Schrödinger equation (Equation 2.5) yields an infinite collection of solutions ($\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ...), each with its associated value of the separation constant (E_1, E_2, E_3, ...); thus there is a different wave function for each **allowed energy**:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2t/\hbar}, \quad \ldots.$$

Now (as you can easily check for yourself) the (time-*de*pendent) Schrödinger equation (Equation 2.1) has the property that any linear combination[5] of solutions

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[4] Whenever confusion might arise, I'll put a "hat" (^) on the operator, to distinguish it from the dynamical variable it represents.

[5] A **linear combination** of the functions $f_1(z), f_2(z), \ldots$ is an expression of the form

$$f(z) = c_1 f_1(z) + c_2 f_2(z) + \cdots,$$

where $c_1, c_2, \ldots$ are any (complex) constants.

is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x,t)=\sum_{n=1}^{\infty}c_n\psi_n(x)e^{-iE_nt/\hbar}. \qquad [2.15]$$

It so happens that *every* solution to the (time-dependent) Schrödinger equation can be written in this form—it is simply a matter of finding the right constants (c_1, c_2, ...) so as to fit the initial conditions for the problem at hand. You'll see in the following sections how all this works out in practice, and in Chapter 3 we'll put it into more elegant language, but the main point is this: Once you've solved the time-*in*dependent Schrödinger equation, you're essentially *done*; getting from there to the general solution of the time-*de*pendent Schrödinger equation is, in principle, simple and straightforward.

A lot has happened in the last four pages, so let me recapitulate, from a somewhat different perspective. Here's the generic problem: You're given a (time-independent) potential $V(x)$, and the starting wave function $\Psi(x,0)$; your job is to find the wave function, $\Psi(x,t)$, for any subsequent time t. To do this you must solve the (time-dependent) Schrödinger equation (Equation 2.1). The strategy[6] is first to solve the time-*in*dependent Schrödinger equation (Equation 2.5); this yields, in general, an infinite set of solutions ($\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ...), each with its own associated energy (E_1, E_2, E_3, ...). To fit $\Psi(x,0)$ you write down the general linear combination of these solutions:

$$\Psi(x,0)=\sum_{n=1}^{\infty}c_n\,\psi_n(x); \qquad [2.16]$$

the miracle is that you can *always* match the specified initial state by appropriate choice of the constants c_1, c_2, c_3, ... To construct $\Psi(x,t)$ you simply tack onto each term its characteristic time dependence, $\exp(-iE_nt/\hbar)$:

$$\boxed{\Psi(x,t)=\sum_{n=1}^{\infty}c_n\psi_n(x)e^{-iE_nt/\hbar}=\sum_{n=1}^{\infty}c_n\Psi_n(x,t).} \qquad [2.17]$$

The separable solutions themselves,

$$\Psi_n(x,t)=\psi_n(x)e^{-iE_nt/\hbar}, \qquad [2.18]$$

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[6] Occasionally you can solve the time-dependent Schrödinger equation without recourse to separation of variables—see, for instance, Problems 2.49 and 2.50. But such cases are extremely rare.

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are *stationary* states, in the sense that all probabilities and expectation values are independent of time, but this property is emphatically *not* shared by the general solution (Equation 2.17); the energies are different, for different stationary states, and the exponentials do not cancel, when you calculate $|\Psi|^2$.

Example 2.1 Suppose a particle starts out in a linear combination of just *two* stationary states:

$$\Psi(x, 0) = c_1\psi_1(x) + c_2\psi_2(x).$$

(To keep things simple I'll assume that the constants c_n and the states $\psi_n(x)$ are *real.*) What is the wave function $\Psi(x, t)$ at subsequent times? Find the probability density, and describe its motion.

Solution: The first part is easy:

$$\Psi(x, t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar},$$

where E_1 and E_2 are the energies associated with ψ_1 and ψ_2. It follows that

$$|\Psi(x, t)|^2 = (c_1\psi_1 e^{iE_1t/\hbar} + c_2\psi_2 e^{iE_2/\hbar})(c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2/\hbar})$$

$$= c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos[(E_2 - E_1)t/\hbar].$$

(I used **Euler's formula**, $\exp i\theta = \cos\theta + i\sin\theta$, to simplify the result.) Evidently the probability density *oscillates* sinusoidally, at an angular frequency $(E_2 - E_1)/\hbar$; this is certainly *not* a stationary state. But notice that it took a *linear combination* of states (with different energies) to produce motion.[7]

***Problem 2.1** Prove the following three theorems:

(a) For normalizable solutions, the separation constant E must be *real*. *Hint:* Write E (in Equation 2.7) as $E_0 + i\Gamma$ (with E_0 and Γ real), and show that if Equation 1.20 is to hold for all t, Γ must be zero.

(b) The time-independent wave function $\psi(x)$ can always be taken to be *real* (unlike $\Psi(x, t)$, which is necessarily complex). This doesn't mean that every solution to the time-independent Schrödinger equation *is* real; what it says is that if you've got one that is *not*, it can always be expressed as a linear combination of solutions (with the same energy) that *are*. So you *might as well* stick to ψ's that are real. *Hint:* If $\psi(x)$ satisfies Equation 2.5, for a given E, so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.

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[7] This is nicely illustrated by an applet at the Web site http://thorin.adnc.com/~topquark/quantum/deepwellmain.html.

(c) If $V(x)$ is an **even function** (that is, $V(-x) = V(x)$) then $\psi(x)$ can always be taken to be either even or odd. *Hint:* If $\psi(x)$ satisfies Equation 2.5, for a given E, so too does $\psi(-x)$, and hence also the even and odd linear combinations $\psi(x) \pm \psi(-x)$.

$*$**Problem 2.2** Show that E must exceed the minimum value of $V(x)$, for every normalizable solution to the time-independent Schrödinger equation. What is the classical analog to this statement? *Hint:* Rewrite Equation 2.5 in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi;$$

if $E < V_{\text{min}}$, then ψ and its second derivative always have the *same sign*—argue that such a function cannot be normalized.

2.2 THE INFINITE SQUARE WELL

Suppose

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases} \qquad [2.19]$$

(Figure 2.1). A particle in this potential is completely free, except at the two ends ($x = 0$ and $x = a$), where an infinite force prevents it from escaping. A classical model would be a cart on a frictionless horizontal air track, with perfectly elastic bumpers—it just keeps bouncing back and forth forever. (This potential is artificial, of course, but I urge you to treat it with respect. Despite its simplicity—or rather, precisely *because* of its simplicity—it serves as a wonderfully accessible test case for all the fancy machinery that comes later. We'll refer back to it frequently.)

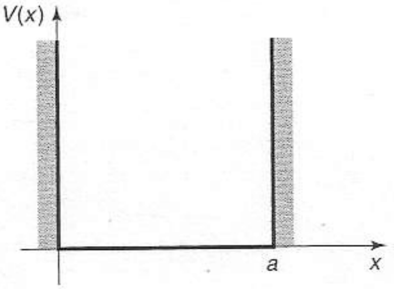

FIGURE 2.1: The infinite square well potential (Equation 2.19).

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9).

Outside the well, $\psi(x) = 0$ (the probability of finding the particle there is zero). *Inside* the well, where $V = 0$, the time-independent Schrödinger equation (Equation 2.5) reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \qquad [2.20]$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \qquad [2.21]$$

(By writing it in this way, I have tacitly assumed that $E \geq 0$; we know from Problem 2.2 that $E < 0$ won't work.) Equation 2.21 is the classical **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A\sin kx + B\cos kx, \qquad [2.22]$$

where A and B are arbitrary constants. Typically, these constants are fixed by the **boundary conditions** of the problem. What *are* the appropriate boundary conditions for $\psi(x)$? Ordinarily, *both* ψ *and* $d\psi/dx$ *are continuous*, but where the potential goes to infinity only the first of these applies. (I'll *prove* these boundary conditions, and account for the exception when $V = \infty$, in Section 2.5; for now I hope you will trust me.)

Continuity of $\psi(x)$ requires that

$$\psi(0) = \psi(a) = 0, \qquad [2.23]$$

so as to join onto the solution outside the well. What does this tell us about A and B? Well,

$$\psi(0) = A\sin 0 + B\cos 0 = B,$$

so $B = 0$, and hence

$$\psi(x) = A\sin kx. \qquad [2.24]$$

Then $\psi(a) = A\sin ka$, so either $A = 0$ (in which case we're left with the trivial—non-normalizable—solution $\psi(x) = 0$), or else $\sin ka = 0$, which means that

$$ka = 0,\ \pm\pi,\ \pm 2\pi,\ \pm 3\pi,\ \ldots \qquad [2.25]$$

But $k = 0$ is no good (again, that would imply $\psi(x) = 0$), and the negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and we can absorb the minus sign into A. So the *distinct* solutions are

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \ldots \qquad [2.26]$$

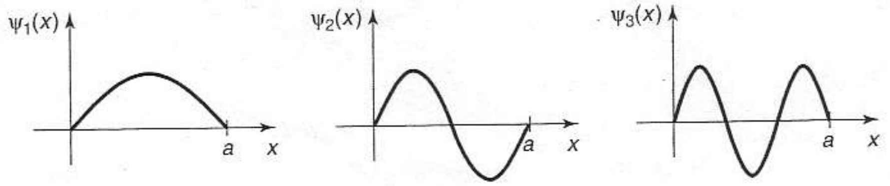

FIGURE 2.2: The first three stationary states of the infinite square well (Equation 2.28).

Curiously, the boundary condition at $x = a$ does not determine the constant A, but rather the constant k, and hence the possible values of E:

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.} \qquad [2.27]$$

In radical contrast to the classical case, a quantum particle in the infinite square well cannot have just *any* old energy—it has to be one of these special **allowed** values.[8] To find A, we *normalize* ψ:

$$\int_0^a |A|^2 \sin^2(kx)\,dx = |A|^2\frac{a}{2} = 1, \quad \text{so} \quad |A|^2 = \frac{2}{a}.$$

This only determines the *magnitude* of A, but it is simplest to pick the positive real root: $A = \sqrt{2/a}$ (the phase of A carries no physical significance anyway). Inside the well, then, the solutions are

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right).} \qquad [2.28]$$

As promised, the time-independent Schrödinger equation has delivered an infinite set of solutions (one for each positive integer n). The first few of these are plotted in Figure 2.2. They look just like the standing waves on a string of length a; ψ_1, which carries the lowest energy, is called the **ground state**, the others, whose energies increase in proportion to n^2, are called **excited states**. As a collection, the functions $\psi_n(x)$ have some interesting and important properties:

1. They are alternately **even** and **odd**, with respect to the center of the well: ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.[9]

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[8] Notice that the quantization of energy emerged as a rather technical consequence of the boundary conditions on solutions to the time-independent Schrödinger equation.

[9] To make this symmetry more apparent, some authors center the well at the origin (running it from $-a$ to $+a$). The even functions are then cosines, and the odd ones are sines. See Problem 2.36.

2. As you go up in energy, each successive state has one more **node** (zero-crossing): ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.

3. They are mutually **orthogonal**, in the sense that

$$\int \psi_m(x)^* \psi_n(x)\, dx = 0, \qquad [2.29]$$

whenever $m \neq n$. *Proof*:

$$\begin{aligned}
\int \psi_m(x)^* \psi_n(x)\, dx &= \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right) dx \\
&= \frac{1}{a}\int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)\right] dx \\
&= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m+n}{a}\pi x\right)\right\}\Bigg|_0^a \\
&= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)}\right\} = 0.
\end{aligned}$$

Note that this argument does *not* work if $m = n$. (Can you spot the point at which it fails?) In that case normalization tells us that the integral is 1. In fact, we can combine orthogonality and normalization into a single statement:[10]

$$\boxed{\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn},} \qquad [2.30]$$

where δ_{mn} (the so-called **Kronecker delta**) is defined in the usual way,

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases} \qquad [2.31]$$

We say that the ψ's are **orthonormal**.

4. They are **complete**, in the sense that any *other* function, $f(x)$, can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right). \qquad [2.32]$$

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[10] In this case the ψ's are *real*, so the * on ψ_m is unnecessary, but for future purposes it's a good idea to get in the habit of putting it there.

I'm not about to *prove* the completeness of the functions $\sin(n\pi x/a)$, but if you've studied advanced calculus you will recognize that Equation 2.32 is nothing but the **Fourier series** for $f(x)$, and the fact that "any" function can be expanded in this way is sometimes called **Dirichlet's theorem.**[11]

The coefficients c_n can be evaluated—for a given $f(x)$—by a method I call **Fourier's trick**, which beautifully exploits the orthonormality of $\{\psi_n\}$: Multiply both sides of Equation 2.32 by $\psi_m(x)^*$, and integrate.

$$\int \psi_m(x)^* f(x)\,dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^*\psi_n(x)\,dx = \sum_{n=1}^{\infty} c_n\delta_{mn} = c_m. \qquad [2.33]$$

(Notice how the Kronecker delta kills every term in the sum except the one for which $n = m$.) Thus the nth coefficient in the expansion of $f(x)$ is[12]

$$\boxed{c_n = \int \psi_n(x)^* f(x)\,dx.} \qquad [2.34]$$

These four properties are extremely powerful, and they are not peculiar to the infinite square well. The first is true whenever the potential itself is a symmetric function; the second is universal, regardless of the shape of the potential.[13] Orthogonality is also quite general—I'll show you the proof in Chapter 3. Completeness holds for all the potentials you are likely to encounter, but the proofs tend to be nasty and laborious; I'm afraid most physicists simply *assume* completeness, and hope for the best.

The stationary states (Equation 2.18) of the infinite square well are evidently

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}. \qquad [2.35]$$

I claimed (Equation 2.17) that the most general solution to the (time-dependent) Schrödinger equation is a linear combination of stationary states:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}. \qquad [2.36]$$

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[11] See, for example, Mary Boas, *Mathematical Methods in the Physical Sciences*, 2d ed. (New York: John Wiley, 1983), p. 313; $f(x)$ can even have a finite number of finite discontinuities.

[12] It doesn't matter whether you use m or n as the "dummy index" here (as long as you are consistent on the two sides of the equation, of course); *whatever* letter you use, it just stands for "any positive integer."

[13] See, for example, John L. Powell and Bernd Crasemann, *Quantum Mechanics* (Addison-Wesley, Reading, MA, 1961), p. 126.

(If you doubt that this *is* a solution, by all means *check* it!) It remains only for me to demonstrate that I can fit any prescribed initial wave function, $\Psi(x, 0)$, by appropriate choice of the coefficients c_n:

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

The completeness of the ψ's (confirmed in this case by Dirichlet's theorem) guarantees that I can always express $\Psi(x, 0)$ in this way, and their orthonormality licenses the use of Fourier's trick to determine the actual coefficients:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0)\, dx. \qquad [2.37]$$

That *does* it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n, using Equation 2.37, and then plug these into Equation 2.36 to obtain $\Psi(x, t)$. Armed with the wave function, we are in a position to compute any dynamical quantities of interest, using the procedures in Chapter 1. And this same ritual applies to *any* potential—the only things that change are the functional form of the ψ's and the equation for the allowed energies.

Example 2.2 A particle in the infinite square well has the initial wave function

$$\Psi(x, 0) = Ax(a - x), \quad (0 \leq x \leq a),$$

for some constant A (see Figure 2.3). *Outside* the well, of course, $\Psi = 0$. Find $\Psi(x, t)$.

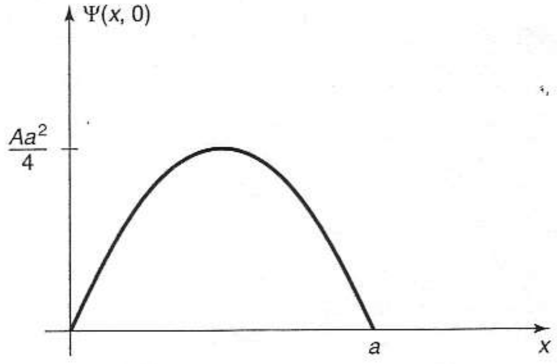

FIGURE 2.3: The starting wave function in Example 2.2.

Solution: First we need to determine A, by normalizing $\Psi(x,0)$:

$$1 = \int_0^a |\Psi(x,0)|^2\,dx = |A|^2 \int_0^a x^2(a-x)^2\,dx = |A|^2\frac{a^5}{30},$$

so

$$A = \sqrt{\frac{30}{a^5}}.$$

The nth coefficient is (Equation 2.37)

$$\begin{aligned}
c_n &= \sqrt{\frac{2}{a}}\int_0^a \sin\left(\frac{n\pi}{a}x\right)\sqrt{\frac{30}{a^5}}\,x(a-x)\,dx \\
&= \frac{2\sqrt{15}}{a^3}\left[a\int_0^a x\sin\left(\frac{n\pi}{a}x\right)dx - \int_0^a x^2\sin\left(\frac{n\pi}{a}x\right)dx\right] \\
&= \frac{2\sqrt{15}}{a^3}\left\{a\left[\left(\frac{a}{n\pi}\right)^2\sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right. \\
&\qquad \left.-\left[2\left(\frac{a}{n\pi}\right)^2 x\sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2-2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right\} \\
&= \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0)\right] \\
&= \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0)-\cos(n\pi)\right], \\
&= \begin{cases} 0, & \text{if } n \text{ is even,} \\ 8\sqrt{15}/(n\pi)^3, & \text{if } n \text{ is odd.} \end{cases}
\end{aligned}$$

Thus (Equation 2.36):

$$\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5\ldots} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right)e^{-in^2\pi^2\hbar t/2ma^2}.$$

Loosely speaking, c_n tells you the "amount of ψ_n that is contained in Ψ." Some people like to say that $|c_n|^2$ is the "probability of finding the particle in the nth stationary state," but this is bad language; the particle is in the state Ψ, *not* Ψ_n, and, anyhow, in the laboratory you don't "find a particle to be in a particular state"—you *measure* some *observable*, and what you get is a *number*. As we'll see in Chapter 3, what $|c_n|^2$ tells you is *the probability that a measurement of the* *energy would yield the value* E_n (a competent measurement will always return *one* of the "allowed" values—hence the name—and $|c_n|^2$ is the probability of getting the *particular* value E_n).

Of course, the *sum* of these probabilities should be 1,

$$\boxed{\sum_{n=1}^{\infty} |c_n|^2 = 1.} \tag{2.38}$$

Indeed, this follows from the normalization of Ψ (the c_n's are independent of time, so I'm going to do the proof for $t = 0$; if this bothers you, you can easily generalize the argument to arbitrary t).

$$\begin{aligned}
1 = \int |\Psi(x,0)|^2\,dx &= \int \left(\sum_{m=1}^{\infty} c_m \psi_m(x)\right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x)\right) dx \\
&= \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \int \psi_m(x)^* \psi_n(x)\,dx \\
&= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} c_m^* c_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2.
\end{aligned}$$

(Again, the Kronecker delta picks out the term $m = n$ in the summation over m.)

Moreover, the expectation value of the energy must be

$$\boxed{\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n,} \tag{2.39}$$

and this too can be checked directly: The time-independent Schrödinger equation (Equation 2.12) says

$$H\psi_n = E_n \psi_n, \tag{2.40}$$

so

$$\begin{aligned}
\langle H \rangle = \int \Psi^* H \Psi\,dx &= \int \left(\sum c_m \psi_m\right)^* H \left(\sum c_n \psi_n\right) dx \\
&= \sum\sum c_m^* c_n E_n \int \psi_m^* \psi_n\,dx = \sum |c_n|^2 E_n.
\end{aligned}$$

Notice that the probability of getting a particular energy is independent of time, and so, *a fortiori*, is the expectation value of H. This is a manifestation of **conservation of energy** in quantum mechanics.

Example 2.3 In Example 2.2 the starting wave function (Figure 2.3) closely resembles the ground state ψ_1 (Figure 2.2). This suggests that $|c_1|^2$ should dominate, and in fact

$$|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.998555\ldots .$$

The rest of the coefficients make up the difference:[14]

$$\sum_{n=1}^{\infty} |c_n|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^6} = 1.$$

The expectation value of the energy, in this example, is

$$\langle H \rangle = \sum_{n=1,3,5,\ldots}^{\infty} \left(\frac{8\sqrt{15}}{n^3\pi^3}\right)^2 \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{480\hbar^2}{\pi^4 ma^2} \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^4} = \frac{5\hbar^2}{ma^2}.$$

As one might expect, it is very close to $E_1 = \pi^2\hbar^2/2ma^2$—slightly *larger*, because of the admixture of excited states.

Problem 2.3 Show that there is no acceptable solution to the (time-independent) Schrödinger equation for the infinite square well with $E = 0$ or $E < 0$. (This is a special case of the general theorem in Problem 2.2, but this time do it by explicitly solving the Schrödinger equation, and showing that you cannot meet the boundary conditions.)

∗Problem 2.4 Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$, σ_x, and σ_p, for the nth stationary state of the infinite square well. Check that the uncertainty principle is satisfied. Which state comes closest to the uncertainty limit?

∗Problem 2.5 A particle in the infinite square well has as its initial wave function an even mixture of the first two stationary states:

$$\Psi(x, 0) = A[\psi_1(x) + \psi_2(x)].$$

---

[14] You can look up the series

$$\frac{1}{1^6} + \frac{1}{3^6} + \frac{1}{5^6} + \cdots = \frac{\pi^6}{960}$$

and

$$\frac{1}{1^4} + \frac{1}{3^4} + \frac{1}{5^4} + \cdots = \frac{\pi^4}{96}$$

in math tables, under "Sums of Reciprocal Powers" or "Riemann Zeta Function."

(a) Normalize $\Psi(x, 0)$. (That is, find A. This is very easy, if you exploit the orthonormality of ψ_1 and ψ_2. Recall that, having normalized Ψ at $t = 0$, you can rest assured that it *stays* normalized—if you doubt this, check it explicitly after doing part (b).)

(b) Find $\Psi(x, t)$ and $|\Psi(x, t)|^2$. Express the latter as a sinusoidal function of time, as in Example 2.1. To simplify the result, let $\omega \equiv \pi^2\hbar/2ma^2$.

(c) Compute $\langle x \rangle$. Notice that it oscillates in time. What is the angular frequency of the oscillation? What is the amplitude of the oscillation? (If your amplitude is greater than $a/2$, go directly to jail.)

(d) Compute $\langle p \rangle$. (As Peter Lorre would say, "Do it ze *kveek* vay, Johnny!")

(e) If you measured the energy of this particle, what values might you get, and what is the probability of getting each of them? Find the expectation value of H. How does it compare with E_1 and E_2?

Problem 2.6 Although the *overall* phase constant of the wave function is of no physical significance (it cancels out whenever you calculate a measurable quantity), the *relative* phase of the coefficients in Equation 2.17 *does* matter. For example, suppose we change the relative phase of ψ_1 and ψ_2 in Problem 2.5:

$$\Psi(x, 0) = A[\psi_1(x) + e^{i\phi}\psi_2(x)],$$

where ϕ is some constant. Find $\Psi(x, t)$, $|\Psi(x, t)|^2$, and $\langle x \rangle$, and compare your results with what you got before. Study the special cases $\phi = \pi/2$ and $\phi = \pi$. (For a graphical exploration of this problem see the applet in footnote 7.)

∗**Problem 2.7** A particle in the infinite square well has the initial wave function[15]

$$\Psi(x, 0) = \begin{cases} Ax, & 0 \le x \le a/2, \\ A(a - x), & a/2 \le x \le a. \end{cases}$$

(a) Sketch $\Psi(x, 0)$, and determine the constant A.

(b) Find $\Psi(x, t)$.

---

[15] There is no restriction in principle on the *shape* of the starting wave function, as long as it is normalizable. In particular, $\Psi(x, 0)$ need not have a continuous derivative—in fact, it doesn't even have to be a *continuous* function. However, if you try to calculate $\langle H \rangle$ using $\int \Psi(x, 0)^* H \Psi(x, 0)\, dx$ in such a case, you may encounter technical difficulties, because the second derivative of $\Psi(x, 0)$ is ill-defined. It works in Problem 2.9 because the discontinuities occur at the end points, where the wave function is zero anyway. In Problem 2.48 you'll see how to manage cases like Problem 2.7.

(c) What is the probability that a measurement of the energy would yield the value E_1?

(d) Find the expectation value of the energy.

Problem 2.8 A particle of mass m in the infinite square well (of width a) starts out in the left half of the well, and is (at $t = 0$) equally likely to be found at any point in that region.

(a) What is its initial wave function, $\Psi(x, 0)$? (Assume it is real. Don't forget to normalize it.)

(b) What is the probability that a measurement of the energy would yield the value $\pi^2\hbar^2/2ma^2$?

Problem 2.9 For the wave function in Example 2.2, find the expectation value of H, at time $t = 0$, the "old fashioned" way:

$$\langle H \rangle = \int \Psi(x, 0)^* \hat{H} \Psi(x, 0)\, dx.$$

Compare the result obtained in Example 2.3, using Equation 2.39. *Note:* because $\langle H \rangle$ is independent of time, there is no loss of generality in using $t = 0$.

2.3 THE HARMONIC OSCILLATOR

The paradigm for a classical harmonic oscillator is a mass m attached to a spring of force constant k. The motion is governed by **Hooke's law**,

$$F = -kx = m\frac{d^2x}{dt^2}$$

(ignoring friction), and the solution is

$$x(t) = A\sin(\omega t) + B\cos(\omega t),$$

where

$$\omega \equiv \sqrt{\frac{k}{m}} \qquad [2.41]$$

is the (angular) frequency of oscillation. The potential energy is

$$V(x) = \frac{1}{2}kx^2; \qquad [2.42]$$

its graph is a parabola.

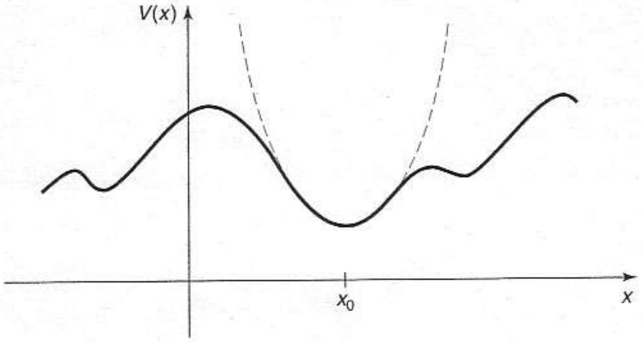

FIGURE 2.4: Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

Of course, there's no such thing as a *perfect* harmonic oscillator—if you stretch it too far the spring is going to break, and typically Hooke's law fails long before that point is reached. But practically any potential is *approximately* parabolic, in the neighborhood of a local minimum (Figure 2.4). Formally, if we expand $V(x)$ in a **Taylor series** about the minimum:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots,$$

subtract $V(x_0)$ (you can add a constant to $V(x)$ with impunity, since that doesn't change the force), recognize that $V'(x_0) = 0$ (since x_0 is a minimum), and drop the higher-order terms (which are negligible as long as $(x - x_0)$ stays small), we get

$$V(x) \cong \frac{1}{2}V''(x_0)(x - x_0)^2,$$

which describes simple harmonic oscillation (about the point x_0), with an effective spring constant $k = V''(x_0)$.[16] That's why the simple harmonic oscillator is so important: Virtually *any* oscillatory motion is approximately simple harmonic, as long as the amplitude is small.

The *quantum* problem is to solve the Schrödinger equation for the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 \qquad [2.43]$$

(it is customary to eliminate the spring constant in favor of the classical frequency, using Equation 2.41). As we have seen, it suffices to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi. \qquad [2.44]$$

---

[16] Note that $V''(x_0) \geq 0$, since by assumption x_0 is a *minimum*. Only in the rare case $V''(x_0) = 0$ is the oscillation not even approximately simple harmonic.

In the literature you will find two entirely different approaches to this problem. The first is a straightforward "brute force" solution to the differential equation, using the **power series method**; it has the virtue that the same strategy can be applied to many other potentials (in fact, we'll use it in Chapter 4 to treat the Coulomb potential). The second is a diabolically clever algebraic technique, using so-called **ladder operators**. I'll show you the algebraic method first, because it is quicker and simpler (and a lot more fun);[17] if you want to skip the power series method for now, that's fine, but you should certainly plan to study it at some stage.

2.3.1 Algebraic Method

To begin with, let's rewrite Equation 2.44 in a more suggestive form:

$$\frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi, \tag{2.45}$$

where $p \equiv (\hbar/i)d/dx$ is, of course, the momentum operator. The basic idea is to *factor* the Hamiltonian,

$$H = \frac{1}{2m}[p^2 + (m\omega x)^2]. \tag{2.46}$$

If these were *numbers*, it would be easy:

$$u^2 + v^2 = (iu + v)(-iu + v).$$

Here, however, it's not quite so simple, because p and x are *operators*, and operators do not, in general, **commute** (xp is not the same as px). Still, this does motivate us to examine the quantities

$$\boxed{a_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x)} \tag{2.47}$$

(the factor in front is just there to make the final results look nicer).

Well, what *is* the product a_-a_+?

$$\begin{aligned} a_-a_+ &= \frac{1}{2\hbar m\omega}(ip + m\omega x)(-ip + m\omega x) \\ &= \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2 - im\omega(xp - px)]. \end{aligned}$$

---

[17] We'll encounter some of the same strategies in the theory of angular momentum (Chapter 4), and the technique generalizes to a broad class of potentials in **super-symmetric quantum mechanics** (see, for example, Richard W. Robinett, *Quantum Mechanics*, (Oxford U.P., New York, 1997), Section 14.4).

As anticipated, there's an extra term, involving $(xp - px)$. We call this the **commutator** of x and p; it is a measure of how badly they *fail* to commute. In general, the commutator of operators A and B (written with square brackets) is

$$[A, B] \equiv AB - BA. \tag{2.48}$$

In this notation,

$$a_- a_+ = \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2] - \frac{i}{2\hbar}[x, p]. \tag{2.49}$$

We need to figure out the commutator of x and p. *Warning:* Operators are notoriously slippery to work with in the abstract, and you are bound to make mistakes unless you give them a "test function," $f(x)$, to act on. At the end you can throw away the test function, and you'll be left with an equation involving the operators alone. In the present case we have:

$$[x, p]f(x) = \left[x\frac{\hbar}{i}\frac{d}{dx}(f) - \frac{\hbar}{i}\frac{d}{dx}(xf)\right] = \frac{\hbar}{i}\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) = i\hbar f(x). \tag{2.50}$$

Dropping the test function, which has served its purpose,

$$\boxed{[x, p] = i\hbar.} \tag{2.51}$$

This lovely and ubiquitous result is known as the **canonical commutation relation**.[18]

With this, Equation 2.49 becomes

$$a_- a_+ = \frac{1}{\hbar\omega}H + \frac{1}{2}, \tag{2.52}$$

or

$$H = \hbar\omega\left(a_- a_+ - \frac{1}{2}\right). \tag{2.53}$$

Evidently the Hamiltonian does *not* factor perfectly—there's that extra $-1/2$ on the right. Notice that the ordering of a_+ and a_- is important here; the same argument, with a_+ on the left, yields

$$a_+ a_- = \frac{1}{\hbar\omega}H - \frac{1}{2}. \tag{2.54}$$

In particular,

$$[a_-, a_+] = 1. \tag{2.55}$$

---

[18] In a deep sense all of the mysteries of quantum mechanics can be traced to the fact that position and momentum do not commute. Indeed, some authors take the canonical commutation relation as an *axiom* of the theory, and use it to *derive* $p = (\hbar/i)d/dx$.

So the Hamiltonian can equally well be written

$$H = \hbar\omega\left(a_+a_- + \frac{1}{2}\right). \qquad [2.56]$$

In terms of $a_\pm$, then, the Schrödinger equation[19] for the harmonic oscillator takes the form

$$\hbar\omega\left(a_\pm a_\mp \pm \frac{1}{2}\right)\psi = E\psi \qquad [2.57]$$

(in equations like this you read the upper signs all the way across, or else the lower signs).

Now, here comes the crucial step: I claim that *if ψ satisfies the Schrödinger equation with energy E,* (that is: $H\psi = E\psi$), *then $a_+\psi$ satisfies the Schrödinger equation with energy $(E + \hbar\omega)$: $H(a_+\psi) = (E + \hbar\omega)(a_+\psi)$. Proof:*

$$\begin{aligned} H(a_+\psi) &= \hbar\omega\left(a_+a_- + \frac{1}{2}\right)(a_+\psi) = \hbar\omega\left(a_+a_-a_+ + \frac{1}{2}a_+\right)\psi \\ &= \hbar\omega a_+\left(a_-a_+ + \frac{1}{2}\right)\psi = a_+\left[\hbar\omega\left(a_+a_- + 1 + \frac{1}{2}\right)\psi\right] \\ &= a_+(H + \hbar\omega)\psi = a_+(E + \hbar\omega)\psi = (E + \hbar\omega)(a_+\psi). \end{aligned}$$

(I used Equation 2.55 to replace a_-a_+ by $a_+a_- + 1$, in the second line. Notice that whereas the ordering of a_+ and a_- *does* matter, the ordering of $a_\pm$ and any *constants*—such as $\hbar$, ω, and E—does *not*; an operator commutes with any constant.)

By the same token, $a_-\psi$ is a solution with energy $(E - \hbar\omega)$:

$$\begin{aligned} H(a_-\psi) &= \hbar\omega\left(a_-a_+ - \frac{1}{2}\right)(a_-\psi) = \hbar\omega a_-\left(a_+a_- - \frac{1}{2}\right)\psi \\ &= a_-\left[\hbar\omega\left(a_-a_+ - 1 - \frac{1}{2}\right)\psi\right] = a_-(H - \hbar\omega)\psi = a_-(E - \hbar\omega)\psi \\ &= (E - \hbar\omega)(a_-\psi). \end{aligned}$$

Here, then, is a wonderful machine for generating new solutions, with higher and lower energies—if we could just find *one* solution, to get started! We call $a_\pm$ **ladder operators**, because they allow us to climb up and down in energy; a_+ is the **raising operator**, and a_- the **lowering operator**. The "ladder" of states is illustrated in Figure 2.5.

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[19] I'm getting tired of writing "time-independent Schrödinger equation," so when it's clear from the context which one I mean, I'll just call it the "Schrödinger equation."

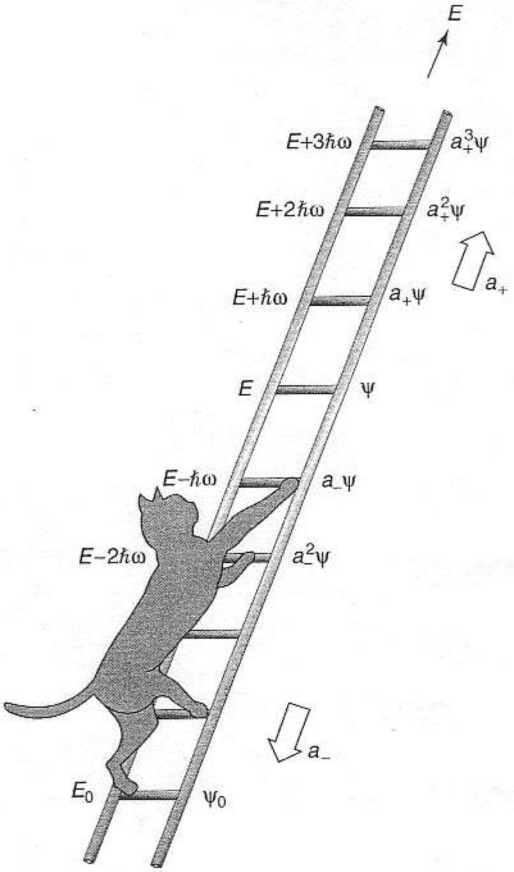

FIGURE 2.5: The "ladder" of states for the harmonic oscillator.

But wait! What if I apply the lowering operator repeatedly? Eventually I'm going to reach a state with energy less than zero, which (according to the general theorem in Problem 2.2) does not exist! At some point the machine must fail. How can that happen? We know that $a_-\psi$ is a new solution to the Schrödinger equation, but *there is no guarantee that it will be normalizable*—it might be zero, or its square-integral might be infinite. In practice it is the former: There occurs a "lowest rung" (call it ψ_0) such that

$$a_-\psi_0 = 0. \qquad [2.58]$$

We can use this to determine $\psi_0(x)$:

$$\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega x\right)\psi_0 = 0,$$

or

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x \psi_0.$$

This differential equation is easy to solve:

$$\int \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar} \int x\, dx \quad \Rightarrow \quad \ln \psi_0 = -\frac{m\omega}{2\hbar} x^2 + \text{constant},$$

so

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}.$$

We might as well normalize it right away:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\, dx = |A|^2 \sqrt{\frac{\pi\hbar}{m\omega}},$$

so $A^2 = \sqrt{m\omega/\pi\hbar}$, and hence

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}.} \qquad [2.59]$$

To determine the energy of this state we plug it into the Schrödinger equation (in the form of Equation 2.57), $\hbar\omega(a_+a_- + 1/2)\psi_0 = E_0\psi_0$, and exploit the fact that $a_-\psi_0 = 0$:

$$E_0 = \frac{1}{2}\hbar\omega. \qquad [2.60]$$

With our foot now securely planted on the bottom rung (the ground state of the quantum oscillator), we simply apply the raising operator (repeatedly) to generate the excited states,[20] increasing the energy by $\hbar\omega$ with each step:

$$\boxed{\psi_n(x) = A_n(a_+)^n\psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2}\right)\hbar\omega,} \qquad [2.61]$$

where A_n is the normalization constant. By applying the raising operator (repeatedly) to ψ_0, then, we can (in principle) construct all[21] the stationary states of

---

[20] In the case of the harmonic oscillator it is customary, for some reason, to depart from the usual practice, and number the states starting with $n = 0$, instead of $n = 1$. Obviously, the lower limit on the sum in a formula such as Equation 2.17 should be altered accordingly.

[21] Note that we obtain *all* the (normalizable) solutions by this procedure. For if there were some *other* solution, we could generate from it a second ladder, by repeated application of the raising and lowering operators. But the bottom rung of this new ladder would have to satisfy Equation 2.58, and since that leads inexorably to Equation 2.59, the bottom rungs would be the same, and hence the two ladders would in fact be identical.

the harmonic oscillator. Meanwhile, without ever doing that explicitly, we have determined the allowed energies.

Example 2.4 Find the first excited state of the harmonic oscillator.

Solution: Using Equation 2.61,

$$\begin{aligned}\psi_1(x) = A_1 a_+ \psi_0 &= \frac{A_1}{\sqrt{2\hbar m\omega}}\left(-\hbar\frac{d}{dx} + m\omega x\right)\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \\ &= A_1\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\sqrt{\frac{2m\omega}{\hbar}}\, x e^{-\frac{m\omega}{2\hbar}x^2}.\end{aligned} \qquad [2.62]$$

We can normalize it "by hand":

$$\int |\psi_1|^2\, dx = |A_1|^2 \sqrt{\frac{m\omega}{\pi\hbar}}\left(\frac{2m\omega}{\hbar}\right)\int_{-\infty}^{\infty} x^2 e^{-\frac{m\omega}{\hbar}x^2}\, dx = |A_1|^2,$$

so, as it happens, $A_1 = 1$.

I wouldn't want to calculate ψ_{50} this way (applying the raising operator fifty times!), but never mind: In *principle* Equation 2.61 does the job—except for the normalization.

You can even get the normalization algebraically, but it takes some fancy footwork, so watch closely. We know that $a_\pm \psi_n$ is *proportional* to $\psi_{n\pm 1}$,

$$a_+\psi_n = c_n \psi_{n+1}, \quad a_-\psi_n = d_n \psi_{n-1} \qquad [2.63]$$

but what are the proportionality factors, c_n and d_n? First note that for "any"[22] functions $f(x)$ and $g(x)$,

$$\int_{-\infty}^{\infty} f^*(a_\pm g)\, dx = \int_{-\infty}^{\infty} (a_\mp f)^* g\, dx. \qquad [2.64]$$

(In the language of linear algebra, $a_\mp$ is the **hermitian conjugate** of $a_\pm$.)

Proof:

$$\int_{-\infty}^{\infty} f^*(a_\pm g)\, dx = \frac{1}{\sqrt{2\hbar m\omega}}\int_{-\infty}^{\infty} f^*\left(\mp\hbar\frac{d}{dx} + m\omega x\right) g\, dx,$$

---

[22] Of course, the integrals must *exist*, and this means that $f(x)$ and $g(x)$ must go to zero at $\pm\infty$.

and integration by parts takes $\int f^*(dg/dx)\,dx$ to $-\int(df/dx)^*g\,dx$ (the boundary terms vanish, for the reason indicated in footnote 22), so

$$\int_{-\infty}^{\infty} f^*(a_\pm g)\,dx = \frac{1}{\sqrt{2\hbar m\omega}}\int_{-\infty}^{\infty}\left[\left(\pm\hbar\frac{d}{dx}+m\omega x\right)f\right]^* g\,dx = \int_{-\infty}^{\infty}(a_\mp f)^* g\,dx.$$

QED

In particular,

$$\int_{-\infty}^{\infty}(a_\pm\psi_n)^*(a_\pm\psi_n)\,dx = \int_{-\infty}^{\infty}(a_\mp a_\pm\psi_n)^*\psi_n\,dx.$$

But (invoking Equations 2.57 and 2.61)

$$a_+a_-\psi_n = n\psi_n, \quad a_-a_+\psi_n = (n+1)\psi_n, \qquad [2.65]$$

so

$$\int_{-\infty}^{\infty}(a_+\psi_n)^*(a_+\psi_n)\,dx = |c_n|^2\int_{-\infty}^{\infty}|\psi_{n+1}|^2\,dx = (n+1)\int_{-\infty}^{\infty}|\psi_n|^2\,dx,$$

$$\int_{-\infty}^{\infty}(a_-\psi_n)^*(a_-\psi_n)\,dx = |d_n|^2\int_{-\infty}^{\infty}|\psi_{n-1}|^2\,dx = n\int_{-\infty}^{\infty}|\psi_n|^2\,dx.$$

But since ψ_n and $\psi_{n\pm1}$ are normalized, it follows that $|c_n|^2 = n+1$ and $|d_n|^2 = n$, and hence

$$\boxed{a_+\psi_n = \sqrt{n+1}\,\psi_{n+1}, \quad a_-\psi_n = \sqrt{n}\,\psi_{n-1}.} \qquad [2.66]$$

Thus

$$\psi_1 = a_+\psi_0, \quad \psi_2 = \frac{1}{\sqrt{2}}a_+\psi_1 = \frac{1}{\sqrt{2}}(a_+)^2\psi_0,$$

$$\psi_3 = \frac{1}{\sqrt{3}}a_+\psi_2 = \frac{1}{\sqrt{3\cdot2}}(a_+)^3\psi_0, \quad \psi_4 = \frac{1}{\sqrt{4}}a_+\psi_3 = \frac{1}{\sqrt{4\cdot3\cdot2}}(a_+)^4\psi_0,$$

and so on. Clearly

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n\psi_0,} \qquad [2.67]$$

which is to say that the normalization factor in Equation 2.61 is $A_n = 1/\sqrt{n!}$ (in particular, $A_1 = 1$, confirming our result in Example 2.4).

As in the case of the infinite square well, the stationary states of the harmonic oscillator are orthogonal:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \delta_{mn}. \qquad [2.68]$$

This can be proved using Equation 2.65, and Equation 2.64 twice—first moving a_+ and then moving a_-:

$$\begin{aligned}\int_{-\infty}^{\infty} \psi_m^* (a_+ a_-) \psi_n \, dx &= n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx \\ &= \int_{-\infty}^{\infty} (a_- \psi_m)^* (a_- \psi_n) \, dx = \int_{-\infty}^{\infty} (a_+ a_- \psi_m)^* \psi_n \, dx \\ &= m \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx.\end{aligned}$$

Unless $m = n$, then, $\int \psi_m^* \psi_n \, dx$ must be zero. Orthonormality means that we can again use Fourier's trick (Equation 2.34) to evaluate the coefficients, when we expand $\Psi(x, 0)$ as a linear combination of stationary states (Equation 2.16), and $|c_n|^2$ is again the probability that a measurement of the energy would yield the value E_n.

Example 2.5 Find the expectation value of the potential energy in the nth state of the harmonic oscillator.

Solution:

$$\langle V \rangle = \left\langle \frac{1}{2} m \omega^2 x^2 \right\rangle = \frac{1}{2} m \omega^2 \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx.$$

There's a beautiful device for evaluating integrals of this kind (involving powers of x or p): Use the definition (Equation 2.47) to express x and p in terms of the raising and lowering operators:

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a_+ + a_-); \quad p = i \sqrt{\frac{\hbar m \omega}{2}} (a_+ - a_-). \qquad [2.69]$$

In this example we are interested in x^2:

$$x^2 = \frac{\hbar}{2m\omega} \left[(a_+)^2 + (a_+ a_-) + (a_- a_+) + (a_-)^2 \right].$$

So

$$\langle V \rangle = \frac{\hbar \omega}{4} \int \psi_n^* \left[(a_+)^2 + (a_+ a_-) + (a_- a_+) + (a_-)^2 \right] \psi_n \, dx.$$

But $(a_+)^2\psi_n$ is (apart from normalization) ψ_{n+2}, which is orthogonal to ψ_n, and the same goes for $(a_-)^2\psi_n$, which is proportional to ψ_{n-2}. So those terms drop out, and we can use Equation 2.65 to evaluate the remaining two:

$$\langle V\rangle = \frac{\hbar\omega}{4}(n+n+1) = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right).$$

As it happens, the expectation value of the potential energy is exactly *half* the total (the other half, of course, is kinetic). This is a peculiarity of the harmonic oscillator, as we'll see later on.

∗Problem 2.10

(a) Construct $\psi_2(x)$.

(b) Sketch ψ_0, ψ_1, and ψ_2.

(c) Check the orthogonality of ψ_0, ψ_1, and ψ_2, by explicit integration. *Hint:* If you exploit the even-ness and odd-ness of the functions, there is really only one integral left to do.

∗Problem 2.11

(a) Compute $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, and $\langle p^2\rangle$, for the states ψ_0 (Equation 2.59) and ψ_1 (Equation 2.62), by explicit integration. *Comment:* In this and other problems involving the harmonic oscillator it simplifies matters if you introduce the variable $\xi \equiv \sqrt{m\omega/\hbar}\,x$ and the constant $\alpha \equiv (m\omega/\pi\hbar)^{1/4}$.

(b) Check the uncertainty principle for these states.

(c) Compute $\langle T\rangle$ (the average kinetic energy) and $\langle V\rangle$ (the average potential energy) for these states. (No new integration allowed!) Is their sum what you would expect?

∗Problem 2.12 Find $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, $\langle p^2\rangle$, and $\langle T\rangle$, for the nth stationary state of the harmonic oscillator, using the method of Example 2.5. Check that the uncertainty principle is satisfied.

Problem 2.13 A particle in the harmonic oscillator potential starts out in the state

$$\Psi(x,0) = A[3\psi_0(x) + 4\psi_1(x)].$$

(a) Find A.

(b) Construct $\Psi(x,t)$ and $|\Psi(x,t)|^2$.

(c) Find $\langle x\rangle$ and $\langle p\rangle$. Don't get too excited if they oscillate at the classical frequency; what would it have been had I specified $\psi_2(x)$, instead of $\psi_1(x)$? Check that Ehrenfest's theorem (Equation 1.38) holds for this wave function.

(d) If you measured the energy of this particle, what values might you get, and with what probabilities?

Problem 2.14 A particle is in the ground state of the harmonic oscillator with classical frequency ω, when suddenly the spring constant quadruples, so $\omega' = 2\omega$, without initially changing the wave function (of course, Ψ will now *evolve* differently, because the Hamiltonian has changed). What is the probability that a measurement of the energy would still return the value $\hbar\omega/2$? What is the probability of getting $\hbar\omega$? [*Answer:* 0.943.]

2.3.2 Analytic Method

We return now to the Schrödinger equation for the harmonic oscillator,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi, \qquad [2.70]$$

and solve it directly, by the series method. Things look a little cleaner if we introduce the dimensionless variable

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x; \qquad [2.71]$$

in terms of ξ the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \qquad [2.72]$$

where K is the energy, in units of $(1/2)\hbar\omega$:

$$K \equiv \frac{2E}{\hbar\omega}. \qquad [2.73]$$

Our problem is to solve Equation 2.72, and in the process obtain the "allowed" values of K (and hence of E).

To begin with, note that at very large ξ (which is to say, at very large x), ξ^2 completely dominates over the constant K, so in this regime

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi, \qquad [2.74]$$

which has the approximate solution (check it!)

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2}. \qquad [2.75]$$

The B term is clearly not normalizable (it blows up as $|x| \to \infty$); the physically acceptable solutions, then, have the asymptotic form

$$\psi(\xi) \to (\ \ )e^{-\xi^2/2}, \quad \text{at large } \xi. \tag{2.76}$$

This suggests that we "peel off" the exponential part,

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}, \tag{2.77}$$

in hopes that what remains, $h(\xi)$, has a simpler functional form than $\psi(\xi)$ itself.[23] Differentiating Equation 2.77,

$$\frac{d\psi}{d\xi} = \left(\frac{dh}{d\xi} - \xi h\right) e^{-\xi^2/2},$$

and

$$\frac{d^2\psi}{d\xi^2} = \left(\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\xi^2 - 1)h\right) e^{-\xi^2/2},$$

so the Schrödinger equation (Equation 2.72) becomes

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K - 1)h = 0. \tag{2.78}$$

I propose to look for solutions to Equation 2.78 in the form of *power series* in ξ:[24]

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j. \tag{2.79}$$

Differentiating the series term by term,

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} ja_j\xi^{j-1},$$

and

$$\frac{d^2h}{d\xi^2} = 2a_2 + 2\cdot 3a_3\xi + 3\cdot 4a_4\xi^2 + \cdots = \sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}\xi^j.$$

---

[23] Note that although we invoked some approximations to *motivate* Equation 2.77, what follows is *exact*. The device of stripping off the asymptotic behavior is the standard first step in the power series method for solving differential equations—see, for example, Boas (footnote 11), Chapter 12.

[24] This is known as the **Frobenius method** for solving a differential equation. According to Taylor's theorem, *any* reasonably well-behaved function can be expressed as a power series, so Equation 2.79 ordinarily involves no loss of generality. For conditions on the applicability of the method, see Boas (footnote 11) or George B. Arfken and Hans-Jurgen Weber, *Mathematical Methods for Physicists*, 5th ed., Academic Press, Orlando (2000), Section 8.5.

Putting these into Equation 2.78, we find

$$\sum_{j=0}^{\infty}\left[(j+1)(j+2)a_{j+2}-2ja_j+(K-1)a_j\right]\xi^j=0. \qquad [2.80]$$

It follows (from the uniqueness of power series expansions[25]) that the coefficient of *each power* of ξ must vanish,

$$(j+1)(j+2)a_{j+2}-2ja_j+(K-1)a_j=0,$$

and hence that

$$a_{j+2}=\frac{(2j+1-K)}{(j+1)(j+2)}a_j. \qquad [2.81]$$

This **recursion formula** is entirely equivalent to the Schrödinger equation. Starting with a_0, it generates all the even-numbered coefficients:

$$a_2=\frac{(1-K)}{2}a_0, \quad a_4=\frac{(5-K)}{12}a_2=\frac{(5-K)(1-K)}{24}a_0, \quad \dots,$$

and starting with a_1, it generates the odd coefficients:

$$a_3=\frac{(3-K)}{6}a_1, \quad a_5=\frac{(7-K)}{20}a_3=\frac{(7-K)(3-K)}{120}a_1, \quad \dots.$$

We write the complete solution as

$$h(\xi)=h_{\text{even}}(\xi)+h_{\text{odd}}(\xi), \qquad [2.82]$$

where

$$h_{\text{even}}(\xi)\equiv a_0+a_2\xi^2+a_4\xi^4+\cdots$$

is an even function of ξ, built on a_0, and

$$h_{\text{odd}}(\xi)\equiv a_1\xi+a_3\xi^3+a_5\xi^5+\cdots$$

is an odd function, built on a_1. Thus Equation 2.81 determines $h(\xi)$ in terms of two arbitrary constants (a_0 and a_1)—which is just what we would expect, for a second-order differential equation.

However, not all the solutions so obtained are *normalizable*. For at very large j, the recursion formula becomes (approximately)

$$a_{j+2}\approx\frac{2}{j}a_j,$$

---

[25] See, for example, Arfken (footnote 24), Section 5.7.

with the (approximate) solution

$$a_j \approx \frac{C}{(j/2)!},$$

for some constant C, and this yields (at large ξ, where the higher powers dominate)

$$h(\xi) \approx C \sum \frac{1}{(j/2)!} \xi^j \approx C \sum \frac{1}{j!} \xi^{2j} \approx C e^{\xi^2}.$$

Now, if h goes like $\exp(\xi^2)$, then ψ (remember ψ?—that's what we're trying to calculate) goes like $\exp(\xi^2/2)$ (Equation 2.77), which is precisely the asymptotic behavior we *didn't* want.[26] There is only one way to wiggle out of this: For normalizable solutions *the power series must terminate*. There must occur some "highest" j (call it n), such that the recursion formula spits out $a_{n+2} = 0$ (this will truncate *either* the series h_{even} *or* the series h_{odd}; the *other* one must be zero from the start: $a_1 = 0$ if n is even, and $a_0 = 0$ if n is odd). For physically acceptable solutions, then, Equation 2.81 requires that

$$K = 2n + 1,$$

for some non-negative integer n, which is to say (referring to Equation 2.73) that the *energy* must be

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad \text{for } n = 0, 1, 2, \ldots . \qquad [2.83]$$

Thus we recover, by a completely different method, the fundamental quantization condition we found algebraically in Equation 2.61.

It seems at first rather surprising that the quantization of energy should emerge from a technical detail in the power series solution to the Schrödinger equation, but let's look at it from a different perspective. Equation 2.70 has solutions, of course, for *any* value of E (in fact, it has *two* linearly independent solutions for every E). But almost all of these solutions blow up exponentially at large x, and hence are not normalizable. Imagine, for example, using an E that is slightly *less* than one of the allowed values (say, $0.49\hbar\omega$), and plotting the solution (Figure 2.6(a)); the "tails" fly off to infinity. Now try an E slightly *larger* (say, $0.51\hbar\omega$); the "tails" now blow up in the *other* direction (Figure 2.6(b)). As you tweak the parameter in tiny increments from 0.49 to 0.51, the tails flip over when you pass through 0.5—only at *precisely* 0.5 do the tails go to zero, leaving a normalizable solution.[27]

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[26] It's no surprise that the ill-behaved solutions are still contained in Equation 2.81; this recursion relation is equivalent to the Schrödinger equation, so it's *got* to include both the asymptotic forms we found in Equation 2.75.

[27] It is possible to set this up on a computer, and discover the allowed energies "experimentally." You might call it the **wag the dog** method: When the tail wags, you know you've just passed over an allowed value. See Problems 2.54–2.56.

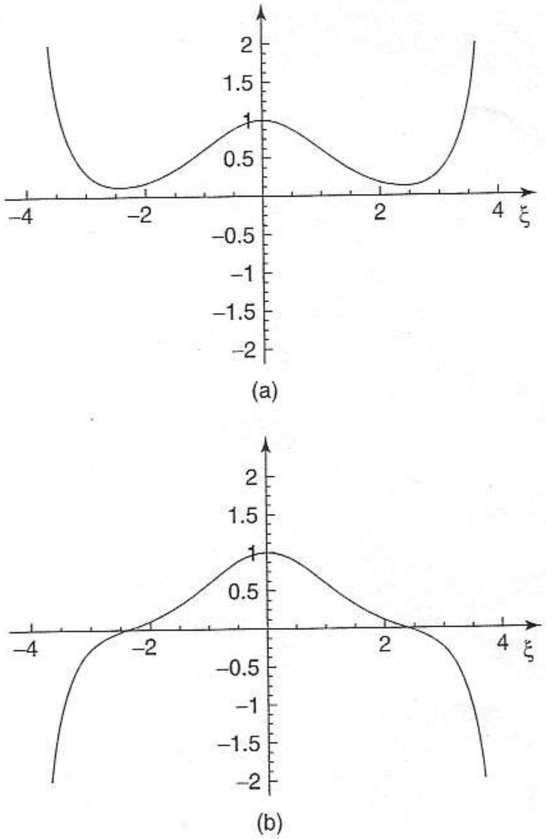

FIGURE 2.6: Solutions to the Schrödinger equation for (a) $E = 0.49\,\hbar\omega$, and (b) $E = 0.51\,\hbar\omega$.

For the allowed values of K, the recursion formula reads

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j. \qquad [2.84]$$

If $n = 0$, there is only one term in the series (we must pick $a_1 = 0$ to kill h_{odd}, and $j = 0$ in Equation 2.84 yields $a_2 = 0$):

$$h_0(\xi) = a_0,$$

and hence

$$\psi_0(\xi) = a_0 e^{-\xi^2/2}$$

(which, apart from the normalization, reproduces Equation 2.59). For $n = 1$ we take $a_0 = 0$,[28] and Equation 2.84 with $j = 1$ yields $a_3 = 0$, so

$$h_1(\xi) = a_1\xi,$$

and hence

$$\psi_1(\xi) = a_1\xi e^{-\xi^2/2}$$

(confirming Equation 2.62). For $n = 2$, $j = 0$ yields $a_2 = -2a_0$, and $j = 2$ gives $a_4 = 0$, so

$$h_2(\xi) = a_0(1 - 2\xi^2),$$

and

$$\psi_2(\xi) = a_0(1 - 2\xi^2)e^{-\xi^2/2},$$

and so on. (Compare Problem 2.10, where this last result was obtained by algebraic means.)

In general, $h_n(\xi)$ will be a polynomial of degree n in ξ, involving even powers only, if n is an even integer, and odd powers only, if n is an odd integer. Apart from the overall factor (a_0 or a_1) they are the so-called **Hermite polynomials**, $H_n(\xi)$.[29] The first few of them are listed in Table 2.1. By tradition, the arbitrary multiplicative factor is chosen so that the coefficient of the highest power of ξ is 2^n. With this convention, the normalized[30] stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi)e^{-\xi^2/2}. \qquad [2.85]$$

They are identical (of course) to the ones we obtained algebraically in Equation 2.67.

TABLE 2.1: The first few Hermite polynomials, $H_n(\xi)$.

$$H_0 = 1,$$
$$H_1 = 2\xi,$$
$$H_2 = 4\xi^2 - 2,$$
$$H_3 = 8\xi^3 - 12\xi,$$
$$H_4 = 16\xi^4 - 48\xi^2 + 12,$$
$$H_5 = 32\xi^5 - 160\xi^3 + 120\xi.$$

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[28] Note that there is a completely different set of coefficients a_j for each value of n.

[29] The Hermite polynomials have been studied extensively in the mathematical literature, and there are many tools and tricks for working with them. A few of these are explored in Problem 2.17.

[30] I shall not work out the normalization constant here; if you are interested in knowing how it is done, see for example Leonard Schiff, *Quantum Mechanics*, 3rd ed., McGraw-Hill, New York (1968), Section 13.

In Figure 2.7(a) I have plotted $\psi_n(x)$ for the first few n's. The quantum oscillator is strikingly different from its classical counterpart—not only are the energies quantized, but the position distributions have some bizarre features. For instance, the probability of finding the particle outside the classically allowed range (that is, with x greater than the classical amplitude for the energy in question) is *not* zero (see Problem 2.15), and in all odd states the probability of finding the particle at the center is zero. Only at large n do we begin to see some resemblance to the classical case. In Figure 2.7(b) I have superimposed the classical position distribution on the quantum one (for $n = 100$); if you smoothed out the bumps, the two would fit pretty well (however, in the classical case we are talking about the distribution of positions over *time* for *one* oscillator, whereas in the quantum case we are talking about the distribution over an *ensemble* of identically prepared systems).[31]

Problem 2.15 In the ground state of the harmonic oscillator, what is the probability (correct to three significant digits) of finding the particle outside the classically allowed region? *Hint:* Classically, the energy of an oscillator is $E = (1/2)ka^2 = (1/2)m\omega^2a^2$, where a is the amplitude. So the "classically allowed region" for an oscillator of energy E extends from $-\sqrt{2E/m\omega^2}$ to $+\sqrt{2E/m\omega^2}$. Look in a math table under "Normal Distribution" or "Error Function" for the numerical value of the integral.

Problem 2.16 Use the recursion formula (Equation 2.84) to work out $H_5(\xi)$ and $H_6(\xi)$. Invoke the convention that the coefficient of the highest power of ξ is 2^n to fix the overall constant.

****Problem 2.17** In this problem we explore some of the more useful theorems (stated without proof) involving Hermite polynomials.

(a) The **Rodrigues formula** says that

$$H_n(\xi) = (-1)^n e^{\xi^2}\left(\frac{d}{d\xi}\right)^n e^{-\xi^2}. \qquad [2.86]$$

Use it to derive H_3 and H_4.

(b) The following recursion relation gives you H_{n+1} in terms of the two preceding Hermite polynomials:

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi). \qquad [2.87]$$

Use it, together with your answer in (a), to obtain H_5 and H_6.

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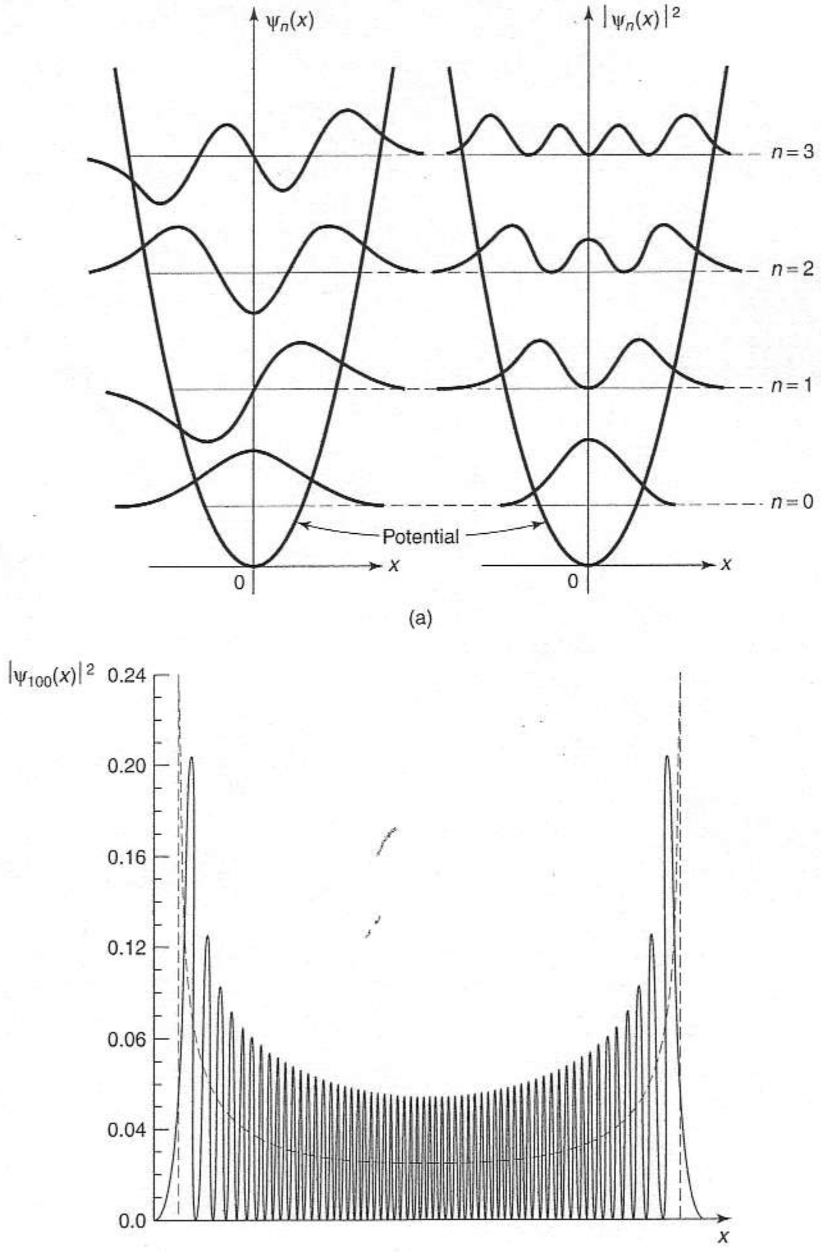
[31] The parallel is perhaps more direct if you interpret the classical distribution as an ensemble of oscillators all with the same energy, but with random starting times.



(b)

FIGURE 2.7: (a) The first four stationary states of the harmonic oscillator. This material is used by permission of John Wiley & Sons, Inc.; Stephen Gasiorowicz, *Quantum Physics*, John Wiley & Sons, Inc., 1974. (b) Graph of $|\psi_{100}|^2$, with the classical distribution (dashed curve) superimposed.

2.4 THE FREE

(c) If you differentiate an nth-order polynomial, you get a polynomial of order $(n-1)$. For the Hermite polynomials, in fact,

$$\frac{dH_n}{d\xi} = 2nH_{n-1}(\xi). \tag{2.88}$$

Check this, by differentiating H_5 and H_6.

(d) $H_n(\xi)$ is the nth z-derivative, at $z = 0$, of the **generating function** $\exp(-z^2 + 2z\xi)$; or, to put it another way, it is the coefficient of $z^n/n!$ in the Taylor series expansion for this function:

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi). \tag{2.89}$$

Use this to rederive H_0, H_1, and H_2.

2.4 THE FREE PARTICLE

We turn next to what *should* have been the simplest case of all: the free particle ($V(x) = 0$ everywhere). Classically this would just mean motion at constant velocity, but in quantum mechanics the problem is surprisingly subtle and tricky. The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \tag{2.90}$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{2.91}$$

So far, it's the same as inside the infinite square well (Equation 2.21), where the potential is also zero; this time, however, I prefer to write the general solution in exponential form (instead of sines and cosines), for reasons that will appear in due course:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \tag{2.92}$$

Unlike the infinite square well, there are no boundary conditions to restrict the possible values of k (and hence of E); the free particle can carry *any* (positive) energy. Tacking on the standard time dependence, $\exp(-iEt/\hbar)$,

$$\Psi(x,t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}. \tag{2.93}$$

Now, *any* function of x and t that depends on these variables in the special combination $(x \pm vt)$ (for some constant v) represents a wave of fixed profile, traveling in the $\mp x$-direction, at speed v. A fixed point on the waveform (for example, a maximum or a minimum) corresponds to a fixed value of the argument, and hence to x and t such that

$$x \pm vt = \text{constant}, \quad \text{or} \quad x = \mp vt + \text{constant}.$$

Since every point on the waveform is moving along with the same velocity, its *shape* doesn't change as it propagates. Thus the first term in Equation 2.93 represents a wave traveling to the *right*, and the second represents a wave (of the same energy) going to the *left*. By the way, since they only differ by the *sign* in front of k, we might as well write

$$\Psi_k(x,t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)}, \tag{2.94}$$

and let k run negative to cover the case of waves traveling to the left:

$$k \equiv \pm\frac{\sqrt{2mE}}{\hbar}, \quad \text{with} \begin{cases} k > 0 \Rightarrow & \text{traveling to the right,} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases} \tag{2.95}$$

Evidently the "stationary states" of the free particle are propagating waves; their wavelength is $\lambda = 2\pi/|k|$, and, according to the de Broglie formula (Equation 1.39), they carry momentum

$$p = \hbar k. \tag{2.96}$$

The speed of these waves (the coefficient of t over the coefficient of x) is

$$v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}. \tag{2.97}$$

On the other hand, the *classical* speed of a free particle with energy E is given by $E = (1/2)mv^2$ (pure kinetic, since $V = 0$), so

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}}. \tag{2.98}$$

Apparently the quantum mechanical wave function travels at *half* the speed of the particle it is supposed to represent! We'll return to this paradox in a moment—there is an even more serious problem we need to confront first: *This wave function is not normalizable*. For

$$\int_{-\infty}^{+\infty} \Psi_k^*\Psi_k\,dx = |A|^2 \int_{-\infty}^{+\infty} dx = |A|^2(\infty). \tag{2.99}$$

In the case of the free particle, then, the separable solutions do not represent physically realizable states. A free particle cannot exist in a stationary state; or, to put it another way, *there is no such thing as a free particle with a definite energy*.

But that doesn't mean the separable solutions are of no use to us, for they play a *mathematical* role that is entirely independent of their *physical* interpretation. The general solution to the time-dependent Schrödinger equation is still a linear combination of separable solutions (only this time it's an *integral* over the continuous variable k, instead of a *sum* over the discrete index n):

$$\boxed{\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m} t)}\, dk.} \qquad [2.100]$$

(The quantity $1/\sqrt{2\pi}$ is factored out for convenience; what plays the role of the coefficient c_n in Equation 2.17 is the combination $(1/\sqrt{2\pi})\phi(k)\,dk$.) Now *this* wave function *can* be normalized (for appropriate $\phi(k)$). But it necessarily carries a *range* of k's, and hence a range of energies and speeds. We call it a **wave packet**.[32]

In the generic quantum problem, we are *given* $\Psi(x,0)$, and we are asked to *find* $\Psi(x,t)$. For a free particle the solution takes the form of Equation 2.100; the only question is how to determine $\phi(k)$ so as to match the initial wave function:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx}\, dk. \qquad [2.101]$$

This is a classic problem in Fourier analysis; the answer is provided by **Plancherel's theorem** (see Problem 2.20):

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx}\, dk \Longleftrightarrow F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx}\, dx.} \qquad [2.102]$$

$F(k)$ is called the **Fourier transform** of $f(x)$; $f(x)$ is the **inverse Fourier transform** of $F(k)$ (the only difference is in the sign of the exponent). There is, of course, some restriction on the allowable functions: The integrals have to *exist*.[33] For our purposes this is guaranteed by the physical requirement that $\Psi(x,0)$ itself

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[32] Sinusoidal waves extend out to infinity, and they are not normalizable. But *superpositions* of such waves lead to interference, which allows for localization and normalizability.

[33] The necessary and sufficient condition on $f(x)$ is that $\int_{-\infty}^{\infty} |f(x)|^2 dx$ be *finite*. (In that case $\int_{-\infty}^{\infty} |F(k)|^2 dk$ is also finite, and in fact the two integrals are equal.) See Arfken (footnote 24), Section 15.5.

be normalized. So the solution to the generic quantum problem, for the free particle, is Equation 2.100, with

$$\boxed{\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x,0)e^{-ikx}\, dx.} \qquad [2.103]$$

Example 2.6 A free particle, which is initially localized in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x,0) = \begin{cases} A, & \text{if } -a < x < a, \\ 0, & \text{otherwise,} \end{cases}$$

where A and a are positive real constants. Find $\Psi(x,t)$.

Solution: First we need to normalize $\Psi(x,0)$:

$$1 = \int_{-\infty}^{\infty} |\Psi(x,0)|^2\, dx = |A|^2 \int_{-a}^{a} dx = 2a|A|^2 \;\Rightarrow\; A = \frac{1}{\sqrt{2a}}.$$

Next we calculate $\phi(k)$, using Equation 2.103:

$$\begin{aligned} \phi(k) &= \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2a}} \int_{-a}^{a} e^{-ikx}\, dx = \frac{1}{2\sqrt{\pi a}} \left.\frac{e^{-ikx}}{-ik}\right|_{-a}^{a} \\ &= \frac{1}{k\sqrt{\pi a}}\left(\frac{e^{ika} - e^{-ika}}{2i}\right) = \frac{1}{\sqrt{\pi a}}\frac{\sin(ka)}{k}. \end{aligned}$$

Finally, we plug this back into Equation 2.100:

$$\Psi(x,t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{\sin(ka)}{k} e^{i(kx - \frac{\hbar k^2}{2m}t)}\, dk. \qquad [2.104]$$

Unfortunately, this integral cannot be solved in terms of elementary functions, though it can of course be evaluated numerically (Figure 2.8). (There are, in fact, precious few cases in which the integral for $\Psi(x,t)$ (Equation 2.100) *can* be calculated explicitly; see Problem 2.22 for a particularly beautiful example.)

It is illuminating to explore the limiting cases. If a is very small, the starting wave function is a nicely localized spike (Figure 2.9(a)). In this case we can use the small angle approximation to write $\sin(ka) \approx ka$, and hence

$$\phi(k) \approx \sqrt{\frac{a}{\pi}};$$

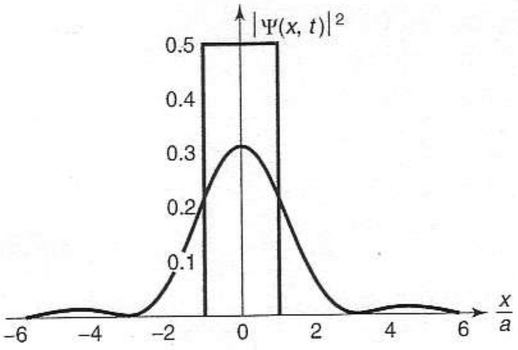
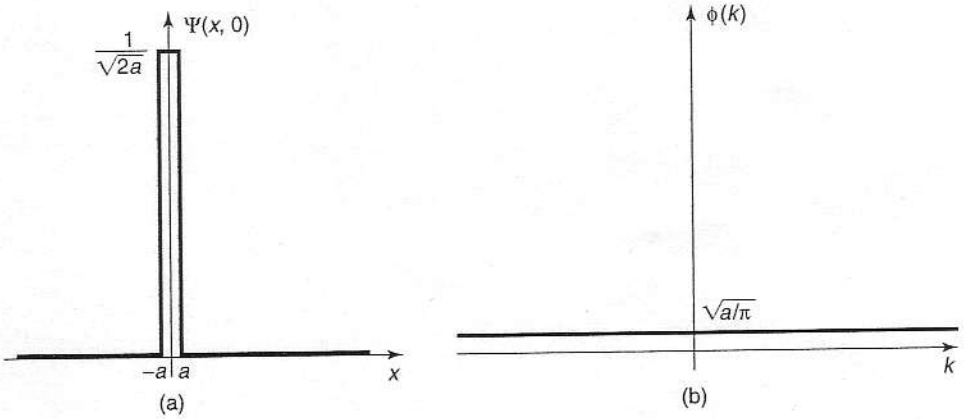


FIGURE 2.8: Graph of $|\Psi(x, t)|^2$ (Equation 2.104) at $t = 0$ (the rectangle) and at $t = ma^2/\hbar$ (the curve).



(a)

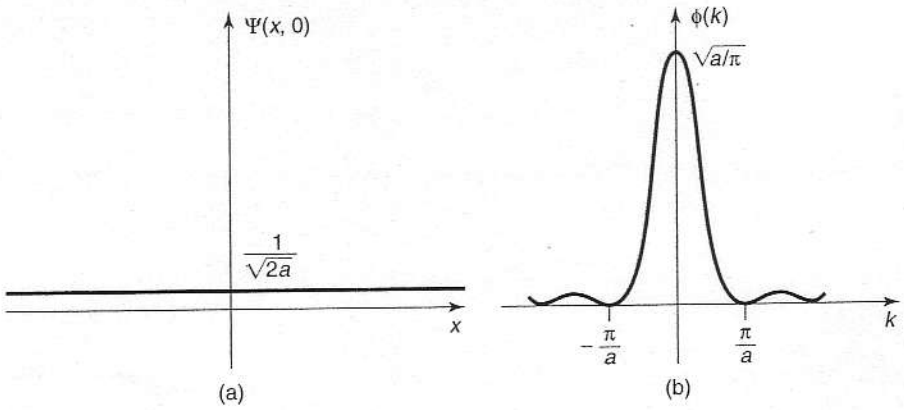
(b)

FIGURE 2.9: Example 2.6, for small a. (a) Graph of $\Psi(x, 0)$. (b) Graph of $\phi(k)$.

it's *flat*, since the k's cancelled out (Figure 2.9(b)). This is an example of the uncertainty principle: If the spread in *position* is small, the spread in *momentum* (and hence in k—see Equation 2.96) must be large. At the other extreme (*large* a) the spread in position is broad (Figure 2.10(a)) and

$$\phi(k) = \sqrt{\frac{a}{\pi}} \frac{\sin(ka)}{ka}.$$

Now, $\sin z/z$ has its maximum at $z = 0$, and drops to zero at $z = \pm\pi$ (which, in this context, means $k = \pm\pi/a$). So for large a, $\phi(k)$ is a sharp spike about $k = 0$ (Figure 2.10(b)). This time it's got a well-defined momentum but an ill-defined position.



(a) (b)

FIGURE 2.10: Example 2.6, for large a. (a) Graph of $\Psi(x, 0)$. (b) Graph of $\phi(k)$.

I return now to the paradox noted earlier: the fact that the separable solution $\Psi_k(x, t)$ in Equation 2.94 travels at the "wrong" speed for the particle it ostensibly represents. Strictly speaking, the problem evaporated when we discovered that Ψ_k is not a physically realizable state. Nevertheless, it is of interest to discover how information about velocity *is* contained in the free particle wave function (Equation 2.100). The essential idea is this: A wave packet is a superposition of sinusoidal functions whose amplitude is modulated by ϕ (Figure 2.11); it consists of "ripples" contained within an "envelope." What corresponds to the particle velocity is not the speed of the individual ripples (the so-called **phase velocity**), but rather the speed of the envelope (the **group velocity**)—which, depending on the nature of the waves, can be greater than, less than, or equal to, the velocity of the ripples that go to make it up. For waves on a string, the group velocity is the same as the phase velocity. For water waves it is one-half the phase velocity, as you may have noticed when you toss a rock into a pond (if you concentrate on a particular ripple, you will see it build up from the rear, move forward through the group, and fade away at the front, while the group as a whole propagates out at half the speed). What I need to show is that for the wave function of a free particle in quantum mechanics

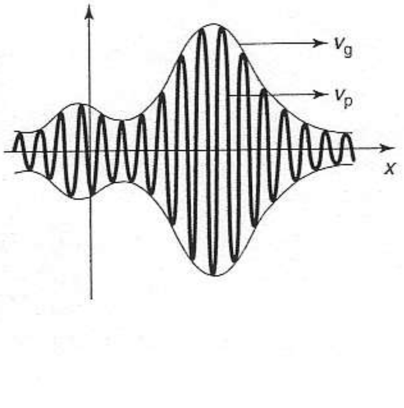


FIGURE 2.11: A wave packet. The "envelope" travels at the group velocity; the "ripples" travel at the phase velocity.

the group velocity is *twice* the phase velocity—just right to represent the classical particle speed.

The problem, then, is to determine the group velocity of a wave packet with the general form

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx-\omega t)}\, dk.$$

(In our case $\omega = (\hbar k^2/2m)$, but what I have to say now applies to *any* kind of wave packet, regardless of its **dispersion relation**—the formula for ω as a function of k.) Let us assume that $\phi(k)$ is narrowly peaked about some particular value k_0. (There is nothing *illegal* about a broad spread in k, but such wave packets change shape rapidly—since different components travel at different speeds—so the whole notion of a "group," with a well-defined velocity, loses its meaning.) Since the integrand is negligible except in the vicinity of k_0, we may as well Taylor-expand the function $\omega(k)$ about that point, and keep only the leading terms:

$$\omega(k) \cong \omega_0 + \omega_0'(k - k_0),$$

where ω_0' is the derivative of ω with respect to k, at the point k_0.

Changing variables from k to $s \equiv k - k_0$ (to center the integral at k_0), we have

$$\Psi(x,t) \cong \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i[(k_0+s)x-(\omega_0+\omega_0' s)t]}\, ds.$$

At $t = 0$,

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)x}\, ds,$$

and at later times

$$\Psi(x,t) \cong \frac{1}{\sqrt{2\pi}} e^{i(-\omega_0 t + k_0 \omega_0' t)} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)(x-\omega_0' t)}\, ds.$$

Except for the shift from x to $(x - \omega_0' t)$, the integral is the same as the one in $\Psi(x, 0)$. Thus

$$\Psi(x,t) \cong e^{-i(\omega_0 - k_0\omega_0')t}\, \Psi(x - \omega_0' t, 0). \qquad [2.105]$$

Apart from the phase factor in front (which won't affect $|\Psi|^2$ in any event) the wave packet evidently moves along at a speed ω_0':

$$v_{\text{group}} = \frac{d\omega}{dk} \qquad [2.106]$$

(evaluated at $k = k_0$). This is to be contrasted with the ordinary phase velocity

$$v_{\text{phase}} = \frac{\omega}{k}. \qquad [2.107]$$

In our case, $\omega = (\hbar k^2/2m)$, so $\omega/k = (\hbar k/2m)$, whereas $d\omega/dk = (\hbar k/m)$, which is twice as great. This confirms that it is the group velocity of the wave packet, not the phase velocity of the stationary states, that matches the classical particle velocity:

$$v_{\text{classical}} = v_{\text{group}} = 2v_{\text{phase}}. \qquad [2.108]$$

Problem 2.18 Show that $[Ae^{ikx} + Be^{-ikx}]$ and $[C\cos kx + D\sin kx]$ are equivalent ways of writing the same function of x, and determine the constants C and D in terms of A and B, and vice versa. *Comment:* In quantum mechanics, when $V = 0$, the exponentials represent *traveling* waves, and are most convenient in discussing the free particle, whereas sines and cosines correspond to *standing* waves, which arise naturally in the case of the infinite square well.

Problem 2.19 Find the probability current, J (Problem 1.14) for the free particle wave function Equation 2.94. Which direction does the probability current flow?

****Problem 2.20** This problem is designed to guide you through a "proof" of Plancherel's theorem, by starting with the theory of ordinary Fourier series on a *finite* interval, and allowing that interval to expand to infinity.

(a) Dirichlet's theorem says that "any" function $f(x)$ on the interval $[-a, +a]$ can be expanded as a Fourier series:

$$f(x) = \sum_{n=0}^{\infty}[a_n \sin(n\pi x/a) + b_n \cos(n\pi x/a)].$$

Show that this can be written equivalently as

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/a}.$$

What is c_n, in terms of a_n and b_n?

(b) Show (by appropriate modification of Fourier's trick) that

$$c_n = \frac{1}{2a}\int_{-a}^{+a} f(x)e^{-in\pi x/a}\,dx.$$

(c) Eliminate n and c_n in favor of the new variables $k = (n\pi/a)$ and $F(k) = \sqrt{2/\pi}\,ac_n$. Show that (a) and (b) now become

$$f(x) = \frac{1}{\sqrt{2\pi}}\sum_{n=-\infty}^{\infty} F(k)e^{ikx}\,\Delta k; \quad F(k) = \frac{1}{\sqrt{2\pi}}\int_{-a}^{+a} f(x)e^{-ikx}\,dx,$$

where Δk is the increment in k from one n to the next.

(d) Take the limit $a \to \infty$ to obtain Plancherel's theorem. *Comment:* In view of their quite different origins, it is surprising (and delightful) that the two formulas—one for $F(k)$ in terms of $f(x)$, the other for $f(x)$ in terms of $F(k)$—have such a similar structure in the limit $a \to \infty$.

Problem 2.21 A free particle has the initial wave function

$$\Psi(x,0) = Ae^{-a|x|},$$

where A and a are positive real constants.

(a) Normalize $\Psi(x,0)$.

(b) Find $\phi(k)$.

(c) Construct $\Psi(x,t)$, in the form of an integral.

(d) Discuss the limiting cases (a very large, and a very small).

***Problem 2.22 The gaussian wave packet.** A free particle has the initial wave function

$$\Psi(x,0) = Ae^{-ax^2},$$

where A and a are constants (a is real and positive).

(a) Normalize $\Psi(x,0)$.

(b) Find $\Psi(x,t)$. *Hint:* Integrals of the form

$$\int_{-\infty}^{+\infty} e^{-(ax^2+bx)}\,dx$$

can be handled by "completing the square": Let $y \equiv \sqrt{a}\,[x + (b/2a)]$, and note that $(ax^2+bx) = y^2 - (b^2/4a)$. *Answer:*

$$\Psi(x,t) = \left(\frac{2a}{\pi}\right)^{1/4} \frac{e^{-ax^2/[1+(2i\hbar at/m)]}}{\sqrt{1+(2i\hbar at/m)}}.$$

(c) Find $|\Psi(x,t)|^2$. Express your answer in terms of the quantity

$$w \equiv \sqrt{\frac{a}{1+(2\hbar at/m)^2}}.$$

Sketch $|\Psi|^2$ (as a function of x) at $t = 0$, and again for some very large t. Qualitatively, what happens to $|\Psi|^2$, as time goes on?

(d) Find $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, $\langle p^2\rangle$, σ_x, and σ_p. *Partial answer:* $\langle p^2\rangle = a\hbar^2$, but it may take some algebra to reduce it to this simple form.

(e) Does the uncertainty principle hold? At what time t does the system come closest to the uncertainty limit?
