CHAPTER 2

THE 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—how do you go about solving the Schrödinger equation? I shall assume for all of this chapter (and most of this book) that the potential,[1] 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*,

$$\Psi(x, t) = \psi(x) f(t), \qquad [2.1]$$

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

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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*.

For separable solutions we have

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

(*ordinary* derivatives, now), and the Schrödinger equation (Equation 1.1) reads

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

Or, dividing through by ψf:

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V. \tag{2.2}$$

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

$$i\hbar \frac{1}{f} \frac{df}{dt} = E,$$

or

$$\frac{df}{dt} = -\frac{iE}{\hbar} f, \tag{2.3}$$

and

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

or

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V \psi = E \psi.} \tag{2.4}$$

Separation of variables has turned a *partial* differential equation into two *ordinary* differential equations (Equations 2.3 and 2.4). The first of these 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 ψf). Then

$$f(t) = e^{-iEt/\hbar}. \tag{2.5}$$

The second (Equation 2.4) is called the **time-independent Schrödinger equation**; we can go no further with it until the potential $V(x)$ is specified.

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

The rest of this chapter will be devoted to solving the time-independent Schrödinger equation, for a variety of simple potentials. But before we get to that I would like to consider further the question: *What's so great about separable solutions?* After all, *most* solutions to the (time-dependent) Schrödinger equation do *not* take the form $\psi(x) f(t)$. I offer three answers—two of them physical and one mathematical:

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

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar},$$ [2.6]

does (obviously) depend on t, the probability density

$$|\Psi(x, t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar} \psi e^{-iEt/\hbar} = |\psi(x)|^2$$ [2.7]

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

$$\langle Q(x, p)\rangle = \int \psi^* Q(x, \frac{\hbar}{i}\frac{d}{dx})\psi \, dx.$$ [2.8]

Every expectation value is constant in time; we might as well drop the factor $f(t)$ 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**:

$$H(x, p) = \frac{p^2}{2m} + V(x).$$ [2.9]

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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$ [2.10]

Thus the time-independent Schrödinger equation (Equation 2.4) can be written

$$\hat{H}\psi = E\psi,$$ [2.11]

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

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

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi \, dx = E \int |\psi|^2 \, dx = E. \qquad [2.12]$$

(Note 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 standard deviation in H is given by

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0. \qquad [2.13]$$

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 2.4) 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**:

$$\Psi_1(x, t) = \psi_1(x)e^{-iE_1 t/\hbar}, \quad \Psi_2(x, t) = \psi_2(x)e^{-iE_2 t/\hbar}, \ldots$$

Now (as you can easily check for yourself) the (time-*de*pendent) Schrödinger equation (Equation 1.1) has the property that any linear combination[5] of solutions is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x)e^{-iE_n t/\hbar}. \qquad [2.14]$$

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

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[5]A linear combination of the functions $f_1(z)$, $f_2(z)$, ... 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.

Schrödinger equation, you're essentially done; getting from there to the general solution of the time-*de*pendent Schrödinger equation is simple and straightforward.

⋆Problem 2.1 Prove the following theorems:

(a) For normalizable solutions, the separation constant E must be *real*. *Hint*: Write E (in Equation 2.6) 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) ψ can always be taken to be *real* (unlike Ψ, which is necessarily complex). *Note*: 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 in Equation 2.14 you *might as well* stick to ψ's that are real. *Hint*: If $\psi(x)$ satisfies the time-independent Schrödinger equation for a given E, so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.

(c) If $V(x)$ is an *even* function [i.e., $V(-x) = V(x)$], then $\psi(x)$ can always be taken to be either even or odd. *Hint*: If $\psi(x)$ satisfies the time-independent Schrödinger equation 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 2.4 in the form

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

if $E < V_{min}$, 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

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases} \qquad [2.15]$$

(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 awfully artificial, but I urge you to treat it with respect. Despite its simplicity—or rather,
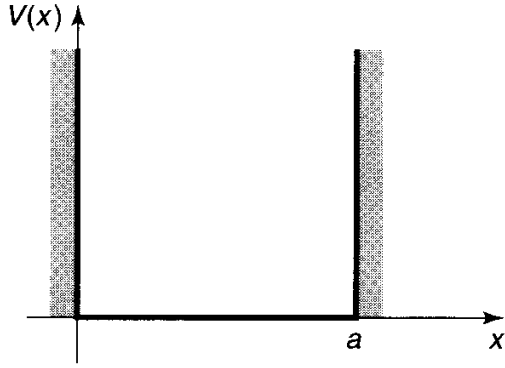
Figure 2.1:   The infinite square well potential (Equation 2.15).

precisely *because* of its simplicity—it serves as a wonderfully accessible test case for all the fancy stuff that comes later. We'll refer back to it frequently.)

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 2.4) reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$ [2.16]

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$ [2.17]

(By writing it in this way, I have tacitly assumed that $E \geq 0$; we know from Problem 2.2 that $E < 0$ doesn't work.) Equation 2.17 is the (classical) **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A\sin kx + B\cos kx,$$ [2.18]

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 $V = \infty$, later on; for now I hope you will trust me.)

Continuity of $\psi(x)$ requires that

$$\psi(0) = \psi(a) = 0,$$ [2.19]

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

$$\psi(x) = A\sin kx.$$ [2.20]

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

$$ka = 0, \quad \pm\pi, \quad \pm 2\pi, \quad \pm 3\pi, \ldots.$$ [2.21]

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

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \ldots. \qquad [2.22]$$

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:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \qquad [2.23]$$

In sharp contrast to the classical case, a quantum particle in the infinite square well cannot have just *any* old energy—only these special **allowed** values. Well, how *do* we fix the constant A? Answer: 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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right). \qquad [2.24]$$

As promised, the time-independent Schrödinger equation has delivered an infinite set of solutions, one for each 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 group, 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.[6])

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.

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[6]To make this symmetry more apparent, some authors center the well at the origin (so that it runs from $-a/2$ to $+a/2$. The even functions are then cosines, and the odd ones are sines. See Problem 2.4.
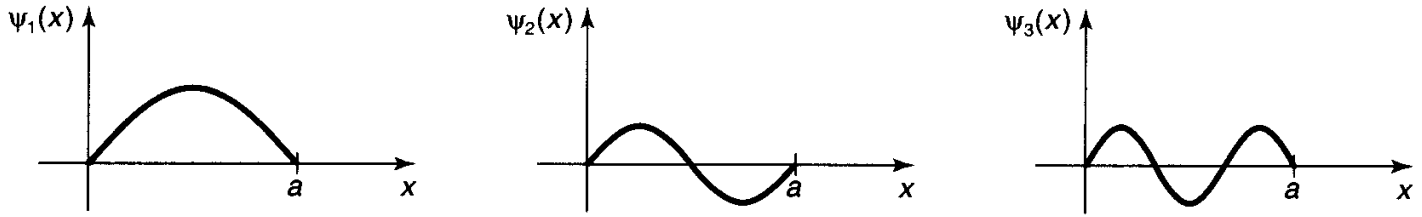
Figure 2.2: The first three stationary states of the infinite square well (Equation 2.24).

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

$$\int \psi_m(x)^* \psi_n(x)\, dx = 0, \qquad\qquad [2.25]$$

whenever $m \neq n$. Proof

$$\int \psi_m(x)^* \psi_n(x)\, dx = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx$$

$$= \frac{1}{a} \int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right] dx$$

$$= \left\{ \frac{1}{(m-n)\pi} \sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi} \sin\left(\frac{m+n}{a}\pi x\right) \right\} \Big|_0^a$$

$$= \frac{1}{\pi} \left\{ \frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)} \right\} = 0.$$

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[7]:

$$\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn}, \qquad\qquad [2.26]$$

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

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases} \qquad\qquad [2.27]$$

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:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right). \qquad\qquad [2.28]$$

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[7]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 $\sqrt{2/a}\sin(n\pi x/a)$, but if you've studied advanced calculus you will recognize that Equation 2.28 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**.[8] The expansion 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 2.28 by $\psi_m(x)^*$, and integrate.

$$\int \psi_m(x)^* f(x)\, dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\, dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m. \quad [2.29]$$

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

$$c_m = \int \psi_m(x)^* f(x)\, dx. \quad [2.30]$$

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 an even function; the second is universal, regardless of the shape of the potential.[9] 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 2.6) for the infinite square well are evidently

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad [2.31]$$

I claimed (Equation 2.14) that the most general solution to the (time-dependent) Schrödinger equation is a linear combination of stationary states:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad [2.32]$$

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. According to Equation 2.32,

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

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

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

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:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0)\, dx. \qquad [2.33]$$

That does it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n, using Equation 2.33, and then plug these into Equation 2.32 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.

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 Solve the time-independent Schrödinger equation with appropriate boundary conditions for an infinite square well centered at the origin [$V(x) = 0$, for $-a/2 < x < +a/2$; $V(x) = \infty$ otherwise]. Check that your allowed energies are consistent with mine (Equation 2.23), and confirm that your ψ's can be obtained from mine (Equation 2.24) by the substitution $x \rightarrow x - a/2$.

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*Problem 2.5 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 2.6 A particle in the infinite square well has as its initial wave function an even mixture of the first two stationary states:

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

(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 in terms of sinusoidal functions of time, eliminating the exponentials with the help of **Euler's formula**: $e^{i\theta} = \cos\theta + i \sin\theta$.) Let $\omega \equiv \pi^2\hbar/2ma^2$.

(c) Compute $\langle x \rangle$. Notice that it oscillates in time. What is the 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) Find the expectation value of H. How does it compare with E_1 and E_2?

(f) A *classical* particle in this well would bounce back and forth between the walls. If its energy is equal to the expectation value you found in (e), what is the frequency of the classical motion? How does it compare with the quantum frequency you found in (c)?

Problem 2.7 Although the *overall* phase constant of the wave function is of no physical significance (it cancels out whenever you calculate a measureable quantity), the *relative* phase of the expansion coefficients in Equation 2.14 *does* matter. For example, suppose we change the relative phase of ψ_1 and ψ_2 in Problem 2.6:

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

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 $\phi = \pi$.

∗Problem 2.8 A particle in the infinite square well has the initial wave function

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

(a) Normalize $\Psi(x, 0)$. Graph it. Which stationary state does it most closely resemble? On that basis, estimate the expectation value of the energy.

(b) Compute $\langle x \rangle$, $\langle p \rangle$, and $\langle H \rangle$, at $t = 0$. (*Note:* This time you cannot get $\langle p \rangle$ by differentiating $\langle x \rangle$, because you only know $\langle x \rangle$ at one instant of time.) How does $\langle H \rangle$ compare with your estimate in (a)?

∗Problem 2.9 Find $\Psi(x, t)$ for the initial wave function in Problem 2.8. Evaluate c_1, c_2, and c_3 numerically, to five decimal places, and comment on these numbers. (c_n tells you, roughly speaking, how much ψ_n is "contained in" Ψ.) Suppose you measured the energy at time $t_0 > 0$, and got the value E_3. Knowing that immediate repetition of the measurement must return the same value, what can you say about the coefficients c_n *after* the measurement? (This is an example of the "collapse of the wave function", which we discussed briefly in Chapter 1.)

∗Problem 2.10 The wave function (Equation 2.14) has got to be normalized; given that the ψ_n's are orthonormal, what does this tell you about the coefficients c_n? *Answer:*

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \tag{2.34}$$

(In particular, $|c_n|^2$ is always ≤ 1.) Show that

$$\langle H \rangle = \sum_{n=1}^{\infty} E_n |c_n|^2. \tag{2.35}$$

Incidentally, it follows that $\langle H \rangle$ is constant in time, which is one manifestation of **conservation of energy** in quantum mechanics.

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**,

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

(as always, we ignore friction), and the solution is

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

where

$$\omega \equiv \sqrt{\frac{k}{m}} \tag{2.36}$$

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

$$V(x) = \frac{1}{2}kx^2; \tag{2.37}$$

its graph is a parabola.

Of course, there's no such thing as a *perfect* simple 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 2.3). 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], the potential becomes

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

which describes simple harmonic oscillation (about the point x_0), with an effective spring constant $k = V''(x_0)$.[10] 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.

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[10]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.
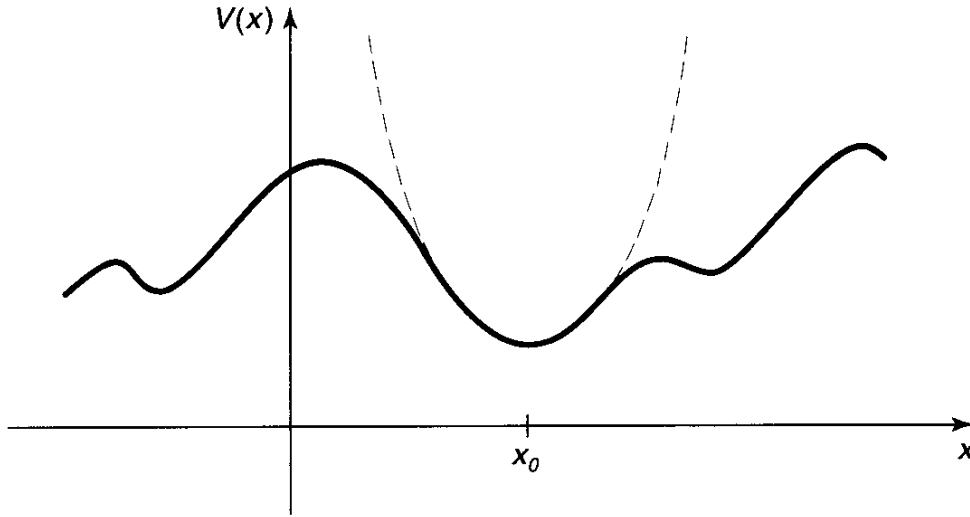
Figure 2.3:   Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

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

$$V(x) = \frac{1}{2}m\omega^2 x^2 \qquad [2.38]$$

(it is customary to eliminate the spring constant in favor of the classical frequency, using Equation 2.36). As we have seen, it suffices to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi. \qquad [2.39]$$

In the literature you will find two entirely different approaches to this problem. The first is a straighforward "brute force" solution to the differential equation, using the method of **power series expansion**; 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 more fun); if you want to skip the analytic 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 2.39 in a more suggestive form:

$$\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right]\psi = E\psi. \qquad [2.40]$$

The idea is to *factor* the term in square brackets. If these were *numbers*, it would be easy:

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

Here, however, it's not quite so simple, because u and v are *operators*, and operators do not, in general, **commute** (uv is not the same as vu). Still, this does invite us to take a look at the expressions

$$a_\pm \equiv \frac{1}{\sqrt{2m}} \left(\frac{\hbar}{i} \frac{d}{dx} \pm im\omega x \right). \qquad [2.41]$$

What *is* their product, $a_- a_+$? *Warning*: Operators can be 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

$$(a_- a_+)f(x) = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} - im\omega x \right) \left(\frac{\hbar}{i} \frac{d}{dx} + im\omega x \right) f(x)$$

$$= \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} - im\omega x \right) \left(\frac{\hbar}{i} \frac{df}{dx} + im\omega x f \right)$$

$$= \frac{1}{2m} \left[-\hbar^2 \frac{d^2 f}{dx^2} + \hbar m\omega \frac{d}{dx}(xf) - \hbar m\omega x \frac{df}{dx} + (m\omega x)^2 f \right]$$

$$= \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 + (m\omega x)^2 + \hbar m\omega \right] f(x).$$

[I used $d(xf)/dx = x(df/dx) + f$ in the last step.] Discarding the test function, we conclude that

$$a_- a_+ = \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 + (m\omega x)^2 \right] + \frac{1}{2} \hbar\omega. \qquad [2.42]$$

Evidently Equation 2.40 does *not* factor perfectly—there's an extra term $(1/2)\hbar\omega$. However, if we pull this over to the other side, the Schrödinger equation[11] becomes

$$(a_- a_+ - \frac{1}{2} \hbar\omega)\psi = E\psi. \qquad [2.43]$$

Notice that the ordering of the factors a_+ and a_- is important here; the same argument, with a_+ on the left, yields

$$a_+ a_- = \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 + (m\omega x)^2 \right] - \frac{1}{2} \hbar\omega. \qquad [2.44]$$

Thus

$$a_- a_+ - a_+ a_- = \hbar\omega, \qquad [2.45]$$

---

[11] 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.

and the Schrödinger equation can also be written

$$(a_+ a_- + \frac{1}{2}\hbar\omega)\psi = E\psi. \qquad [2.46]$$

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

$$(a_+ a_- + \frac{1}{2}\hbar\omega)(a_+\psi) = (a_+ a_- a_+ + \frac{1}{2}\hbar\omega a_+)\psi$$

$$= a_+(a_- a_+ + \frac{1}{2}\hbar\omega)\psi = a_+[(a_- a_+ - \frac{1}{2}\hbar\omega)\psi + \hbar\omega\psi]$$

$$= a_+(E\psi + \hbar\omega\psi) = (E + \hbar\omega)(a_+\psi). \text{ QED}$$

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

$$(a_- a_+ - \frac{1}{2}\hbar\omega)(a_-\psi) = a_-(a_+ a_- - \frac{1}{2}\hbar\omega)\psi$$

$$= a_-[(a_+ a_- + \frac{1}{2}\hbar\omega)\psi - \hbar\omega\psi] = a_-(E\psi - \hbar\omega\psi)$$

$$= (E - \hbar\omega)(a_-\psi).$$

Here, then, is a wonderful machine for grinding out new solutions, with higher and lower energies—if we can 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 called the **raising operator**, and a_- the **lowering operator**. The "ladder" of states is illustrated in Figure 2.4.

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. Problem 2.11 rules out the latter possibility. Conclusion: There must occur a "lowest rung" (let's call it ψ_0) such that

$$a_-\psi_0 = 0. \qquad [2.47]$$

That is to say,

$$\frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d\psi_0}{dx} - im\omega x\psi_0\right) = 0,$$
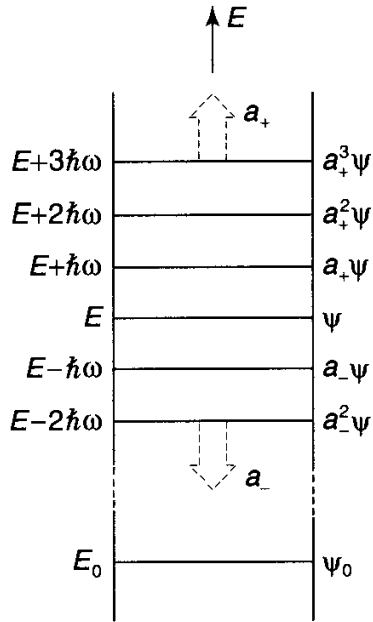
Figure 2.4: The ladder of stationary states for the simple harmonic oscillator.

or

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

This differential equation for ψ_0 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

$$\psi_0(x) = A_0 e^{-\frac{m\omega}{2\hbar}x^2}. \tag{2.48}$$

To determine the energy of this state, we plug it into the Schrödinger equation (in the form of Equation 2.46), $(a_+a_- + (1/2)\hbar\omega)\psi_0 = E_0\psi_0$, and exploit the fact that $a_-\psi_0 = 0$. Evidently

$$E_0 = \frac{1}{2}\hbar\omega. \tag{2.49}$$

With our foot now securely planted on the bottom rung[12] (the ground state of the quantum oscillator), we simply apply the raising operator to generate the excited states[13]:

$$\psi_n(x) = A_n(a_+)^n e^{-\frac{m\omega}{2\hbar}x^2}, \quad \text{with } E_n = (n + \frac{1}{2})\hbar\omega. \tag{2.50}$$

---

[12]Note that there can only be *one* ladder, because the lowest state is uniquely determined by Equation 2.47. Thus we have in fact obtained *all* the (normalizable) solutions.

[13]In the case of the harmonic oscillator, it is convenient to depart from our usual custom and number the states starting with $n = 0$ instead of $n = 1$. Obviously, the lower limit on the sum in equations such as Equation 2.14 should be altered accordingly.

(This method does not immediately determine the normalization factor A_n; I'll let you work that out for yourself in Problem 2.12.) For example,

$$\psi_1 = A_1 a_+ e^{-\frac{m\omega}{2\hbar}x^2} = A_1 \frac{1}{\sqrt{2m}} \left(\frac{\hbar}{i} \frac{d}{dx} + im\omega x \right) e^{-\frac{m\omega}{2\hbar}x^2}$$

$$= \frac{A_1}{\sqrt{2m}} \left[\frac{\hbar}{i} \left(-\frac{m\omega}{\hbar}x \right) e^{-\frac{m\omega}{2\hbar}x^2} + im\omega x e^{-\frac{m\omega}{2\hbar}x^2} \right],$$

which simplifies to

$$\psi_1(x) = (iA_1\omega\sqrt{2m})x e^{-\frac{m\omega}{2\hbar}x^2}. \qquad [2.51]$$

I wouldn't want to calculate ψ_{50} in this way, but never mind: We have found all the allowed energies, and in principle we have determined the stationary states—the rest is just computation.

Problem 2.11 Show that the lowering operator cannot generate a state of infinite norm (i.e., $\int |a_-\psi|^2 dx < \infty$, if ψ itself is a normalized solution to the Schrödinger equation). What does this tell you in the case $\psi = \psi_0$? *Hint*: Use integration by parts to show that

$$\int_{-\infty}^{\infty} (a_-\psi)^*(a_-\psi)\,dx = \int_{-\infty}^{\infty} \psi^*(a_+a_-\psi)\,dx.$$

Then invoke the Schrödinger equation (Equation 2.46) to obtain

$$\int_{-\infty}^{\infty} |a_-\psi|^2\,dx = E - \frac{1}{2}\hbar\omega,$$

where E is the energy of the state ψ.

∗∗Problem 2.12

(a) The raising and lowering operators generate new solutions to the Schrödinger equation, but these new solutions are not correctly normalized. Thus $a_+\psi_n$ is *proportional* to ψ_{n+1}, and $a_-\psi_n$ is *proportional* to ψ_{n-1}, but we'd like to know the precise proportionality constants. Use integration by parts and the Schrödinger equation (Equations 2.43 and 2.46) to show that

$$\int_{-\infty}^{\infty} |a_+\psi_n|^2\,dx = (n+1)\hbar\omega, \quad \int_{-\infty}^{\infty} |a_-\psi_n|^2\,dx = n\hbar\omega,$$

and hence (with i's to keep the wavefunctions real)

$$a_+\psi_n = i\sqrt{(n+1)\hbar\omega}\,\psi_{n+1}, \qquad [2.52]$$

$$a_-\psi_n = -i\sqrt{n\hbar\omega}\,\psi_{n-1}. \qquad [2.53]$$

(b) Use Equation 2.52 to determine the normalization constant A_n in Equation 2.50. (You'll have to normalize ψ_0 "by hand".) *Answer:*

$$A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{(-i)^n}{\sqrt{n!(\hbar\omega)^n}}. \qquad [2.54]$$

∗Problem 2.13 Using the methods and results of this section,

(a) Normalize ψ_1 (Equation 2.51) by direct integration. Check your answer against the general formula (Equation 2.54).

(b) Find ψ_2, but don't bother to normalize it.

(c) Sketch ψ_0, ψ_1, and ψ_2.

(d) Check the orthogonality of ψ_0, ψ_1, and ψ_2. *Note:* If you exploit the evenness and oddness of the functions, there is really only one integral left to evaluate explicitly.

∗Problem 2.14 Using the results of Problems 2.12 and 2.13,

(a) Compute $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$, for the states ψ_0 and ψ_1. *Note:* In this and most problems involving the harmonic oscillator, it simplifies the notation 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 $\langle T \rangle$ and $\langle V \rangle$ for these states (no new integration allowed!). Is their sum what you would expect?

2.3.2 Analytic Method

We return now to the Schrödinger equation for the harmonic oscillator (Equation 2.39):

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

Things look a little cleaner if we introduce the dimensionless variable

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x; \qquad [2.55]$$

in terms of ξ, the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \qquad [2.56]$$