(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 $E < V_{\min}$, 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.)

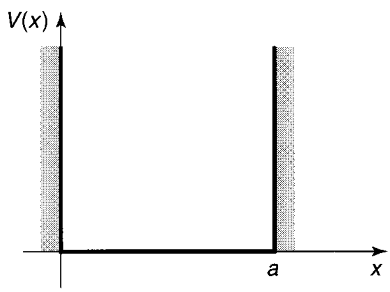

FIGURE 2.1: The infinite square well potential (Equation 2.19).

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

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

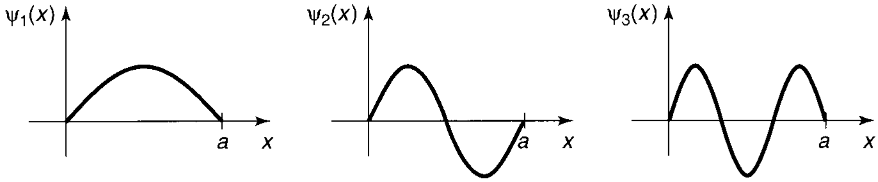

FIGURE 2.2: The first three stationary states of the infinite square well (Equation 2.28).

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:

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

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

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

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]

---

[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:

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

---

[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:

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

---

[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

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

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

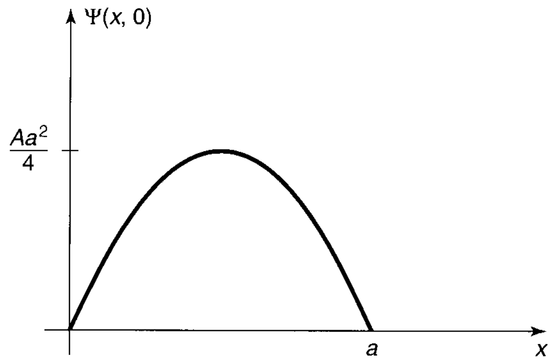

FIGURE 2.3: The starting wave function in Example 2.2.

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)

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

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.