2. THE SCHRÖDINGER EQUATION. BOUND STATES

The central object in quantum mechanics is the wave or state function Ψ, which is a function of the space (and spin) coordinates of the system and time, and from which anything knowable about the system can be obtained. For a while, our system will be a single spinless particle, and what is knowable about the particle is less complete than what is assumed in classical mechanics. The evolution of Ψ in time is given by a partial differential equation, the time-dependent Schrödinger equation, which we introduce first in one space dimension. Separation of space and time variables for this equation leads to the time-independent Schrödinger equation, an eigenvalue equation whose eigenvalues are the possible energies of the system. After brief mention of provisional "rules" of quantum mechanics (detailed formalism can await some experience with what the formalism addresses), we find the energy states of a particle bound in an infinite square well, a finite square well, and a delta-function well. In quantum mechanics, the possible energies of a bound particle are discrete (i.e., quantized), not continuous. Mathematically, the problems are similar to finding the normal modes of classical vibrating systems.

We next step into three space dimensions, and find the energy states of a particle in a three-dimensional rectangular box and (for the case of no angular momentum) a spherical box. We also find the ground states of the harmonic oscillator and hydrogen. With examples in hand, we survey general qualitative properties of bound states. Finally, we develop two ways to get partial or approximate information about bound states without solving the Schrödinger equation.

We can now do some physics. The Problems include simplified models for the polarizability of hydrogen, the bound state of a proton and neutron, and (invoking the Pauli exclusion principle) the absorption frequencies of certain simple molecules, the ground state of the gas of free electrons in a metal, and the radius of a white dwarf star.

2·1. THE SCHRÖDINGER EQUATION

Quantum mechanics is new physics—it cannot be derived from what went before. New physics can only be guessed at using intelligence and imagination guided by attention to results of experiments. Quantum mechanics was first discovered, in a matrix form, by Heisenberg in 1925. A few months later, Schrödinger discovered a differential-equation form, and after a brief period of confusion the two forms were shown to be equivalent. Physicists in 1925 were much more familiar with differential equations than with matrices (Heisenberg didn't know that the arrays he developed were matrices), and Schrödinger soon, for the most part, won the field. Here we develop Schrödinger's form. However, we shall later need the matrix form too—it is particularly useful for angular momentum.

Schrödinger's search began with a talk he gave on de Broglie's ideas about associating a wave with a particle. After the talk, someone remarked that where there was a wave there ought to be a wave equation. So we begin by reviewing very briefly the simplest classical wave equation.

Classical wave equations—A string of mass per unit length μ is stretched along the x axis under tension T. The string undergoes small transverse oscillations, where "small" means that the transverse displacement $y(x, t)$ and the slope $\partial y/\partial x$ are never large. Under these conditions the tension remains, to a good approximation, constant. Application of $F = ma$ to an infinitesimal length of the string leads to

$$\text{tension} \times \text{curvature} = \text{mass per unit length} \times \text{transverse acceleration} ,$$

or

$$\frac{\partial^2 y}{\partial x^2} = \frac{\mu}{T}\frac{\partial^2 y}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} .$$

Here $v \equiv \sqrt{T/\mu}$ is the speed with which a wave will sweep down the string if it is shaken at one end. You can shake a long string at one end, with any frequency, and get a traveling wave. Or you can pluck a string that is fixed at its ends and excite various of a *discrete* set of fundamental and overtone frequencies to get a standing wave. The spectrum of frequencies for *traveling* waves is continuous; for *standing* waves it is discrete.

The equation for electromagnetic waves in vacuum, derived from Maxwell's equations, has the same form as the string equation:

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \Psi}{\partial t^2} ,$$

where Ψ is any transverse component of the electric or the magnetic field (E_y, E_z, B_y, B_z) and c is the speed of light. And again there are both traveling waves, as when light radiates from the Sun or radio waves radiate from an antenna, and standing waves, as in a laser cavity. There are many other physical systems for which an equation of the same form applies, and there are more complicated equations for waves traveling, for example, in inhomogeneous or absorbing media.

[Missing: A paragraph on the advantages of using complex amplitudes such as $\Psi(x, t) = Ae^{2\pi i(x/\lambda - t/\tau)}$.]

If a sinusoidal wave sweeps down a long string, or if one of the normal modes of a string fixed at its ends is excited, each bit of the string undergoes simple harmonic motion. In

either case, the energy *density* at a point along the string is proportional to the square of the amplitude of the motion at that point. Similarly, electric and magnetic energy densities u_E and u_B are proportional to the squares of the electric and magnetic field strengths E and B: $u_E = \epsilon_0 E^2/2$ and $u_B = B^2/2\mu_0$, where ϵ_0 and μ_0 are the permittivity and permeability constants of free space.

Pieces of a puzzle—There are three pieces of our guessing at a wave equation for a particle.

(1) The nonrelativistic relation between the kinetic energy K, the mass m, and the momentum p of a particle is $K = p^2/2m$. Then the total energy is

$$E = \frac{p^2}{2m} + V(x,t) \ ,$$

where $V(x,t)$ is the potential energy (we stay in one space dimension for the time being). The total energy written in terms of p (as opposed to the velocity v) and x and t is the Hamiltonian H.

(2) The particle aspects E and p of a photon and the wave aspects—the frequency ν, the period $\tau = 1/\nu$, the angular frequency $\omega \equiv 2\pi\nu$, the wavelength λ, and the wave number $k \equiv 2\pi/\lambda$—are related by

$$E = h\nu = \frac{h}{\tau} = \hbar\omega \quad \text{and} \quad p = \frac{h}{\lambda} = \hbar k \ .$$

Then any one of $E = pc$ or $\nu = c/\lambda$ or $\omega = ck$ for a photon follows from any other. De Broglie borrowed the relation $p = h/\lambda$ to apply to particles, and thereby was able to "explain" certain quantization rules due to Bohr and to Sommerfeld and Wilson that predated a full quantum mechanics.

(3) The complex expression for a wave of well-defined wavelength and frequency— whether a wave on a string or a sound wave in air or a light wave in vacuum—is

$$\Psi(x,t) = Ae^{2\pi i(x/\lambda - t/\tau)} = Ae^{i(kx - \omega t)} \ .$$

For a photon, the relations in (2) above let us write $\Psi(x,t)$ as

$$\Psi(x,t) = Ae^{i(px - Et)/\hbar} \ .$$

Inventing an equation—For now, our physical system will be a single particle with mass m. We are after a partial differential equation in the variables x and t that somehow embodies the physical relation $E = p^2/2m + V$ in (1) above. We first assume that *both* of the relations in (2) above—$E = \hbar\omega$ and $p = \hbar k$—apply to particles as well as to photons. (It will no longer be the case, however, that $E = pc$ or $\omega = ck$.) We also assume that, for a *free* particle having well-defined energy and momentum (or frequency and wavelength), the *solution* of the equation we are after has the form of $\Psi(x,t)$ in (3) above,

$$\Psi(x,t) = Ae^{i(px - Et)/\hbar} \ .$$

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Taking partial derivatives of this $\Psi(x,t)$, we get

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar}\Psi, \quad \text{or} \quad -i\hbar\frac{\partial \Psi}{\partial x} = p\Psi ,$$

and

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}\Psi, \quad \text{or} \quad i\hbar\frac{\partial \Psi}{\partial t} = E\Psi .$$

Since the kinetic energy involves p^2, we take a *second* derivative with respect to x:

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi, \quad \text{or} \quad -\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi .$$

Thus we may write

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \quad \text{and} \quad -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m}\Psi .$$

Finally, since for a free particle $E = p^2/2m$, we equate the left sides of these last two equations, and have

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} .$$

And that is the Schrödinger equation for a free particle having energy E and momentum p. It is first order in the time derivative, and second order in the space derivative. The solution of the equation is, by (reverse) construction,

$$\Psi(x,t) = Ae^{i(px-Et)/\hbar} .$$

When there is a potential energy $V(x,t)$, we simply add on a term $V(x,t)\Psi(x,t)$, to get

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi(x,t) .$$

(It is E and p, not x or t or functions thereof, that call for differential operations.) This is the full *time-dependent Schrödinger equation*. When $V = V(x,t)$, the solutions will no longer be of the form $Ae^{i(px-Et)/\hbar}$.

The terms on the right side of the Schrödinger equation came from the Hamiltonian, $H = p^2/2m + V$. In classical mechanics, H is a stand-alone function of the position and momentum of a particle, and gives the energy. In quantum mechanics, H is an *operator*,

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V ,$$

which operates on a wave function Ψ, an object that does not exist in classical mechanics. We shall mark the quantum-mechanical H (and, later on, other operators) with a hat, and shall often write the Schrödinger equation in a short form,

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

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Much of Chap. 4, on the formalism of quantum mechanics, will be about operators.

The above argument for Schrödinger's equation might give the impression that Schrödinger discovered it in an afternoon. In fact it took some months. Of course the proof of the equation is that its solutions are in accord with experiments. This Schrödinger showed in a remarkable series of papers that laid the foundations for much of nonrelativistic quantum mechanics. The development of the brilliant work of both Heisenberg and Schrödinger is described in Chap. 5 of *The Conceptual Development of Quantum Mechanics* by M. Jammer (McGraw-Hill, New York, 1966). It is well worth a browse.

2·2. THE WAVE FUNCTION

The wave function—What does the solution $\Psi(x,t)$ of the Schrödinger equation represent? What is it that waves? The answer came from Born: The *probability* that the particle would be found between x and $x + dx$ at t is

$$P(x,t)\,dx = |\Psi(x,t)|^2\,dx = \Psi^*(x,t)\Psi(x,t)\,dx \ .$$

Thus $|\Psi(x,t)|^2$ is a probability *density*, and $\Psi(x,t)$ is a probability *amplitude*. As with classical waves, the square of an amplitude gives a density, but here it is a density of probability, not of energy. And here the amplitude is, as we shall see, unavoidably complex, so that the absolute value is needed. Since the particle is somewhere, $\Psi(x,t)$ is "normalized" by requiring that

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\,dx = 1 \ .$$

Since probabilities are dimensionless, $|\Psi(x,t)|^2$ has (in one space dimension) the dimension of inverse length.

Mean values—We throw an unbiased die. All six outcomes $n = 1, 2, \ldots, 6$ are equally likely, and *some* outcome is certain. Thus the probabilities are normalized if

$$\sum_{1}^{6} P(n) = 1 \ ,$$

and then $P(n) = 1/6$ for all n. The probability that the result of a throw will be 3 is $P(3) = 1/6$. *Before* a throw we have a probability distribution; *after* a throw we have an experimental result.

Given the $P(n)$, we can calculate the expected average or mean $\bar{n}$ of the value of the showing face were we to throw the die, say, 1000 times (or throw 1000 dice once). We simply weight the various possible results with their probabilities and sum over all possible results:

$$\bar{n} \ = \ \sum_{\text{possible results}} \text{result} \times \text{probability of result} \ = \ \sum_{1}^{6} n\,P(n) \ = \ 3\tfrac{1}{2} \ .$$

Of course, an actual experiment with 1000 throws would be unlikely to give $\bar{n} = 3\tfrac{1}{2}$ exactly. In the same way, we can calculate the mean of n^2, or of any other function $f(n)$ of n:

$$\overline{n^2} = \sum_{1}^{6} n^2 P(n) = \frac{91}{6} \quad \text{and} \quad \overline{f(n)} = \sum_{1}^{6} f(n)\,P(n) \ .$$

When the possible results of a measurement form a continuum, such as the position x of a particle, the sum over a discrete set of results is replaced by an integral over a continuous range. The normalization is

$$\int\limits_{\text{range of } x} P(x)\,dx = 1\ ,$$

where $P(x)\,dx$ is the probability of getting a result between x and $x + dx$ on making a measurement. Given the quantum-mechanical $P(x,t) = |\Psi(x,t)|^2$, we can calculate the mean value of x at time t:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x\,|\Psi(x,t)|^2\,dx\ .$$

Anticipating notation to be introduced in Chap. 4, we denote quantum-mechanical mean values with angular brackets, not overbars. The mean of a function $f(x)$ of x at time t would be

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x)\,|\Psi(x,t)|^2\,dx\ .$$

There will be much more about mean values in Chap. 4.

Rules—Here and in the next Section, we state five "rules" concerning the meaning and interpretation of quantum mechanics. The full meaning of these rules will not be immediately apparent, and they are provisional—they will be revised and extended in Chap. 4.

Rule 1: The state of a particle is completely specified by a wave function $\Psi(x,t)$. Anything knowable about the particle can be obtained from its wave function, but what is knowable is less complete than what is assumed in classical mechanics. For example, a particle does not simultaneously have both a definite position and a definite energy.

Rule 2: The Schrödinger equation $i\hbar\,\partial\Psi/\partial t = \hat{H}\Psi$ tells how $\Psi(x,t)$ evolves in time—until a measurement is made. Measurement can cause an abrupt change in the wave function.

2·3. THE TIME-DEPENDENT EQUATION. ENERGY STATES

Product solutions—Suppose, as will usually be the case, that the potential energy depends only on x, not on t: $V = V(x)$. Then we try to find solutions of the Schrödinger equation having the product form

$$\Psi(x,t) = \psi(x)\,T(t)\ .$$

The aim is to get separate *ordinary* differential equations in x and t. Ordinary differential equations are easier to solve than partial differential equations. Afterwards, we can put the pieces, $\psi(x)$ and $T(t)$, back together again.

Putting our trial solution into the Schrödinger equation, $i\hbar\,\partial\Psi/\partial t = \hat{H}\Psi$, we get

$$i\hbar\psi\,\frac{dT}{dt} = T\left(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,\psi\right).$$

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We write ordinary derivatives here because T depends only of t, ψ only on x. Dividing by ψT, we get

$$\frac{i\hbar}{T}\frac{dT}{dt} = \frac{1}{\psi}\left(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,\psi\right).$$

We have managed to move all t dependence to the left side of the equation, and all x dependence to the right. This separation would not have been possible had V depended on t as well as on x.

Now comes the crux of the argument. The variables x and t are independent: either can be varied at will without regard to the other. Suppose we fix x and vary t. Then only the left side of our equation could change; the right side depends only on x, which is fixed. However, if the right side doesn't change, then neither can the left side, since the two sides are equal. The same result follows of course if we fix t and vary x—neither side can change. Therefore, for a product solution to exist, each side of the separated equation must be constant, no matter how x and t vary; and, again, the two sides are equal. The constant to which they are equal is a *separation constant*, E. Thus we obtain two ordinary differential equations,

$$i\hbar\frac{dT}{dt} = ET \quad \text{and} \quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,\psi = \hat{H}\psi = E\psi\ .$$

The other Schrödinger equation—Starting with the time-*dependent* Schrödinger equation, $i\hbar\,\partial\Psi/\partial t = \hat{H}\Psi$, we have derived the time-*independent* Schrödinger equation, $\hat{H}\psi = E\psi$. This is an eigenvalue equation: an operation on ψ—do the various things to ψ that are specified on the left of the equation—is to give ψ back again multiplied by some constant E. And the operator acting on ψ is just the Hamiltonian $\hat{H}$, the energy operator, which is why we call the separation constant E.

There is a different eigenvalue problem for every $V(x)$. Suppose, for some $V(x)$, we have found the eigenvalues E_n and eigenfunctions $\psi_n(x)$ of $\hat{H}\psi_n = E_n\psi_n$. (Many examples to follow!) The physical significance is:

Rule 3: The only possible result of a (good) measurement of the energy of the system is one of the eigenvalues. For a particle bound to a limited region of space the *spectrum* of energy eigenvalues will be discrete, not continuous.

Rule 4: And if, say, the result of the measurement at $t = 0$ is E_6, then immediately afterwards the system is in the corresponding state $\psi_6(x)$. Conversely, if the particle is in the state $\Psi_6(x, t)$, then E_6 will be obtained on measuring the energy.

These two rules will be generalized later on.

Time dependence—To get the time dependence of an eigenstate having eigenvalue E_n, we go back to the differential equation for $T(t)$:

$$\frac{i\hbar}{T}\frac{dT}{dt} = E_n\ .$$

Then

$$\int_{T(0)}^{T(t)}\frac{dT}{T} = -\frac{iE_n}{\hbar}\int_0^t dt\ ,$$

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and

$$T_n(t) = e^{-iE_n t/\hbar} \ .$$

(We shall absorb a multiplicative constant $T(0)$ into $\psi_n(x)$.) Whenever V is independent of time, the equation for $T(t)$ always has the same form, independent of the Hamiltonian, and the dependence of an energy eigenstate on time is $e^{-iE_n t/\hbar}$. Of course, the *values* of E_n depend entirely upon the Hamiltonian.

Thus the product solutions of the time-*dependent* Schrödinger equation are

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_n t/\hbar} \ .$$

The free-particle wave function of Sec. 1 has this same form: $\Psi(x,t) = Ae^{ipx/\hbar}e^{-iEt/\hbar}$. For bound (localized) states, we normalize the eigenstates so that

$$\int_{-\infty}^{+\infty} |\Psi_n(x,t)|^2\, dx = \int_{-\infty}^{+\infty} |\psi_n(x)|^2\, dx = 1 \ ,$$

as is required by the probability interpretation of $|\Psi(x,t)|^2$. Note that $|\Psi_n(x,t)|^2$ is independent of time.

Properties of wave functions—Any physical wave function, classical or quantum mechanical, has certain properties. (1) It is a single-valued function of position and time: it has *a* value at x and t. (2) It is finite in magnitude at all x and t; nature doesn't have infinite amplitudes. (3) It is finite in extent; nature doesn't have infinitely *long* amplitudes.

Because $\Psi(x,t)$ is finite in magnitude and extent, the integral $\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\, dx$ is finite (or "square integrable") and $\Psi(x,t)$ is normalizable. Now in fact the only wave function we have seen so far, $\Psi(x,t) = A\, e^{i(px-Et)/\hbar}$, is not normalizable; it was assumed to have an exact momentum p (or wavelength $\lambda = h/p$), and Fourier analysis tells us that no wave finite in extent does so. Thus $\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\, dx = |A|^2 \int_{-\infty}^{+\infty} dx$ is infinite. Nevertheless, as a mathematical simplification and a physical idealization, $\Psi(x,t) = A\, e^{i(px-Et)/\hbar}$ is highly useful. The idealization of a single wavelength is, of course, made through much of every optics text. We can defer further discussion of such amplitudes until Chap. 3. All other wave functions in this Chapter will be obviously normalizable.

[Missing: A proof (1) that $\psi(x)$ is continuous everywhere, (2) that $d\psi/dx$ is continuous except where $V(x)$ takes an infinite jump, and (3) that $d^2\psi/dx^2$ is continuous except where $V(x)$ takes a jump, finite or infinite.]

Superposition—The product solutions, taken separately, are not the only solutions of the time-*dependent* Schrödinger equation. Consider the linear sum—or *superposition*—of any two product solutions, $\Psi_1(x,t)$ and $\Psi_2(x,t)$:

$$\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t) = c_1\psi_1(x)e^{-iE_1 t/\hbar} + c_2\psi_2(x)e^{-iE_2 t/\hbar} \ ,$$

where c_1 and c_2 are arbitrary constants. Now $i\hbar\, \partial/\partial t$ operating on each term multiplies it by its energy, E_1 or E_2, and $\hat{H}$ does exactly the same thing. So, putting $\Psi(x,t)$ into the time-dependent equation, $i\hbar\, \partial\Psi/\partial t = \hat{H}\Psi$, we get the same thing on both sides of the equation, namely

$$c_1 E_1 \Psi_1 + c_2 E_2 \Psi_2 \ .$$

Thus the superposition of two product solutions is a solution of $i\hbar\,\partial\Psi/\partial t = \hat{H}\Psi$. Pretty clearly, a linear superposition $\Psi(x,t) = \sum c_n \Psi_n(x,t)$ of any number of product solutions would be a solution. Note that $c_1\psi_1(x) + c_2\psi_2(x)$ is *not* a solution of the time-*independent* Schrödinger equation. (What would we use for E?)

Now we can see where time dependence of a probability density will come from: the cross terms in $|\Psi(x,t)|^2$ when $\Psi(x,t)$ is a superposition of two or more states with different energies.

Each product solution is a kind of "unit vector," and the full set of product solutions provides a "basis" for constructing general solutions, much as the unit vectors $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ in ordinary space provide a basis for constructing ordinary three-dimensional vectors. Our "components" here are the constants c_1, c_2, ... For now, this is just a bare hint of what is to come, but the general formalism will make much use of this geometrical analogy in order to make matters more intuitive and visualizable. We shall need all such help we can get.

> *Rule 5*: Any linear superposition of possible states of a system is a possible state of the system.

We shall see that some of the deepest consequences of quantum mechanics result from superposition. For the rest of this Chapter, however, we simply solve the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, for a number of different potential energies $V(x)$. These examples are important in their own right, and it is better to gain some familiarity with the methods and results of quantum mechanics before addressing the general formalism.

2·4. THE INFINITE SQUARE WELL

We consider a particle of mass m confined to a one-dimensional box of length L. The potential energy is (see Fig. 1)

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{outside the box .} \end{cases}$$
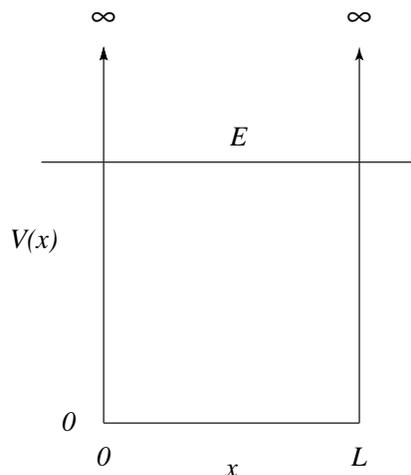

Figure 1. The infinite square well.

The particle is excluded from regions in which $V(x) = \infty$. The classical analogue is a ball bouncing elastically between two rigid walls. However, since we are doing a *wave* mechanics, our solutions will resemble those for a guitar string tied down at $x = 0$ and L.

Inside the box, the time-independent Schrödinger equation is

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

We may write this as

$$\psi'' + k^2\psi = 0 \ ,$$

where primes indicate differentiation and $k^2 \equiv 2mE/\hbar^2$. The general solution of this ordinary, linear, homogeneous, second-order, constant-coefficient differential equation is

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

where A and B are arbitrary constants.

Since the particle is confined to the box, the wave function outside the box is zero. Continuity of $\psi(x)$, like continuity of a guitar string tied down at $x = 0$ and L, requires that

$$\psi(0) = 0 \quad \text{and} \quad \psi(L) = 0 \ .$$

From $\psi(0) = 0$, it follows that $A = 0$. Then from $\psi(L) = 0$, it follows either that $B = 0$, in which case $\psi(x)$ is zero everywhere and we have no physics, or that $kL = n\pi$, where $n = 1, 2, 3, \ldots$ Thus our eigenfunctions are

$$\psi_n(x) = B\sin\left(\frac{n\pi x}{L}\right),$$

for $0 \le x \le L$. We normalize these so that

$$\int_0^L |\psi_n(x)|^2 \, dx = |B|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \ .$$

Since the average height of $\sin^2(n\pi x/L)$ over $0 \le x \le L$ is $1/2$, the integral itself is $L/2$; then, with a choice of phase to make B real and positive, $B = \sqrt{2/L}$. Thus our normalized eigenfunctions are

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right).$$

From the definition $k^2 = 2mE/\hbar^2$, the corresponding eigenvalues are

$$E_n = \frac{\hbar^2 k^2}{2m} = n^2\frac{\pi^2\hbar^2}{2mL^2} = n^2 E_1 \ ,$$

where $E_1 \equiv \pi^2\hbar^2/2mL^2$ and $n = 1, 2, 3, \ldots$

We have thus found that the possible energies of the system are discrete, or *quantized*, and that there is only one wave function for each energy. In Sec. 9, we shall show that the energy is quantized because the particle is bound, and that there is only one wave function

for each bound energy because here there is only one space dimension. Note that when the energy is E_n, there is only a probability distribution, $|\psi_n(x)|^2$, not a definite value, for the position of the particle.

Figure 2(a) shows the lowest energy levels and eigenfunctions. Although the *physics* here is of course very different, the functions themselves are exactly the fundamental and overtone oscillation patterns (normal modes) of a guitar string. In the ground state, one half wavelength fits between 0 and L; in the $n = 2$ state, two half wavelengths fit in L; for the nth level,

$$n\frac{\lambda}{2} = L ,$$

where $n = 1, 2, 3, \ldots$ Using the de Broglie relation $p = h/\lambda$, we get

$$p = \frac{nh}{2L} = \frac{n\pi\hbar}{L} .$$

Then

$$E_n = \frac{p^2}{2m} = n^2\frac{\pi^2\hbar^2}{2mL^2} ,$$

just as before.

In Fig. 2(a), the ground-state wave function $\psi_1(x)$ never crosses the x axis; that is, $\psi_1(x)$ has no nodes (the tie-downs at $x = 0$ and L due to the infinities in $V(x)$ don't count here as nodes). And $\psi_2(x)$ crosses once, $\psi_3(x)$ crosses twice, and so on. Higher energy states have more nodes because higher energies mean higher momenta and thus shorter wavelengths. Count nodes and you know which wave function it is.

The potential energy here is symmetric about $x = L/2$; that is, $V(L/2 - x) = V(L/2 + x)$. When the potential energy is symmetric about some point, then the first, third, fifth, … wave functions are symmetric about this point too (have *even* or *positive parity*); but the second, fourth, … wave functions are antisymmetric (have *odd* or *negative parity*). That is, $\psi_1(L/2 - x) = \psi_1(L/2 + x)$, but $\psi_2(L/2 - x) = -\psi_2(L/2 + x)$; and so on. We prove this property for the general symmetric $V(x)$ in Sec. 9. It means that the probability *densities* $|\psi_n(x)|^2$ of energy eigenstates in symmetric potential wells are always symmetric about the point of symmetry; see Fig. 2(b).

Figure 2(b) also shows the normalized *classical* probability density. Classically, a particle of given energy is moving at constant speed; if 1000 snapshots were taken of the particle at random times, it would with equal likelihood be found anywhere in the well. Thus the probability density is $1/L$ for $0 \leq x \leq L$. Obviously, the classical and quantum-mechanical distributions are different; this too we discuss in Sec. 9.

2·5. THE FINITE SQUARE WELL

Figure 3 shows the potential energy for the finite square well:

$$V(x) = \begin{cases} -V_0 & \text{for } -L/2 < x < +L/2 \\ 0 & \text{outside the central region} \end{cases} ,$$

where $V_0 > 0$. The potential energy is symmetric about the midpoint of the well, and we place the origin at the midpoint, so that $V(-x) = V(+x)$ for all x. Placing the origin at

the symmetry point of $V(x)$ will make the symmetries of our solutions more apparent. Here we are after the *bound-state* energy eigenvalues and eigenfunctions. Bound states will have negative energies between $-V_0$ and 0: $-V_0 < -|E| \le 0$. We consider positive energies for this $V(x)$ in Chap. 3.
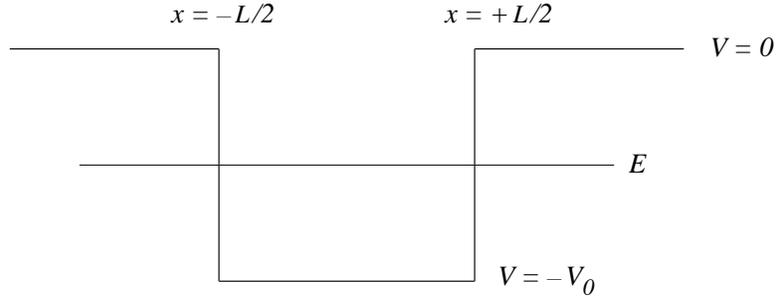

Figure 3. The finite square well.

Piecewise solutions—The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,\psi = E\psi \qquad \text{or} \qquad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\big[E - V(x)\big]\psi = 0 \ .$$

Let ψ_-, ψ_c, and ψ_+ represent $\psi(x)$ in the left-hand, central, and right-hand regions (see Fig. 3). In the central region, where $V(x) = -V_0$, we may write the Schrödinger equation as

$$\psi_c'' + k^2\psi_c = 0 \ ,$$

where primes indicate differentiation and

$$k^2 \equiv \frac{2m}{\hbar^2}(E - V) = \frac{2m}{\hbar^2}(V_0 - |E|) > 0 \ ,$$

so that k is real. The general solution in the central region then is

$$\psi_c(x) = B\cos kx + C\sin kx \ ,$$

where B and C are arbitrary constants.

To the left of the well, the Schrödinger equation is

$$\psi_-'' - q^2\psi_- = 0 \ ,$$

where

$$q^2 \equiv -\frac{2mE}{\hbar^2} = \frac{2m|E|}{\hbar^2} > 0 \ ,$$

so that q is real. The general solution is

$$\psi_-(x) = Ae^{+qx} + A'e^{-qx} \ ,$$

where A and A' are arbitrary. However, e^{-qx} increases without limit as x goes toward $-\infty$; and since $\psi(x)$ must be everywhere finite, we discard this part of the mathematical solution

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on physical grounds, leaving $\psi_-(x) = Ae^{+qx}$. In the same way, the physical solution to the right of the well must be $\psi_+(x) = De^{-qx}$.

We shall also need the first derivatives of the wave functions:

$$d\psi_-/dx = +qAe^{+qx}$$
$$d\psi_c/dx = -kB\sin kx + kC\cos kx$$
$$d\psi_+/dx = -qDe^{-qx} \ .$$

Boundary conditions—We have altogether five unknowns, the four multiplicative constants A, B, C, and D, and the energy E, which is buried in the definitions of k and q. It is one of our requirements that both $\psi(x)$ and (except at an infinite jump of V) its first derivative be continuous everywhere. We thus have four constraints, two at each wall, and these lead to the energy eigenvalues and to elimination of three of the four multiplicative constants. The last constant would come from normalizing $\psi(x)$.

At $x = -L/2$, we set $\psi_- = \psi_c$ and $d\psi_-/dx = d\psi_c/dx$:

$$Ae^{-qL/2} = B\cos(kL/2) - C\sin(kL/2)$$
$$qAe^{-qL/2} = kB\sin(kL/2) + kC\cos(kL/2) \ ,$$

where we have used $\sin(-\phi) = -\sin\phi$ and $\cos(-\phi) = \cos\phi$. Letting $\theta \equiv kL/2$ and dividing the second equation by the first, we get

$$q = k\left(\frac{B\sin\theta + C\cos\theta}{B\cos\theta - C\sin\theta}\right) \ .$$

In the same way, over at $x = +L/2$, we get

$$q = k\left(\frac{B\sin\theta - C\cos\theta}{B\cos\theta + C\sin\theta}\right) \ .$$

Equating the two expressions for q/k and cross multiplying, we get

$$(B^2 + C^2)\sin\theta\cos\theta + BC(\sin^2\theta + \cos^2\theta) = (B^2 + C^2)\sin\theta\cos\theta - BC(\sin^2\theta + \cos^2\theta) \ .$$

This reduces at once to $BC = -BC$, or to $BC = 0$. Thus either $C = 0$ or $B = 0$. (Why is the case $B = C = 0$ of no interest?) We consider the two cases in turn.

Symmetric and antisymmetric solutions—When $C = 0$, the solution in the central region is $\psi_c(x) = B\cos kx$, an even function of x. Thus $\psi_c(-L/2) = \psi_c(+L/2)$, and the boundary conditions require that $A = D$: the solutions are even functions of x, with oscillations within the well and mirror-image decaying exponentials to either side. Also, when $C = 0$, we have $q = k\tan\theta$.

When $B = 0$, the solution in the central region is $\psi_c(x) = C\sin kx$, an odd function of x. Thus $\psi_c(-L/2) = -\psi_c(+L/2)$, and the boundary conditions give that $A = -D$: the solutions are odd functions of x, with oscillations within the well and upside-down mirror-image decaying exponentials to either side. And now we have $q = -k\cot\theta$. But $\cot\theta = -\tan(\theta + \pi/2)$, so we may write this as $q = k\tan(\theta + \pi/2)$.

The energy eigenvalues for the even and odd solutions will come from the equations $q = k \tan\theta$ and $q = k \tan(\theta + \pi/2)$, which we rewrite. From the previous definitions

$$k^2 \equiv \frac{2m}{\hbar^2}(V_0 - |E|) \quad \text{and} \quad q^2 \equiv \frac{2m|E|}{\hbar^2} \;,$$

we have

$$\frac{q^2}{k^2} = \frac{|E|}{V_0 - |E|} = \frac{V_0}{V_0 - |E|} - 1 \;.$$

Remembering the definition of θ and defining a new parameter θ_0,

$$\theta^2 \equiv k^2 \frac{L^2}{4} = \frac{2m}{\hbar^2}(V_0 - |E|)\frac{L^2}{4} \quad \text{and} \quad \theta_0^2 \equiv \frac{2m}{\hbar^2} V_0 \frac{L^2}{4} \;,$$

we have

$$\frac{q^2}{k^2} = \frac{\theta_0^2}{\theta^2} - 1 \;.$$

Thus finally our equations to be solved are

$$\tan\theta = \left(\frac{\theta_0^2}{\theta^2} - 1\right)^{1/2} \quad \text{and} \quad \tan\left(\theta + \frac{\pi}{2}\right) = \left(\frac{\theta_0^2}{\theta^2} - 1\right)^{1/2} \;.$$

All the parameters in the problem—m, $\hbar$, L, and V_0—are in θ_0, and only in this combination do they determine the energy eigenvalues.

Energy eigenvalues—Our equations have the form $f(\theta) = g(\theta)$, and we are after the roots—the values of θ for which the equations are true. Because the equations are transcendental, we can only find the roots graphically or numerically, not algebraically. To see how to get roots graphically, consider the simple equation $x = x^2$. In Fig. 4(a), we plot separately the two sides, our $f(x)$ and $g(x)$, versus x. The roots of the equation are the values of x at which the two curves intersect—just where the two functions are equal. Alternatively, we may plot the function $h(x) \equiv f(x) - g(x)$; see Fig. 4(b). Now the solutions are the roots of $h(x) = 0$, the crossings of $h(x)$ with the x axis. Often $f(x)$ and $g(x)$ are simple and familiar enough to sketch, and from the sketch we can get at least an idea of where the roots lie. On the other hand, an attack with a computer will usually go after the roots of $h(x) = 0$. Many calculators have a built-in routine for finding the roots of a function.

Back to our problem. Figure 5 shows the branches, all identical in form, of $\tan\theta$ and $\tan(\theta + \pi/2)$, our $f(\theta)$ here, as alternating solid and dashed curves, endlessly repeating. It also shows the function

$$g(\theta) = \left(\frac{\theta_0^2}{\theta^2} - 1\right)^{1/2}$$

for three different values of θ_0. In each case, $g(\theta)$ is large when $\theta \ll \theta_0$, swoops down as θ increases, and strikes the θ axis vertically at $\theta = \theta_0$. Since $\theta_0^2 \equiv mV_0L^2/2\hbar^2$, a wider or deeper well means a larger value of θ_0 and more intersections of $g(\theta)$ with the tangent curves—more roots. The positions of the intersections, and thus the values of the roots,

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are entirely determined by the single parameter θ_0. For $\theta_0 < \pi/2$, there is only one bound state; for $\pi/2 \leq \theta_0 < \pi$, there are two bound states; and so on.

Each root gives an energy eigenvalue. Let θ_1, θ_2, ... be the roots in order of increasing magnitude. The ratio

$$\frac{\theta_n^2}{\theta_0^2} = \frac{V_0 - |E_n|}{V_0}$$

gives the nth level as a *fraction of the way up from the bottom* of the well. Or

$$E_n = -\left(1 - \frac{\theta_n^2}{\theta_0^2}\right) V_0$$

gives E_n in terms of V_0. Larger roots give less negative values of E_n.

Here are the energies, as fractions of V_0 when measured from the *bottom* of the well, for $\theta_0 = 1$, 4, and 9:

θ_0	$n =$	1	2	3	4	5	6
1		0.5462	...	...	...	...	...
4		0.0980	0.3827	0.8079	...	...	...
		(1.0)	(3.905)	(8.244)	...	...	...
9		0.0247	0.0984	0.2203	0.3886	0.5995	0.8427
		(1.0)	(3.984)	(8.919)	(15.73)	(24.27)	(34.12)

Numbers in parentheses are the ratios of energies (as measured from the bottom) to the ground-state energy. As θ_0 gets larger, they approach the $1 : 4 : 9 : \ldots$ ratios of the infinite square well. Figure 6 shows the energy levels and eigenfunctions for $\theta_0 = 4$.

If, for a given L, V_0 is made very large, then so is θ_0, and the lowest roots intersect the tangent curves high up, so that $\theta_n \approx n\pi/2$, where $n = 1, 2, \ldots$ (see Fig. 5). These roots lead to energies, measured from the bottom of the well, of

$$V_0 - |E_n| = \frac{2\hbar^2}{mL^2}\theta_n^2 \approx n^2 \frac{\pi^2 \hbar^2}{2mL^2} \ ,$$

which are, not surprisingly, those of the infinite square well. Note from Fig. 5 that the roots, and therefore the energy levels, for a finite square well will alternate with those for the infinite well of the same width. Thus if, say, there are 20 levels with $E_n < V_0$ in an infinite square well of width L, there will be either 20 or 21 levels in the finite well of depth V_0 and the same width.

2·6. THE DELTA-FUNCTION WELL

A limiting case—Figure 7(a) shows a limiting case of the finite square well—a very narrow, very deep well, where the product of the width and depth is finite:

$$L \to 0, \quad V_0 \to \infty, \quad \text{and} \quad g \equiv LV_0 \text{ is finite .}$$

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(This g is not the $g(\theta)$ of Sec. 5.) In this limit, the ruling parameter θ_0, which is proportional to $V_0^{1/2}L$, is zero. This puts the only crossing of the $\tan\theta$ and $(\theta_0^2/\theta^2 - 1)^{1/2}$ curves right at the origin, which tells us that there is only one bound state but fails to provide a value for E. However, $\tan\theta = (\theta_0^2/\theta^2 - 1)^{1/2}$ came from $q = k\tan\theta$, where $\theta \equiv kL/2$. Since the solution θ is here very small, $q = k\tan\theta$ reduces to $q = k^2L/2$. Then, since $q^2 = 2m|E|/\hbar^2$ and $k^2 = 2m(V_0 - |E|)/\hbar^2$, we have

$$\left(\frac{2m|E|}{\hbar^2}\right)^{1/2} = \frac{2m}{\hbar^2}(V_0 - |E|)\frac{L}{2} = \frac{mg}{\hbar^2} \ .$$

The last step follows because (1) $LV_0 = g$, and (2) an infinite $|E|$ will not solve the equation (why not?), and so $|E|L = 0$. Solving for E, we get

$$E = -|E| = -\frac{mg^2}{2\hbar^2} \ .$$

as the energy of the only bound state. Figure 7(b) shows the wave function, which has the usual decaying exponentials outside the well and a kink at $x = 0$.

The Dirac delta function—Figure 8 shows two sequences of functions that grow ever taller and narrower while the areas under the curves remain constant at unity. The common limit of these (and of similar) sequences is the Dirac function $\delta(x)$, which has these defining properties:

$$\delta(x) = 0 \text{ for } x \neq 0, \quad \text{and} \quad \int \delta(x)\,dx = 1$$

if the range of integration includes $x = 0$. The integral is (by convention) dimensionless, so $\delta(x)$ has the dimension of inverse length. To put the spike at $x = a$ instead of at $x = 0$, we write $\delta(x - a)$. The δ function is also sometimes called the impulse function.

In applications, $\delta(x - a)$ is most often found multiplying an ordinary function $f(x)$ in an integrand, as in $\int f(x)\,\delta(x - a)\,dx$. Since $f(x)$ is then multiplied by zero everywhere except at $x = a$, only its value at $x = a$ matters:

$$\int f(x)\,\delta(x - a)\,dx = \int f(a)\,\delta(x - a)\,dx = f(a)\int \delta(x - a)\,dx = f(a) \ ,$$

when the range of integration includes $x = a$. Thus, for example,

$$\int_0^\pi e^{i\theta}\,\delta(\theta - \pi/2)\,d\theta = i \ .$$

We can do no better here than quote from Chap. 5, "The Impulse Symbol ," of the fine book, *The Fourier Integral and Its Applications*, by R.N. Bracewell (3rd ed., McGraw Hill, 2000). "The important attribute of an impulse is the integral; the precise details of form [rectangular, gaussian, ...] are unimportant ... Point masses, point charges, point sources, concentrated forces ... and the like are familiar and accepted entities in physics. Of course, these things do not exist. Their conceptual value stems from the fact that the impulse response ... may be indistinguishable ... from the response due to a physically

realizable pulse. It is then a convenience to have a name for pulses which are so brief and intense that making them any briefer and more intense does not matter."

The delta-function well—We solve the narrow, deep well again, writing the potential energy in terms of $\delta(x)$ and integrating the Schrödinger equation directly. The integral $\int V(x)\,dx$ across a finite square well is $-V_0 L$, so we may here write $V(x) = -V_0 L\,\delta(x) = -g\delta(x)$. The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\big[V(x) - E\big]\psi = -\frac{2m}{\hbar^2}\big[g\,\delta(x) + E\big]\psi\ .$$

As was the case for the finite square well, $\psi_+(x) = Ae^{-qx}$ and $\psi_-(x) = Ae^{+qx}$; and here $\psi_\pm(0) = A$ (see Fig. 7(b)). We integrate the equation over the infinitesimal range $-\epsilon \le x \le +\epsilon$. The left side gives

$$\int_{-\epsilon}^{+\epsilon} \frac{d^2\psi}{dx^2}\,dx = \left.\frac{d\psi_+}{dx}\right|_{+\epsilon} - \left.\frac{d\psi_-}{dx}\right|_{-\epsilon} = -qA - qA\ .$$

The right side gives

$$-\frac{2m}{\hbar^2}\int_{-\epsilon}^{+\epsilon}\big[g\,\delta(x) + E\big]\psi(x)\,dx = -\frac{2mg}{\hbar^2}A\ ,$$

since the interval of integration is infinitesimal and ψ and E are both finite. Equating the two sides of the integrated Schrödinger equation, we get

$$q \equiv \left(\frac{2m|E|}{\hbar^2}\right)^{1/2} = \frac{mg}{\hbar^2}\ ,$$

or, once again, $E = -mg^2/2\hbar^2$.

The result would be the same for a very narrow, very deep gaussian or triangular well: "... the precise details of form are unimportant ..."

2·7. SCHRÖDINGER IN THREE DIMENSIONS

Rectangular coordinates—In three dimensions and rectangular coordinates, the classical Hamiltonian is

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z, t)\ .$$

By symmetry, the quantum-mechanical operators for p_x, p_y, and p_z must certainly all have the same form, so $\hat{p}_y = -i\hbar\,\partial/\partial y$, etc. Thus the time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + V(x, y, z, t)\,\Psi\ ,$$

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where now $\Psi = \Psi(x, y, z, t)$. The quantity in parentheses is the Laplacian operator ∇^2 operating on Ψ, so we may write the equation more compactly as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \ .$$

When V does not depend on t, so that $V = V(x, y, z)$, we again look for solutions that separate space and time: $\Psi(x, y, z, t) = \psi(x, y, z)\, T(t)$. Just as before, we get

$$\frac{i\hbar}{T} \frac{dT}{dt} = \frac{1}{\psi} \left(-\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z)\, \psi \right) = E \ .$$

The equation for $T(t)$ is the same as it was for one dimension. However, now our time-independent equation is still a partial differential equation,

$$\hat{H}\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z)\, \psi = E\psi \ .$$

If, for some V, we find an eigenvalue E_n of this equation, the time dependence of the corresponding wave function Ψ_n will again be $\exp(-iE_n t/\hbar)$.

Suppose the potential energy is a *sum* of three functions, one for each variable:

$$V(x, y, z) = V_x(x) + V_y(y) + V_z(z) \ .$$

Then the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V_x(x)\psi - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial y^2} + V_y(y)\psi - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial z^2} + V_z(z)\psi = E\psi \ .$$

As usual, we try to break this into separate ordinary differential equations. Putting a product form $\psi(x, y, z) = X(x)Y(y)Z(z)$ into the equation and dividing by XYZ, we get

$$\frac{1}{X} \left(-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} + V_x(x)X \right) + \frac{1}{Y} \left(-\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} + V_y(y)Y \right) + \frac{1}{Z} \left(-\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} + V_z(z)Z \right) = E \ .$$

The first term depends only on x, the second only on y, etc. And x, y, and z are independent variables. Suppose we fix y and z and vary x. Then only the first term in the above equation could vary; but if it did the equation would not remain true. We conclude that, for a product solution to exist, each of the three terms on the left of the equation must be constant; call the constant values E_x, E_y, and E_z. Then $E_x + E_y + E_z = E$, and

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} + V_x(x)X = E_x X \ ,$$

with equations of the same form for Y and Z. These are just one-dimensional Schrödinger equations. If we can solve them, getting eigenvalues and eigenfunctions E_{n_x} and $X_{n_x}(x)$, etc., then our three-dimensional product solutions are

$$\psi_{n_x n_y n_z}(x, y, z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z) \quad \text{with} \quad E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} \ .$$

The eigenvalues are sums of one-dimensional eigenvalues and the eigenfunctions are products of one-dimensional eigenfunctions.

As an example, consider a particle confined to a three-dimensional rectangular box of sides a, b, and c. The potential energy is the *sum* of

$$V_x(x) = 0 \text{ for } 0 \leq x \leq a, \ \infty \text{ otherwise}$$
$$V_y(y) = 0 \text{ for } 0 \leq y \leq b, \ \infty \text{ otherwise}$$
$$V_z(z) = 0 \text{ for } 0 \leq z \leq c, \ \infty \text{ otherwise} .$$

The *sum* confines the particle to the box. The separation of variables leads to three one-dimensional box problems. The boundary conditions are that $\psi = 0$ on the six faces of the box. The eigenvalues are

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right),$$

where $n_i = 1, 2, \ \ldots$ And the eigenfunctions are

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{abc}} \sin \left(\frac{n_x \pi x}{a} \right) \sin \left(\frac{n_y \pi y}{b} \right) \sin \left(\frac{n_z \pi z}{c} \right)$$

for points (x, y, z) inside the box. Note that the x-dependent factor in ψ makes $\psi = 0$ on the $x = 0$ and $x = a$ faces of the box, etc.

Spherical coordinates—In spherical coordinates, the spatial variables are r, θ, and ϕ, defined as shown in Fig. 9. Rectangular and spherical coordinates are related by

$$x = r \sin \theta \cos \phi , \quad y = r \sin \theta \sin \phi , \quad z = r \cos \theta .$$
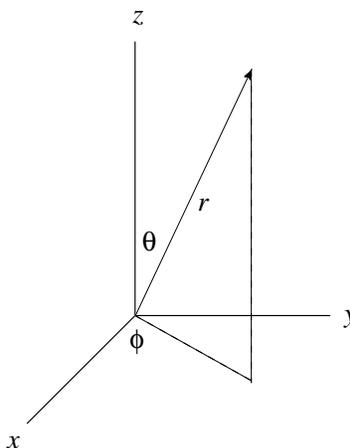

Figure 9. Spherical coordinates.

The ranges of the spherical variables are

$$0 \leq r \leq \infty , \quad 0 \leq \theta \leq \pi , \quad 0 \leq \phi \leq 2\pi .$$

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The angle θ is like latitude, except it is measured from the north pole (positive z axis) to the south instead of up and down from the equator; and ϕ is like longitude, except it is measured all the way around to the "east." Note that r is always nonnegative. What are the coordinates of the point antipodal to the point (r, θ, ϕ)?

When the potential energy is central—that is, when $V = V(r)$—it is nearly always far easier to work in spherical coordinates. The Laplacian operator in spherical coordinates is derived in courses on vector analysis, and once in a lifetime is enough. The time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r} \frac{\partial^2 (r\psi)}{\partial r^2} + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right] + V(r)\,\psi = E\psi \;,$$

where now $\psi = \psi(r, \theta, \phi)$. The first term in $\nabla^2 \psi$ is often written as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial\psi}{\partial r} \right) \;,$$

but the two forms are equivalent (prove it), and we shall prefer the one with r next to ψ.

The Schrödinger equation in spherical coordinates certainly looks formidable, and it will be awhile before we tackle it. We note, however, that there will be a subset of solutions that are *spherically symmetric*—solutions in which $\psi = \psi(r)$, with no θ or ϕ dependence. (In Chap. 7, we shall find that no angular dependence means that the angular momentum is zero.) Then the terms involving $\partial\psi/\partial\theta$ and $\partial\psi/\partial\phi$ are zero, and the Schrödinger equation, somewhat rearranged, greatly simplifies to the *ordinary* differential equation

$$\frac{d^2(r\psi)}{dr^2} + \frac{2m}{\hbar^2} \left[E - V(r) \right] r\psi = 0 \;;$$

or, with $u(r) \equiv r\psi(r)$,

$$\frac{d^2 u}{dr^2} + \frac{2m}{\hbar^2} \left[E - V(r) \right] u = 0 \;.$$

This equation is for $u(r)$, not $\psi(r)$, but it has exactly the same form as the *one*-dimensional equation for $\psi(x)$,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left[E - V(x) \right] \psi = 0 \;.$$

However, whereas the range of x is $-\infty$ to $+\infty$, the range of r, again, is 0 to $+\infty$. Also, since $u(r) = r\psi(r)$ and $\psi(r)$ is everywhere finite, $u(0)$ is zero—a boundary condition.

In spherical coordinates, the infinitesimal volume element is $r^2 \sin\theta\, dr\, d\theta\, d\phi$. The normalization integral is

$$\int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |\psi(r, \theta, \phi)|^2\, r^2 \sin\theta\, dr\, d\theta\, d\phi = 1 \;.$$

When ψ depends only on r, this becomes

$$4\pi \int_0^{\infty} |\psi(r)|^2\, r^2\, dr = 4\pi \int_0^{\infty} |u(r)|^2\, dr = 1 \;.$$

For the integral to in fact be finite, it is necessary that $u(r)$, not just $\psi(r)$, vanish as $r \to \infty$.

As an example, consider a particle of mass m confined to the interior of a sphere of radius R:

$$V(r) = \begin{cases} 0 & \text{for } 0 \le r \le R \\ \infty & \text{for } r > R . \end{cases}$$

For the subset of solutions that are spherically symmetric, where $\psi = \psi(r)$, the eigenvalue problem is

$$\frac{d^2 u}{dr^2} + \frac{2mE}{\hbar^2} u = 0 ,$$

with $u(0) = u(R) = 0$. This is mathematically identical to the one-dimensional infinite-square-well problem for $\psi(x)$,

$$\frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 ,$$

with $\psi(0) = \psi(L) = 0$. Equations of the same form have solutions of the same form. Thus the *spherically symmetric* solutions here are

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mR^2} \quad \text{and} \quad \psi_n(r) = \frac{1}{\sqrt{2\pi R}} \frac{1}{r} \sin\left(\frac{n\pi r}{R}\right) ,$$

for $0 \le r \le R$. Why is the normalization here different from that for the one-dimensional well?

2·8. THE TWO MOST IMPORTANT BOUND STATES

Forces and potential energies—The Hooke's-law force is

$$F(x) = -kx \ \text{ in one dimension} , \quad \mathbf{F}(\mathbf{r}) = -kr\,\hat{\mathbf{r}} \ \text{ in three} ,$$

where k is the force constant and $\hat{\mathbf{r}}$ is the unit vector in the radial direction. The angular frequency of the classical oscillator is $\omega = \sqrt{k/m}$, and we shall use $m\omega^2$ in place of k. The corresponding potential energies, from $F(x) = -dV/dx$ or $F(r) = -dV/dr$, are

$$V(x) = -\int_0^x (-m\omega^2 x)dx = +\frac{1}{2}m\omega^2 x^2 \quad \text{and} \quad V(r) = -\int_0^r (-m\omega^2 r)dr = +\frac{1}{2}m\omega^2 r^2 ,$$

where $V(0) = 0$.

The Coulomb force is

$$\mathbf{F}(\mathbf{r}) = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \hat{\mathbf{r}} = -\frac{ke^2}{r^2} \hat{\mathbf{r}} ,$$

where on the right we take the charges to be $+e$ and $-e$, as for the proton and electron in hydrogen; and for brevity we let $k \equiv 1/4\pi\epsilon_0$. The potential energy is

$$V(r) = -\int_\infty^r \left(-\frac{ke^2}{r^2}\right) dr = -\frac{ke^2}{r} ,$$

where $V(\infty) = 0$.

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Figure 10 shows these two potential energies. Note that we took the oscillator potential energy to be zero at the origin, where the force is zero, whereas we took the Coulomb potential energy to be zero at infinity, where the force is zero. Provided that we do so consistently, we can always add a constant to potential energies, but we cannot calculate the oscillator potential energy integrating from infinity or the Coulomb energy integrating from zero. Why not?

The Hooke's-law and Coulomb forces are the most important forces giving bound states. In classical mechanics, they are the only two power-law forces that give as bound orbits closed ellipses encircling the center of force. Solving the Schrödinger equation for these forces will take much work later on, but we can here get the *ground-state* solutions, which are the most important ones, by judicious guessing.

Harmonic-oscillator ground state—The time-independent Schrödinger equation for the one-dimensional oscillator is

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

The ground-state wave function will have to be symmetric about $x = 0$, have no nodes, vanish as $x \to \pm\infty$ fast enough for $\psi(x)$ to be square integrable, and be finite, continuous, and differentiable over the entire range $-\infty < x < +\infty$. Since there are no discontinuities in $V(x)$, there are no *piecewise* solutions—one function is to do the job for all x.

The Schrödinger equation tells us that we need a $\psi(x)$ whose second derivative has the form $(cx^2 + d)\psi$. A moment's scribbling shows that

$$\psi(x) = e^{-ax^2}$$

is such a function, and that it also satisfies all the other requirements. This is the gaussian function, the bell-shaped curve that occurs in statistics and other fields. Exponentials with negative exponents die away nicely, and the exponent $-ax^2$ makes the function symmetric. Putting this $\psi(x)$ into the Schrödinger equation shows that it is indeed a solution, provided (1) that $a = m\omega/2\hbar$, and (2) that $E = \hbar\omega/2$. The details are left for a Problem.

It remains to normalize $\psi(x)$. As the integral is important and the method clever, we do it. We calculate the *area* integral

$$\left(\int_{-\infty}^{+\infty} e^{-2ax^2}\,dx\right)\left(\int_{-\infty}^{+\infty} e^{-2ay^2}\,dy\right) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-2a(x^2+y^2)}dx\,dy \; .$$

This is the *square* of the integral we are after. (Why are there 2's in the exponents?) First, we transform to polar coordinates, where $x^2 + y^2 = r^2$ and the area element is $r\,dr\,d\theta$, and the integral becomes

$$\int_0^\infty\int_0^{2\pi} e^{-2ar^2}\,r\,dr\,d\theta = 2\pi\int_0^\infty e^{-2ar^2}\,r\,dr \; .$$

Then we substitute s for r^2, so that $ds = 2r\,dr$, and the integral is easy to do:

$$\pi\int_0^\infty e^{-2as}\,ds = \pi\left(\frac{e^{-2as}}{-2a}\right)_0^\infty = \frac{\pi}{2a} \; .$$

Thus

$$\int_{-\infty}^{+\infty} e^{-2ax^2}\, dx = \sqrt{\frac{\pi}{2a}} = \sqrt{\frac{\pi\hbar}{m\omega}}\ ,$$

and our ground-state energy and normalized wave function are

$$E_0 = \frac{\hbar\omega}{2} \quad \text{and} \quad \psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}\ .$$

For the oscillator (as opposed to square wells), the numbering of states starts with zero, not one. As we shall see in Chap. 5, this follows the way polynomials that occur in the full solution of the oscillator problem are numbered. Figure 11(a) shows E_0 and $\psi_0(x)$.

Hydrogen-atom ground state—In Sec. 7, we saw that the Schrödinger equation with a central potential energy greatly simplifies when ψ has no θ or ϕ dependence. In that case, we had

$$\frac{d^2(r\psi)}{dr^2} + \frac{2m}{\hbar^2}\Big[E - V(r)\Big]r\psi = 0\ .$$

For the Coulomb potential energy, $V(r) = -ke^2/r$, we have

$$\frac{d^2(r\psi)}{dr^2} + \frac{2m}{\hbar^2}\left(E + \frac{ke^2}{r}\right)r\psi = 0\ .$$

Even in this case of no angular dependence, there are an infinite number of bound-state ($E < 0$) solutions, but here we are only after the ground state. The Schrödinger equation tells us that we need a $u(r) = r\psi(r)$ whose second derivative has the form $(c + d/r)\, u$. The function $u(r) = re^{-br}$, or $\psi(r) = e^{-br}$, satisfies this and all other requirements, provided (1) that $b = mke^2/\hbar^2 = 1/a_0$, where $a_0 = 0.529 \times 10^{-10}$ m is the Bohr radius, and (2) that $E = -mk^2e^4/2\hbar^2 = -13.6$ eV. The normalized wave function is

$$\psi_1(r) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}\ .$$

We again leave details for a Problem. Figure 11(b) shows E_1 and $\psi_1(x)$.

It is often useful to consider the electron to be smeared out over a "cloud" whose volume charge density is $\rho(r) = -e\,|\psi(r)|^2$. The integral of $\rho(r)$ over space is of course $-e$.

If we move along, say, the x axis, there is a kink (a discontinuity in slope) in ψ_1 on passing through the origin. Why (physically) is there one here but not for the harmonic oscillator?

2·9. QUALITATIVE PROPERTIES OF BOUND STATES (to be written)

(1) The energies of bound states are quantized.

(2) The bound energy eigenstates over $-\infty < x < +\infty$ are nondegenerate.

(3) The bound energy eigenfunctions over $-\infty < x < +\infty$ may be taken to be real.

(4) The lowest bound-state energy E_1 lies above the minimum of $V(x)$.

(5) An eigenfunction is concave toward the x axis (oscillatory) in regions of x where $E > V(x)$ but is convex toward the axis in regions where $E < V(x)$.

(6) The number of nodes increases with energy.

(7) For large n, the quantum probability distributions $|\psi_n(x)|^2$ on average track classical distributions.

(8) For large n, in $E > V(x)$ regions, the wave function amplitude is larger where $V(x)$ is shallower.

(9) If $V(-x) = V(+x)$, then the eigenfunctions are alternately even and odd.

See Chap. 3 of French and Taylor, *Introduction to Quantum Physics*, for a number of examples on the relations between $\psi(x)$ and $V(x)$.

2·10. DIMENSIONS AND SCALING

Sometimes we can learn a lot from an equation, without actually solving it, simply by considering the quantities upon which the solutions must depend.

Harmonic oscillator—We look again at the Schrödinger equation for the harmonic oscillator,

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

The energy eigenvalues can only depend upon the following quantities: a quantum number n, perhaps some other pure numbers such as 2 or π, and the parameters that appear in the equation, $\hbar$, m, and ω. Parameters not in the equation are of course irrelevant—if you're not part of the problem, you're not part of the solution.

What can we deduce? The equation for the eigenvalues, $E_n = ?$, will of course have to be dimensionally correct. Let M, L, and T represent the fundamental physical dimensions of mass, length, and time. Then the dimensions of energy are

$$\dim(E) = ML^2T^{-2} \qquad (\text{think } E = mc^2) \ ,$$

and the dimensions of m, ω, and $\hbar$ are

$$\dim(m) = M$$
$$\dim(\omega) = T^{-1} \qquad (\text{think } \omega = 2\pi/\tau)$$
$$\dim(\hbar) = ML^2T^{-1} \qquad (\text{think } E = \hbar\omega) \ .$$

The only way to construct a quantity having the dimensions of energy from the three parameters is to take $\hbar$ to get the L^2 dependence, and then multiply it by ω to complete the T^{-2} dependence. Therefore this much—that $E \propto \hbar\omega$—comes without knowing any more about the Schrödinger equation than the parameters that occur in it. Of course, we already knew that $\hbar\omega$ has the dimensions of energy, but perhaps we hadn't noticed that it is the only combination of the available parameters that does so.

Hydrogen atom—The Schrödinger equation for the hydrogen atom is

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{ke^2}{r}\psi = E\psi \ .$$

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Here the parameters are $\hbar$, m, $k \equiv 1/4\pi\epsilon_0$, and e. Now k has to go with e^2 in order to cancel the charge units (coulomb^2); and

$$\dim(ke^2) = ML^3T^{-2} \qquad (\text{think } V = -ke^2/r) \ .$$

To construct a quantity having the dimensions of energy, we write

$$\dim(E) = [\dim(\hbar)]^a \ [\dim(m)]^b \ [\dim(ke^2)]^c \ ,$$

or

$$ML^2T^{-2} = (ML^2T^{-1})^a M^b (ML^3T^{-2})^c \ .$$

Here a, b, and c are numbers to be obtained by matching the powers of M, L, and T on the two sides of the equation. The constraints are

$$1 = a + b + c \ , \quad 2 = 2a + 3c \ , \quad \text{and} \quad -2 = -a - 2c \ ,$$

and the sole solution is $a = -2$, $b = +1$, and $c = +2$. Thus the dependence of the eigenvalues on the parameters has to be

$$E_n \propto -(\hbar)^{-2}(m)^{+1}(ke^2)^{+2} = -mk^2e^4/\hbar^2 \ .$$

The minus sign is a reminder that for this potential, $V(r) = -ke^2/r$, the bound states have negative energies. Thus if, say, m increases, the energies become lower (more negative), not higher.

Uses of dimensional results—We can use results obtained from dimensional arguments in the following ways:

(1) *To estimate the energies and sizes of ground states*—If we multiply either of the above results, $\hbar\omega$ or $-mk^2e^4/\hbar^2$, by 1/2, we get exactly the ground-state energy of the corresponding system—see Sec. 8. In general, the combination of parameters that makes an energy gives an order-of-magnitude estimate of the ground-state energy. In the same way, for these and other power-law potentials, only one combination of parameters makes a length, a combination that can serve as an estimate of the size of the ground state.

(2) *To see how energies and sizes "scale" when a parameter changes*—Our result for the hydrogen atom involves, in the numerator, the square of the product of the charges of the electron and proton. Thus a single-electron atom with nuclear charge Ze would have bound-state energies Z^2 times as large as the hydrogen energies. Similarly, the mass dependence—properly, m is the *reduced* mass, $\mu = mM/(m + M)$—shows that the positronium atom, e^+e^-, has bound-state energies closely one-half as large as those of hydrogen.

(3) *To see how energies and sizes depend upon a quantum number*—When a quantum number appears in an equation, it goes with $\hbar$. Some of the relations we have seen or shall see are

$$E_n = n^2 \frac{\pi^2\hbar^2}{2mL^2}, \ \ E_n = -\frac{1}{n^2}\frac{mk^2e^4}{2\hbar^2}, \ \ E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \ \ |\mathbf{L}| = \sqrt{\ell(\ell+1)}\,\hbar, \ \ L_z = m_\ell\hbar \ .$$

In each equation, the quantum number, n or ℓ or m_ℓ, to leading order goes with $\hbar$. (We shall put this relationship on a firmer footing in the next Section.) Having determined from

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a dimensional argument where $\hbar$ goes, we know pretty well where the associated quantum number goes. Thus for the oscillator and the hydrogen atom, we have

$$E_n \approx n\hbar\omega \quad \text{and} \quad E_n \approx -\frac{1}{n^2}\frac{mk^2e^4}{\hbar^2} \ .$$

We come close to the true eigenvalues,

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{and} \quad E_n = -\frac{1}{n^2}\frac{mk^2e^4}{2\hbar^2} \ ,$$

using nothing more from the Schrödinger equation than the relevant parameters and an approximate rule, "n goes with $\hbar$." We may already know the exact eigenvalues here, but we now have a way to learn something quickly should we encounter the potential energy $V(x) = b\,|x|$, say, or $V(x) = cx^4$.

Remarks—Dimensional and scaling methods have a distinguished ancestry that includes Lord Rayleigh and Fourier and goes all the way back to Galileo. However, the full power of the methods were developed largely by Buckingham in the 1910's. Our examples above were very elementary. Often there is more than one way to construct a quantity of interest because there are many parameters—there is more than one way to construct an energy when $V(r) = ar^2 - b/r$. Nevertheless, dimensional analysis leads to a reduction of the number of "degrees of freedom"—always a blessing. Then scaling permits, for example, the experimental testing of the design of an airplane wing, or the investigation of cratering due to explosives or asteroid impacts, for values of the parameters that are far from the "real" values but are experimentally accessible. Dimensional methods are invaluable when, as in fluid mechanics, the equations are known but are in many situations too difficult to solve, or when, as often in biomechanics, there is no equation from which to read the relevant parameters. The art in the latter case—and in many engineering applications—is to decide which of a multitude of parameters are important and which are not. For the atom, the art was Bohr's.

For an introduction to dimensional analysis, see P.W. Bridgman, *Dimensional Analysis*, (Yale University Press, New Haven, 1949). For examples both physical and biological and further references, see T.A. McMahon and J.T. Bonner, *On Size and Life*, (Scientific American Library, New York, 1983).

2·11. FITTING WAVELENGTHS IN A WELL

We look for an easier way to get energy eigenvalues than solving the Schrödinger equation. We "invent" a method that is indeed sometimes easier, but it will usually only give approximate results. We start with what we already know about the infinite square well and the harmonic oscillator. Figure 11 shows the lowest eigenstates for these cases. As the energy increases, there are more oscillations of the wave function. For the harmonic oscillator, there are more both because there are more oscillations per unit distance in x and because the oscillations extend over a larger range of x as the turning points—the values of x at which $E = V(x)$—move out.

Infinite square well—We consider again the infinite square well. The de Broglie wavelength λ is related to the momentum p by $\lambda = h/p$; and in the well $E = p^2/2m$. Thus

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \ .$$

Let us calculate the number of wavelengths in the well for *any* E, not just for those values of E that make $n\lambda/2 = L$. The infinitesimal *fraction* of a wavelength in the infinitesimal distance dx is dx/λ. Then the

$$\text{number of wavelengths between 0 and } L \ = \int_0^L \frac{dx}{\lambda} = \frac{L}{\lambda} = \frac{\sqrt{2mE}}{h}L \ ,$$

since here λ (for a given E) is constant. To fit properly in the well, we want the number of wavelengths in the distance L to be $n/2$, where $n = 1, 2, \ldots$ Equating the right side of the above equation to $n/2$ leads at once to the quantized energies $E_n = n^2\pi^2\hbar^2/2mL^2$.

So far there is nothing new—we made much the same argument in Sec. 4. However, we now have a two-step recipe for more general application: (1) Find the number of wavelengths between the turning points for any value of E. (2) Decide how many wavelengths we ought to have between the turning points. Think of slowly raising up the E line, like a high-jump bar, on a $V(x)$ diagram. At certain heights, the line "clicks" into a value that gives a proper number of wavelengths.

Harmonic oscillator—When $V(x)$ is not constant, then neither is the de Broglie wavelength. However, in regions of x where $E > V(x)$, we can still define a "local" wavelength using

$$\lambda(x) = \frac{h}{p(x)} = \frac{h}{\sqrt{2m(E - V(x))}} \ .$$

And then we can still calculate how the number of wavelengths between turning points x_1 and x_2 depends on E, using our varying $\lambda(x)$:

$$\text{number of wavelengths between } x_1 \text{ and } x_2 \ = \int_{x_1}^{x_2} \frac{dx}{\lambda(x)} = \frac{1}{h} \int_{x_1}^{x_2} \sqrt{2m(E - V(x))} \ dx \ .$$

For the oscillator, $V(x) = \frac{1}{2}m\omega^2 x^2$ and the turning points are at $\pm a$, where $a = \sqrt{2E/m\omega^2}$. Thus the number of wavelengths between $-a$ and $+a$ is

$$\frac{1}{h} \int_{-a}^{+a} \sqrt{2m\left(E - \frac{1}{2}m\omega^2 x^2\right)} \ dx \ .$$

Note that here both the integrand and the limits of integration are functions of E.

A change of variable, $y \equiv x/a$, changes the limits to ± 1 and the integral to

$$\frac{2E}{h\omega} \int_{-1}^{+1} \sqrt{1 - y^2} \ dy = \frac{E}{2\hbar\omega} \ .$$

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The integral itself is $\pi/2$; see Fig. 12. Thus for the oscillator the number of wavelengths between the turning points is proportional to E.
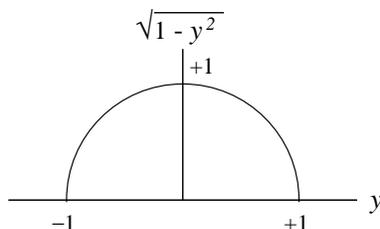

Figure 12. The area under the half circle is $\pi/2$.

The next question is: What do we now set $E/2\hbar\omega$ equal to? That is, how many wavelengths do we *want* between the turning points? The wave functions for the infinite square well are entirely oscillatory, and the oscillations bring the wave function all the way back to the x axis at $x = 0$ and L. The wave functions for the oscillator, however, are finally brought back to the x axis by the decaying exponentials outside the turning points. Thus, for the oscillator ground state, we don't need a whole half wavelength between the turning points; but we do need at least a bit of a wavelength in the $E > V(x)$ region to turn the wave function over to connect with the decaying exponentials. Suppose we minimize our maximum error by choosing midway between half a wavelength and none at all. Setting the number of wavelengths, $E/2\hbar\omega$, equal to $1/4$, we get $E_0 = \hbar\omega/2$. Perfect!

Instead of *guessing* the number of wavelengths that we need (and finding that we get the correct result), we could (and would, had we got an incorrect result) have *used* the correct result to get the number of wavelengths. But there is often something to be learned by first trying to puzzle out what a reasonable answer might be.

To get each higher energy eigenvalue, we simply add another half wavelength: $E/2\hbar\omega = 3/4, 5/4, \ldots$; see Fig. 10. This gives $E_n = (n + 1/2)\hbar\omega$, where $n = 0, 1, 2, \ldots$ And this, as we shall see (after much work) in Chap. 5, is exact for all n.

Bouncing particle—We now have a method that gives exact energy eigenvalues for the infinite square well and for the harmonic oscillator. Again: (1) Find the number of wavelengths between the turning points for any value of E. (2) Decide how many wavelengths we ought to have between the turning points; this depends on whether or not ψ has to got to zero at a turning point.

Let us try it for a particle of mass m bouncing elastically on a floor. With the floor at $z = 0$, the potential energy is

$$V(z) = \begin{cases} \infty & \text{for } z < 0 \\ mgz & \text{for } z \geq 0 \end{cases} .$$

The turning points are at $z = 0$ and $z = E/mg$, and the number of wavelengths between them as a function of E is

$$\frac{1}{h} \int_0^{E/mg} \sqrt{2m(E - mgz)} \; dz .$$

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With a change of variable, $y \equiv mgz/E$, this becomes

$$\sqrt{2mE} \, \frac{E}{mgh} \int_0^1 \sqrt{1-y} \, dy = \frac{1}{gh}\sqrt{\frac{2E^3}{m}}\left(-\frac{2}{3}\right)(1-y)^{3/2}\bigg|_0^1 = \frac{1}{3\pi gh}\sqrt{\frac{2E^3}{m}} \, .$$

For the ground ($n = 1$) state, we here want neither 1/4 nor 1/2 but 3/8 of a wavelength (why?); and for the nth state we want $\left(\frac{n}{2} - \frac{1}{8}\right)$ wavelengths, with $n = 1, 2, \ldots$ Thus

$$\frac{1}{3\pi g\hbar}\sqrt{\frac{2E^3}{m}} = \left(\frac{n}{2} - \frac{1}{8}\right) ,$$

or

$$E_n \approx \left[\frac{3\pi}{\sqrt{8}}\left(n - \frac{1}{4}\right)\right]^{2/3}(mg^2\hbar^2)^{1/3} ,$$

where we have separated the purely numerical factors from those having dimensions.

Here for a few values of n is what we get compared with true answers obtained numerically:

n =	1	2	3	5	10
$\left[\frac{3\pi}{\sqrt{8}}\left(n - \frac{1}{4}\right)\right]^{2/3}$ =	1.842	3.240	4.379	6.304	10.182
True =	1.856	3.245	4.382	6.305	10.183

The larger the value of n, the better the result.

Remarks—[Not written.]

PROBLEMS

> *"He wants to have done it, but he doesn't want to do it,"*
> from *Running the Amazon* by Joe Kane

1. *A sloshing particle.*

At $t = 0$, the wave function for a particle in an infinite square well is

$$\Psi(x,0) = \frac{1}{\sqrt{2}}\left[\psi_1(x) + \psi_2(x)\right] ,$$

where ψ_1 and ψ_2 are the two lowest normalized energy eigenfunctions.

(a) Show that $\Psi(x,0)$ is normalized.

(b) Calculate the mean value $\langle x(t)\rangle = \int_0^L x \, |\Psi(x,t)|^2 \, dx$. (Some of the integrals are zero, by symmetry; and trigonometric identities will reduce the others to the form $\int x \cos ax \, dx$.) Note that $\langle x(t)\rangle$ oscillates with an angular frequency $\omega = (E_2 - E_1)/\hbar$.

(c) Sketch $|\Psi(x,t)|^2$ versus x at $t = 0$ and after half a period of the oscillation.

2. *The finite square well, I.*

Use a calculator or computer to verify the numbers in the $\theta_0 = 9$ row of the table at the end of Sec. 5. Get *your* numbers to 5-place accuracy, and draw to scale the energy-level diagram. Show where the first six energies of an infinite square well of the same width would be.

3. *The finite square well, II.*

A particle of mass m in a finite square well of width L and depth V_0 has just barely five (or six, or seven ...) bound states. Find the energy levels (in terms of V_0) to 4-place accuracy. Then draw to scale the energy-level diagram.

4. *The Heaviside step function.*

The Heaviside step function is

$$H(x) = \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x > 0 \end{cases}.$$

(a) Show that $\int_{-\infty}^{x} \delta(x)\, dx = H(x)$.

(b) Show that $dH(x)/dx = \delta(x)$. One way is to consider the derivative of an approximation to $H(x)$ that ramps up in a straight line from 0 at $x = -\epsilon$ to 1 at $x = +\epsilon$. Then let $\epsilon \to 0$.

(c) The symbol $H(x - a)$ places the step at $x = a$. Sketch $H(x) - H(x - a)$ and its derivative.

5. *A one-dimensional crystal.*

(a) We might model the potential energy of a particle in a one-dimensional crystal using a very long line of identical δ functions at the sites of the atoms:

$$V(x) = -g \left[\cdots + \delta(x + b) + \delta(x) + \delta(x - b) + \delta(x - 2b) + \cdots \right],$$

where b is the spacing between the atoms. What is the ground-state energy of a particle of mass m in this $V(x)$?

(b) Snip off a string of N of these "atomic sites" and join the cut ends to make a ring molecule of length Nb. What now is the lowest energy?

6. *The double-delta well.*

The double-δ potential energy,

$$V(x) = -g \left[\delta(x - a) + \delta(x + a) \right],$$

has, depending on the parameters a and g and the mass m, either one or two bound states.

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(a) Sketch the wave functions for the bound states, assuming two exist.

(b) Write down the form of the wave functions in regions I (use a coefficient A), II (use B and C), and III (use D) when $E < 0$. Use parity considerations to write the even-parity (E_1) wave function in terms of just A and B. Do the same for the odd-parity (E_2) wave function.

(c) Use the (dis)continuity conditions on $\psi(x)$ and $d\psi/dx$ at $x = +a$ to get

$$e^{-2qa} = 2qa/\Lambda - 1$$

as the equation that determines E_1. Here $q^2 \equiv 2m|E|/\hbar^2$ and $\Lambda \equiv 2mga/\hbar^2$.

(d) Sketch $\exp(-2qa)$ and $(2qa/\Lambda - 1)$ as functions of qa. Show that the only crossing occurs for qa somewhere between Λ and $\Lambda/2$. Thus find bounds on E_1 in terms of m, g, a, and $\hbar$.

(e) Show that the equation that determines E_2 is

$$-e^{-2qa} = 2qa/\Lambda - 1 .$$

Sketch the two sides and show that there is no physical $(qa > 0)$ solution unless $\Lambda > 1$.

7. *Oscillator and hydrogen-atom ground states.*

(a) Show that $\psi(x) = e^{-ax^2}$ is a solution of the Schrödinger equation for the oscillator, provided (1) that $a = m\omega/2\hbar$, and (2) that $E = \hbar\omega/2$.

(b) Show that $\psi(r) = e^{-br}$ is a solution of the Schrödinger equation for the hydrogen atom, provided (1) that $b = mke^2/\hbar^2 = 1/a_0$, where a_0 is the Bohr radius, and (2) that $E = -mk^2e^4/2\hbar^2$. Normalize the wave function.

8. *The hydrogen ground state.*

(a) A hydrogen atom is in its ground state. If space is divided into identical infinitesimal cubes, in which cube is the electron most likely to be found? If instead space is divided into shells of infinitesimal thickness, like the layers of an onion, centered on the proton, what is the radius of the shell in which the electron is most likely to be found?

(b) Calculate the mean radius $\langle r \rangle = 4\pi \int_0^\infty r\,|\psi(r)|^2\,r^2\,dr$.

(c) Calculate the mean value of $V(r)$. What then, without calculation, is the mean value of the kinetic energy K?

9. *Polarizability of hydrogen.*

When a hydrogen atom is placed in an electric field $\mathcal{E}$, the proton and electron are pushed in opposite directions. Thus an electric dipole moment $p = ed$ is induced, where d is the offset of the center of charge of the electron "cloud" from the proton. For fields attainable in the laboratory, p is proportional to $\mathcal{E}$: $p = \alpha \mathcal{E}$, where α is the *polarizability*.

Find α by modeling the electron cloud as a spherical charge density given by $\rho(r) = -e\,|\psi(r)|^2$, where $\psi(r)$ is the ground-state wave function; assume that ρ is not distorted by the field.

Hint: What is the electric field due to a spherical charge distribution a distance d from its center? For attainable fields, d will be far smaller than the Bohr radius a_0. The answer here, $\alpha = 3\pi\epsilon_0\,a_0^3$, is one-sixth of the true value; a detailed calculation takes into account the distortion of the cloud.

10. *Integrating by differentiating.*

Let

$$I_n = \int_{-\infty}^{+\infty} x^n e^{-bx^2}\,dx \ .$$

Then $I_n = 0$ when n is odd; and we showed in Sec. 8 that $I_0 = \sqrt{\pi/b}$. By taking derivatives of I_0 with respect to b, show that

$$I_2 = \frac{1}{2b}\,I_0\ , \quad I_4 = \frac{3}{4b^2}\,I_0\ ,$$

and get a general expression for I_n when n is even.

"...when guys at MIT or Princeton had trouble doing a certain integral, it was because they couldn't do it by the standard methods they had learned at school ... Then I'd come along and try differentiating under the integral sign, and often it worked. So I got a great reputation for doing integrals, only because my box of tricks was different from everybody else's." From *Surely You're Joking, Mr. Feynman* (W.W. Norton, New York, 1985).

11. *Reading wave functions.*

Part (a) of the figure shows the lowest eigenfunctions for the potential well shown in part (b). Show with horizontal lines on (a copy of) the energy diagram the approximate energies of these five states.

Note: These figures are traced from an early paper on the quantum-mechanical tunneling of an outer electron between the atoms of a diatomic molecule (F. Hund, 1927), as reproduced in *Physics Today*, August 2002, p. 45.

12. *Another wave function.*

Part (a) of the figure shows one of the energy eigenfunctions for the potential well shown in part (b).

(a) Which eigenfunction is it?

(b) Is the energy of this state above or below the top of the central plateau in the well?

(c) Sketch the ground-state and first-excited-state wave functions. In particular, get the curvatures of the wave functions in the various regions right.

13. *Half wells.*

The energy eigenvalues and normalized eigenfunctions for a potential energy $V(x)$ that is symmetric about $x = 0$ are E_1, E_2, E_3, ... and $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ... What are the eigenvalues and normalized eigenfunctions for

$$V_{1/2}(x) = \begin{cases} \infty & \text{for } x < 0 \\ V(x) & \text{for } x > 0 \end{cases} ?$$

14. *The deuteron.*

The nuclear force, which binds protons and neutrons (nucleons) together into nuclei, is very strong but of very short range. The only bound state of *two* nucleons is the deuteron. The constituent proton and neutron each have a mass of about 939 MeV/c^2, and the binding energy is 2.23 MeV. Model the deuteron with the spherical well

$$V(r) = \begin{cases} -V_0 & \text{for } r < R \\ 0 & \text{for } r > R . \end{cases}$$

Let $R = 2$ fm $= 2 \times 10^{-15}$ m.

(a) What limiting value of V_0 would make impossible any bound state? Hint: See the preceding problem, and don't forget to use the reduced mass.

(b) What is the value of V_0 for the deuteron?

15. *Simplest solutions of eigenvalue equations.*

Finding the full set of solutions of an eigenvalue equation may be a formidible task, but finding the simplest one or two solutions, which are the most important ones, is sometimes trivial. Always take a minute to look.

(a) Find *by inspection* (that is, in your head) two linearly independent eigenfunctions and the corresponding eigenvalues ϵ of this equation for $h(x)$:

$$-h'' + 2xh' + h = \epsilon h .$$

This equation will appear in Chap. 5, on the harmonic oscillator.

(b) Find by inspection the simplest eigenfunction and the corresponding eigenvalue λ of this equation for $P(\theta)$:

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) = \lambda P .$$

One of $\sin\theta$ and $\cos\theta$ is another eigenfunction. Which one, and what is its λ? This equation will appear in Chap. 7, on angular momentum.

16. *Dimensional analysis.*

(a) Find the only way to construct a length from the parameters in the Schrödinger equation for the harmonic oscillator. Compare the result with the classical amplitude of oscillation when the energy is $\hbar\omega/2$.

(b) Find the only way to construct a length from the parameters in the Schrödinger equation for the hydrogen atom. Compare the result with the Bohr radius.

(c) How would you expect the characteristic length of each system to vary with its quantum number n?

17. *A bouncing particle.*

(a) Construct quantities having the dimensions of energy and of length when the potential energy is $V(z) = mgz$ for $z > 0$ and $V(z) = \infty$ for $z < 0$.

(b) An electron bounces on a horizontal surface. In its lowest energy states, the electron stays near the surface, held there by gravity. Show that the minimum thickness of the layer in which the electron is likely to be found is about 1 mm. Why is this so large?

Note: Experiments have been done on very low-energy ("ultracold") bouncing neutrons.

18. *Energy levels for $V(x) = bx^4$.*

Use the method of fitting wavelengths in a well to show that the energy eigenvalues for $V(x) = bx^4$ are approximately

$$E_n \approx \left(3\sqrt{\frac{\pi}{2} \frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})}} \right)^{4/3} \left(\frac{\left(n - \frac{1}{2}\right) \hbar\, b^{1/4}}{\sqrt{m}} \right)^{4/3} = 1.3765 \left(\frac{\left(n - \frac{1}{2}\right) \hbar\, b^{1/4}}{\sqrt{m}} \right)^{4/3}.$$

Here Γ is the gamma function, and $n = 1, 2, \ldots$ All needed mathematics can be found in the reference given in the "Advice to Students." Note that a dimensional analysis would give the dimensional factor here as well as the approximate dependence on n. Fitting wavelengths replaces n with $n - 1/2$ and gives the approximate numerical factor 1.3765.

The true values of E_n for $n = 1, 3,$ and 5, in units of $(\hbar b^{1/4}/\sqrt{m})^{4/3}$, are 0.668, 4.697, and 10.24. Show that the approximate equation is 18% off for $n = 1$ but is already within 1% for $n = 3$.

The remaining Problems approximate finite potential wells with infinite square wells. They also invoke the Pauli exclusion principle, which we shall eventually discuss, but which is probably familiar from a course on chemistry or modern physics, in which it is used to explain the periodicity of the elements. The principle states that no more than two electrons can go in a given spatial quantum state in a well. Thus in a one-, two-, or three-dimensional well, no more than two electrons can have the same quantum number(s) n, or (n_x, n_y), or (n_x, n_y, n_z). Problems 21 and 22 follow on Problem 20.

19. *Absorption frequencies of certain molecules.*

Certain simple hydrocarbons consist of a linear chain of an even number $N = 4, 6, 8, \ldots$ of carbon atoms, with hydrogen atoms attached as shown schematically for the simplest of them, butadiene. They also have N "π electrons," electrons that have free run of the length of the chain (ask a chemist).

Model the chain as a one-dimensional infinite square well of length $L = Nd$, where $d = 1.4 \times 10^{-10}$ m is the length per carbon atom. (The chain extends a distance $d/2$ beyond the end carbon atoms.) According to the Pauli principle, the ground state for butadiene, for example, has got its four π electrons, two each in the $n = 1$ and 2 levels of the well.
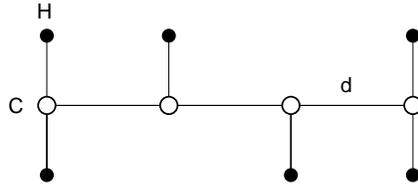
Find the lowest excitation energies (in eV) and the corresponding wavelengths of the absorbed light for $N = 4$, 6, 8, 10, and 12. In what part of the electromagnetic spectrum are each of these wavelengths? When the wavelength is in the visible part of the spectrum, the color of a molecule is complementary to the color of the absorbed light.
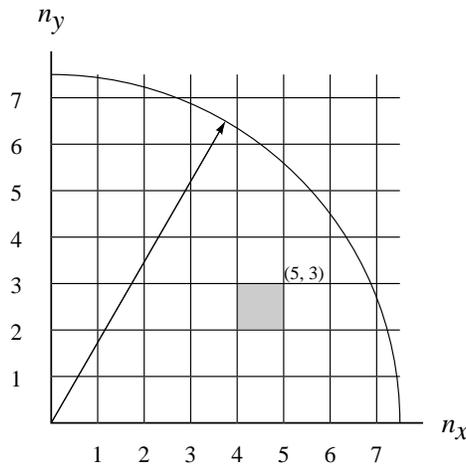
20. *Electrons in a box.*

In a block of metal such as copper, there is about one free electron per atom. These electrons move about freely through the background of the positive ions like the molecules of a gas in a box, the walls of which are the boundaries of the block. At normal temperatures, the electrons nearly all lie in the lowest states possible consistent with the Pauli principle; the electrons are then said to be degenerate.

In a two-dimensional square box of side L, the energy levels are

$$E_{n_x n_y} = (n_x^2 + n_y^2) \frac{\pi^2 \hbar^2}{2mL^2} ,$$

where n_x and $n_y = 1, 2, \ldots$ We may associate each pair of quantum numbers (n_x, n_y) with a point and with a square on a grid, as shown in the figure.

(a) Show that the number of different (n_x, n_y) states having $n_x^2 + n_y^2 \le n_0^2$, where n_0 is a very large number, is $\pi n_0^2/4$.

(b) According to the Pauli principle, there can be no more than two electrons in a given (n_x, n_y) state. If there are a large number N of electrons in this box in the lowest states possible, show that the energy of the "top" electron—the "Fermi energy" E_F—is

$$E_F = \frac{2\pi N}{A} \frac{\hbar^2}{2m} ,$$

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where $A = L^2$ is the area of the box.

(c) Show that the average energy of an electron in this lowest state is $\overline{E} = E_F/2$.

(d) Three dimensions should now be easy: For a cube of side L and volume V, show that the number of different (n_x, n_y, n_z) states having $n_x^2 + n_y^2 + n_z^2 \leq n_0^2$, where n_0 is a large number, is $\pi n_0^3/6$. Show that here

$$E_F = \left(\frac{3\pi^2 N}{V}\right)^{2/3} \frac{\hbar^2}{2m} \quad \text{and} \quad \overline{E} = \frac{3}{5}E_F \ .$$

Thus the *total* energy of a completely degenerate electron gas is $E_e = \frac{3}{5}NE_F$. Note that E_F, and thus also E_e, increase as the number density N/V increases.

21. *The free-electron gas in copper.*

The atomic number of copper is 29, its atomic mass is 63.5 g/mol, and its density is 8.96. There is one free electron per atom. Find the Fermi energy E_F and the corresponding "Fermi temperature" T_F, where $E_F = kT_F$, and $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant.

A puzzle before the discovery of quantum mechanics was why the gas of free electrons contributes little to the heat capacity of a metal. On classical principles (the equipartition theorem), the average energy per free electron ought to be $\frac{3}{2}kT$, and the gas of them ought to contribute an amount $\frac{3}{2}R$ to the molar heat capacity, where $R = N_A k$ is the ideal gas constant. The quantum answer to the puzzle is that at ordinary temperatures nearly all the electrons are in the lowest quantum states possible, and thus only the small fraction of them near the top of the "Fermi sea" can be easily excited—somewhat as only the water molecules near the surface of an actual sea can evaporate. The high Fermi temperature indicates that, on a scale of kT for normal temperatures, the Fermi sea is deep. Thus most of the free electrons indeed lie far below the surface and have no way to absorb thermal energies—all nearby states are already occupied.

22. *Radius of a white-dwarf star.*

Many stars end up as white dwarfs. When fuel is exhausted, a star cools down and contracts under gravity; it is prevented from collapse only because squeezing the now highly degenerate electrons into a smaller volume would increase the total energy E_e of the electron gas more than it would decrease the gravitational potential energy E_g. If we model the star as a uniformly dense sphere, then E_g is

$$E_g = -\frac{3}{5}\frac{GM^2}{R} \ ,$$

where G is Newton's constant and M and R are the mass and radius of the star.

(a) Find the radius R that minimizes $E_e + E_g$. The mass of the star comes almost entirely from nucleons (protons and neutrons), each of mass μ, and there are about equal numbers of electrons, protons, and neutrons. All the electrons are free. Write R in terms of m, μ, and M. Is there anything surprising about the dependence of R on M?

(b) Evaluate R for $M = 2.0 \times 10^{30}$ kg, the mass of the Sun. Data: $m = 9.1 \times 10^{-31}$ kg, $\mu = 1.7 \times 10^{-27}$ kg, $G = 6.7 \times 10^{-11}$ m^3 kg^{-1} s^{-2}. Compare the density of this white dwarf with the density of nuclei, about 2×10^{17} kg/m^3.

FIGURE CAPTIONS

Fig. 1. The infinite square well.

Fig. 2. (a) The lowest energy levels E_n and eigenfunctions $\psi_n(x)$ of the infinite square well. The energy lines are used as x axes to draw the corresponding eigenfunctions. (b) The lowest probability densities $|\psi_n(x)|^2$.

Fig. 3. The finite square well.

Fig. 4. (a) The solutions of $x = x^2$ are the values of x at the crossings of x and x^2. (b) They are also the values of x at the crossings of $x - x^2$ with the x axis.

Fig. 5. The solutions of $\tan\theta = (\theta_0^2/\theta^2 - 1)^{1/2}$ and $\tan(\theta + \pi/2) = (\theta_0^2/\theta^2 - 1)^{1/2}$ are the values of θ at the crossings of the curves. Here $(\theta_0^2/\theta^2 - 1)^{1/2}$ is drawn for the three values $\theta_0 = 1$, 4, and 9.

Fig. 6. The energy levels and eigenfunctions of the finite square well when $\theta_0 = 4$.

Fig. 7. (a) A very narrow, very deep square well. (b) The wave function for the only bound state of this well.

Fig. 8. Two sequences of functions that grow ever taller and narrower while the areas under the curves remain constant at unity.

Fig. 9. Spherical coordinates.

Fig. 10. Potential energies for (a) the harmonic oscillator, and (b) the hydrogen atom. Also shown are the ground-state energies and wave functions.

Fig. 11. The lowest energy wave functions for the infinite square well and for the harmonic oscillator.

Fig. 12. The area under the half circle is $\pi/2$.