

## The Schrödinger Equation in One Dimension

### Introduction

We have defined a complex wave function  $\Psi(x, t)$  for a particle and interpreted it such that  $|\Psi(x, t)|^2 dx$  gives the probability that the particle is at position  $x$  (within a region of length  $dx$ ) at time  $t$ . How does one solve for this wave function? Presumably, it obeys some kind of wave equation similar to the wave equation that describes classical waves (tension waves, pressure wave, electromagnetic waves). The classical wave equation, which is a differential equation, can be solved subject to conditions imposed by the particular system being studied. For example, the equation describing the waves generated by a plucked guitar string must be solved subject to the condition that the ends of the string are fixed. Such conditions are called *boundary conditions*, and the solutions of the wave equation must be consistent with them. These solutions give one a complete description of the dynamical behavior of the wave disturbance in the medium.

For a single, classical particle, one solves Newton's second law  $\vec{F} = m\vec{a}$  (which is also a differential equation) to find the dynamical behavior of the particle. Newton's second law is solved subject to boundary conditions (e.g., initial position and velocity) and the solutions  $x(t)$  and  $v(t)$  (one dimensional) give all the information about the dynamics of the particle for all time. Our quantum wave equation will play the same role in quantum mechanics as Newton's second law does in classical mechanics. It will represent the fundamental equation of motion of a matter wave, which when solved subject to boundary conditions, will give us the wave function  $\Psi(\vec{r}, t)$ .  $\Psi(\vec{r}, t)$  provides a complete statistical description of the dynamics of the particle in terms of average values for the dynamical quantities such as energy, momentum and position.<sup>1</sup>

Like Newton's second law, our quantum wave equation cannot be derived. It must be postulated and then shown to be consistent with experiment. What are some of the properties that the quantum wave equation should have?

(1) Linear, homogeneous differential equation. This ensures that the principle of superposition is valid, i.e., if  $\Psi_1$  is a solution and  $\Psi_2$  is a solution, then  $\Psi_1 + \Psi_2$  is also a solution. We saw that we can construct a wave packet from a superposition of pure sinusoidal waves. If the elementary waves are solutions to the quantum wave equation, then superposition ensures that the wave packet will be a solution also.

(2) It must be consistent with the de Broglie-Einstein relations. Thus, total energy  $E = hf = \hbar\omega$ . Momentum  $p$  of particle is given by  $p = h/\lambda = \hbar k$ .

(3) It must be consistent with the conservation of energy, which we expect to remain valid in quantum mechanics. Thus,  $K + U = E$ , where  $K$  is kinetic energy,  $U$  is potential energy, and  $E$  is total energy, which is conserved.

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<sup>1</sup> Do flow chart: Equation of motion+B.C.  $\rightarrow \Psi(x, t) \rightarrow \langle p \rangle, \langle x \rangle, \langle E \rangle$

In this course, we shall deal exclusively with non-relativistic particles. Hence,  $K = p^2/2m$ , and  $E$  represents the total mechanical energy (i.e., the sum of the kinetic and potential energies, *not* the relativistic mass-energy).

### Obtaining the Schrodinger Wave Equation

Let us now construct our wave equation by reverse engineering, i.e., we start with a wave function solution and work backwards to obtain the equation. We shall first postulate the wave function for the simplest conceivable system: a free particle. We saw that a pure sinusoidal wave can be represented by

$$\Psi_1(x, t) = A \cos(kx - \omega t). \quad (7.1)$$

This wave has a single precise value of wave number  $k$  (momentum  $\hbar k$ ) and single frequency  $\omega$  (energy  $\hbar\omega$ ). The momentum and energy do not change with time, which is consistent with the behavior of a free particle. Note also that the Heisenberg Uncertainty Principle tells us that since  $\Delta E = 0$ , the particle has the same precise energy for all time, and since  $\Delta p = 0$ , it has the same precise momentum in all space. [We know that  $\int_{-\infty}^{\infty} |\Psi_1|^2 dx \rightarrow \infty$  but we shall overlook this detail in our subsequent discussion.<sup>2</sup> All other properties of the wave are well-behaved, and the bad behavior at infinity will not affect the construction of our wave equation.]

Now, the harmonic wave

$$\Psi_2(x, t) = B \sin(kx - \omega t). \quad (7.2)$$

is just as good a representation of a free particle as Eq. (7.1).<sup>3</sup> So is the superposed solution

$$\Psi(x, t) = \Psi_1(x, t) + \Psi_2(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t). \quad (7.3)$$

### Mathematical Aside: Complex Numbers

We now find it convenient to introduce the complex exponential

$$e^{i\theta} = \cos\theta + i \sin\theta, \quad (7.4)$$

which is called Euler's formula. Eq. (7.4) can be proved by using the power series expansions for  $e^x$ ,  $\cos x$ , and  $\sin x$ .

Proof:

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \dots$$

$$e^{i\theta} = 1 + i\theta + \frac{1}{2!}(i\theta)^2 + \frac{1}{3!}(i\theta)^3 + \dots = 1 + i\theta - \frac{1}{2!}\theta^2 - \frac{1}{3!}i\theta^3 + \dots$$

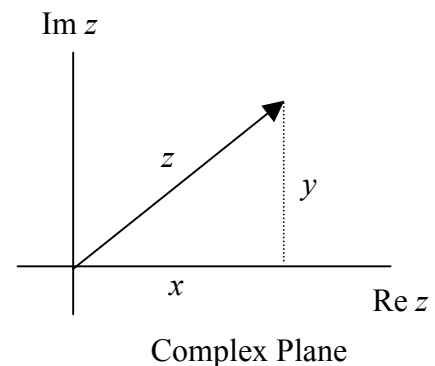
$$\cos\theta = 1 - \frac{1}{2!}\theta^2 + \frac{1}{4!}\theta^4 - \dots$$

$$\sin\theta = \theta - \frac{1}{3!}\theta^3 + \frac{1}{5!}\theta^5 - \dots$$

$$i \sin\theta = i\theta - \frac{1}{3!}i\theta^3 + \frac{1}{5!}i\theta^5 - \dots$$

$$\cos\theta + i \sin\theta = 1 + i\theta - \frac{1}{2!}\theta^2 - \frac{1}{3!}i\theta^3 + \dots = e^{i\theta}.$$

Consider complex number  $z = x + iy$



<sup>2</sup> We can always find appropriate solutions by superposition.

<sup>3</sup> Plot with *Mathematica*

The *complex conjugate* of  $z$  is  $z^* = x - iy$ . The complex conjugate of any complex number is obtained by replacing  $i$  by  $-i$  wherever it occurs. Note that  $|z|^2 = x^2 + y^2 = z^*z$ .

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We have argued that we can represent our free particle by the superposition  $\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$ . Since  $i$  is a constant, we can use the complex exponential instead of this sum:

$$\Psi(x, t) = Ce^{i(kx - \omega t)}. \quad (\text{Free particle traveling in } +x \text{ direction}) \quad (7.5)$$

Also,

$$\Psi(x, t) = De^{-i(kx + \omega t)}. \quad (\text{Free particle traveling in } -x \text{ direction}) \quad (7.6)$$

Let us take a snapshot of our wave function, i.e., we fix the time, and so we can concentrate on the spatial variation. Then our wave function Eq. (7.5) becomes

$$\psi(x) = Ce^{ikx}. \quad (7.7)$$

Now, from the de Broglie relation, the kinetic energy  $K = p^2/2m = \hbar^2 k^2/2m$ . From Eq. (7.7),

$$\frac{d^2\psi}{dx^2} = -k^2 Ce^{ikx} = -k^2 \psi.$$

Hence,

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = -\left(\frac{\hbar^2 k^2}{2m}\right) \psi = -K\psi.$$

Now, for a free particle,  $U = 0$ , so  $E = K$ . If  $U$  is not zero, then  $K = E - U$ . Substituting in the above equation yields

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = -(E - U)\psi,$$

or,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x). \quad (7.8)$$

Eq. (7.8) is the *Time-Independent Schrodinger Equation* (TISE) in one dimension.

Recall that we did not derive the TISE, we simple constructed a differential equation that is consistent with the free-particle wave function. Other equations could have been constructed, but it has been found that the TISE is the only one that is consistent with experimental results in a large number of different physical systems.

We have suppressed the time dependence. This may initially seen to be a significant limitation. In fact, the general form of the Schrodinger Equation is known as the *Time-Dependent Schrodinger Equation* (TDSE):

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x, t)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}. \quad (7.9)$$

When the potential energy is independent of time (true for many interesting systems), wave functions satisfying the TDSE can always be written as (in 1 D)

$$\Psi(x, t) = \psi(x)e^{-i\omega t}, \quad (7.10)$$

where  $\psi(x)$  satisfies the TISE and  $\omega = E / \hbar$ . Note that the free particle wave function falls into this category ( $U = 0$ ):  $\Psi_{\text{fp}}(x, t) = C e^{i(kx - \omega t)} = \underbrace{C e^{ikx}}_{\psi(x)} e^{-i\omega t}$ .

Thus, in cases where  $U$  is not a function of  $t$ , one solves the TISE to find the appropriate function  $\Psi(x)$  and then the time-dependent wave functions  $\Psi(x, t)$  are obtained by tacking on the  $e^{-i\omega t}$  factor.

### Stationary States

The solutions  $\Psi(x, t)$  obtained when  $U$  is not a function of  $t$  correspond to states that have a definite energy  $E$ , which remains constant in time (consistent with the HUP). These wave functions are called *energy eigenfunctions* and the corresponding values of energy are the *energy eigenvalues*. Notice that the probability density for an energy eigenfunction is independent of time:

$$|\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t) = \psi^*(x)e^{i\omega t}\psi(x)e^{-i\omega t} = |\psi(x)|^2. \quad (7.11)$$

Thus, energy eigenfunctions are called *stationary states*. Note that it is essential that the time-dependent part of the wave function be a complex number; otherwise, the time dependence would not disappear when the square of the modulus of the wave function is calculated. Energy eigenfunctions play a very important role in quantum mechanics for several reasons. One reason is that energy is frequently measured in experiments and so the energy eigenvalues are experimentally accessible. A second reason is that all functions (well-behaved) can be expressed as linear combinations (i.e., a superposition) of energy eigenfunctions.

### Characteristics of the Wave Function and Boundary Conditions

For the rest of the chapter, we focus on the behavior of the solutions  $\psi(x)$  to the Time-Independent Schrodinger Equation. We shall consider only cases in the potential energy is independent of time; hence, the solution to the Time-Dependent Schrodinger Equation can be obtained simply by multiplying  $\psi(x)$  by the time-dependent exponential factor discussed above.

Acceptable solutions to the TISE must be continuous (well-behaved) everywhere, including at boundaries between regions of different potential energies. This ensures that the probability density  $|\psi(x)|^2$  is continuous. Also, the first derivative of  $\psi$  must be continuous at the boundaries provided that changes in potential energy are finite.<sup>4</sup> Finally,  $\psi$  must go to zero at infinity. We list the boundary conditions that must be satisfied by the energy eigenfunctions:

- 1)  $\psi$  is continuous across a boundary between two potential-energy functions.
- 2)  $d\psi/dx$  is continuous across a boundary at which the change in potential energy is finite.<sup>5</sup>
- 3)  $\psi$  should be zero at infinity. This ensures that  $\int_{\text{all space}} |\psi(x)|^2 dx$  is finite.

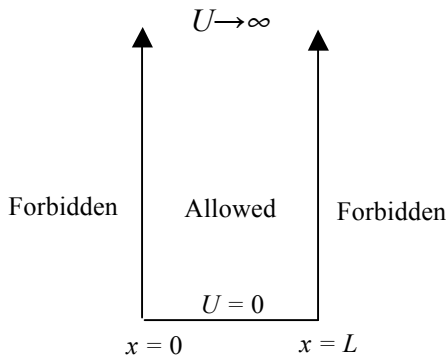
<sup>4</sup> Changes in  $\psi$  with distance, i.e., the slope, must be continuous.

<sup>5</sup> In quantum mechanics, potential energy functions are usually referred to as “potentials.”

Let us now apply the TISE to a simple system - a particle in an infinitely deep potential well.

### Particle in a One-Dimensional Rigid Box (Infinite Square Well)

The potential energy is infinitely large outside the region  $0 < x < L$ , and zero within that region. Hence, the particle is confined within the box. The TISE for the particle within the box is given by



$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x), \quad (7.12)$$

since  $U = 0$  inside box. Rewriting Eq. (7.12) yields

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0. \quad (7.13)$$

Let us set

$$k^2 = \frac{2mE}{\hbar^2}, \quad (7.14)$$

so that

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0. \quad (7.15)$$

The general solution to Eq. (7.15) is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \quad (7.16)$$

Note that there are two unknown constants because we have solved a 2<sup>nd</sup>-order differential equation by integrating twice.<sup>6</sup> Also, note that the general solution is a linear combination (superposition) of the two solutions  $Ae^{ikx}$  and  $Be^{-ikx}$ . These solutions should not surprise us because the particle is “free” inside the box. Outside the box, i.e.,  $x < 0$  and  $x > L$ ,  $\psi(x) = 0$ , as we shall see below.

Now we need to satisfy the boundary conditions. At  $x = 0$  and  $x = L$ ,  $\psi(x)$  must be zero because the particle cannot escape the box (it would require an infinite amount of energy).<sup>7</sup>  $\psi(0) = 0$  implies that  $A + B = 0$ , from Eq. (7.16). Thus,  $A = -B$ , and we can write

$$\psi(x) = A(e^{ikx} - e^{-ikx}). \quad (7.17)$$

But,

$$\sin kx = \frac{e^{ikx} - e^{-ikx}}{2i}. \quad (7.18)$$

Thus, we can rewrite our wave function as

$$\psi(x) = C \sin kx, \quad (7.19)$$

where  $C = 2iA$ .

<sup>6</sup> Two integrations give two constants.

<sup>7</sup> We have invoked the continuity of the wave function.

$\psi(L) = 0$  implies that

$$\begin{aligned} C \sin kL &= 0, \text{ i.e.,} \\ \sin kL &= 0, \end{aligned} \tag{7.20}$$

since  $C \neq 0$  (or there would be no wave function and no particle). This means that the values of  $k$  are restricted:

$$\begin{aligned} kL &= n\pi, \text{ i.e.,} \\ k &= \frac{n\pi}{L}, \quad n = 1, 2, 3, \dots \end{aligned} \tag{7.21}$$

Thus,  $k$  is quantized. Note that the de Broglie wavelength  $\lambda = 2\pi/k = 2L/n$ . This is the identical result obtained for standing waves on a string of length  $L$  that is fixed at both ends. Thus, the wave functions for a particle in a 1D box are standing waves. [Note:  $\sin kx = (e^{ikx} - e^{-ikx})/2i$  is the superposition of two traveling waves of equal and opposite momenta. (The time dependence is suppressed.)]

From Eq. (7.14), we have

$$E = \frac{\hbar^2 k^2}{2m}. \tag{7.22}$$

Substituting for  $k$  yields

$$E \equiv E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots \tag{7.23}$$

Thus, the energy of the particle is *quantized*. Note that the quantization arises from the satisfaction of the boundary conditions. The ground state energy<sup>8</sup> is given by setting  $n = 1$ :

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2}. \tag{7.24}$$

Notice that this ground-state energy is just the zero-point energy for this system, since  $U = 0$  inside the box. Note also that it is consistent with the zero-point energy derived from the uncertainty principle:  $K_{av} \geq \hbar^2/2mL^2$ .

We can write the general expression for the energy in terms of the ground state energy:

$$E_n = n^2 E_1. \tag{7.25}$$

Notice that the change in energy between consecutive levels increases as  $n$  increases.<sup>9</sup>

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<sup>8</sup> Lowest-energy state.

<sup>9</sup> Picture: Rohlf, p. 198

Since the total energy  $E$  of the particle in the well is always less than the potential energy everywhere outside the well ( $U = \infty$ ), the particle is trapped or *bound*. Thus, the energies given above are the *bound-state* energies<sup>10</sup> for a particle in a 1-D infinite square well.

To complete our solution, we need to evaluate the constant  $C$  in the wave function. In order to do this, we impose the condition that the wave function has to be *normalized*, i.e., the probability of finding the particle anywhere in space is 1. This means that

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1. \quad (7.26)$$

Since  $\psi_n(x) = 0$  outside of the box, then the relation above can be rewritten as

$$\int_0^L |\psi_n(x)|^2 dx = 1. \quad (7.27)$$

Now  $\psi_n(x) = C \sin(n\pi x/L)$  so substituting for  $\psi_n(x)$  yields

$$|C|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1, \quad (7.28)$$

or  $|C|^2 (L/2) = 1$ , i.e.,  $|C| = \sqrt{2/L}$ . We customarily choose  $C$  to be real, so we find

$$C = \sqrt{\frac{2}{L}}. \quad (7.29)$$

$C$  is called the *normalization constant*. Thus, the complete wave function is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}. \quad (7.30)$$

### Probability Densities

[Show graphs]

Note that the points where  $\psi_n(x) = 0$ , i.e., the *nodes*, the probability density is zero always.

Thus, if a measurement of the position of the particle is made, the particle will never be found at the nodes. However, at the points midway between the nodes where the wave amplitude is greatest (*antinodes*), the probability density is maximum, so the particle will most likely be found at those positions, when a single position measurement is made. If multiple measurements are made on a single particle or single measurements made on multiple identical particles, the particle will most frequently be found at the antinodes.

Given that the probability density, i.e., probability *per unit length* in one dimension, is  $|\psi(x)|^2$ , the probability of finding the particle between positions  $x_1$  and  $x_2$  is

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<sup>10</sup> There are an infinite number of bound state energies for the infinitely deep well.

$$P = \int_{x_1}^{x_2} |\psi(x)|^2 dx. \quad (7.31)$$

### Expectation Values

The probability density tells us how likely it is (per unit of length) for the particle to be found at a certain position when a single measurement is made, or equivalently, how frequently it will be found at that position when many identical measurements are made (with the system in the same state). If we made many such measurements of position, the average value or *expectation value* of the position is calculated as

$$\langle x \rangle = \int_{-\infty}^{\infty} |\psi(x)|^2 x dx. \quad (7.32)$$

Eq. (7.32) is strictly correct only if  $\psi(x)$  is normalized. The expectation value as defined in Eq. (7.32) is consistent with our notion of the average: we take each value of  $x$ , weight it with its frequency of occurrence, sum the weighted values of  $x$ , and then divide by the total number of measurements. Note that the frequency divided by the total number of measurements is just the probability of occurrence of that particular value of  $x$ .

Note also that the probability density for every state of the infinite square well is symmetric about the midpoint of the well. It follows that  $\langle x \rangle = L/2$  for all states (we prove this below).

Example: [Krane 1<sup>st</sup> ed. p. 127-128]

An electron is trapped in a one-dimensional region of length  $1.0 \times 10^{-10}$  m (a typical atomic diameter). (a) How much energy must be supplied to excite the electron from the ground state to the first excited state? (b) In the ground state, what is the probability of finding the electron in the region from  $x = 0.090 \times 10^{-10}$  m to  $0.110 \times 10^{-10}$  m? (c) In the first excited state, what is the probability of finding the electron between  $x = 0$  and  $x = 0.250 \times 10^{-10}$  m? (d) Show that the average value of  $x$  is  $L/2$  independent of quantum state.

Solution

$$(a) E_1 = \frac{\hbar^2 \pi^2}{2mL^2} = \frac{(1.05 \times 10^{-34} \text{ J} \cdot \text{s})^2 (3.14)^2}{2(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^{-10} \text{ m})^2} = 6.0 \times 10^{-18} \text{ J} = 37 \text{ eV}.$$

In the ground state, the energy is  $E_1$ . In the first excited state, the energy is  $4E_1$ . The difference, which is the energy that must be supplied, is  $3E_1$  or 111 eV.

(b) From Eq. (7.31),

$$\text{probability} = \int_{x_1}^{x_2} |\psi_1(x)|^2 dx = \frac{2}{L} \int_{0.090 \text{ \AA}}^{0.110 \text{ \AA}} \sin^2\left(\frac{\pi x}{L}\right) dx = \left( \frac{x}{L} - \frac{1}{2\pi} \sin \frac{2\pi x}{L} \right) \Bigg|_{0.090 \text{ \AA}}^{0.110 \text{ \AA}} = 0.0038 = 0.38\%.$$



Finite Square Well

$$(c) \text{ Probability} = \int_{x_1}^{x_2} |\psi_2(x)|^2 dx = \frac{2}{L} \int_0^{0.250A} \sin^2\left(\frac{2\pi x}{L}\right) dx = \left(\frac{x}{L} - \frac{1}{4\pi} \sin\frac{4\pi x}{L}\right) \Big|_0^{0.250A} = 0.25.$$

Rounded Well

(This result is of course what we would expect by inspection of the graph of  $\psi_2(x)$ . The interval from  $x = 0$  to  $x = L/4$  contains 25 percent of the total area under the  $|\psi_2(x)|^2$  curve.)

(d) We use Eq. (7.32). Since  $\psi_n(x)$  except for  $0 \leq x \leq L$ , we use 0 and  $L$  as the limits of integration.

$$\langle x \rangle = \int_0^L |\psi_n(x)|^2 x dx = \frac{2}{L} \int_0^L \sin^2(n\pi x/L) x dx.$$

This can be integrated by parts or found in integral tables; the result is

$$\langle x \rangle = \frac{L}{2}.$$

Note that as we had argued above, this result is independent of  $n$ . Thus, knowledge of the average position of the particle yields no information about its quantum state.

The greater the energy of a state, the more nodes the corresponding wave function has. The ground state has no nodes, the first excited state has one node, and so on. This is consistent with the de Broglie-Einstein relations because more nodes mean a shorter wavelength, and a shorter wavelength means greater momentum, which in turn implies greater kinetic energy. [See [www.falstad.com](http://www.falstad.com) for simulations.]

**Particle in a Non-Rigid Box (Finite Well)**

[Show Google image of “Quantum Corral.” This is a finite circular well.]

Very few interesting problems in quantum mechanics can be solved analytically, i.e., giving solutions that are standard functions. To solve realistic problems, the TISE has to be solved numerically. Before we look at the numerical method of solution, let us look at some general properties of the solutions to the TISE for a finite potential well.



We consider a single particle moving such that it has a potential energy, given by one of the functions given above.<sup>11</sup> For specificity, let us focus on the rounded well. Now,  $E = K + U(x)$ . Classically, if  $E < U_0$ , then the particle is *bound*. It can move between the turning points  $x_1$  and  $x_2$  where  $E = U(x)$  i.e.,  $K = 0$ . The particle is forbidden from entering the regions where  $E < U(x)$ . If  $E > U_0$ , then the motion is unbounded.

Let us examine the quantum mechanical situation. The TISE is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + [U(x) - E]\psi(x) = 0. \quad (7.33)$$

In the region inside the well where  $U(x) = 0$ , the acceptable solutions should be very similar to the standing wave solutions obtained for the infinite well. However, the boundary conditions in this case are different. Since  $U(x)$  is finite,  $\psi(x)$  is not zero at the boundary. To see why, let us look at the form of the solutions outside the well, i.e., in the classically forbidden region. In this region,  $U(x) > E$ . Let us assume for the moment that the well is almost square, so that  $U(x) \approx U_0$ . After some rearrangement, the TISE becomes

$$\frac{d^2\psi(x)}{dx^2} - \frac{2m}{\hbar^2}(U_0 - E)\psi(x) = 0. \quad (7.34)$$

For a fixed value of  $E$ ,  $\frac{2m}{\hbar^2}(U_0 - E)$  is a positive constant. Let us set

$$\alpha^2 = \frac{2m}{\hbar^2}(U_0 - E). \quad (7.35)$$

Eq. (7.34) becomes

$$\frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) = 0. \quad (7.36)$$

The solutions are *real* exponentials:

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x}. \quad (7.37)$$

Now as  $x \rightarrow +\infty$ ,  $e^{\alpha x}$  blows up. Thus, for an acceptable wave function,  $A = 0$ . Hence,  $\psi(x) = Be^{-\alpha x}$  ( $x > L$ ). Similarly, as  $x \rightarrow -\infty$ ,  $e^{-\alpha x}$  blows up so we must set  $B = 0$ . So,  $\psi(x) = Ae^{\alpha x}$  ( $x < 0$ ). Note that  $\psi(x) \neq 0$  in the classically forbidden region. However, the wave function decays exponentially with  $x$ .

The solutions inside and outside the well must match at the boundary for the wave function to be continuous. Also, the first derivative of  $\psi$  must be continuous. The satisfaction of all the boundary conditions will select the correct values of  $E$ , i.e., only for certain *quantized* values of  $E$  will the boundary conditions be satisfied.<sup>12</sup> Let us look more closely at how the boundary conditions and the quantization of  $E$  are related.

<sup>11</sup> Picture: p 100 Six Ideas

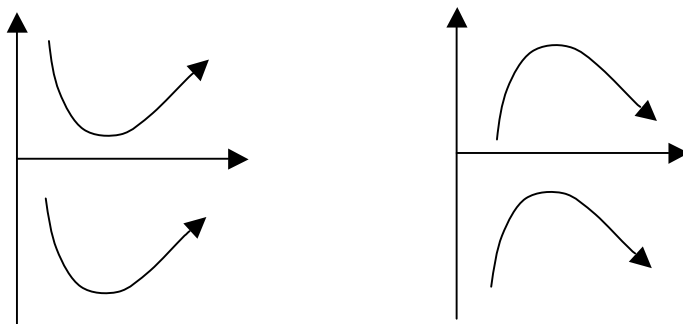
<sup>12</sup> For a *physically acceptable* solution.

$$\psi \quad \frac{d^2\psi}{dx^2} > 0$$

$$\psi \quad \frac{d^2\psi}{dx^2} < 0$$

### How the Energy Eigenfunctions Curve

We note that the second derivative of a function gives an indication of the *curvature* of the function.  $d\psi/dx$  is the slope and  $\frac{d}{dx}(d\psi/dx) = d^2\psi/dx^2$  is the slope of the slope, i.e., the rate of change of the slope. If  $d^2\psi/dx^2 > 0$ , the slope increases and the function curves upward. If  $d^2\psi/dx^2 < 0$ , then the slope decreases and the function curves downward.



Now the Schrödinger equation can be written as  $d^2\psi(x)/dx^2 - (2m/\hbar^2)[U(x) - E]\psi(x) = 0$ , i.e.,  $d^2\psi(x)/dx^2 = f(x)\psi(x)$ , where  $f(x) \equiv (2m/\hbar^2)[U(x) - E]$ . Now in the classically allowed region,  $f(x)$  is negative, since  $E > U(x)$ . Hence, the sign of  $d^2\psi/dx^2$  is always opposite that of  $\psi(x)$ . Thus, if  $\psi(x) > 0$ ,  $d^2\psi/dx^2 < 0$  and the function bends *towards* the  $x$ -axis (downward). Further, when  $\psi(x) < 0$ ,  $d^2\psi/dx^2 > 0$ ,  $\psi(x)$  curves upward, i.e., *toward* the  $x$ -axis. This means  $\psi(x)$  will be oscillatory.<sup>13</sup> If  $f(x)$  is large in magnitude (large kinetic energy<sup>14</sup>),  $\psi(x)$  oscillates rapidly (many nodes).

In contrast, if  $f(x)$  is positive<sup>15</sup>, then  $d^2\psi/dx^2$  and  $\psi(x)$  always have the same sign and so  $\psi(x)$  always *curves away* from the  $x$ -axis. The exponential solutions  $e^{\pm\alpha x}$  found previously have this property. Hence, to obtain a solution to the TISE that is physically acceptable for a bound state, the wave function and its slope at the boundary must be such that the wavelike solution inside the well matches a decaying exponential outside the well. This will occur only for particular values of energy  $E$ . For other values of energy, even slightly different from the allowed  $E$  values, matching at the boundaries will be satisfied for exponentials which curve completely away from the  $x$ -axis, i.e., the wave function blows up at  $-\infty$  or  $+\infty$ . Note that the wave functions that blow up at infinity are *mathematically* acceptable solutions, but not physically acceptable ones. Even for physically acceptable solutions, there is a finite probability that the particle is in the classically forbidden region.<sup>16</sup>

<sup>13</sup> or wavelike

<sup>14</sup>  $E - U = K$

<sup>15</sup> Classically forbidden region

<sup>16</sup> Pictures: Figs 8.15-17, 8.19 T&Z, p. 215 Six Ideas

## Summary of Rules for Sketching Wave Functions

From: "Six Ideas That Shaped Physics" by Thomas Moore.

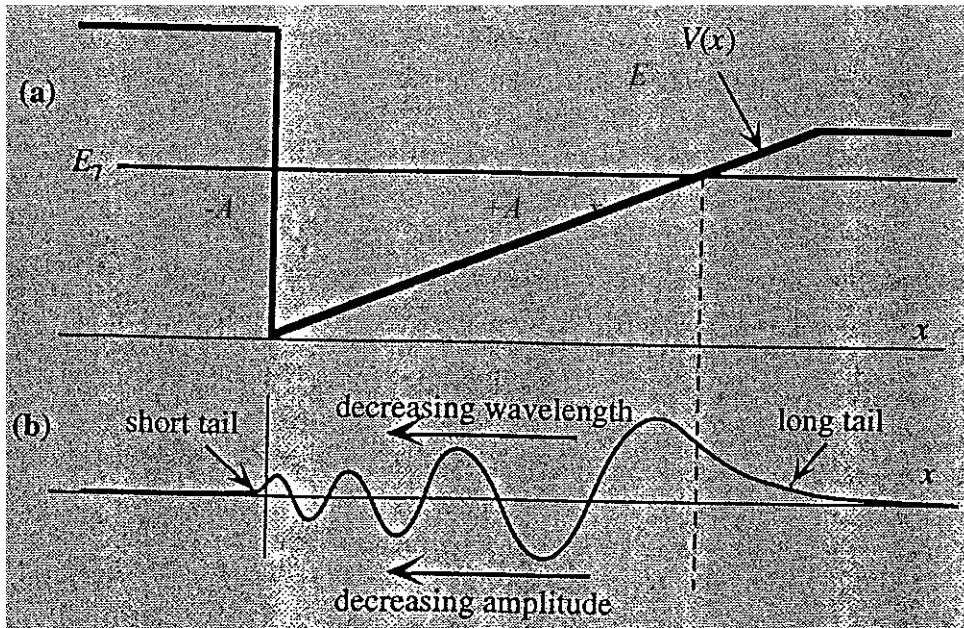
1. Solutions to the Schrodinger equation curve toward the  $x$ -axis in classically-allowed regions and away from the  $x$  axis in classically-forbidden regions. Implication: Solutions are wavelike in allowed regions and exponential-like in forbidden regions.
2. The curvature of solutions increases with  $|E - U(x)|$ . Note that  $|E - U(x)|$  corresponds to the distance between the energy line and the potential energy curve on a potential energy graph. Implications:
  - a. In classically-allowed regions, the *local wavelength* of the wavelike part of the solution gets shorter (i.e., there are more nodes) as  $|E - U(x)|$  increases.
  - b. In classically-forbidden regions, the length of any exponential-like tail gets shorter as  $|E - U(x)|$  increases.
3. The local amplitude of the wavelike part of a solutions decreases as the value of  $|E - U(x)|$  increases. The reason is that  $|E - U(x)|$  is the kinetic energy for wavelike solutions. Where  $|E - U(x)|$  is larger, the particle is moving faster and thus is less probable to be found than in a region where  $|E - U(x)|$  is smaller. Thus, the amplitude of  $\psi(x)$  decreases.
4. Solutions are always continuous and smooth (no kinks) as long as any discontinuous jumps in  $U(x)$  are finite.
5. Physically reasonable wave functions remain finite as  $|x| \rightarrow \infty$ .
  - a. The exponential-like parts of physically reasonable solutions for *bound* quantum particles must actually decrease to zero as  $|x| \rightarrow \infty$  in the classically forbidden regions that flank the central allowed region.
  - b. Only certain quantized energy values  $E_n$  give rise to physically reasonable solutions (that is, energy eigenfunctions) for bound quantum particles.
6. Energy eigenfunctions for bound quantum particles have an integer number of nodes in the central classically-allowed region: the more nodes the greater the corresponding energy. The energy eigenfunction corresponding to the quantum particle's lowest possible energy  $E_1$  has no nodes in its wavelike part. The eigenfunction corresponding to the quantum particle's second lowest energy  $E_2$  has one node and so on.

Example:

Sketch the energy eigenfunction corresponding to the seventh lowest possible energy for a quantum particle whose potential energy as a function of  $x$  is shown below.

Energy

$U(x)$



[From "Six Ideas That Shaped Physics"]

### The Harmonic Oscillator

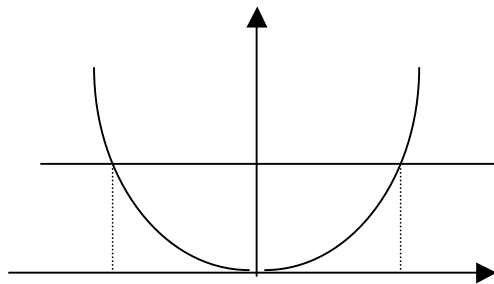
A harmonic oscillator is a system that executes simple harmonic motion (SHM). There are many examples of such systems in classical physics, e.g., the simple pendulum for small vibrational amplitudes<sup>17</sup>, and a spring-mass system.

In a spring-mass system, recall that the force exerted by the spring on the mass is given by Hooke's law:

$$F = -kx, \quad (7.38)$$

where  $k$  is the spring constant. The potential energy of the mass is given by

$$U = \frac{1}{2}kx^2. \quad (7.39)$$



<sup>17</sup> In this and many other systems, the motion is approx. SHM

Classically, the oscillator has turning points at  $x = \pm A$ , where  $E = U$ . (See figure above.) Quantum mechanically, we expect wave functions qualitatively similar to those of the finite square well, with non-zero exponentially decaying values in the classically forbidden region where  $E < U$ . Quantitative results can be obtained by solving the TISE:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} kx^2 \psi(x) = E\psi(x). \quad (7.40)$$

Classically, the oscillator has a single angular frequency given by  $\omega = \sqrt{k/m}$ , from which we obtain  $k = m\omega^2$ . Rewriting Eq. (7.40) in terms of  $\omega$  gives

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x). \quad (7.41)$$

It is not simple to obtain the solution to Eq. (7.41) so we shall just state the results. (The solution is discussed in more detail in a more advanced course.) The energy  $E$ , as expected, is quantized because of boundary conditions ( $\psi(x) \rightarrow 0$  as  $x \rightarrow \infty$ ). The result is

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \dots \quad (7.42)$$

Notes: (1) The ground state energy  $E_0 = \frac{1}{2} \hbar\omega$ , which is the zero-point energy. In solids, atoms execute (approximately) SHM. Thus, even at  $T = 0$  K, atoms have energy due to the zero-point energy. For helium, the zero-point energy is large enough to keep it from freezing at ordinary pressures even at  $T = 0$  K!

(2) The spacing between successive energy levels is constant.

#### Properties of Harmonic Oscillator Wave Functions

- Oscillatory in classically allowed region
- Exponentially decaying in classically forbidden regions
- Analytic solutions are Hermite functions

The great utility of the harmonic oscillator in physics is that many physical systems are oscillatory, and for small amplitude oscillations, SHM is an excellent approximation.<sup>18</sup>

#### **Quantum Mechanics Application: The Scanning Tunneling Microscope**

If the total energy of a quantum particle is less than the potential energy of a barrier of finite width, there is a non-zero probability that the particle can traverse the barrier even though  $E < U$  in the region of the barrier. This process is called *tunneling*. There is no classical analog. The phenomenon of quantum tunneling underlies the operation of the Scanning Tunneling Microscope (STM). The STM allows the imaging of conductive surfaces with atomic-scale resolution. The STM permits single atoms to be imaged routinely. Its inventors, G. Binnig and H. Rohrer, were awarded the Nobel Prize in 1986.

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<sup>18</sup> Pictures: p. 105 Six Ideas; p. 133 Krane; Table 8.1 p. 211 TZ&D