41.3 A Particle in a Rigid Box: Energies and Wave Functions

FIGURE 41.3 A particle in a rigid box of length L.

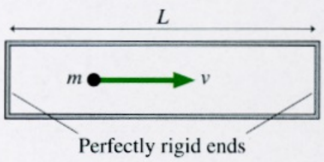


FIGURE 41.3 shows a particle of mass m confined in a rigid, one-dimensional box of length L. The walls of the box are assumed to be perfectly rigid, and the particle undergoes perfectly elastic reflections from the ends. This situation is known as a "particle in a box."

A classical particle bounces back and forth between the walls of the box. There are no restrictions on the speed or kinetic energy of a classical particle. In contrast, a wave-like particle characterized by a de Broglie wavelength sets up a standing wave as it reflects back and forth. In Chapters 25 and 39, we found that a standing de Broglie wave automatically leads to energy quantization. That is, only certain discrete energies are allowed. However, our hypothesis of a de Broglie standing wave was just a guess, with no real justification, because we had no theory about how a wave-like particle ought to behave.

20.2 ActivPhysics ONLINE

We will now revisit this problem from the new perspective of quantum mechanics. The basic questions we want to answer in this, and any quantum-mechanics problem, are:

- What are the allowed energies of the particle?
- What is the wave function associated with each energy?
- In which part of the box is the particle most likely to be found?

We can use Problem-Solving Strategy 41.1 to answer these questions.

Model: Identify a Potential-Energy Function

By a *rigid box* we mean a box whose walls are so sturdy that they can confine a particle no matter how fast the particle moves. Furthermore, the walls are so stiff that they do not flex or give as the particle bounces. No real container has these attributes, so the rigid box is a *model* of a situation in which a particle is extremely well confined. Our first task is to characterize the rigid box in terms of a potential-energy function.

Let's establish a coordinate axis with the boundaries of the box at $x = 0$ and $x = L$. The rigid box has three important characteristics:

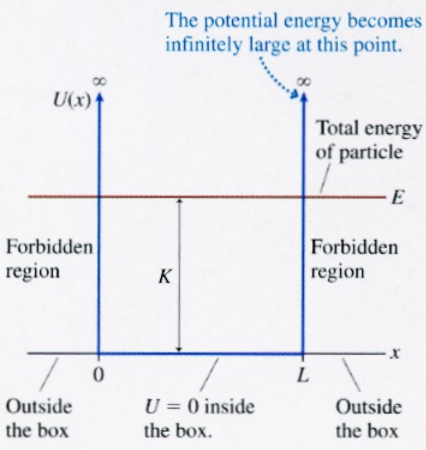
1. The particle can move freely between 0 and L at constant speed and thus with constant kinetic energy.
2. No matter how much kinetic energy the particle has, its turning points are at $x = 0$ and $x = L$.
3. The regions $x < 0$ and $x > L$ are forbidden. The particle cannot leave the box.

A potential-energy function that describes the particle in this situation is

$$U_{\text{rigid box}}(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & x < 0 \quad \text{or} \quad x > L \end{cases} \tag{41.9}$$

Inside the box, the particle has only kinetic energy. The infinitely high potential-energy barriers prevent the particle from ever having $x < 0$ or $x > L$ no matter how much kinetic energy it may have. It is this potential energy for which we want to solve the Schrödinger equation.

FIGURE 41.4 The energy diagram of a particle in a rigid box of length L.



Visualize: Establish Boundary Conditions

FIGURE 41.4 is the energy diagram of a particle in the rigid box. You can see that $U = 0$ and $E = K$ inside the box. The upward arrows labeled ∞ indicate that the potential energy becomes infinitely large at the walls of the box ($x = 0$ and $x = L$).

NOTE ► Figure 41.4 is not a picture of the box. It is a graphical representation of the particle's kinetic and potential energy. ◄

Next, we need to establish the boundary conditions that the solution must satisfy. Because it is physically impossible for the particle to be outside the box, we require

$$\psi(x) = 0 \quad \text{for } x < 0 \quad \text{or} \quad x > L \tag{41.10}$$

That is, there is zero probability of finding the particle outside the box.

Furthermore, the wave function must be a *continuous* function. That is, there can be no break in the wave function at any point. Because the solution is zero everywhere outside the box, continuity requires that the wave function inside the box obey the two conditions

$$\psi(\text{at } x = 0) = 0 \quad \text{and} \quad \psi(\text{at } x = L) = 0 \tag{41.11}$$

In other words, as **FIGURE 41.5** shows, the oscillating wave function inside the box must go to zero at the boundaries to be continuous with the wave function outside the box. This requirement of the wave function is equivalent to saying that a standing wave on a string must have a node at the ends.

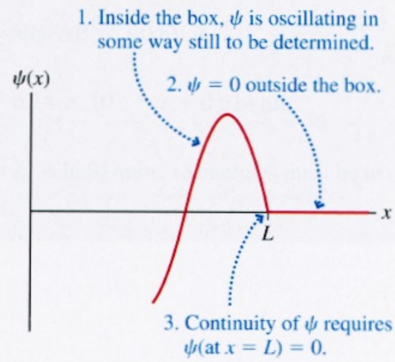


FIGURE 41.5 Applying boundary conditions to the wave function of a particle in a box.

Solve I: Find the Wave Functions

At all points *inside* the box the potential energy is $U(x) = 0$. Thus the Schrödinger equation inside the box is

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \tag{41.12}$$

There are two aspects to solving this equation:

1. For what values of E does Equation 41.12 have physically meaningful solutions?
2. What are the solutions $\psi(x)$ for those values of E?

To begin, let's simplify the notation by defining $\beta^2 = 2mE/\hbar^2$. Equation 41.12 is then

$$\frac{d^2\psi}{dx^2} = -\beta^2\psi(x) \tag{41.13}$$

We're going to solve this differential equation by guessing! Can you think of any functions whose second derivative is a *negative* constant times the function itself? Two such functions are

$$\psi_1(x) = \sin\beta x \quad \text{and} \quad \psi_2(x) = \cos\beta x \tag{41.14}$$

Both are solutions to Equation 41.13 because

$$\frac{d^2\psi_1}{dx^2} = \frac{d^2}{dx^2}(\sin\beta x) = -\beta^2\sin\beta x = -\beta^2\psi_1(x)$$

$$\frac{d^2\psi_2}{dx^2} = \frac{d^2}{dx^2}(\cos\beta x) = -\beta^2\cos\beta x = -\beta^2\psi_2(x)$$

Furthermore, these are *independent* solutions because $\psi_2(x)$ is not a multiple or a rearrangement of $\psi_1(x)$. Consequently, according to Equation 41.8, the general solution to the Schrödinger equation for the particle in a rigid box is

$$\psi(x) = A\sin\beta x + B\cos\beta x \tag{41.15}$$

where

$$\beta = \frac{\sqrt{2mE}}{\hbar} \tag{41.16}$$

The constants A and B must be determined by using the boundary conditions of Equation 41.11. First, the wave function must go to zero at $x = 0$. That is,

$$\psi(\text{at } x = 0) = A \cdot 0 + B \cdot 1 = 0 \tag{41.17}$$

This boundary condition can be satisfied only if $B = 0$. The $\cos\beta x$ term may satisfy the differential equation in a mathematical sense, but it is not a physically meaningful solution for this problem because it does not satisfy the boundary conditions. Thus the physically meaningful solution is

$$\psi(x) = A\sin\beta x$$

The wave function must also go to zero at $x = L$. That is,

$$\psi(\text{at } x = L) = A\sin\beta L = 0 \tag{41.18}$$

This condition could be satisfied by $A = 0$, but then we wouldn't have a wave function at all! Fortunately, that isn't necessary. This boundary condition is also satisfied if $\sin\beta L = 0$, which requires

$$\beta L = n\pi \quad \text{or} \quad \beta = \frac{n\pi}{L} \qquad n = 1, 2, 3, \ldots \tag{41.19}$$

Notice that n starts with 1, not 0. The value $n = 0$ would give $\beta = 0$ and make $\psi = 0$ at all points, a physically meaningless solution.

Thus the solutions to the Schrödinger equation for a particle in a rigid box are

$$\psi_n(x) = A\sin\beta_n x = A\sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \ldots \tag{41.20}$$

We've found a whole *family* of solutions, each corresponding to a different value of the integer n. These wave functions represent the stationary states of the particle in the box. The constant A remains to be determined.

Solve II: Find the Allowed Energies

Equation 41.16 defined β. Equation 41.19 then placed restrictions on the possible values of β:

$$\beta_n = \frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{L} \qquad n = 1, 2, 3, \ldots \tag{41.21}$$

where the value of β and the energy associated with the integer n have been labeled β_n and E_n. We can solve for E_n by squaring both sides:

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} = n^2\frac{h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots \tag{41.22}$$

where, in the last step, we used the definition $\hbar = h/2\pi$. **For a particle in a box, these energies are the only values of E for which there are physically meaningful solutions to the Schrödinger equation.**

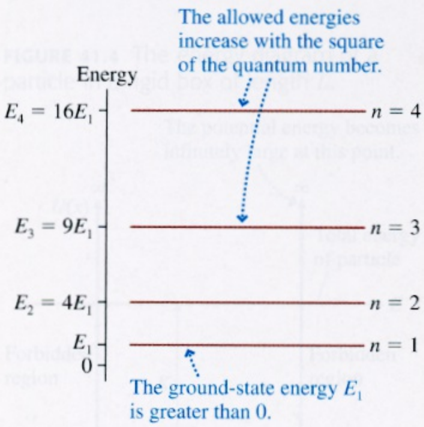
We have found that the particle's energy is quantized! It is useful to write the energies of the stationary states as

$$E_n = n^2E_1 \tag{41.23}$$

where E_n is the energy of the stationary state with *quantum number n*. The smallest possible energy $E_1 = h^2/8mL^2$ is the energy of the $n = 1$ *ground state*. These allowed energies are shown in the *energy-level diagram* of FIGURE 41.6. Recall, from Chapter 39, that an energy-level diagram is not a graph (the horizontal axis doesn't represent anything) but a "ladder" of allowed energies.

Equation 41.22 is identical to the energies we found in Chapter 39 by requiring the de Broglie wave of a particle in a box to form a standing wave. Only now we have a theory that tells not only the energies but also the wave functions.

FIGURE 41.6 The energy-level diagram for a particle in a box.



EXAMPLE 41.1 An electron in a box

An electron is confined to a rigid box. What is the length of the box if the energy difference between the first and second states is 3.0 eV?

MODEL Model the electron as a particle in a rigid one-dimensional box of length L.

SOLVE The first two quantum states, with $n = 1$ and $n = 2$, have energies E_1 and $E_2 = 4E_1$. Thus the energy difference between the states is

$$\Delta E = 3E_1 = \frac{3h^2}{8mL^2} = 3.0 \text{ eV} = 4.8 \times 10^{-19} \text{ J}$$

The length of the box for which $\Delta E = 3.0$ eV is

$$L = \sqrt{\frac{3h^2}{8m\Delta E}} = 6.14 \times 10^{-10} \text{ m} = 0.614 \text{ nm}$$

ASSESS The expression for E_1 is in SI units, so energies must be in J, not eV.

Solve III: Normalize the Wave Functions

We can determine the constant A by requiring the wave functions to be normalized. The normalization condition, which we found in Chapter 40, is

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

This is the mathematical statement that the particle must be *somewhere* on the x-axis. The integration limits extend to $\pm\infty$, but here we need to integrate only from 0 to L because the wave function is zero outside the box. Thus

$$\int_0^L |\psi_n(x)|^2 dx = A_n^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \tag{41.24}$$

or

$$A_n = \left[\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx\right]^{-1/2} \tag{41.25}$$

We placed a subscript n on A_n because it is possible that the normalization constant is different for each wave function in the family. This is a standard integral. We will leave it as a homework problem for you to show that its value, for any n, is

$$A_n = \sqrt{\frac{2}{L}} \qquad n = 1, 2, 3, \ldots \tag{41.26}$$

We now have a complete solution to the problem. The normalized wave function for the particle in quantum state n is

$$\psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right) & 0 \le x \le L \\ 0 & x < 0 \text{ and } x > L \end{cases} \tag{41.27}$$

41.4 A Particle in a Rigid Box: Interpreting the Solution

Our solution to the quantum-mechanical problem of a particle in a box tells us that:

1. The particle must have energy $E_n = n^2 E_1$, where $n = 1, 2, 3, \ldots$ is the quantum number. $E_1 = h^2/8mL^2$ is the energy of the $n = 1$ ground state.
2. The wave function for a particle in quantum state n is

$$\psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right) & 0 \le x \le L \\ 0 & x < 0 \text{ and } x > L \end{cases}$$

These are the stationary states of the system.