7.5: The Quantum Particle in a Box

Learning Objectives

By the end of this section, you will be able to:

- Describe how to set up a boundary-value problem for the stationary Schrödinger equation
- Explain why the energy of a quantum particle in a box is quantized
- Describe the physical meaning of stationary solutions to Schrödinger's equation and the connection of these solutions with time-dependent quantum states
- Explain the physical meaning of Bohr's correspondence principle

In this section, we apply Schrödinger's equation to a particle bound to a one-dimensional box. This special case provides lessons for understanding quantum mechanics in more complex systems. The energy of the particle is quantized as a consequence of a standing wave condition inside the box.

Consider a particle of mass m that is allowed to move only along the *x*-direction and its motion is confined to the region between hard and rigid walls located at $x = 0$ and at $x = L$ (Figure $7.5.1$). Between the walls, the particle moves freely. This physical situation is called the *infinite square well*, described by the potential energy function

$$U(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \; and \; x > L \end{cases} \tag{7.5.1}$$

Combining this equation with Schrödinger's time-independent wave equation gives

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x), \; for \, 0 \leq x \leq L \tag{7.5.2}$$

where E is the *total energy of the particle*. What types of solutions do we expect? The energy of the particle is a positive number, so if the value of the wavefunction is positive (right side of the equation), the curvature of the wavefunction is negative, or concave down (left side of the equation). Similarly, if the value of the wavefunction is negative (right side of the equation), the curvature of the wavefunction is positive or concave up (left side of equation). This condition is met by an oscillating wavefunction, such as a sine or cosine wave. Since these waves are confined to the box, we envision standing waves with fixed endpoints at $x = 0$ and $x = L$.

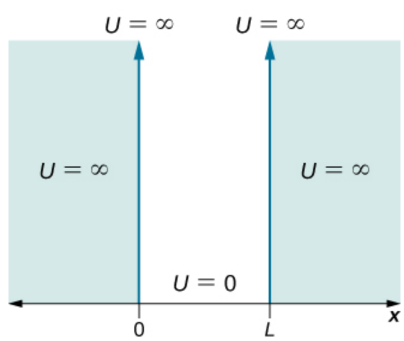

Figure $7.5.1$: The potential energy function that confines the particle in a one-dimensional box

Solutions $\psi(x)$ to this equation have a probabilistic interpretation. In particular, the square $|\psi(x)|^2$ represents the probability density of finding the particle at a particular location *x*. This function must be integrated to determine the probability of finding the particle in some interval of space. We are therefore looking for a normalizable solution that satisfies the following normalization condition:

$$\int_0^L dx|\psi(x)|^2 = 1. \tag{7.5.3}$$

The walls are rigid and impenetrable, which means that the particle is never found beyond the wall. Mathematically, this means that the solution must vanish at the walls:

$$\psi(0)=\psi(L)=0. \tag{7.5.4}$$

We expect oscillating solutions, so the most general solution to this equation is

$$\psi_k(x)=A_k\ \cos\ kx+B_k\ \sin\ kx \tag{7.5.5}$$

where k is the wave number, and A_k and B_k are constants. Applying the boundary condition expressed by Equation 7.5.3 gives

$$\psi_k(0)=A_k\ \cos(k\cdot 0)+B_k\ \sin(k\cdot 0)=A_k=0. \tag{7.5.6}$$

Because we have $A_k=0$, the solution must be

$$\psi_k(x)=B_k\ \sin\ kx. \tag{7.5.7}$$

If B_k is zero, then $\psi_k(x)=0$ for all values of x and the normalization condition (Equation 7.5.3) cannot be satisfied. Assuming $B_k\neq 0$, Equation 7.5.4 for $x=L$ then gives

$$0=B_k\ \sin(kL)\Rightarrow \sin(kL)=0\Rightarrow kL=n\pi,\ n=1,2,3,\ldots \tag{7.5.8}$$

We discard the $n=0$ solution because $\psi(x)$ for this quantum number would be zero everywhere—an un-normalizable and therefore unphysical solution. Substituting Equation 7.5.7 into Equation 7.5.2 gives

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(B_k\sin(kx))=E(B_k\sin(kx)). \tag{7.5.9}$$

Computing these derivatives leads to

$$E=E_k=\frac{\hbar^2k^2}{2m}. \tag{7.5.10}$$

According to de Broglie, $p=\hbar k$, so this expression implies that the total energy is equal to the kinetic energy, consistent with our assumption that the "particle moves freely." Combining the results of Equation 7.5.8 and 7.5.10 gives

$$E_n=n^2\frac{\pi^2\hbar^2}{2mL^2},\ n=1,2,3,\ldots \tag{7.5.11}$$

Strange!

Equation 7.5.11 argues that a particle bound to a one-dimensional box can only have certain discrete (quantized) values of energy. Further, the particle *cannot* have a zero kinetic energy—it is impossible for a particle bound to a box to be "at rest."

To evaluate the allowed wavefunctions that correspond to these energies, we must find the normalization constant B_n. We impose the normalization condition Equation 7.5.3 on the wavefunction

$$\psi_n(x)=B_n\ \sin\ \frac{n\pi x}{L} \tag{7.5.12}$$

We start with the normalization condition (Equation 7.5.3)

$$1 = \int_0^L dx |\psi_n(x)|^2 \tag{7.5.13}$$

$$= \int_0^L dx\, B_n^2 \sin^2 \frac{n\pi}{L} x \tag{7.5.14}$$

$$= B^2 n \int_0^2 dx\, \sin^2 \frac{n\pi}{L} x \tag{7.5.15}$$

$$= B_n^2 \frac{L}{2} \tag{7.5.16}$$

$$\Rightarrow B_n = \sqrt{\frac{2}{L}}. \tag{7.5.17}$$

Hence, the wavefunctions that correspond to the energy values given in Equation 7.5.11 are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L},\ n = 1, 2, 3, \ldots \tag{7.5.18}$$

For the lowest energy state or ground state energy, we have

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2},\ \psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right). \tag{7.5.19}$$

All other energy states can be expressed as

$$E_n = n^2 E_1,\ \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \tag{7.5.20}$$

The index n is called the **energy quantum number** or **principal quantum number**. The state for $n = 2$ is the first excited state, the state for $n = 3$ is the second excited state, and so on. The first three quantum states (for n = 1, 2, and 3) of a particle in a box are shown in Figure 7.5.2. The wavefunctions in Equation 7.5.20 are sometimes referred to as the "states of definite energy." Particles in these states are said to occupy **energy levels**, which are represented by the horizontal lines in Figure 7.5.2. Energy levels are analogous to rungs of a ladder that the particle can "climb" as it gains or loses energy.

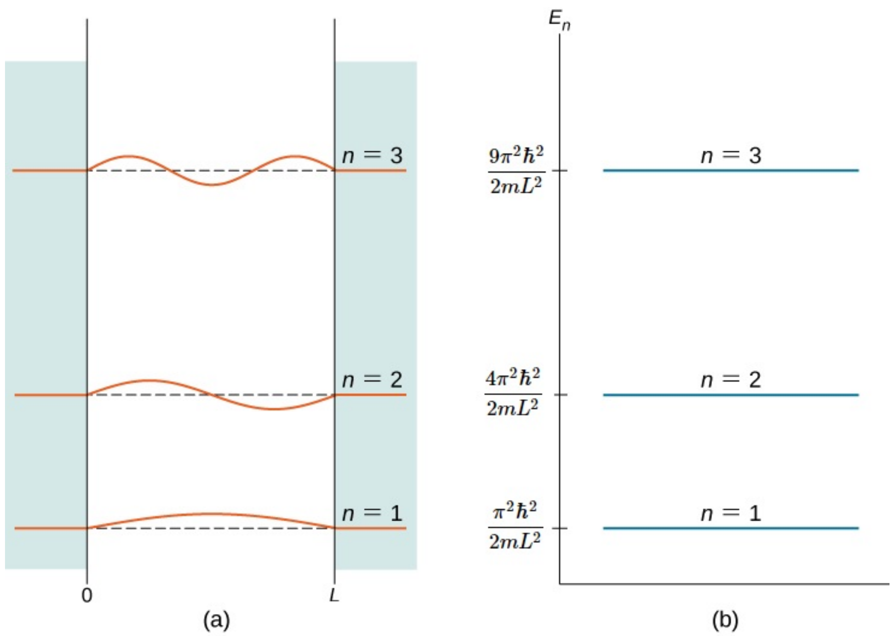

Figure 7.5.2: The first three quantum states of a quantum particle in a box for principal quantum numbers n = 1,2,and 3: (a) standing wave solutions and (b) allowed energy states.

Stationary States

The wavefunctions in Equation 7.5.20 are also called **stationary states** and **standing wave states**. These functions are "stationary," because their probability density functions, $|\Psi(x,t)|^2$, do not vary in time, and "standing waves" because their real and imaginary parts oscillate up and down like a standing wave—like a rope waving between two children on a playground. Stationary states are states of definite energy (Equation 7.5.20), but linear combinations of these states, such as $\psi(x) = a\psi_1 + b\psi_2$ (also solutions to Schrödinger's equation) are states of mixed energy.

Energy quantization is a consequence of the boundary conditions. If the particle is not confined to a box but wanders freely, the allowed energies are continuous. However, in this case, only certain energies ($E_1, 4E_1, 9E_1, \ldots$) are allowed. The energy difference between adjacent energy levels is given by

$$\Delta E_{n+1,n} = E_{n+1} - E_n = (n+1)^2 E_1 - n^2 E_1 = (2n+1)E_1. \tag{7.5.21}$$

Conservation of energy demands that if the energy of the system changes, the energy difference is carried in some other form of energy. For the special case of a charged particle confined to a small volume (for example, in an atom), energy changes are often carried away by photons. The frequencies of the emitted photons give us information about the energy differences (spacings) of the system and the volume of containment—the size of the "box" (Equation 7.5.19).

Example 7.5.1: A Simple Model of the Nucleus

Suppose a proton is confined to a box of width $L = 1.00 \times 10^{-14} m$ (a typical nuclear radius). What are the energies of the ground and the first excited states? If the proton makes a transition from the first excited state to the ground state, what are the energy and the frequency of the emitted photon?

Strategy

If we assume that the proton confined in the nucleus can be modeled as a quantum particle in a box, all we need to do is to use Equation 7.5.11 to find its energies E_1 and E_2. The mass of a proton is $m = 1.76 \times 10^{-27} kg$. The emitted photon carries away the energy difference $\Delta E = E_2 - E_1$. We can use the relation $E_f = hf$ to find its frequency *f*.

Solution

The ground state:

$$\begin{aligned} E_1 &= \frac{\pi^2\hbar^2}{2mL^2} \\ &= \frac{\pi^2(1.05\times10^{-34} J\cdot s)}{2(1.67\times10^{-27} kg)(1.00\times10^{-14} m)^2} \\ &= 3.28\times10^{-13} J \\ &= 2.05\, MeV \end{aligned}$$

The first excited state:

$$E_2 = 2^2 E_1 = 4(2.05\, MeV) = 8.20\, MeV. \tag{7.5.22}$$

The energy of the emitted photon is

$$E_f = \Delta E = E_2 - E_1 = 8.20\, MeV - 2.05\, MeV = 6.15\, MeV. \tag{7.5.23}$$

The frequency of the emitted photon is

$$f = \frac{E_f}{h} = \frac{6.15\, MeV}{4.14\times10^{-21} MeV\cdot s} = 1.49\times10^{21} Hz. \tag{7.5.24}$$

Significance

This is the typical frequency of a gamma ray emitted by a nucleus. The energy of this photon is about 10 million times greater than that of a visible light photon.

The expectation value of the position for a particle in a box is given by

$$\langle x\rangle = \int_0^L dx\, \psi_n^*(x) x \psi_n(x) = \int_0^L dx\, x|\psi_n^*(x)|^2 = \int_0^L dx\, x \frac{2}{L} sin^2\, \frac{n\pi x}{L} = \frac{L}{2}. \tag{7.5.25}$$

We can also find the expectation value of the momentum or average momentum of a large number of particles in a given state:

$$\langle p\rangle = \int_0^L dx \psi_n^*(x)\left[-i\hbar \frac{d}{dx}\psi_n(x)\right] \tag{7.5.26}$$

$$= -i\hbar \int_0^L dx \sqrt{\frac{2}{L}}\, \sin\, \frac{n\pi x}{L}\left[\frac{d}{dx}\sqrt{\frac{2}{L}}\, \sin\, \frac{n\pi x}{L}\right] \tag{7.5.27}$$

$$= -i\frac{2\hbar}{L}\int_0^L dx\, \sin\, \frac{n\pi x}{L}\left[\frac{n\pi}{L}\cos\, \frac{n\pi x}{L}\right] \tag{7.5.28}$$

$$= -i\frac{2n\pi\hbar}{L^2}\int_0^L dx \frac{1}{2}\sin\, \frac{2n\pi x}{L} \tag{7.5.29}$$

$$= -i\frac{n\pi\hbar}{L^2}\frac{L}{2n\pi}\int_0^{2\pi n} d\varphi\, \sin\, \varphi \tag{7.5.30}$$

$$= -i\frac{\hbar}{2L}\cdot 0 \tag{7.5.31}$$

$$= 0. \tag{7.5.32}$$

Thus, for a particle in a state of definite energy, the average position is in the middle of the box and the average momentum of the particle is zero—as it would also be for a classical particle. Note that while the minimum energy of a classical particle can be zero (the particle can be at rest in the middle of the box), the minimum energy of a quantum particle is nonzero and given by Equation 7.5.19. The average particle energy in the *nth* quantum state—its expectation value of energy—is

$$E_n = \langle E\rangle = n^2\frac{\pi^2\hbar^2}{2m}. \tag{7.5.33}$$

The result is not surprising because the standing wave state is a state of definite energy. Any energy measurement of this system must return a value equal to one of these allowed energies.

Our analysis of the quantum particle in a box would not be complete without discussing Bohr's correspondence principle. This principle states that for large quantum numbers, the laws of quantum physics must give identical results as the laws of classical physics. To illustrate how this principle works for a quantum particle in a box, we plot the probability density distribution

$$|\psi_n(x)|^2 = \frac{2}{L}sin^2(n\pi x/L) \tag{7.5.34}$$

for finding the particle around location x between the walls when the particle is in quantum state ψ_n. Figure $7.5.3$ shows these probability distributions for the ground state, for the first excited state, and for a highly excited state that corresponds to a large quantum number. We see from these plots that when a quantum particle is in the ground state, it is most likely to be found around the middle of the box, where the probability distribution has the largest value. This is not so when the particle is in the first excited state because now the probability distribution has the zero value in the middle of the box, so there is no chance of finding the particle there. When a quantum particle is in the first excited state, the probability distribution has two maxima, and the best chance of finding the particle is at positions close to the locations of these maxima. This quantum picture is unlike the classical picture.

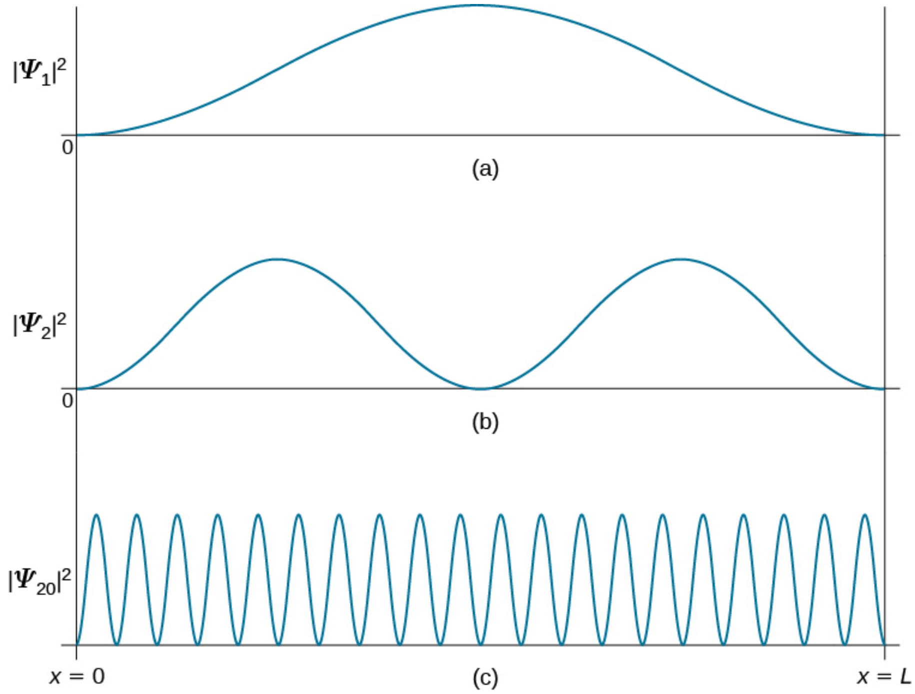

Figure 7.5.3: The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$.

The probability density of finding a classical particle between x and $x + \Delta x$ depends on how much time Δt the particle spends in this region. Assuming that its speed u is constant, this time is $\Delta t = \Delta x/u$, which is also constant for any location between the walls. Therefore, the probability density of finding the classical particle at x is uniform throughout the box, and there is no preferable location for finding a classical particle. This classical picture is matched in the limit of large quantum numbers. For example, when a quantum particle is in a highly excited state, shown in Figure 7.5.3, the probability density is characterized by rapid fluctuations and then the probability of finding the quantum particle in the interval Δx does not depend on where this interval is located between the walls.

Example 7.5.2: A Classical Particle in a Box

A small 0.40-kg cart is moving back and forth along an air track between two bumpers located 2.0 m apart. We assume no friction; collisions with the bumpers are perfectly elastic so that between the bumpers, the car maintains a constant speed of 0.50 m/s. Treating the cart as a quantum particle, estimate the value of the principal quantum number that corresponds to its classical energy.

Strategy

We find the kinetic energy K of the cart and its ground state energy E_1 as though it were a quantum particle. The energy of the cart is completely kinetic, so $K = n^2 E_1$ (Equation 7.5.20). Solving for n gives $n = (K/E_1)^{1/2}$.

Solution

The kinetic energy of the cart is

$$K = \frac{1}{2}mu^2 = \frac{1}{2}(0.40\,kg)(0.50\,m/s)^2 = 0.050\,J. \tag{7.5.35}$$

The ground state of the cart, treated as a quantum particle, is

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} = \frac{\pi^2(1.05\times10^{-34}\,J\cdot s)^2}{2(0.40\,kg)(2.0\,m)^2} = 1.700\times10^{-68}\,J. \tag{7.5.36}$$

Therefore,

$$n = (K/E_1)^{1/2} = (0.050/1.700\times10^{-68})^{1/2} = 1.2\times10^{33}. \tag{7.5.37}$$

Significance

We see from this example that the energy of a classical system is characterized by a very large quantum number. Bohr's correspondence principle concerns this kind of situation. We can apply the formalism of quantum mechanics to any kind of system, quantum or classical, and the results are correct in each case. In the limit of high quantum numbers, there is no advantage in using quantum formalism because we can obtain the same results with the less complicated formalism of classical mechanics. However, we cannot apply classical formalism to a quantum system in a low-number energy state.

Exercise 7.5.1

(a) Consider an infinite square well with wall boundaries $x = 0$ and $x = L$. What is the probability of finding a quantum particle in its ground state somewhere between $x = 0$ and $x = L/4$? (b) Repeat question (a) for a classical particle.

Solution

a. 9.1%; b. 25%

Having found the stationary states $\psi_n(x)$ and the energies E_n by solving the time-independent Schrödinger equation (Equation 7.5.2), we use Equation 7.4.12 to write wavefunctions $\Psi_n(x,t)$ that are solutions of the time-dependent Schrödinger's equation given by Equation 7.4.7. For a particle in a box this gives

$$\Psi_n(x,t) = e^{-i\omega_n t}\psi_n(x) = \sqrt{\frac{2}{L}}e^{-iE_nt/\hbar} sin \frac{n\pi x}{L}, \, n = 1, 2, 3, ... \tag{7.5.38}$$

where the energies are given by Equation 7.5.11.

The quantum particle in a box model has practical applications in a relatively newly emerged field of optoelectronics, which deals with devices that convert electrical signals into optical signals. This model also deals with nanoscale physical phenomena, such as a nanoparticle trapped in a low electric potential bounded by high-potential barriers.

Contributors and Attributions

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