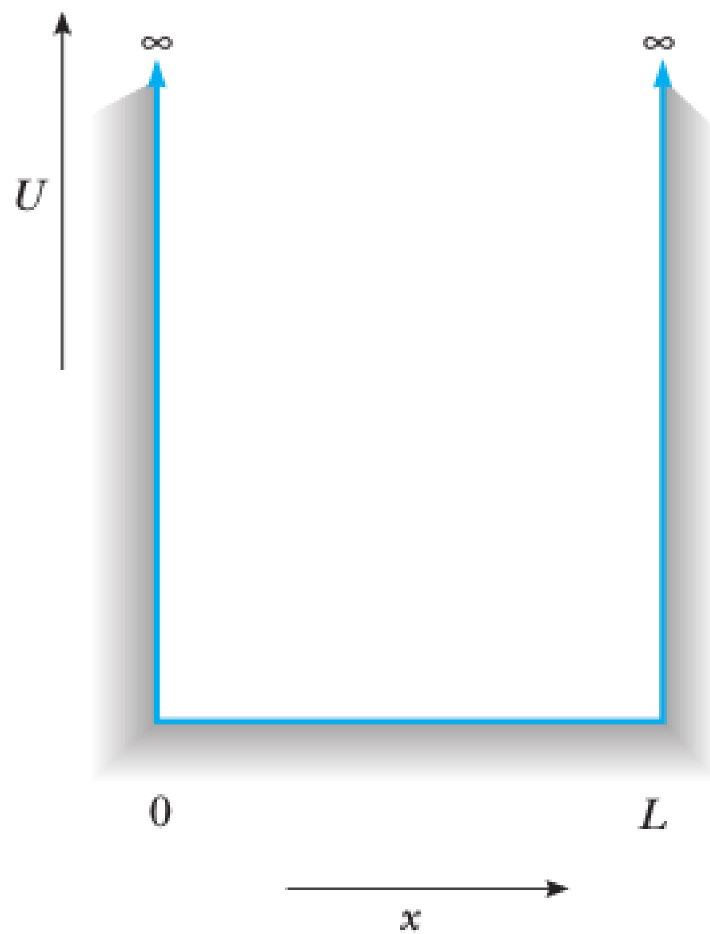
Particle in an Infinite Potential Well

We consider the simplest non-trivial problem in quantum mechanics. In one dimension the motion of the particle is bound an infinite potential well. Mathematically, the potential is defined by

$$\begin{aligned} V(x) &= 0 \text{ for } 0 < \text{x} < \text{L} \\ &= \infty \text{ for all other x} \end{aligned}$$



It is also called *particle in a box* problem. We want to solve the time independent Schroedinger's equation

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

for the potential of the infinite potential well. Equivalently, we want to solve the **eigenvalue** problem for the inifinte potential well.

We look for solutions with finite value of energy. Hence, the only allowed solution for $x \leq 0$ and $x \geq L$ is $\psi(x) = 0$, because the potential energy in these regions is infinite. For $0 < x < L$, the Schroedinger's equation is

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

This is better written as

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} &= -\frac{2mE}{\hbar^2}\psi(x) \\ &= -k^2\psi(x), \end{aligned} \tag{1}$$

where we defined $k^2 = 2mE/\hbar^2$ or $E = \hbar^2 k^2/2m$.

As mentioned in the class, we look for solutions which satisfy the conditions on wave functions:

- They should be single valued.
- They should be square-integrable.
- They should be continuous.
- We **can not** insist on continuity of $d\psi/dx$ everywhere because the potential is infinite at $x = 0$ and $x = L$. At these two points, the second derivative diverges which means that the derivative is discontinuous. That, in turn, means the solution will have a **kink** at these two points.

The differential equation in eq. (1) is a very well-known differential equation. It is the same equation that is satisfied by the simple pendulum, in the limit of small oscillations. Hence the solutions are linear combinations of $\sin(kx)$ and $\cos(kx)$. (In principle, we can write the solution as linear combination of the complex functions, e^{ikx} and e^{-ikx}. We will not do that here because imposing the boundary conditions on these functions is more awkward compared to imposing them on the trigonometric functions.)

The most general solution is

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

We argued before that for x outside the box, $\psi(x) = 0$ (no finite energy solution at points where the potential diverges). Hence we must also conclude $\psi(x) = 0$ at $x = 0$ and at $x = L$.

Quantization condition for a Particle in a Box

Since we demand $\psi(x = 0) = 0$, we must have $B = 0$. A has to be non-zero, because we want the wave function to be non-zero. Since we need $\psi(x = L) = 0$, we must have $\sin(kL) = 0$. This leads to the **Quantization Condition**

$$kL = n\pi \text{ where } n = 1, 2, 3, ...$$

That is, k is allowed to take only **discrete** values $k_n = n\pi/L$, unlike in the case of free particle where the value k is unrestricted.

Substituting k_n in the expression for energy, we get

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2\pi^2 n^2}{8mL^2}.$$

Energy is QUANTIZED! The particle is allowed to take only discrete values of energy. And if it makes transitions between them, the emitted energy will have some pre-determined spectrum, similar to the case of hydrogen atom.

Energy Eigenstates and Eigenvalues

We denote the wave function with wave number k_n as $\phi_n(x)$. These functions are the energy eigenfunctions and $\phi_n(x)$ has energy eigenvalue E_n. That is

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\phi_n(x)}{dx^2} &= \frac{\hbar^2 k_n^2}{2m}\phi_n(x) \\ &= \frac{n^2\pi^2\hbar^2}{2mL^2}\phi_n(x) = E_n\phi_n(x) \end{aligned} \tag{2}$$

Demanding that the energy eigenstates should be normalized, we get

$$\int_{-\infty}^{+\infty} |\phi_n(x)|^2 dx = \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) = 1$$

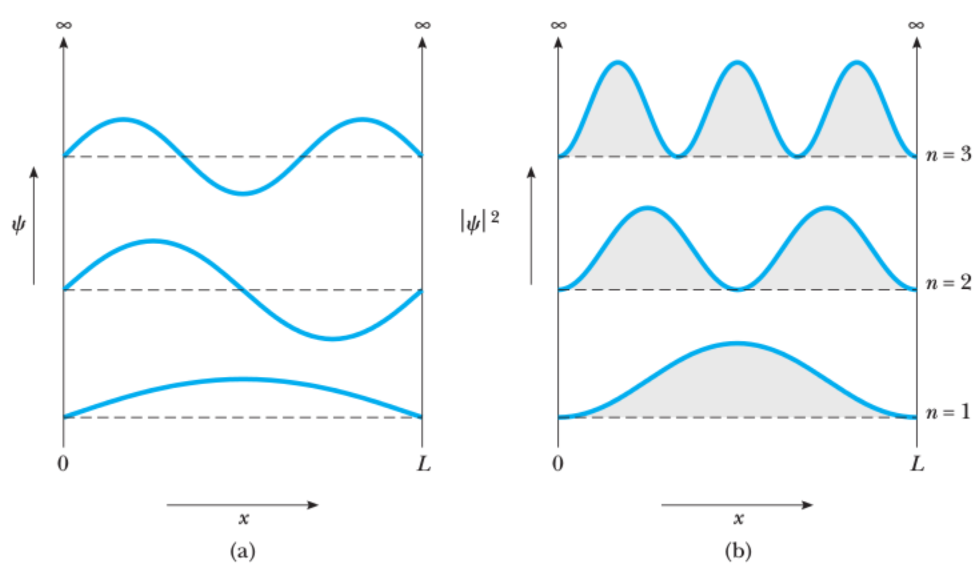
gives the normalization constant $A = \sqrt{2/L}$. It is the same for all the states. It is independent of n in this problem.

The first few energy eigenstates and their corresponding eigenvalues are

$$\begin{aligned}
\phi_1(x) &= \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), \; E_1 = \frac{\pi^2\hbar^2}{2mL^2} \\
\phi_2(x) &= \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right), \; E_2 = \frac{4\pi^2\hbar^2}{2mL^2} \; \ldots \\
\phi_n(x) &= \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \; E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}
\end{aligned}$$

Notation: A general wavefunction is denoted by $\psi(x)$. In any given problem, the energy eigenstates are denoted by $\phi_n(x)$.

Graphs of Energy Eigenstates



Symmetry Properties of Energy Eigenstates

- The states with odd n are even under the transformation $x \to (L-x)$, whereas the states with even n are odd under this transformation. In particular the ground state is even and so is the potential.

- **Theorem**: If the potential has a symmetry, the lowest energy state (called the **ground state**) has the same symmetry.

- The above symmetry is called **Parity** and it is one of the most important symmetries of nature. It dictates which atomic transitions are allowed and which are forbidden.

- It was a shock to many people when it was experimentally demonstrated that beta decay does not have this symmetry.

- The ground state has no nodes, that is $\phi_1(x) \neq 0$ anywhere within the well. The first excited state has one node, the second excited state has two nodes etc.

- This is a general feature of all problems where Parity is a symmetry. The eigenstates alternate between even and odd and the integer characterizing the eigenstate also gives the number of nodes.

General Properties of Energy Eigenstates

- In classical mechanics, if the potential is zero, then the lowest energy is zero. But here the lowest allowed energy is non-zero!

- Because the height of the potential is taken to be infinite, we have an infinite number of bound states. In most cases, the height (or depth) of the potential well is finite. In such cases, we will have only a limited number of bound states.

- States with very large n behave essentially like classical particles.

- The energy eigenstates are **orthogonal** to one another.

$$\int_{-\infty}^{+\infty} \phi_m^*(x)\phi_n(x)dx = \int_0^L \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = 0 \text{ if m} \neq \text{n.}$$

- The energy eigenstates form an orthonormal basis set. Any arbitrary wavefunction for a particle in a box can be written as

$$\psi(x) = \sum_n c_n \phi_n(x).$$

Meaning of Eigenvalues and Eigenstates

- Suppose the particle is in the ground state of the infinite potential well.

$$\psi(x,t) = \phi_1(x) \exp\left(\frac{-iE_1 t}{\hbar}\right).$$

  I do an experiment where I measure the energy of the particle.

- What result do I get? Since the particle is in the ground state, my measurement gives the result E_1.

- What happens to the particle, after I have made the measurement? In this case, **nothing**.

- Why? An energy measurement makes the wave function **collapse** into one of the energy eigenstates. Since the original state is an energy eigenstate, it remains in the same state after the energy measurement.

- Once again I start with the particle in the ground state, but this time I measure its momentum.

- The ground state can be written as the linear combination linear combination

$$\phi_1(x) = \sqrt{2/L}\sin(\pi x/L) = \frac{\sqrt{2/L}}{2i}\left[\exp(i\pi x/L) - \exp(-i\pi x/L)\right].$$

- So the ground state (and every other state in this problem) are linear combinations of two momentum states $\hbar k$ and $-\hbar k$. So the momentum measurement gives one of these two values as a result.

- Suppose we got the answer $\hbar k$. The momentum measurement makes the ground state collapse into a momentum eigenstate. If we immediately make another momentum measurement, we get the result $\hbar k$ again.

- Suppose we wait for a bit and then make the momentum measurement. Now it is possible to get either of the results $\hbar k$ or $-\hbar k$.

- Why is that? Did not our first momentum measurement force the particle into a momentum eigenstate?

- Yes. But then we left the particle alone. The only influence on the particle is only the potential. It is this potential and the kinetic energy which guide the further time evolution of the wave function.

- Our first momentum measurement has forced the particle into one of the two momentum eigenstates of the ground state. Later, this state becomes the usual ground state. When there is no external influence on the particle, the wave function of the particle should be either an energy eignestate or a linear combination of energy eigenstates.

- Here the momentum measurement never took it out of the ground state. Hence at later times, the wave function is the general ground state, not just the $\hbar k$ part of the ground state.