Quantum Mechanics: Particle in a box

Energy of a particle in a box

Consider a particle of mass m, which is trapped inside a one-dimensional box of length L. Inside the box, the particle is free, but the two walls of the box are rigid, and the box can neither penetrate them, nor go out of the box. Thus the potential experienced by the particle is zero inside the box and infinite at the two walls and beyond. The Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}), \tag{1}$$

which can be written in the position representation as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \qquad V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x \geq L, x \leq 0 \end{cases} \tag{2}$$

Notice that since there is only one variable x, we use total derivatives instead of partial derivatives. The time-independent Schrödinger equation can be written as

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \tag{3}$$

This is a 2nd order differential equation, and can be easily solved inside the box, because the potential energy term is zero there. Inside the box the Schrd̈inger equation is

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

which may be written as

$$\left(\frac{d}{dx} + i\frac{\sqrt{2mE}}{\hbar}\right)\left(\frac{d}{dx} - i\frac{\sqrt{2mE}}{\hbar}\right)\psi(x) = 0.$$

The solution of the equation $\left(\frac{d}{dx} - i\frac{\sqrt{2mE}}{\hbar}\right)\psi(x) = 0$ will also be a solution of the above equation. We could have also written the above equation as

$$\left(\frac{d}{dx} - i\frac{\sqrt{2mE}}{\hbar}\right)\left(\frac{d}{dx} + i\frac{\sqrt{2mE}}{\hbar}\right)\psi(x) = 0.$$

In that case, the solution of the equation $\left(\frac{d}{dx} + i\frac{\sqrt{2mE}}{\hbar}\right)\psi(x) = 0$ will also be a solution of the above equation. A second order equation can have only two independent solutions. These two solutions can easily be gotten as

$$\psi_1(x) = e^{ikx}, \qquad \psi_2(x) = e^{-ikx},$$

where $k = \sqrt{2mE}/\hbar$. The general solition will be a linear combination of these two solutions, namely

$$\psi(x) = c_1 e^{ikx} + c_2 e^{-ikx},$$

where c_1, c_2 are undetermined constants. We have gotten the eigenfunction, but we still don't have the energy of the particle. So, what is missing? We have solved the Schrödinger equation *inside* the box, but have left out the boundary, and the region of space outside the box. Instead of putting in infinite potential, which can potentially create problems, we can simply use the physical condition that the particle cannot penetrate the boundary, and thus the probability of finding it *inside* the walls should be zero. From Born's interpretation of the wave-function we have learnt that the $|\psi(x)|^2 dx$ is the probability of finding the particle between x and $x + dx$. The probability *density* of finding the particle at a position x is $|\psi(x)|^2$. Since particle cannot penetrate the walls, we have, $|\psi(0)|^2 = 0$ and $|\psi(L)|^2 = 0$. This in turn means $\psi(0) = 0$ and $\psi(L) = 0$. From the first condition we get $c_2 = -c_1$, which implies

$$\psi(x) = 2ic_1 \sin(kx).$$

The second condition yields

$$\psi(L) = 2ic_1 \sin(kL) = 0,$$

which means $kL = n\pi, \quad n = 1, 2, 3 \ldots.$ We cannot have $n = 0$ because that will make k zero, and the wave-function zero everywhere. The wave-function cannot be zero everywhere, because that would imply that the probability of finding the particle *anywhere* is zero, i.e., the particle does not exist. Thus

$$k = \frac{n\pi}{L}, \quad n = 1, 2, 3 \ldots$$

and there are many eigenfunctions corresponding to those, which we label by n

$$\psi_n(x) = 2ic_1 \sin(n\pi x/L).$$

Recalling the relation of k to energy, we get

$$\frac{\sqrt{2mE_n}}{\hbar} = n\pi$$

or

$$E_n = \frac{n^2 h^2}{8mL^2}, \quad n = 1, 2, 3 \ldots$$

We arrive at a very interesting result which says that the particle which is trapped inside a box, cannot just take any value of energy. There are only fixed, *quantized* values it can take. The energy of the particle is quantized. This is something that never happens in classical mechanics. We shall see later that this quantization of energy is not a special case here, but happens whenver a particle is confined to a small region.

Normalization of the eigenfunctions

Since $|\psi(x)|^2 dx$ is the probability of finding the particle in a small region around x, if we sum it over all x, it should give us the probability of finding the particle in all of space. Since the particle does exist, the probability of finding it anywhere in all of space should be 1:

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x) dx = 1. \tag{4}$$

This is called the *normalization* condition, and must be satisfied by all wave-functions representing a physical system. Using the normalization of all eigenfunctions $\psi_n(x)$, we can find the unknown constant c_1, and get the final normalized eigenfunctions as

$$\psi_n(x) = \sqrt{\tfrac{2}{L}} \sin(n\pi x/L), \quad n = 1, 2, 3 \ldots \tag{5}$$

and we have

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = 1$$

for all $\psi_n(x)$.

Orthogonality of eigenfunctions

Using the expression for the eigenfunctions (5), suppose we evaluate $\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)dx$ where $m \neq n$, what do we get? We find

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)dx = 0.$$

So, we have a lot of eigenfunctions

$$\psi_1, \ \ \psi_2, \ \ \psi_3, \ \ \psi_4, \ \ \psi_5, \ \ \psi_6, \ldots$$

If we multiply them to their own complex conjuge, and integrate, we get 1. If we multiply them to the complex conjuge of a different eigenstate, and integrate, we get 0. There is a close analogy with the unit vectors in the catesian coordinate system

$$\hat{i}, \ \ \hat{j}, \ \ \hat{k}.$$

We know that $\hat{i}\cdot\hat{i} = \hat{j}\cdot\hat{j} = \hat{k}\cdot\hat{k} = 1$, which means they are *unit* vectors. But $\hat{i}\cdot\hat{j} = \hat{j}\cdot\hat{k} = \hat{k}\cdot\hat{i} = 0$, which means they are *orthogonal* or perpendicular to each other. So it appears that $\psi_1, \psi_2, \psi_3, \ldots$ are like unit vectors in some abstract space, and are orthogonal to each other. The 3 unit vectors $\hat{i}, \hat{j}, \hat{k}$ describe a 3-dimensional space. Similarly, the infinite number of eigenfunctions $\psi_1, \psi_2, \psi_3, \ldots$ can be thought of as describing an *infinite-dimensional space*. This space is called the *Hilbert space*.

We know that any arbitrary vector in 3-dimensional space, can be represented in terms of the unit vectors $\hat{i}, \hat{j}, \hat{k}$

$$\vec{A} = a_1\hat{i} + a_2\hat{j} + a_3\hat{k},$$

where a_1, a_2, a_3 are certain constants, specific to the vector $\vec{A}$. Exactly in the same way, *any* wave-function of this particle in the box can represented in terms of the eigenfunctions of Hamiltonian $\psi_1, \psi_2, \psi_3, \ldots$

$$\phi(x) = a_1\psi_1(x) + a_2\psi_2(x) + a_3\psi_3(x) + \ldots,$$

where a_i are certain constants, specific to the wave-function $\phi(x)$.

One might think that this orthogonality of the eigenfunctions of the Hamiltonian may be because of the kind of Hamiltonian or something else. However, we shall see later that this is a generic property - *eigenfunctions of all Hermitian operators are mutually orthogonal*.