1D Particle in a Box

1 Introduction

Every physics undergrad should know how to solve particle in a box, right? But do you understand all the physics (or perhaps math) behind this simple system? Let me first give a brief review on this topic.

Prerequisite: (1) Know how to solve Schrödinger equation (2) Understand eigenvectors and eigenvalues; (3) Momentum space wavefunction (basic Fourier transform); (4) Basic operator

2 Review

Consider 1D particle in a box governed by this Schrödinger equation.

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t) = i\hbar\frac{\partial \Psi}{\partial t} \tag{1}$$

with potential $V(x)$ given by

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{Otherwise} \end{cases} \tag{2}$$

To solve the general wave function $\Psi(x,t)$, we first need to find the energy eigen-states, and then form a linear combination of those states. So, what we do is simply let $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$ and obtain the so called Time Independent Schrödinger Equation (TISE).

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

So basically, we need to solve the energy eigen-states $\psi(x)$ and eigen-energy E. For this particular system, everyone with physics undergrad should agree the following.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad 0 < x < L \tag{4}$$

$$\text{B.C.s} \;\; \psi(0) = \psi(L) = 0 \tag{5}$$

Now the solution to Eq. (4) subjecting to the boundary conditions (5) is just

$$\psi_n(x) = \begin{cases} \sqrt{2/L}\,\sin(k_n x) & 0 < x < L \\ 0 & \text{Otherwise} \end{cases} \tag{6}$$

$$E_n = (\hbar k_n)^2/2m \tag{7}$$

where $k_n = n\pi/L$, $n = 1, 2, 3, \ldots$ Depending on the initial conditions (not given here), we can further obtain $\Psi(x,t)$. But our focus is not here.

3 The Disaster

Question: Find the momentum space representation of the eigen-states for the particle in a box (1D).

I asked this question myself when I was an M. Phil. student and preparing an exercise class for my undergrad student. I thought that it is simple and I decompose ψ_n as follow

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin(k_n x) \tag{8}$$

$$= \frac{1}{2i}\sqrt{\frac{2}{L}}\left[e^{ik_n x} - e^{-ik_n x}\right] \tag{9}$$

So, it is very simple. Why? Because e^{ikx} is an eigen-state of momentum operator $\hat{p}$. By observing Eq. (9), I thought that $\psi_n(x)$ consists of two plane waves travelling in opposite direction. So, the momentum space representation is

$$\phi_n(k) \sim \delta(k - k_n) + \delta(k + k_n) \tag{10}$$

And this is WRONG!!!!

4 Inconsistency

The TISE is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{11}$$

So the Hamiltonian operator is $\hat{H} = \hat{p}^2/2m$.

This is just the free particle Hamiltonian. One would expect that the energy eigenstate is e^{ikx} (not normalizable) which **contradicts** to Eq. (6) (normalizable). Also, the plane wave eigen-energy can take any value (i.e. continuous), which also **contradicts** to Eq. (7) (discrete).

Now, can you spot out what's wrong in the deduction?

5 Solution

The deduction in Sec. 3, is all wrong. In fact, the eigen-state, Eq. (8) is not correct. To be more precise, Eq. (8) is misleading.

The reason is that Eq. (8) only holds on $0 < x < L$. But to consider the actual wave function, we have to specify all the values in the real space (i.e. $-\infty < x < \infty$). Allow me to emphasise once again, the eigen-state of the particle in a box (1D) is given by Eq. (6)

$$\psi_n(x) = \begin{cases} \sqrt{2/L}\,\sin(k_n x) & 0 < x < L \\ 0 & \text{Otherwise} \end{cases} \tag{12}$$

Similarly, the Hamiltonian $\hat{H}$ is **NOT** $\hat{p}^2/2m$ since the potential $V(x)$ is **NOT** identically equal to zero. Having the concept clear, let's find out the momentum representation of $\psi_n(x)$ using Fourier transform.

6 Momentum Space Revisit

The momentum representation of eigen-state $\phi_n(k)$ is

$$\phi_n(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \psi_n(x) e^{-ikx}\, dx \tag{13}$$

Note that the integration domain is $-\infty < x < \infty$. Thus, we have to specify **ALL** the values of $\psi(x)$ in real-space, not just the non-zero region!

Now, since $\psi_n(x) = 0$ for $-\infty < x < 0$ or $L < x < \infty$. Therefore, we only need to integrate from $x = 0$ to $x = L$.

$$\begin{aligned}
\phi_n(k) &= \frac{1}{\sqrt{2\pi}} \int_0^L \sqrt{\frac{2}{L}} \sin(k_n x)\; e^{-ikx}\, dx \qquad (14)\\
&= \frac{1}{2i\sqrt{L\pi}} \int_0^L \left(e^{i(k_n - k)x} - e^{-i(k_n + k)x} \right) dx \qquad (15)\\
&= \frac{1}{2i\sqrt{L\pi}} \left[\frac{e^{i(k_n-k)L} - 1}{i(k_n - k)} + \frac{e^{-i(k_n+k)L} - 1}{i(k_n + k)} \right] \qquad (16)
\end{aligned}$$

Recall that $k_n = n\pi/L$ for $n = 1, 2, 3, \ldots$. Therefore, $e^{ik_nL} = e^{in\pi} = (-1)^n$ and we have

$$\begin{aligned}
\phi_n(k) &= \frac{1}{2i\sqrt{L\pi}} \left[\frac{1}{i(k_n - k)} + \frac{1}{i(k_n + k)} \right] \left[(-1)^n\, e^{-ikL} - 1 \right] \qquad (17)\\
&= \frac{1}{2\sqrt{L\pi}} \left[\frac{2k_n}{k_n^2 - k^2} \right] \left[1 - (-1)^n e^{-ikL} \right] \qquad (18)\\
&= \frac{n\sqrt{\pi L}}{(n\pi)^2 - (kL)^2} \left[1 - (-1)^n e^{-ikL} \right] \qquad (19)
\end{aligned}$$

Great! We now explore the probability distribution of finding a particle with momentum $\hbar k$ (i.e. $|\phi_n(k)|^2$. Remember to take modulues square!) if it is in energy eigenstate.

$$\begin{aligned}
|\phi_n(k)|^2 &= \left[\frac{n\sqrt{\pi L}}{(n\pi)^2 - (kL)^2} \right]^2 \left[1 - (-1)^n e^{-ikL} \right] \left[1 - (-1)^n e^{+ikL} \right] \qquad (20)\\
&= \frac{2n^2\pi L}{\left[(n\pi)^2 - (kL)^2 \right]^2} \left[1 - (-1)^n \cos(kL) \right] \qquad (21)
\end{aligned}$$

Remark
Unlike the wrong deduction in Sec 3, Eq. (21), shows that all k values are allowed! Please also note that for a given value of n, all values of k are allowed even though we have only a single k_n!

Also, $|\phi_n(k)|^2$ is an even function. The amount of plane wave traveling to the right is same as that to the left. Thus, one can easily conclude that $\langle \hat{p} \rangle = 0$ for energy eigen-state. (Try to evaluate yourself the expectation value in real-space and momentum-space!)

7 Advanced Topic

If you are familiar with particle in a box, you probably know that $\langle \hat{x} \rangle = \langle \hat{p} \rangle = 0$ for energy eigen-states. In fact, we can directly obtain this result without solving the Schrödinger equation explictly.

Consider a general TISE in 1D

$$\hat{H}\psi \;=\; \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_n(x) \;=\; E_n\psi_n(x) \tag{22}$$

General in the sense that $V(x)$ is a general function. With a set of appropriate boundary conditions, we can solve for the energy eigen-state $\psi(x)$.

Now, we impose a condition on $V(x)$ such that $V(-x) = V(x)$ (i.e. symmetric potential). With the coordinate transformation $x \to -x$ to Eq. (22), we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_n(-x) \;=\; E_n\psi_n(-x) \tag{23}$$

Note that the PDE, Eq. (23), is identical to Eq. (22). Therefore, $\psi_n(-x)$ is also an energy eigen-state with the same eigen-energy E_n **if the same boundary conditions are satisfied**.

Since 1D quantum system does not have energy degeneracy **for bound states** (See Appendix A), therefore we can conclude that

$$\psi_n(-x) \;=\; \psi_n(x) \tag{24}$$

which is an even function. Therefore, we have $\langle \psi_n | \hat{x} | \psi_n \rangle = 0$.

As a result, the energy eigen-state in momentum space is

$$\begin{aligned}
\phi_n(k) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \psi_n(x)e^{-ikx}\,dx && \text{(25)}\\
&= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \psi_n(-x)e^{+ikx}\,dx \qquad \text{we replace } x \text{ by } -x && \text{(26)}\\
&= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \psi_n(x)e^{-i(-k)x}\,dx \qquad \text{since } \psi_n(-x) = \psi_n(x) && \text{(27)}\\
&= \phi_n(-k) && \text{(28)}
\end{aligned}$$

which is also an even function. Therefore, $\langle \phi_n | \hat{p} | \phi_n \rangle = 0$.

Remark You may notice that Eq. (6) is not symmetric. The reason is that we shifted our origin to the left boundary of the box. (Try to shift the origin back to the centre of the box)

Parity
For such kind of Hamiltonian (in our case, the potential is symmetric), we say that the Hamiltonian has Parity symmetry or invariant under Parity transformation. Mathematically, we write $[\hat{H}, \mathcal{P}] = 0$, where $\mathcal{P}$ is the parity operator. The fundamental operation of Parity operator is $\mathcal{P}\,|x\rangle = |-x\rangle$ (i.e. inversion). For $\mathcal{P}\psi(x) = \pm\psi(x)$. These wavefunctions $\psi(x)$ are said to have definite parity with either even parity (positive) or odd parity (negative).

A 1D No Energy Degeneracy

Energy degeneracy of a quantum system is that more than one energy eigen-states correspond to the same eigen-energy. But for 1D system, there is no energy degeneracy for bound states.

Proof
Let's write down the 1D TISE and we **assume** that two distinct energy eigen-states ψ_n and ψ_m, $n \neq m$, have the same eigen-energy E. We shall prove it by contradiction.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V(x)\psi_n(x) = E\psi_n(x) \tag{29}$$
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_m}{dx^2} + V(x)\psi_m(x) = E\psi_m(x) \tag{30}$$

Multiply Eq. (29) by $\psi_m(x)$ and Eq. (30) by $\psi_n(x)$, we obtain

$$-\frac{\hbar^2}{2m}\psi_m\frac{d^2\psi_n}{dx^2} + \psi_m(x)V(x)\psi_n(x) = E\psi_m(x)\psi_n(x) \tag{31}$$
$$-\frac{\hbar^2}{2m}\psi_n\frac{d^2\psi_m}{dx^2} + \psi_n(x)V(x)\psi_m(x) = E\psi_n(x)\psi_m(x) \tag{32}$$

Subtracting Eq. (31) by Eq. (32), we obtain

$$\psi_n\frac{d^2\psi_m}{dx^2} = \psi_m\frac{d^2\psi_n}{dx^2} \tag{33}$$

Integrate both sides w. r. t. x and perform integration by part:

$$\psi_n(x)\psi_m'(x) - \int \psi_n'(x)\psi_m'(x)\,dx = -\psi_n'(x)\psi_m(x) + \int \psi_m'(x)\psi_n'(x)\,dx + \text{constant} \tag{34}$$
$$\psi_n(x)\psi_m'(x) + \psi_n'(x)\psi_m(x) = \text{constant} \qquad \forall x \tag{35}$$

For bound states (normalizable), we expect that $\psi(x) = 0$ as $x \to \pm\infty$. Therefore, we conclude that the *constant* is zero, and we have

$$\psi_n(x)\psi_m'(x) = \psi_n'(x)\psi_m(x) \tag{36}$$
$$\int \frac{d\psi_m}{\psi_m} = \int \frac{d\psi_n}{\psi_n} \tag{37}$$
$$\psi_m(x) = A\psi_n(x) \tag{38}$$

Since $\psi(x)$ is normalized, we have $A = 1$ and $\psi_m = \psi_n$, which **contradicts** to the assumption that ψ_m and ψ_n are distinct energy eigen-states! Conclusion: No energy degeneracy for 1D bound states.

Warning If we include *spin* in 1D quantum system, then we can have energy degeneracy!