# Lecture 5

# A Particle in a Box

## Study Goal of This Lecture

- Solving a particle in a box
- Know the eignevalue an eigenfunction of particle in a box
- Calculate the expectation value of particle in a box
- Solving a particle in a multidimensional box

## 5.1 Solving a particle in a box

### 5.1.1 General Procedure for Solving the T.I.S.E.

Up to this point we have covered the basic "rules" of quantum mechancis and in the following lectures we will basically repeatedly "practicing" applications of these rules and approximated methods. It takes some work to familize/internalized quantum mechanics rules. We will start with simple/exactly solvable models. Note that we have gone over some mathematics without doing much practices/examples, particularly, we spent quite some time discuss about "measurement", and now we are ready to apply the formalism to real problems. After we have spent some time to practice some simple quantum mechanics problems, we will return to the issue of fundamental rules of quantum mechanics and explicitly state the "postulates" or "ground rules" of quantum mechanic.

Now, lets focus on the applications of quantum mechanics to "solving" simple problems. We spent some time talking about the important of "eigenfunction" and "eigenvalues" of quantum mechanical operators, indeed, we state that a single measurement causes a wavefunction to collapse into a eigenfunction of the associated observable and results an outcome of a value associated with the eigenfunction. It can't be emphasized enough that eigenfunctions of an quantum mechanical operator plays the central role in quantum mechanics. Actually, the Schrödinger equation is an eigenvalue problem.

Eigenfunctions and eigenvalues are important.

$$\hat{H}\psi = E\psi, \quad \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x). \tag{5.1}$$

$\Rightarrow$ eigenfunctions of $\hat{H}$, i.e. energy eigenstates, are important $\Rightarrow$ they represent the likely stable/stationary "energy" states. (In other words, eigenstate of $\hat{H}$ are energetically stable states)

$\hat{H}$ also governs time evolution.

### 5.1.2 Particle in a 1-D box

The simplest quantum mechanical system, hence always the first problem to solve in a quantum mechanic class, is the particle in a one dimensional box. Consider a particle of mass $m$ constrainted to move in a 1-D box of length $a$.

Some declaration or notations:
$\hat{A}\phi_1 = a_1\phi_1$, this is a eigenproblem, $a_1$ is a eigenvalue and $\phi_1$ is a eigenfunction. Eigenfunction = wavefunction = state.

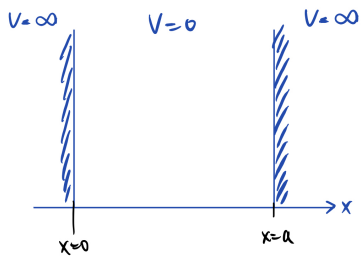


Figure 5.1: Superposition of several wave.

The potential energy is:

$$V(x) = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \le x \le a \\ \infty & \text{if } x > a \end{cases}. \tag{5.2}$$

To solve the Schrödinger equation, we need to write down the Hamiltonian first:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}, \quad \text{for } 0 \leq x \leq a. \tag{5.3}$$

There is no need to consider the range outside the box since the potential energy is infinity. Next, we write down the whole Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \tag{5.4}$$

$$\Rightarrow \frac{d^2}{dx^2}\psi(x) = -k^2\psi(x), \text{ where } k = \sqrt{\frac{2mE}{\hbar}}. \tag{5.5}$$

Here we call it $k$ for a reason.

The general solution of this differential equation is

$$\psi(x) = A\cos(kx) + B\sin(kx). \tag{5.6}$$

Recall that for a physically admissible $\psi(x)$, $\psi(x)$ must satisfy some conditions, such as continuity, smoothness, normalized ... etc.
In this case, $\psi(x) = 0$ outside the box since we requires that $V\psi(x) = 0$ even when $V = \infty$. To avoid discontinuity at $x = 0$ and $x = a$, we must require.

$$\psi(x = 0) = 0, \tag{5.7}$$

$$\psi(x = a) = 0. \tag{5.8}$$

These are boundary conditions. From Equ(5.7), we find

$$A\cos(k \cdot 0) + B\sin(k \cdot 0) = 0 \Rightarrow A = 0. \tag{5.9}$$

and from Equ (5.8), we obtain

$$B\sin(ka) = 0 \Rightarrow ka = n\pi, \ n = 1, 2, 3, \cdots, \tag{5.10}$$

where $n$ is called quantum number, describes discrete eigenstate. $n \neq 0$ because it will make $\psi(x) = 0$.

Q: what does it mean $\psi(x) = 0$ and why it is not valid?

From Equ(5.10), we find that $k$ is not all arbitrary number, the valid $k$ is:

$$k_n = \frac{n\pi}{a}. \tag{5.11}$$

Solving the $E$:

Be careful of distinguishing between $\hbar$ and $h$!

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \times \frac{n^2\pi^2}{a^2} = \frac{n^2 h^2}{8ma^2}. \tag{5.12}$$

corresponding eigenfunction:

$$\psi_n(x) = B\sin(kx) = B\sin\Big(\frac{n\pi x}{a}\Big). \tag{5.13}$$

To determine $B$, we consider the normalization condition

$$1 = \int_0^a \psi_n^*(x)\psi_n(x)dx = |B|^2 \cdot \int_0^a sin^2(\frac{n\pi x}{a})dx \tag{5.14}$$

$$= |B|^2 \cdot \int_0^a \Big[\frac{1}{2} - \frac{1}{2}\cos\Big(\frac{2n\pi x}{a}\Big)\Big]dx$$

$$= |B|^2 \cdot \Big[\frac{1}{2}a - \frac{1}{2}\frac{a}{2n\pi}\sin\Big(\frac{2n\pi x}{a}\Big)\Big|_0^a\Big] = \frac{1}{2}|B|^2 a.$$

$$\therefore B = \sqrt{\frac{2}{a}}, \tag{5.15}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}. \tag{5.16}$$

Any arbitrary $\phi(x)$ can be written as $\phi(x) = \sum_n C_n\psi_n(x)$.

It is easy to show that $\int \psi_n(x)\psi_m(x)dx = 0$ for $n \neq m$, that is $\{\psi_n\}$ are orthornormal. From these eigenfunctions, we can calculate any properties of the particle.

Let's summerize the systematic way of solving the Schrödinger equation :

1. Write down $\hat{H}$
2. Write down Schrödinger equation and simplify.
3. Find general solutions to the Schrödinger equation.
4. Find boundary condtions.
5. Plug in the boundary conditions and find quantization conditions.
6. Find $E_n$ and $\psi_n(x)$.
7. Normalize the eigenfunction.

With the eigenfunctions, we can calculate experimental expectation values when the system is prepared in any of the states (Notice that one wavefunction is one quantum state).

## 5.2 Properties of a Particle in a Box

Let's plot these eigenfunctions → stationary states.

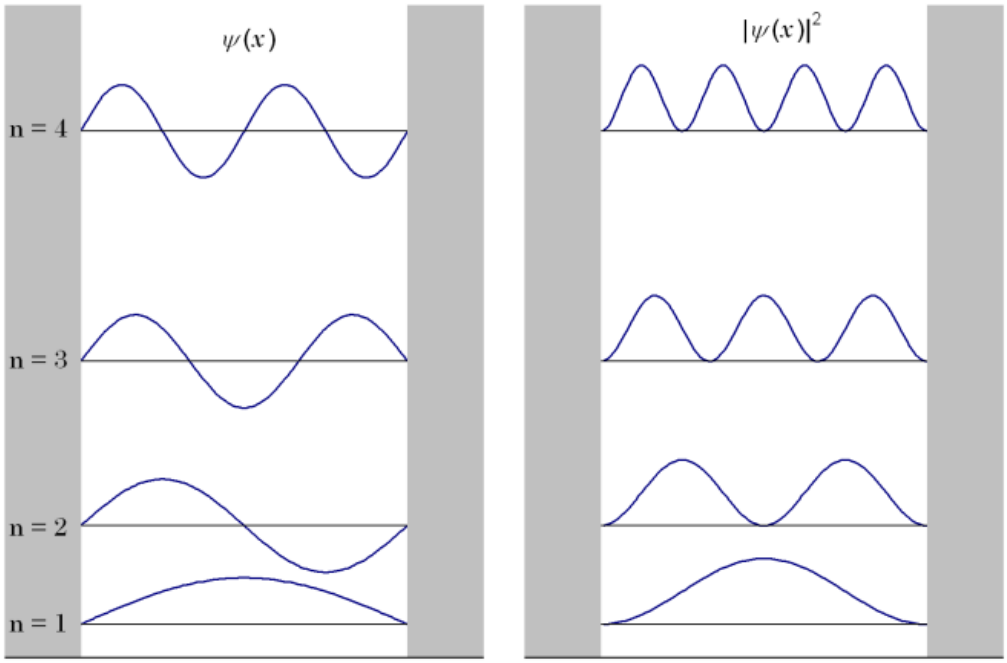


Figure 5.2: Plot of the wavefunction of particle in a box.

Observation:

- Energy $\propto n^2$, not equally spaced
- As $E$ increases, number of nodes increases too (Number of node $= n - 1$.)
- The probability $|\psi(x)|^2$ is more localized in the center at $n = 1$ and then spread out as $n \uparrow$
- The zero point energy is $\frac{h^2}{8mn^2}$
- Energy $\propto \frac{1}{a^2}$, so when size of the box increases, the energy drops rapidlly
- Return to classical state at $n \to \infty$

Note that the particle is not "fixed" localized in space, instead, we can only calculate the "probability" of finding the particle at a position. Now let's calculated

the averageand "width"/spreading of the particle.

For example:

$$\langle x\rangle_n = \int_0^a \psi_n^*(x)\hat{x}\psi_n(x)dx = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}x\sin\frac{n\pi x}{a}dx\frac{2}{a}\int_0^a \sin^2\frac{n\pi x}{a}dx. \quad (5.17)$$

Look up the integral table,

$$\int x\sin^2(ux)dx = \frac{x^2}{4} - \frac{x\sin(2ux)}{4u} - \frac{\cos(2ux)}{8u^2}, \quad (5.18)$$

therefore,

$$\langle x\rangle_n = \frac{2}{a}\times\frac{a^2}{4} = \frac{a}{2} \Leftarrow \text{center of box for all eigenstates.} \quad (5.19)$$

Spreading of the eigenstates:

$$\langle \hat{x}^2\rangle_n = \int_0^a \psi_n^*(x)\hat{x}^2\psi_n(x)dx = \frac{2}{a}\int_0^a x^2\sin^2\frac{n\pi x}{a}dx = (\frac{a}{2\pi n})^2(\frac{4\pi^2n^2}{3}-2), \quad (5.20)$$

so the variance is:

$$\Delta x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{a^2}{3} - \frac{3a^2}{2n^2\pi^2} - \frac{a^2}{4} = \frac{a^2}{12} - \frac{3a^2}{2n^2\pi^2}. \quad (5.21)$$

Therefore,

$$\Delta x = \sqrt{\frac{a^2}{12} - \frac{3a^2}{2n^2\pi^2}}. \quad (5.22)$$

Similarly, we can calculate $\langle p_x\rangle$ and $\langle p_x^2\rangle$. Directly get the result:

$$\langle p_x\rangle = 0, \quad (5.23)$$

$$\langle p_x^2\rangle = \frac{n^2\hbar^2\pi^2}{a^2}, \quad (5.24)$$

thus

$$\Delta p_x = \frac{n\hbar\pi}{a}. \quad (5.25)$$

With Equ(5.22) and Equ(5.25), we obtain:

$$\Delta x\Delta p_x = \frac{\hbar}{2}\sqrt{(\frac{\pi^2}{3}n^2-2)} > \frac{\hbar}{2}. \quad (5.26)$$

As $n\uparrow$, $\Delta x\Delta p_x\uparrow$
The uncertainty principle is a "lower bound".

The Heisenberg uncertainty principle is hold.

## 5.3 Particle in a 3-D box

This can be genrerlized to higher dimensions, consider a box of dimension $a, b, c$ along $x, y, z$ axis. Thus the Schrödinger equation can be written as

$$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\psi(x,y,z)=E\psi(x,y,z). \tag{5.27}$$

Note that $\psi$ is a function of three variables, and the variables in the Hamiltonian are independent. i.e. no terms such as $\frac{\partial}{\partial x}\frac{\partial}{\partial y}$ or $xy\cdots$.

We call this kind of system a "seperable" system. In general, the solution can be written as a "product" of indepedent functions

Independent degree of freedom → product!! To write in a product is a huge reduction of complexity.

$$\psi(x,y,z)=X(x)Y(y)Z(z). \tag{5.28}$$

Plugging into the equation, we obtain:

$$\begin{aligned}-\frac{\hbar^2}{2m}[Y(y)Z(z)\frac{\partial^2}{\partial x^2}X(x)+X(x)Z(z)\frac{\partial^2}{\partial y^2}Y(y)+X(x)Y(y)\frac{\partial^2}{\partial z^2}Z(z)]\\ =EX(x)Y(y)Z(z).\end{aligned} \tag{5.29}$$

Divide by $X(x)Y(y)Z(z)$ on both sides, we obtain

$$-\frac{\hbar^2}{2m}[\frac{1}{X(x)}\frac{\partial^2}{\partial x^2}X(x)+\frac{1}{Y(y)}\frac{\partial^2}{\partial y^2}Y(y)+\frac{1}{Z(z)}\frac{\partial^2}{\partial z^2}Z(z)]=E \tag{5.30}$$

Why it can be expanded in this manner?

$$\Rightarrow\begin{cases}\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X(x)=E_xX(x)\\ \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2}Y(y)=E_yY(y)\\ \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2}Z(z)=E_zZ(z)\end{cases},\ E_x+E_y+E_z=E. \tag{5.31}$$

The original equation is now separated into three independent equations, and we know the solutions ⇒ each one is a 1-D particle in a box.

The solution for 1-D particle in a box is:

$$X(x)=\sqrt{\frac{2}{a}}\sin\Big(\frac{n_x\pi x}{a}\Big). \tag{5.32}$$

Therefore, the wavefunctions of 3-D particle in a box is:

$$\psi_{n_x,n_y,n_z}(x,y,z)=\sqrt{\frac{8}{abc}}\sin\Big(\frac{n_x\pi x}{a}\Big)\sin\Big(\frac{n_y\pi y}{b}\Big)\sin\Big(\frac{n_z\pi z}{c}\Big), \tag{5.33}$$

A product state.

energy is:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}). \tag{5.34}$$

Now the eigenstate are determined by three quantum numbers, i.e. we must assign quantum number for each coordinate to define a state.

Observe from the result above, we could find that:

$$\text{energy} \rightarrow \text{sum, wave function} \rightarrow \text{products}$$

Only for independent subsystems!

For a cubic box, energy levels on all three directions are equal, so

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} 1 & | & 2 & 1 & 1 & | & 2 & 2 & 1 & \cdots \\ 1 & | & 1 & 2 & 1 & | & 2 & 1 & 2 & \cdots \\ 1 & | & 1 & 1 & 2 & | & 1 & 2 & 2 & \cdots \end{pmatrix} \tag{5.35}$$

Degenerate: different wavefunctions (eigenfunctions) with the same energy (eigenvalue).

The first column in the right hand side is the ground state. The second to forth column represent first excited states and it is three-fold degenerate.