

Fundamental of Spectroscopy
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Lecture – 04

A Simple Quantum Mechanical System: Particle in a one Dimensional Box

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The slide features a title bar "A Simple Quantum Model System" in a dark blue box. Below it, the text "Particle in a 1-D box / Particle in an infinite square well" is underlined. A diagram shows two vertical dashed lines representing walls at $x=0$ and $x=a$. The region between the walls is labeled $V=0$, and the regions outside are labeled $V=\infty$. A horizontal axis labeled x is shown below the walls. To the right of the diagram, the potential energy function is written as $V(x) = \begin{cases} 0, & 0 < x < a \\ \infty, & 0 \leq x, x \geq a \end{cases}$. Below the diagram, two questions are posed: "What is the nature of the wave function?" and "How does the wave function evolve in time?". On the right side of the slide, a photograph of a man in a light blue shirt is shown speaking and gesturing with his hands.

In the last couple of lectures, we have looked at the postulates of quantum mechanics. Let us now look at a simple quantum model system, which can help us make those ideas a little more concrete. This model system is called the particle in a 1-D box system or the particle in an infinite square well, besides being a very simple model for us to understand the postulates; we will see that this model is actually applicable in certain cases to explain electronic spectroscopy.

So, we will come back to this later in the class when we are going to discuss electronic spectroscopy. Let us now look at this model. In this model we consider that the particle can move in only 1 spatial dimension let us say the x direction further the particle is confined to a certain region of this x axis. So you can imagine that there are hard walls like this. And as long as the particle is within $x = 0$ and $x = a$, the potential energy of the particle = 0.

However, if it goes $x < 0$, then the potential energy becomes infinity. And similarly if it goes to $x > a$, then the potential energy becomes infinity, we can write the potential energy in the following form. V of $x = 0$ when x is between 0 and a , and it is equal to infinity when $x < 0$, or $x > a$. See that the particle is confined in this region. And the question is, what is the nature of the wave functions of the system and how does the system or the wave function of the system evolve in time.

You can imagine the system to be a particle moving along a rod like this. So, as long as the particle is confined into this region, its potential energy 0, but it cannot go out of this. So, the potential energy is infinite in regions outside this region that it can be.

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The slide contains the following content:

- Title:** Particle in a 1-D Box Solutions
- Diagram:** A potential energy diagram showing a box from $x=0$ to $x=a$. Inside the box, $V=0$. Outside the box, $V=\infty$. The boundaries are marked at $x=0$ and $x=a$.
- Boundary Conditions:** $\psi(0) = 0$ and $\psi(a) = 0$
- Hamiltonian:** $\hat{H} = \hat{K}E + \hat{P}E \rightarrow z_{E=0}, 0 < x < a$
- Schrödinger Equation:** $\hat{H} = \hat{K}E = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}, 0 < x < a$
- Time-Independent Equation:** $i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi, \hat{H} \rightarrow \text{time independent}, \hat{H} \psi = E \psi$

So, let us examine how the solutions of this problem looks like. Here is the diagram of the potential energy which is $V = 0$ in this region $V = \text{infinity}$ in these 2 regions. Now, if the potential energy is infinity, the particle cannot be there and the V function in those regions So, in this region it is 0 and also in this region it is 0. This would imply that because of continuity even further wave function in the region inside the box, this part here, point.

This point here should have the value 0 and also this point here should have the value 0. This will ensure that the way function is continuous at these boundaries. So, we can write these 2 boundary conditions as ψ of $0 = 0$ and ψ of $a = 0$. Now, let us write the Hamiltonian of the system. So, the Hamiltonian which is denoted as H hat is equal to the kinetic energy operator + the potential energy operated now in the region 0 to a , the potential energy is 0 and let us write the Hamiltonian in this region.

So, the Hamiltonian is simply the kinetic energy operator which is $-\hbar^2 / 2m$ square by $d^2 x$ square in the region $0 < x < a$. Let us now look at solving the Schrodinger equation with this the Schrodinger equation as you know is $\hbar \nabla \psi = H \psi$ and because in this case the Hamiltonian does not depend on time. We have seen that solving the Schrodinger equation here becomes equivalent to solving the eigenvalue equation of the Hamiltonian $H \psi = E \psi$. So we are going to solve the eigenvalue equation of the Hamiltonian.

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The slide contains the following handwritten derivations:

- Schrodinger equation: $-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E \psi(x)$
- Rearranged equation: $\frac{d^2 \psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x)$
- General solution: $\psi = A \sin kz + B \cos kz$
- Wave number: $k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{\sqrt{2mE}}{\hbar}$
- Boundary conditions: $\psi(0) = \psi(a) = 0$
- Applying $\psi(0) = 0$: $\psi(0) = A \sin 0 + B \cos 0 = 0 \Rightarrow B = 0$
- Applying $\psi(a) = 0$: $\psi(a) = A \sin ka = 0 \Rightarrow ka = n\pi, n = \text{integers}$
- Wave number: $k = \frac{n\pi}{a}$
- Energy levels: $E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (n\pi/a)^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{8ma^2}$
- Final energy formula: $E = \frac{n^2 h^2}{8ma^2}$

In this case, we have written here, the eigenvalue equation of the Hamiltonian of the particle in a box. So let us see how the solutions of this equation look like. So let us rearrange this a little bit. So $d^2 \psi / dx^2 = -2mE / \hbar^2 \psi$. So we notice here that this is a second order differential equation and ψ of x is some function, which when you differentiate twice, you get the same function back with a constant.

We know that the solution of an equation like this is a sin function, cosine function, most general solution is something like this $\psi = A \sin kx + B \cos kx$. k here would be square root of $2mE / \hbar^2$ or square root of $2mE / \hbar$. Now if you substitute this into the eigenvalue equation here, you can verify that this indeed a solution. Now there are certain conditions on the ψ that we have specified before, which is that ψ at $x = 0$ and ψ at $x = a = 0$.

So let us apply the conditions $\psi(0) = 0$. This gives $\psi(0) = A \sin(0) + B \cos(0) = 0$. Now $\sin(0) = 0$, we know that and $\cos(0) = 1$. So this implies that $B = 0$. Now, the solution has the form $\psi = A \sin kx$. Let us apply the second boundary condition, which is $\psi(a) = 0$. This implies that $A \sin ka = 0$. Now, \sin of this part will be 0, when k of a is some integral multiple of π .

So it could be $\pi, 2\pi, 3\pi$ and so on, and is equal to integers. $k = n\pi/a$, if he substitute this value of k into the expression for the wave function then we get the valid wave function to be $\psi = A \sin n\pi x/a$. And if we substitute this k into the expression for the energy which we have here, then we get $n\pi/a$ which is $k = \sqrt{2mE}/\hbar$ and E therefore becomes $n^2\pi^2\hbar^2/a^2m$. Or if you use that $\hbar = h/2\pi$. Then we get energy = $n^2 h^2 / 8ma^2$.

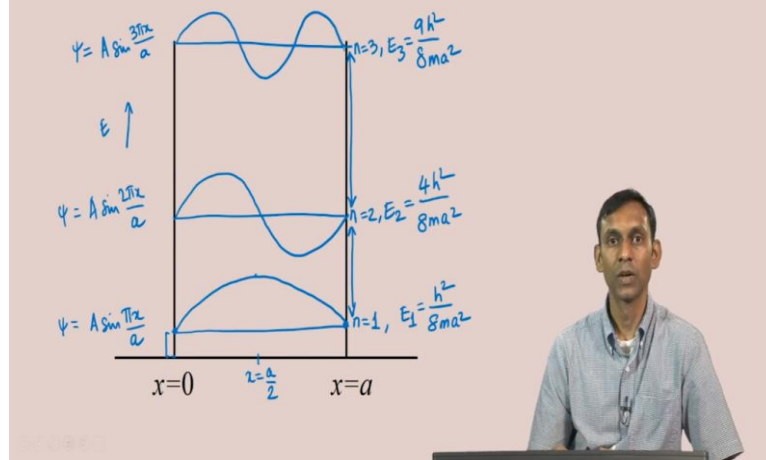
So, this is the energy of the particle in a box and the corresponding eigenfunctions are these where n are integers. So, we see that the energy of the particle is now quantized not all values are allowed, but only values corresponding to this expression when enter integers and similarly the corresponding eigenfunctions are given here, which depends on what n is and n is usually called a quantum number.

Now what integer values can intake it could be 1 2 3 and so on. Now, the question is 0 allowed, if you substitute 0 into this expression, you will see that the wave function becomes simply $\psi = 0$ so, that is not allowed what about negative integers? If you take $n = -1$ for example, then you get $\psi = A \sin -1\pi x/a$. And we see that is nothing but $-$ of A times $\sin \pi x/a$.

So it is essentially the eigenfunction corresponding to $n = 1$, multiplied by -1 . And so it does not really give us a new solution.

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Particle in a 1-D Box Solutions



Let us now examine the form of the eigenfunctions of the particle in a box and the corresponding energies. So here is the particle in a box and the lowest energy corresponds to $n = 1$, which is $E = E_1 = \frac{h^2}{8ma^2}$. And if you put the energy level here, we know that we are not putting it at energy = 0, because even for the lowest quantum number $n = 1$, the energy has a finite value here, now the wave function corresponding to this is $\psi = A \sin \frac{\pi x}{a}$.

So, how does this function look, if you take a point $x = 0$ then the sin value is 0 here, if you take $x = a$ then you get $\sin \pi$, which is the value here $\sin \pi =$ also 0. And if you take $x = a/2$, in that case, you get $\sin \frac{\pi}{2}$ which = 1 and if you do the other points, then you can see that the wave function looks like this. For $n = 2$, which we can draw here the energy is $\frac{4h^2}{8ma^2}$ square. And the wave function is $\psi = A \sin \frac{2\pi x}{a}$, which when we plot looks like this.

And for $n = 3$, now the energy gap here between $n = 2$ and 3, this gap is more than the gap here. Because here now the energy $E_3 = \frac{9h^2}{8ma^2}$ square. And if you draw the wave function there, this eigenfunction is $A \sin \frac{3\pi x}{a}$ which looks something like this.

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Wave Function Normalization

$\Psi(x) = A \sin\left(\frac{n\pi x}{a}\right)$, what is A?

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

$$\int_{-\infty}^{\infty} A^* A \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$|A|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$z = \frac{n\pi x}{a} \quad dz = \frac{n\pi dx}{a}$

$$\frac{a}{n\pi} |A|^2 \int_0^{n\pi} \sin^2 z dz = 1$$

$\Psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$
Normalized eigenfunction

① $\int_0^{\pi} \sin^2 z dz = \int_0^{\pi} \cos^2 z dz = \frac{\pi}{2}$

② $\sin^2 z + \cos^2 z = 1$

$\int_0^{n\pi} \sin^2 z dz = \frac{n\pi}{2}$

$\frac{a}{n\pi} |A|^2 \frac{n\pi}{2} = 1$
 $|A|^2 = \frac{2}{a} \quad A = \sqrt{\frac{2}{a}}$

Let us now examine the properties of these eigenfunctions. So, we have the eigenfunction to be $\psi(x) = A \sin\left(\frac{n\pi x}{a}\right)$. The question is what is A. You will recall that one of the properties of a wave function is that the wave function needs to have $\psi^* \psi$ of the wave function integrated over all space needs to be 1, which is the normalization condition or the condition that the sum of probabilities of finding the particle at any position equal to 1.

So, let us apply this condition for our wave function – from $-\infty$ to ∞ . $A^* A \int_{-\infty}^{\infty} \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$, or we can write this as $|A|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$, because in this case, the probability to be outside the box is 0. So the only place where the wave function has a non-zero value is between 0 and a. And so this becomes $|A|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$. We know make a substitution to solve this integral. So let us substitute $Z = \frac{n\pi x}{a}$. Therefore, $dZ = \frac{n\pi dx}{a}$.

And this integral now becomes $|A|^2 \int_0^{n\pi} \sin^2 Z dZ = 1$. When we substitute A here, this becomes $|A|^2 \frac{a}{n\pi} \int_0^{n\pi} \sin^2 Z dZ = 1$ and this becomes $|A|^2 \frac{a}{n\pi} \frac{n\pi}{2} = 1$. The whole thing multiplied by A over n pi. This integral should be = 1, this integral can be solved by using trigonometry identities, where we convert the $\sin^2 Z$ to $\frac{1 - \cos(2Z)}{2}$ and then integrate. Or you can think of it geometrically in the following way.

So consider this to be the Z axis. And in that the \sin^2 function looks something like this between 0 to pi here, and pi to 2 pi here. And the \cos^2 function is the complementary function, which looks like this. Now you notice that in a cycle, which is from 0 to pi, or between pi to 2 pi, the area under the \sin^2 curve, which is shown here is

equal to the area under the cosine square curve, which I am showing now with a different type of marking.

So the integral $\sin^2 Z \, dZ = \int_0^{\pi} \sin^2 Z \, dZ = \int_0^{\pi} \cos^2 Z \, dZ$ in an interval 0 to π , or any other cycle from π to another $\pi + 1$. Furthermore, we know that $\sin^2 Z + \cos^2 Z$ is always = 1. So this function $\sin^2 Z + \cos^2 Z$ on an average has a value 1. So on an average both these functions $\sin^2 Z$ and $\cos^2 Z$ have a value half and within the interval 0 to π , their integral will become half times π or $\pi / 2$.

This means the integral from 0 to $n\pi$ of $\sin^2 Z \, dZ = n\pi / 2$. If we substitute the value of this integral back here, then we get $a^2 / n\pi \cdot n\pi / 2 = a^2 / 2 = 1$. If we cancel the $n\pi$ here, then you see that $A^2 = 2$ over a and then one of the allowed values for A is $\sqrt{2}$ over a . If you plug this back into the expression of the wave function, the normalized wave function becomes $\psi(x) = \sqrt{2/a} \sin(n\pi x/a)$ which is the final expression for the normalized eigenfunction of the particle box.

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Average Properties

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \int_{\text{all space}} \psi^* \hat{A} \psi \, d\tau$$

$$\langle x \rangle = \frac{2}{a} \int_0^a \sin \frac{n\pi x}{a} \cdot x \cdot \sin \frac{n\pi x}{a} \, dx = \frac{2}{a} \int_0^a x \sin^2 \left(\frac{n\pi x}{a} \right) \, dx = \frac{2}{a} \cdot \frac{a^2}{4} = \frac{a}{2}$$

Center of the box $\langle x \rangle = 0$

$$\langle p \rangle = \frac{2}{a} \int_0^a \sin \frac{n\pi x}{a} \left(-i\hbar \frac{d}{dx} \right) \sin \frac{n\pi x}{a} \, dx = \frac{2}{a} \int_0^a \sin \frac{n\pi x}{a} (-i\hbar) \cos \frac{n\pi x}{a} \cdot \frac{n\pi}{a} \, dx = 0$$

Let us know use this wave function to calculate some average properties, you will recall that the average property of some operator is given by the integral $\psi^* \hat{A} \psi$ this is written in Dirac notation and the integral would be $\int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, d\tau$ over all space. So, let us do this for the position operator in our particular case. So, the average position is $\int_{-\infty}^{\infty} x |\psi|^2 \, dx$ but this can be written as only 0 to a , because that is the only region where wave function exists in all other regions.

It is 0 and therefore, will not contribute to this integral. And the wave function is square root $2/a$ which I can write outside as $2/a \sin n\pi x/a$. And here is the operator which is x multiplied by the wave function again $n\pi x/a dx$. And this is $2/a \int_0^a x \sin^2 n\pi x/a dx$. Now, we can solve this integral by parts. And I will not do this in the interest of time, but if you work it out, you will see that the value of this integral is a square by 4.

And then if you substitute into the expression, you get $2/a$ multiplied by a square by 4 and that = $a/2$. So the average position of the particle is $a/2$, which is the center of the box. This makes sense because the particle can be anywhere. And on an average, just by thinking about it in a symmetric manner, the particle should be on an average right in the middle of the box. Let us now consider the average momentum of the particle.

So, average of P that = $2/a \int_0^a \sin n\pi x/a$ and the momentum operator is $-i\hbar d/dx \sin n\pi x/a dx$. This is equal to $2/a \int_0^a \sin n\pi x/a -i\hbar$, and the differential of \sin is $\cosine n\pi x/a$ multiplied by $n\pi/a dx$, which is $2/a$, multiplied by $-i\hbar n\pi/a$, and then $\int_0^a \sin n\pi x/a \cosine n\pi x/a dx$. And if you solve this integral here, you will find that the value of this is = 0. So the average momentum of the particle in a box is = 0.

Now this again, Make sense, because the particle could be moving to the left or to the right. And on an average the momentum of the particle will be just 0 because momentum has a direction. So, the momentum values on the right will cancel those on the left and on an average the momentum will be 0.

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Time Dependence

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$\phi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}$$

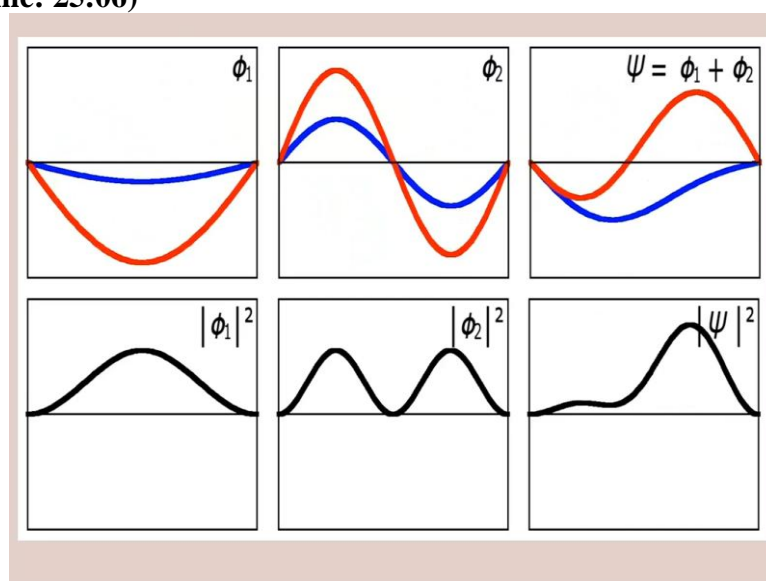
$$= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \left[\cos\left(\frac{E_n t}{\hbar}\right) + i \sin\left(\frac{E_n t}{\hbar}\right) \right]$$

$$\Psi = C_1 \phi_1 + C_2 \phi_2$$

Let us now look at the time dependence of the eigenfunctions of this system. So, we have seen that a general eigenfunction is given by ψ_n of $x = \text{square root of } 2 \text{ over } a \sin n \pi x \text{ over } a$. The time dependent function corresponding to this can be written as $\phi_n(x, t) = \psi_n(x)$ multiplied by e to the power of $-i E_n t / \hbar$. So, if you write this out completely, this will be $\text{square root } 2 \text{ over } a \sin n \pi x \text{ over } a$ and the sin part can be written as the real part \cos of e and $t / \hbar + i \sin e n t / \hbar$.

So, let us look at how the probability density of this wave function evolves in time. And we will also look at how the probability density of wave function which is a linear combination of two eigenfunctions evolves in time.

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You see here, the wave function corresponding to the lowest eigenfunction of the particle in a box in particle, you see the time evolution of this wave function. The real part of this wave function is shown in blue, and the imaginary part is shown in red. As you can see, the real and imaginary parts complement each other, because one is the cosine function, and the other is the sin function. So, as cosine increases, the sin decreases, and that is what you see here, you can now see the second eigenfunction of the particle in a box, and it is time evolution.

Interestingly, the probability density corresponding to both these wave functions, which is shown in the bottom here, does not depend on time. Now, consider the situation where the wave function is a linear combination of the 2 eigenfunctions. In particle, it is an equal linear combination of the 2 eigenfunctions with 50% ψ_1 and 50% ψ_2 . Now, you see that the probability density does depend on time.

And this is consistent with what we have written down before about the time evolution that if a wave function is a linear combination of eigenfunctions it is not a stationary state in that case, the probability density does depend on time.

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The slide, titled "A Model for Spectroscopy", illustrates the relationship between molecular structure and potential energy. It shows three chemical structures of conjugated molecules: ethene, butadiene, and hexatriene. Below each structure is a potential energy diagram. The potential energy is represented by a blue line that is higher at the ends of the molecule and lower in the middle, forming a well. The length of the molecule increases from left to right, and the potential well becomes deeper and wider. Handwritten text on the slide includes "Conjugated molecules" at the top, "Electronic absorption spectroscopy" at the bottom, and "length" with an arrow pointing to the right. A presenter is visible in the bottom right corner of the slide.

The particle box system besides being a simple model to understand quantum mechanics will also serve us as a model to explain electronic spectroscopy for certain classes of molecules. These are conjugated molecules like this, which have double bonds, so, double butadiene like this or a conjugated molecule like this. When there is linear conjugation like this the pi electrons of the system, which are the outermost electrons feel a potential energy, which can be approximately drawn to be of this form.

This is the energy axis here and this is the length of the molecule. So, this potential energy will be more like this in the case of a longer molecule and will have an even longer length in the case of the triply conjugated molecule. The potential energy of this shape implies that the electron is confined to this region and cannot leave. But of course, the walls of this potential energy are not infinite like in the particle box.

Because from the molecule the electron can actually leave however, we will see that the particle in a box is a fairly good approximation to a potential like this. And we will see that based on its eigenvalues, we can explain or model the electronic absorption frequency. We will examine this further when we come to the section on electronic absorption spectroscopy.