**Electronic Properties of the Materials: Computational Approach**
Prof. Somnath Bhowmick
Department of Materials and Engineering
Indian Institute of Technology - Kanpur

Lecture: 03
Schrodinger Equation and Particle in a Box

Hello friends in this lecture we are going to learn about Schrodinger equation and particle in a box. As discussed in the previous lecture draw a model which is based on classical mechanics fails to explain certain things like negative sign of the Hall coefficient heat capacity of electrons etcetera. We need quantum theory for that. In this lecture we are going to learn the basics of quantum theory. We learn the fundamental equation that is the Schrodinger equation and apply it to solve particle in a box problem.

(Refer Slide Time: 00:57)
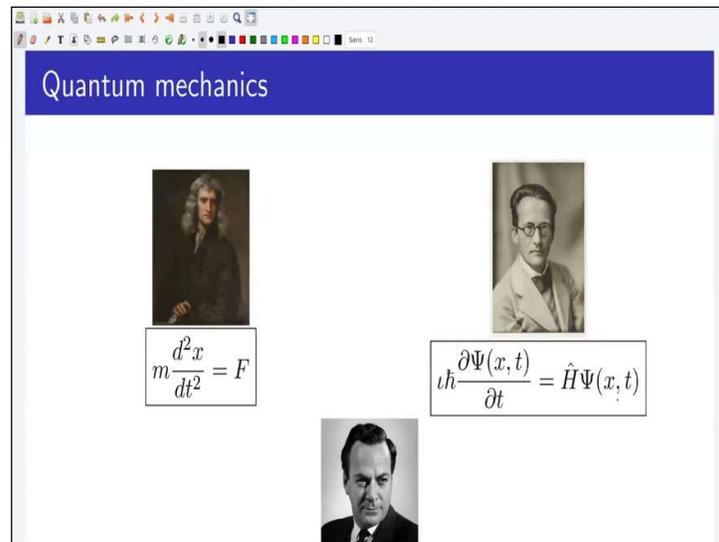
We can start classical mechanics from Newton's second law of motion. Similarly, we can start quantum mechanics from Schrodinger equation. Feynman once stated that I think I can safely say that nobody understands quantum mechanics. In this course we shall not even attempt to understand everything in detail rather we shall focus on getting used to the formalism of quantum mechanics and solve some important problems using this formalism.

(Refer Slide Time: 01:31)

In classical mechanics state of a particle is given by its position and its momentum. We solve Newton's second law of motion $m\frac{d^2x}{dt^2} = F$ with this initial condition $x(0)$ and $p(0)$ and we get $x(t)$ and $p(t)$ for all future time. Similarly in quantum mechanics state of a particle is given by wave function $\Psi(x,t)$. We solve Schrodinger equation and we are given some initial condition $\Psi(x,0)$ and we can get $\Psi(x,t)$ for all future time.

(Refer Slide Time: 02:19)

So, we have to solve this equation we do not know what is H at the moment however you can think of a modified 1d diffusion equation which looks like this

$$i\hbar \frac{1}{\phi}\frac{d\phi}{dt} = \alpha\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E$$

such equations are solved by separation of variables. So, if we replace $\Psi(x,t)$ in this equation what we get is the following

$$i\hbar\psi\frac{d\phi}{dt} = \alpha\phi\frac{d^2\psi}{dx^2}$$

Now divide both the sides by $\phi\psi$. So, if we do that what we get is

$$i\hbar \frac{1}{\phi}\frac{d\phi}{dt} = \alpha\frac{1}{\psi}\frac{d^2\psi}{dx^2}$$

Now you see this is the time dependent part and this is the space dependent part and they have to be equal to some constant which is written as E. Now from this equation what we can write is

$$i\hbar \frac{1}{\phi}\frac{d\phi}{dt} = E$$

and we can solve the time dependent part as

$$\phi \sim e^{-iEt}$$

And the space dependent part we can write as
$$\alpha\frac{d^2\psi}{dx^2} = E$$

Keep in mind that in this slide we have assumed that $\hat{H} = \alpha\frac{d^2}{dx^2}$ and this part is known as the time independent Schrodinger equation and we can write that as $\hat{H}\psi = E\psi$. Note that this is some eigen value problem because this is some operator this is some differential operator.

And it operates on this function psi and I get some constant times the same function that means this is an eigen value problem and we have to solve $\psi(x)$ and E using suitable boundary condition. Once we do that then we can write the time dependent wave function as

$$\psi(x,t) = e^{-i\ /\hbar}$$

(Refer Slide Time: 05:34)

In classical mechanics we solve for $x(t)$ and $p(t)$ and get thermodynamic quantities depending on x, p and these things are solved from Newton's second law of motion. Now, what thermodynamic quantities we are talking about for example we can think of total energy $E(x, p)$ is a function of x. For example, total energy of harmonic oscillator

$$E(x, p) = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

(Refer Slide Time: 07:31)

In quantum mechanics variables are replaced with operators. So, instead of solving for position and momentum what we have to do is that we have to define something called momentum operator which is given by this $-i\hbar\frac{d}{dx}$. So, this is some differential operator or you can define something called $\hat{p}$ square operator which is $-\hbar^2\frac{d^2}{dx^2}$ again some differential operator similarly you can define something called position operator which is just a function x.

You can define some operator for energy and that operator is known as the Hamiltonian operator which is h and this is the kinetic energy operator $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ this is some differential operator and $\hat{V}$ is the potential energy operator. So, thus in this slide we have defined the operator $\hat{H}$ as this and the exact form of time independent Schrodinger equation is

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

In quantum mechanics the first thing that we have to solve is time independent Schrödinger equation and we get the eigen function $\psi(x)$ and eigen value E by doing that. So, once we have solved that then we can write the time dependent wave function as

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

These are known as the stationary states okay let us see why. So, what we do after getting the wave function. What we can do is that we can define something called probability $P(x,t) = \Psi^*(x,t)\Psi(x,t)$ then we can get the position expectation value. So, this is given by psi star of x times the position operator and then we have psi x t dx ok. Similarly, we can get the momentum expectation value and that is given by psi star x and this is the momentum operator and this is the psi x dx and we have to calculate the integral.

Now, note that although the wave function this depends on time however if you calculate the probability density or if you calculate the expectation values then this part e power minus iet by h cross this cancels out because I have psi star and psi okay. So, that will cancel out the time dependent part and that is why these are stationary states however what we have to do is that we can define the general solution like superposition of many, many stationary states.

And if you do that then you get something like this and then this is not a stationary state anymore. Because. Now if you calculate psi starts psi the time part will not cancel out. Note that in this equation E n these are the allowed energy levels which is determined by the boundary condition c n's these are the constants and these are of course the eigen functions.

(Refer Slide Time: 10:04)

In classical mechanics given initial condition x naught p naught position and momentum of a particle is known exactly at any point of time xt. However in quantum mechanics we go for some statistical interpretation and define some probability density. Now if you look at this picture the probability of finding the particle is more here the probability of finding the particle is less here.

Now suppose you measure the position of the particle at some point of time and then you find the particle to be here. Now you can ask the question where was the particle just before the measurement was done? The answer is nowhere. The art of measurement force the particle to take a stand. This point might not be clear at this point of time. However you must appreciate that there exists some indeterminacy in quantum mechanics. What happens when you make some measurement the Oil function collapses shown by this dotted line immediately after the measurement.

(Refer Slide Time: 11:27)

Now there is another kind of uncertainty in quantum mechanics unlike classical we cannot measure position and momentum very accurately simultaneously if we measure the position very accurately momentum measurement becomes inaccurate and vice versa. Consider the 2 wave functions given in this picture. First one is a single wave and the momentum is fixed we can use this lambda is equals to h by p. If I have a single wavelength then p is fixed second one is a superposition of n sine functions. For example if we superpose all of them sine x sine 2x and if we do if we take 10 such terms then we get this picture. Now if you ask where is the particle. Now its position is somewhat localized. However we cannot tell what is its exact momentum because since it is a superposition of so, many waves I do not have a single lambda. So, that means if I measure the position somewhat accurately the momentum measurement becomes inaccurate and it is impossible to go beyond certain limit when you are measuring simultaneously the position and momentum. And the limit is given by the hydrogen bond uncertainty principle delta x delta p it cannot go to zero. So, it is greater than equal to h bar by 2.

(Refer Slide Time: 13:20)

$$\Rightarrow \frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

$V=\infty$ $V=\infty$

$V=0$

ψ_{10}

ψ_3

ψ_2

ψ_1

0 L

- TISE: $\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x),\ k^2 = \frac{2mE}{\hbar^2}$
- $\psi(x) = A\cos(kx) + B\sin(kx)$
- Boundary condition: $\psi(0) = \psi(L) = 0$

$$\psi(x) = B\sin kx$$
$$\psi(L) = B\sin kL = 0$$
$$\sin kL = \sin n\pi$$
$$k_n = \frac{n\pi}{L}$$

- Thus: $A = 0,\ k = \frac{n\pi}{L}$
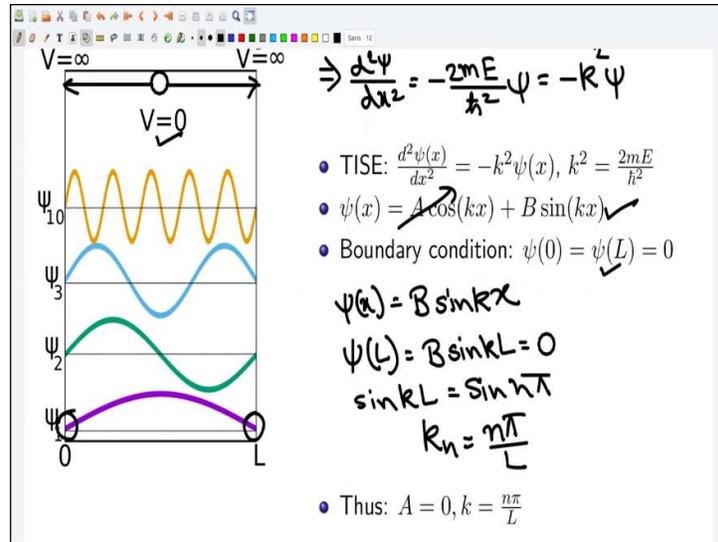
Now let us solve for particle in a box problem. So, you can imagine that this is some, one dimensional box and a particle is confined within the box and it can move along this direction or it can move along this direction and then it collides with the wall and it travels back. Since the particle cannot escape from the box we have infinitely high potential at the box edges however inside the box the potential is zero.

So, let us write the Schrodinger the time independent part of it so h cross square by 2m] d 2 psi dx square + b of x psi is equals to e psi and inside the box V of x is equals to 0. So, we can write d 2 psi dx square is equals to minus 2m E by h square psi and this term we write it as k square. So, we can just write it as minus k square psi. Now a general solution is given by this it is very easy to verify that this will be a general solution.

Because if we take a derivative of cosine or sine twice we get a minus sign ok. Now because of the boundary condition which is given by psi of 0 is equal to psi of l is equals to 0. So, that means the wave function must go to 0 here as well as here because of the boundary condition we see that a has to be equal to 0. Thus the wave function is given by psi of x is equals to B psi kx. Now we can use this part of the boundary condition which tells that psi of L is equals to B sine kL is equals to 0.

And which implies that sine of kL is equals to sine of n pi this implies that k of n has to be equal to n pi by L. Thus we have solve for the eigen function and we can write psi n of x is equals to B sine n pi x by L.

(Refer Slide Time: 16:37)

Since y functions are related to the probability they must be normalized that implies that they must satisfy this. So, we write the eigen functions and let us sine square n pi x by L dx and this integral should give us 1. So, now we can write it as this is like 1 minus cos 2pi nx by L dx is equal to 1 and this part of the integral is going to be 0 which implies that b square by 2 times l is equals to 1 and that gives me the constant B which is equal to root over 2 by L. Thus the eigen function is written in this form.

(Refer Slide Time: 18:07)

We have solved for the eigen functions and we know that k square is given by this and the values of k are given by this. So, from these 2 equations we can solve for the eigen values thus E n is equals to h cross square k n square by 2m and now we know the allowed values of k are given by this and thus we can write this is equal to h cross square n square pi square by 2m L square. The eigen functions as well as eigenvalues.

(Refer Slide Time: 18:57)
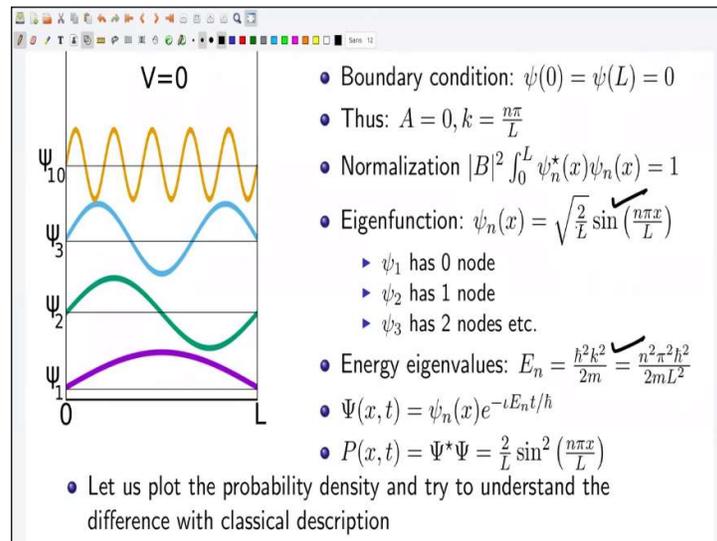
Now let us plot a few eigen functions. So, if you plot psi 1. So, this is Psi 1 this is psi 2 this is Psi 3 and so on and one thing you can note that psi 1 has zero nodes psi 2 has one node and psi 3 has 2 nodes and so on. So, what is the node where the wave function crosses this zero line note that the Oil function is zero at the boundaries but we do not count them as nodes. Only if the wave function crosses the zero line inside the box those things are counted as nodes.

Now once we have solved for the eigen values and eigen functions we can write the time dependent wave function in terms of the eigen functions and the eigen values. Let us try to plot the probability density and understand the difference with the classical description.

(Refer Slide Time: 20:08)
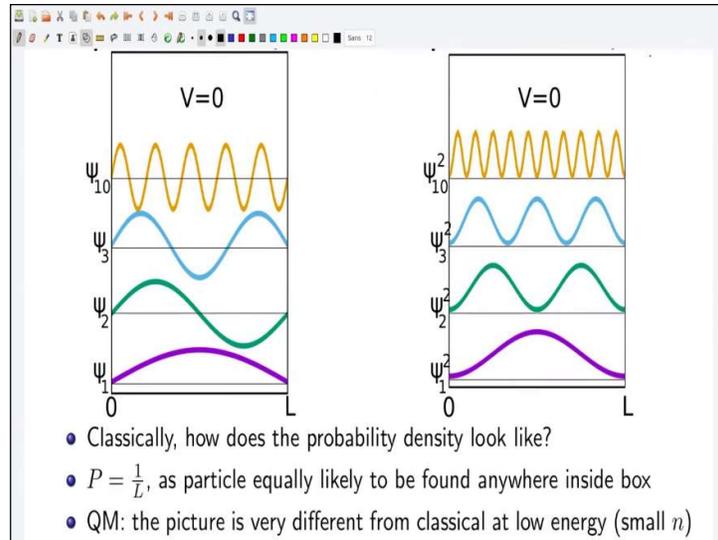
Classically how does the probability density look like. Classically the particle is equally likely to be found anywhere inside the box thus the probability density is given by one over L. However the picture is very different in quantum mechanics. For example if you look at the ground set wave function then the probability density is the highest in the middle of the box. So, if you look at the first excited state then the probability density is very high at these 2 points.

If you look at the second excited state then the probability density is very high at these three points and so on. So, unlike classical the particle is not equally likely to be found anywhere inside the box but the probability density is very high at certain points. However if you look at some high energy then you see that the probability density appears to be more equally distributed inside the box. Thus if we go to very high value of n the quantum mechanical probability density will resemble the classical probability density.

(Refer Slide Time: 21:31)

Particle in a 1D box

- Let us calculate position expectation value for stationary states
- Wave function: $\Psi(x,t) = \psi_n(x)e^{-\iota E_n t/\hbar}$

Position operator :→ $\hat{x} = x$

Square of position operator :→ $\hat{x}\hat{x} = x^2$

- $\langle x \rangle = \int_0^L \Psi^\star(x,t)x\Psi(x,t)dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L}{2}$
- $\langle x^2 \rangle_n = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x^2\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L^2}{3} - \frac{L^2}{2\pi^2 n^2}$

Now let us calculate some expectation values and we start with position expectation value the oil function is given by this. The position operator is just a function x and we can also define square of position operator which is given by a function x square.

(Refer Slide Time: 22:18)

- $\langle x \rangle = \int_0^L \Psi^\star(x,t)x\Psi(x,t)dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L}{2}$
- $\langle x^2 \rangle_n = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x^2\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L^2}{3} - \frac{L^2}{2\pi^2 n^2}$

$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{L^2}{3} - \frac{L^2}{2\pi^2} - \frac{L^2}{4}}$

- $\Delta x_n = \frac{L}{2\pi n}\sqrt{\frac{\pi^2 n^2}{3} - 2}$, wider box − more position uncertainty

Now how do we calculate the expectation values. So, position expectation value is given by psi star times the operator times psi dx and we have to find the integral 0 to l and that turns out to be l by 2. Similarly the expectation value of x square is given by psi star the operator psi and

then you have to calculate the integral and that turns out to be this. Now we can define delta of x which is given by x square and x bar square which is equal to square root of L square by 3 L square by 2 pi square n square minus x square by 4.

And that turns out to be this number and you see that the position uncertainty is proportional to L that means wider the box there is more position uncertainty which makes perfect sense.

(Refer Slide Time: 23:34)

Next we calculate momentum expectation value we know that the momentum operator is given by minus ih + del del x. So, this is some differential operator and similarly we can define square of the momentum operator which is given by minus h cross square delta del x square. Now we calculate momentum expectation value. So, this is given by psi star the momentum operator psi dx and we have to calculate the integral and then this turns out to be equal to zero.

Similarly for p square we write psi star and then this is the p square operator psi dx and if you calculate the integral then this is what you get. Thus we can define momentum or we can write momentum uncertainty as p square average minus the average square and that will just turn out to be since this part is 0 this is just square root of n square pi square h + square by L square delta p varies inversely with L that means wider the box less will be the momentum uncertainty.

(Refer Slide Time: 25:11)

- $\langle x \rangle = \int_0^L \Psi^\star(x,t)x\Psi(x,t)dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L}{2}$ ✔

- $\langle x^2 \rangle_n = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x^2\sin\left(\frac{n\pi x}{L}\right)dx = \frac{L^2}{3} - \frac{L^2}{2\pi^2 n^2}$ ✔

- $\langle p \rangle = \int \Psi^\star\left(-\iota\hbar\frac{\partial}{\partial x}\right)\Psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(-\iota\hbar\frac{\partial}{\partial x}\right)\sin\left(\frac{n\pi x}{L}\right)dx = 0$ ✔

- $\langle p^2 \rangle_n = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right)\sin\left(\frac{n\pi x}{L}\right)dx = \frac{n^2\hbar^2\pi^2}{L^2}$ ✔

- $\Delta x_n \Delta p_n = \left(\frac{L}{2\pi n}\sqrt{\frac{\pi^2 n^2}{3} - 2}\right)\left(\frac{n\pi\hbar}{L}\right) = \frac{\hbar}{2}\sqrt{\frac{\pi^2 n^2}{3} - 2}$ ✔

- Minimum $\Delta x \Delta p = 1.13\left(\frac{\hbar}{2}\right)$ for $n = 1$, uncertainty principle satisfied

- Quantum particle in a box: so far expectation values are static, as we have used *stationary* states

- Classically, x and p does depend on time

- Need more work to get time dependence in quantum particle in a box

The expectation value of x the expectation value of x square the expectation value of p the expectation value of t square we also have calculated the position uncertainty as well as the momentum uncertainty. Now let us multiply them and see whether it satisfies Heisenberg uncertainty principle. So, this is the expression for delta x times delta p and you see that the minimum of this will occur at n equal to 1 and that turns out to be 1.13 times h cross by 2.

Thus uncertainty principle is satisfied. Now must have noticed that in case of quantum particle in a box the expectation values are static. Why this has happened because we have used stationary states. However if you look at classically x and p does depend on time so, can we get this time dependent picture in case of quantum particle in a box? The answer is yes and let us see how do we do that.

(Refer Slide Time: 26:33)
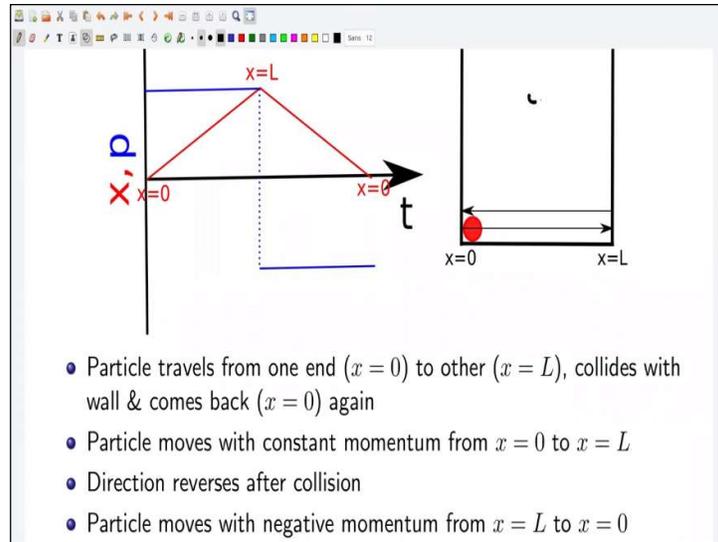
Before we solve the quantum problem let us see what happens classically. So, the particle travels from one end of the box to the other end and then it collides with the wall and comes back in this direction. So, if you plot the position of the particle as a function of time. So, it goes like this. So, it moves from one end to the other and collides with the wall and then it comes back. And if you look at the momentum then the particle moves with constant momentum in this direction after the collision the direction reverses and the particle moves with negative momentum.

(Refer Slide Time: 27:17)
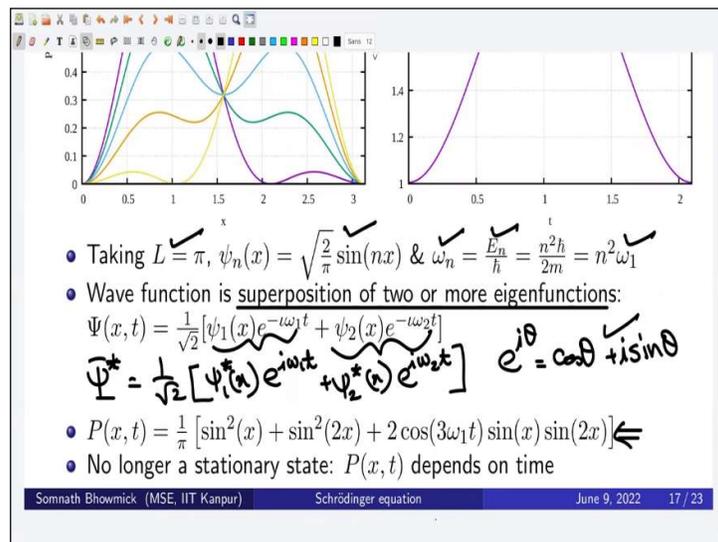
Now we solve for quantum particle in a box. Just to simplify some algebra we will take the box length to be equal to pi such that the eigen functions look like this and we define omega of n as n by h cross and that turns out to be equal to this. Instead of the stationary state we take

some wave function which is superposition of 2 or more eigen functions. So, psi of xt this is the superposition of the ground state and the first excited state eigen function.

Now we can just write psi star is equals to 1 by root 2 psi 1 of x e power I omega 1 t + psi 2 star i omega and we have to use e power i theta is equals to cos theta + i sin theta. Now you can just write psi phi star and using this formula the psi psi star will turn out to be equal to this. Now you see that the probability density is no longer stationary because I have a time dependent part.

(Refer Slide Time: 29:12)
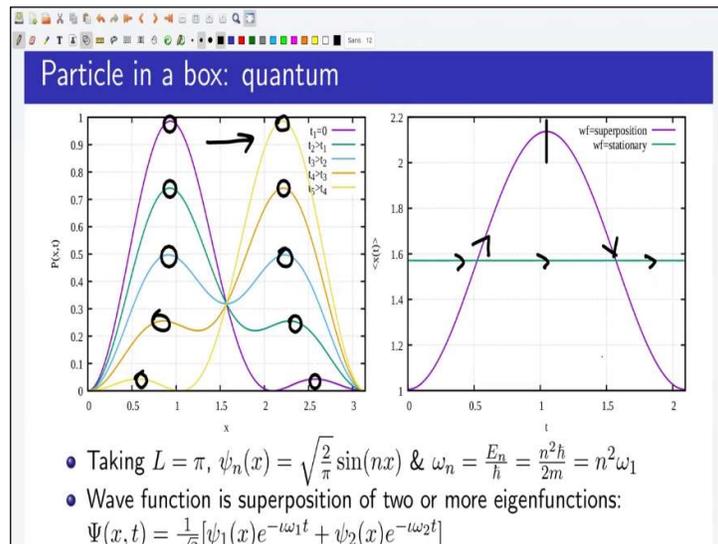
Let us plot t of x t at various different time. So, at time t equal to 0 the probability of finding the particle is very high in the left hand side of the box whereas it is very low in the right hand side of the box. As time progresses the probability of finding the particle in left hand side of the box decreases and the probability of finding the particle in the right hand side of the box increases.

So, at time t 3 the particle is equally likely to be found in the right hand as well as the left hand side and then even further the probability of finding the particle is high in the right hand side and it becomes low in the left hand side. So, it appears that as if the particle is moving from left hand side to the right hand side of the box. Now you can calculate the position expectation value using this formula.

And then you will find that even the position expectation value that also depends on time and if you calculate the integral this is what you get and if you plot this then you see that as time progresses the particle is travelling from left hand side to the right hand side and it supports the collision at this point and then it starts moving in the opposite direction and it comes back. This is unlike the stationary wave function where the position expectation value is not a function of time this remains constant along this line.

(Refer Slide Time: 31:05)

Let us see how to solve a general initial value problem. State of a particle at time t is written using the eigenvalues and eigen functions in this manner. Now psi n and E n are solved from time independent Schrodinger equation for a given potential and boundary condition. Now the question is how do we get c n? We get c n from the initial condition. Before we solve a problem we need to know one important property eigen functions are mutually orthonormal. So, this implies that if we take 2 different eigen functions and then if we calculate this integral 0 to L psi m pi x by L psi n pi x by L dx that will turn out to be equal to 0 because m is not equal to n m and n both of them are integers but they are not equal however if m is equal to n then this integral 0 to L sine square n pi x by L dx that will turn out to be equal to 1.
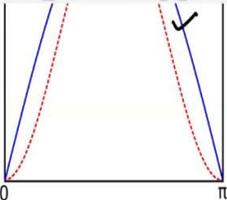
(Refer Slide Time: 32:49)

Now we start by writing the wave function at time t equal to 0. So, if you just put t equal to 0 in this equation what you get is psi x 0 this is no longer a function of time this is just a function of x and that will turn out to be sum over n c n psi n of x. So, now let us see that using this orthonormality condition how do we get this constants c n. So, we write f of x is equal to sum over n c n psi n of x. And what we do is we multiply both the sides by this and then calculate the integral. Now we know that this part of the integral that is delta of mn. So, we can write this as sum over n c n delta. Now you see only the term m equal to n survive okay. So, in that case we can just write c of n as integral 0 to l f of x psi n star x dx. Note the similarity of whatever we have done so, far with the Fourier series.

(Refer Slide Time: 35:09)

Let us solve a problem of particle in a box having initial condition this. The initial condition is plotted here we know that in case of particle in a box the eigen functions are given by this and again we have assumed l equal to pi then we can calculate this constants c n and it turns out to be equal to this. Now you know that cos of n pi is equals to + 1 for n even and this is equal to minus 1 for n on. Thus, the even terms will cancel out and the odd terms will turn out to be like this. Now we write the psi of xt as superposition of all the stationary states. So, this turns out to be c 1 psi 1 x times e power minus i omega 1t and then the c 2 term is 0 because the even terms are 0 and then we have we get like c 3 and so on and in the compact form we can write it like this.

(Refer Slide Time: 36:35)
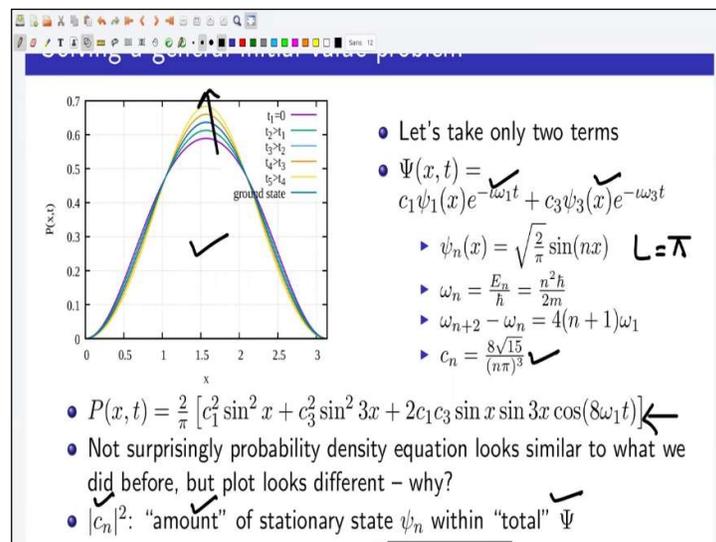
Let us take only 2 terms in the expansion the ground state and only one excited state keep in mind that we are using L equal to pi. In that case the probability density looks like this. Not surprisingly the probability density equation looks very similar to what we did before but the plot looks different. So, mod psi n square this is the amount of stationary state psi n within the total psi and then sum of all the terms should be equal to 1.

So, in this example if you calculate psi c of 1 then you will find that c of 1 square will turn out to be 0.9986 that means the particle is almost entirely in the ground state and very less amount of it is in the excited state. That is why if you plot p of xt as a function of time it appears that all the probability densities they look very similar to the ground state probability densities.

Let us calculate the energy expectation value which is given by psi star the Hamiltonian operator psi dx and you have to calculate the integral let us prove that this is something which is time independent. So, we just work with only 2 states and right psi xt as c 1 psi 1 of x e power minus i omega 1 t + c 3 psi 3 of x e power minus i omega 3 t. So, now we can write the energy expectation value s. So, first we have to write psi star.

So, that is c 1 star psi 1 star e power i omega 1 t + c 3 star psi 3 star e power I omega 3 t this times the Hamiltonian operator times the c 1 psi 1 e power minus i omega 1 t + c 3 psi 3 e power minus i omega 3 t dx. Now note that h times psi 1 is equals to u1 phi 1 right. So, we can just write H psi 1 is equals to e 1 psi 1 and H psi 3 is equals to e 3 psi 3. So, if we do that then we find that this is equal to mod c 1 square E 1. And then we have psi 1 star psi 1 dx + mod c 3 square E 3 integral psi 3 star psi 3 dx. Now you have some other terms which will have psi 1 star psi 3 dx and psi 3 star psi 1 dx because of orthonormality these terms go to 0 and again because of orthonormality this term is equal to 1 and this term is equals to 1. So, which implies that H is equal to mod c 1 square E 1 + mod c 3 square E 3. Now you can take any number of terms and then derive this.

(Refer Slide Time: 41:12)

Now you notice that this is time independent. So, does it mean that every time I measure the energy I get the same value? The answer is no. If we do energy measurement then psi x t will collapse to one of the stationary states. So, that means the psi x 2 will collapse to either the ground state or the excited state and then I measure the corresponding energy E of n. State of the particle before I do the measurement is not a relevant question you do many such measurement and calculate the energy expectation value. Let us assume that c 1 is equals to root 3 by 4 and c 2 is equals to root 1 by 4 and now if you do the energy measurement 100 times then you are expected to get the particle in current ground state 75 times and in excited state 25 times. Now you calculate the average and then you will get this number. Thus mod c n square is nothing but probability of getting an eigenvalue E n in a measurement.

(Refer Slide Time: 42:35)

Let me summarize whatever we have done in the lecture. So, how do we solve a quantum mechanics problem. So, first step is you solve the time independent Schrödinger equation you solve for eigen functions as well as eigen values. Now using the eigen functions and eigen values to construct the time dependent wave function which is given by this. Eigen functions are mutually orthogonal and using this orthonormality or orthogonality we get the values of c n from this equation. Now once we have c n we know what is psi of xt? The wave function. Now position expectation value now can be calculated by using psi star times the position operator psi dx and calculate the integral. Similarly you can calculate the momentum expectation value if you use the momentum operator. Now energy expectation value is given by sum over n c n square E n. And mod of c n square is probability of getting an eigen value E n in a measurement.

And if you add all of them you get a number equal to 1. Energy eigenvalues and eigenfunctions will change depending on the potential and the boundary condition we are using. Rest of the steps remain exactly same. So, let us solve for different potentials and boundary conditions.