Concepts of Chemistry for Engineering
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Lecture No. 05
Quantum mechanics of a free particle

We have established the tenets of quantum mechanics. Now, we are going to slowly get into systems in which quantum mechanics is applicable, and we will see how we can build a description of these systems.

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The first system that we are going to talk about is a particle that is as free as this colorful little bird here. We call it a free particle, what is the meaning of a free particle? We will come to that.

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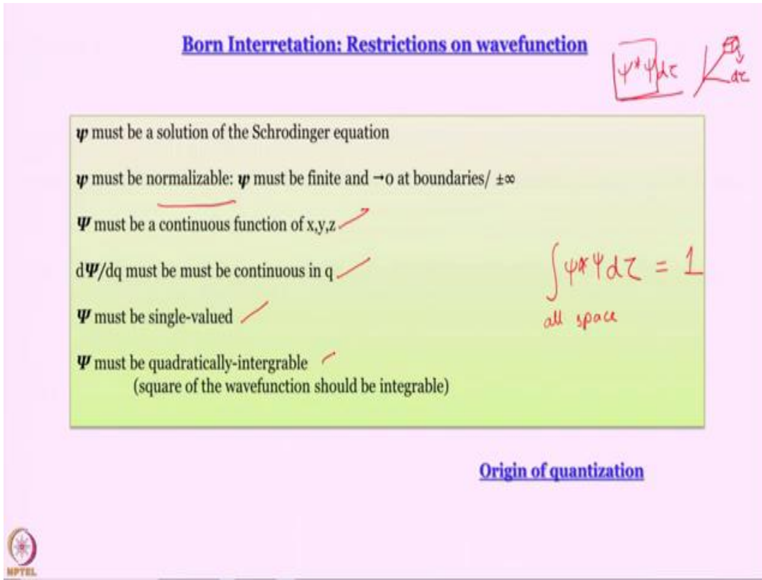

But before we do, let us remind ourselves that so far, we have discussed Schrödinger equation, we have said that Schrödinger equation yields wave functions and this wave functions sorry about the mistake in spelling here, these wave functions are interpreted by Max Born to be associated with what we call probability waves. So, $|\Psi(x,t)|^2$is equal to the probability density that is what we have said.

So, so far, we know that psi has to be a solution of Schrödinger equation, it must be normalizable. Why? Because if $\Psi\Psi^*$ is probability density, then we remember that $\Psi\Psi^*$ or the way it is conventionally written, $\Psi^*\Psi d\tau$ is the probability of finding the particle in a small volume element $d\tau$ at a particular position.

So, if it is Cartesian coordinate $d\tau$ will be dx, dy, dz. So, probability of finding a particle somewhere in space at this point is given by the probability of finding it in this small little box here, which is called the volume element. And we are saying the volume of this volume element is $d\tau$. This is probability and $\Psi\Psi^*$ is probability density.

Naturally, you have to find the particle somewhere in space. So, we write $\int \Psi^* \Psi d\tau$ over all space, I will just write all space here, I think in the last class, I had written - ∞ to + ∞ I will not do that, because you will see what ∞ might mean here. It is not necessarily ∞, ∞, so integrate it over all space that has to be equal to 1 that is your normalization condition.

Next, we said psi has to be continuous. And we will see how this is very useful in our discussion, maybe not in this module, in the next module. Now, $\frac{d\Psi}{dq}$, this has to be continuous in q, we are going to see that, this is not a very rigid condition, this does not really arise out of Born interpretation, it arises out of the requirement that we are writing a second derivative, that is why.

Ψ must be single valued. This of course comes from Born interpretation, you cannot have more than one probability density for a given point. And it has to be quadratically integrable. That these are in a nutshell the conditions that a wave functions must satisfy. And as we are going to see in the next couple of modules, quantization arises out of application of these conditions, imposition of these conditions.

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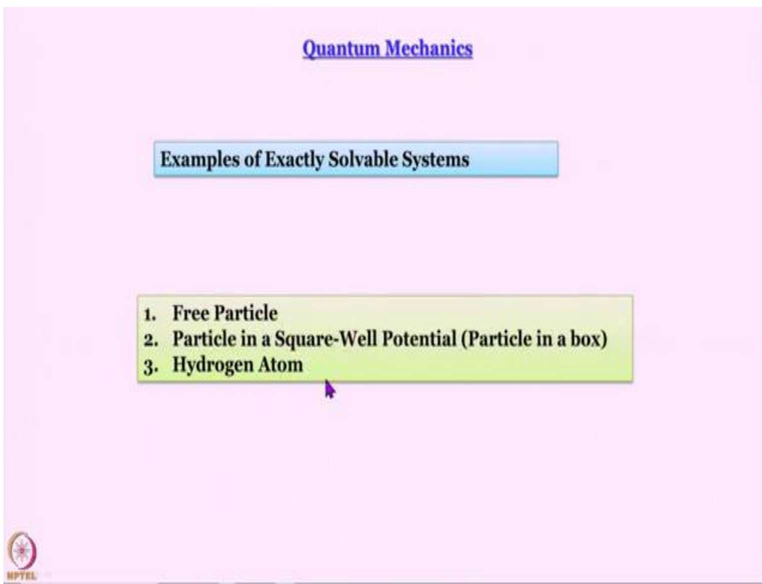

And we will do that. And we will study these three systems. Today we will talk about free particle, then we are going to encage that particle, put it in what is called a square well potential, that is called the particle in a box problem. And finally, we will go on to discuss hydrogen atom.

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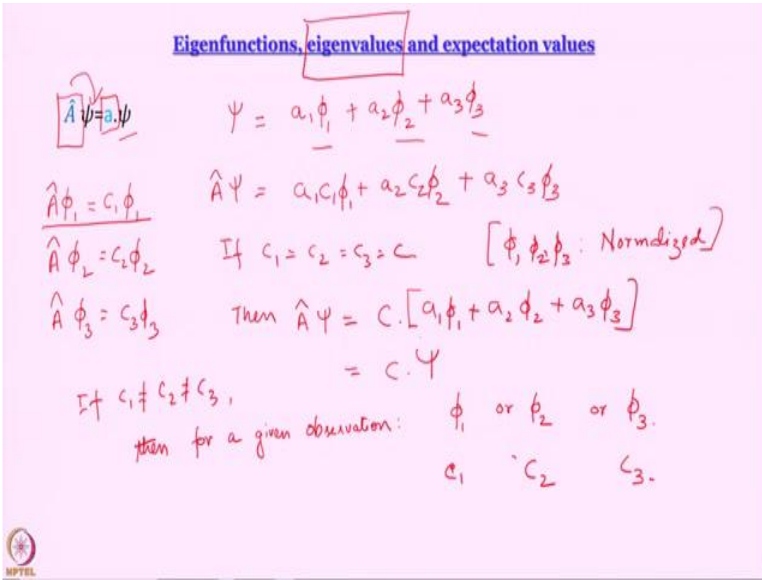

But before that, I want to talk a little bit about Eigen functions, Eigen values and expectation values. And I have been a little lazy. That is why I have not really written these things here. I will write it in real time. So, as we said, the postulates of quantum mechanics tell us that for every observable, we should be able to construct an operator here I am writing Â.

And when this operator operates on the wave function Ψ, we get an Eigen value equation, where the same Ψ is multiplied by a number, that number is called the Eigen value. It is not necessary that always a system will be described by a wave function that is an Eigen function of the operator that we desire. And that is what we will need to understand. You might remember that in the postulates, we had said that the wave function has to be a sum of mutually orthogonal Eigen functions.

So, let us say that I have a wave function Ψ for some system, and we are actually going to encounter a system like this very soon, which is a linear combination of say $a_1\phi_1$, remember I do not necessarily have to write Ψ for a function I can write anything. So, $a_1\phi_1 + a_2\phi_2 + a_3\phi_3$ and these ϕ are such that they are Eigen functions. So, let us say Â operates on the wave function ϕ_1 to give us, I have written 'a' already, so let us say $c_1\phi_1$, let us say Â operates on ϕ_2 to give us $c_2\phi_2$ and Â operates on ϕ_3 to give us $c_3\phi_3$.

Is Ψ an Eigen function of A in that case, let us see. Remember these are all linear operators. So, when Â operates on Ψ, what do I get? I get $a_1c_1\phi_1 + a_2c_2\phi_2 + a_3c_3\phi_3$, where is the $c_1\phi_1$ and

$c_2\phi_2$ coming from? From here. Now, see is there any way in which I can take this $a_1\phi_1 + a_2\phi_2 + a_3\phi_3$ out? This will happen only if $c_1 = c_2 = c_3$. If $c_1 = c_2 = c_3$ equal to some c, then only, only then I am going to get $\hat{A}\Psi = c.[a_1\phi_1 + a_2\phi_2 + a_3\phi_3]$, which is essentially Ψ.

So, now I get c multiplied by Ψ (cΨ). So, the problem now is that, that is the only condition in which it will be an Eigen value equation. So, a linear sum of Eigen functions is an Eigen function, if the constituent Eigen functions ϕ_1, ϕ_2, ϕ_3 here have the same Eigen value. This is something that we are going to use when we talk about p orbitals later on. But this is a very specific case. What is the general case? The general case is that this is not an Eigen function. If c_1, c_2 and c_3 are not equal to each other, then what happens?

Then, what are the values that I will get if I perform some experiment? Remember we had talked about wave function collapse, we had said that the system before measurement exists in an entangled state, when you perform a measurement, it collapses into a particular wave function depending on the experiment you perform, and that is what you see.

So, when you perform an experiment on the system, I am going to see either ϕ_1 or ϕ_2, or ϕ_3. For a given experiment, for or rather let me say for a given observation, the system is going to reveal itself to us either as ϕ_1 or ϕ_2 or ϕ_3. And one thing I forgot to say is that ϕ_1, ϕ_2, ϕ_3, these are all normalized wave functions. So, you are going to see either ϕ_1 or ϕ_2 or ϕ_3.

So, the variable A that you measure, you are going to, for some experiments you are going to see a value of a_1, for some experiments, for some experiments, you are going to see a value of c_1 . For some experiments, you are going to get a value of c_2 . For some you are going to see a value of c_3 . What is the average value that you will get?

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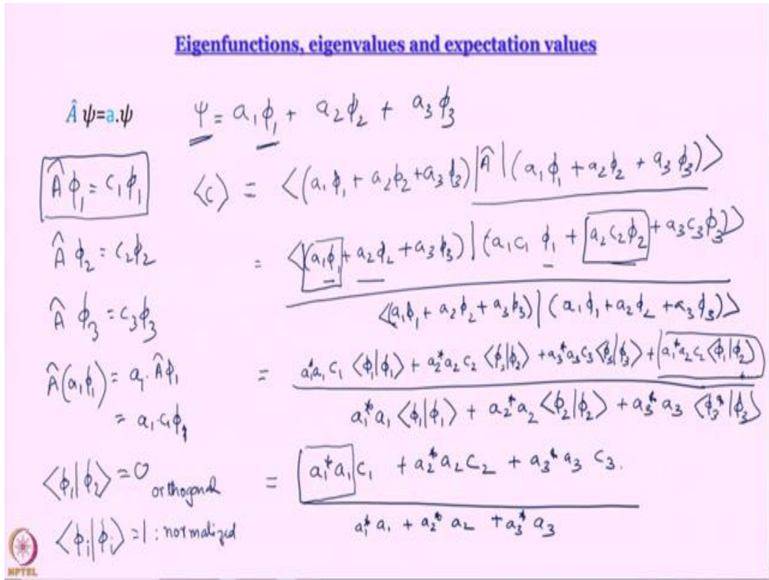

As we said, you are going to see either c_1 or c_2 or c_3. When you perform a particular observation or particular experiment, what is the average value that you will see? Average value of let us say, c, or I could have written Â also, that is going to be if I am using a bad convention, I should have written c as coefficient and A as Eigen value, but that is fine.

So, that is going to be integral. And I hope you remember this Dirac notation, <$(a_1\phi_1 + a_2\phi_2 + a_3\phi_3)|$. Then Â operating on, the second vertical line is absolutely not necessary, it is just written so that it looks a little better, $|a_1\phi_1 + a_2\phi_2 + a_3\phi_3$>. What will I do? First of all, I will work with the ket vector, I will leave the bra vector as it is, and write <$(a_1\phi_1 + a_2\phi_2 + a_3\phi_3)|$.

And now what happens when Â operates on ϕ_1, I get c_1, and a_1 is already there. So, in the ket vector, I get $|(a_1\phi_1 + a_2\phi_2 + a_3\phi_3)$>. I hope you understand what I am doing. When Â operates on ϕ_1, I get $c_1\phi_1$. So, when Â operates on $a_1\phi_1$, I get a_1 . Âϕ_1, that is equal to $a_1 . c_1\phi_1$. These are linear operators remember. And similarly, we can proceed with ϕ_2 and ϕ_3 also.

Now, I will open the bracket and write what I get. I have missed something. In the denominator, I will get something, denominator is also there. I am not writing it in the first line, second line at least I should write. In the denominator I get <$(a_1\phi_1 + a_2\phi_2 + a_3\phi_3)|(a_1\phi_1 + a_2\phi_2 + a_3\phi_3)$>. Because you know, there is no guarantee that this Ψ is normalized. So, in order to normalize it, I have to divide it by this integral $\Psi\Psi^*$.

So, let us go ahead and open this now, what will I get in the numerator? I get well, something like this $a_1^* a_1$ because the coefficients can also be imaginary, multiplied by $c_1 < \phi_1 | \phi_1 >$, there is a first term I get. Similarly, second term I get will be from say ϕ_2 , ϕ_3, so let us just take the ϕ_i terms first.

What will I get there? $a_2^* a_2 \, c_2 < \phi_2 | \phi_2 >$ overall space + $a_3^* a_3 \;\; c_3 < \phi_3 | \phi_3 >$ overall space. And then I just write one more term and not write anything else. Because what will be this one for example, if I take $a_1 \phi_1$ and $a_2 \, c_2 \phi_2$, then I will get a_1^*, remember anything in bra vector is actually complex conjugate $a_1^* a_2$, then I will get c_2 is a constant, it comes out $< \phi_1 | \phi_2 >$ overall space. And I will get many more terms like this.

The problem is $< \phi_1 | \phi_2 >$ overall space is actually 0. Why? Because they are the functions that we said we have defined that ϕ_1, ϕ_2, ϕ_3 are mutually orthogonal. So, the only terms that will survive are the ones on the top. What about the denominator? Well, the three terms that I have written out, this is going to be 0.

What is the denominator? Denominator is going to be $a_1^* a_1 < \phi_1 | \phi_1 >$ + $a_2^* a_2 < \phi_2 | \phi_2 >$ $+ a_3^* a_3 < \phi_3 | \phi_3 >$. Now, see these ϕ_1, ϕ_2, ϕ_3 they are all normalized, so I can write like this now $< \phi_i | \phi_i >$, I can just like write i, i can be 1 or 2 or 3, $< \phi_i | \phi_i >$overall space is actually equal to 1 as they are all normalized.

So, what does the average value turn out to be? It turns out to be $a_1^* a_1 \;\; c_1 + a_2^* a_2 c_2$ + $a_3^* a_3$ c_3 divided by $a_1^* a_1 + a_2^* a_2$ + $a_3^* a_3$. This is your average value. So, it is important to understand what we have just seen, this is a very important aspect of quantum mechanics.

What we have learned is that when you perform a particular experiment, you are going to experience one of these Eigen functions. So, you will get one of their Eigen values, fine. And then when you perform an average measurement, what will be the number of times you observe C1 or C2 or C3 that depends on $a_i^* a_i$. So, mod square of the coefficient of these wave functions gives you the fraction of times you are going to see a particular Eigen value.

This is an important thing in quantum mechanics that we needed to know before we can go ahead further. And we have also learned in the process that if all the Eigen values are the same, then the linear combination is going to be an Eigen function as well. That being said, let us now go ahead and talk about our free particle.

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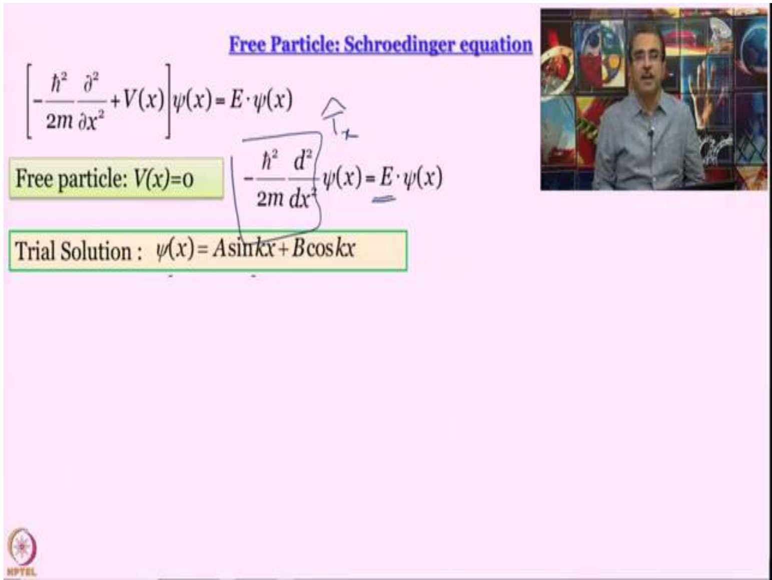

The meaning of free particle is that if you write the Schrödinger equation $[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)]\psi(x)=E.\psi(x)$, this $V(x)$is going to be 0, free particle means we have created a situation where the particle is not under any field of anything in the universe. So, you can think it is like you have an atom and you are provided ionization energy to the electron. So, the electron has just come out of the potential of the atom. Or you can think of a satellite that has just come out of the gravitational potential of earth, that kind of a particle is a free particle.

In fact, you can create free electrons and stuff in equipment, like what are called synchrotrons. So, $V(x)$ going to be equal to 0. So, the Schrödinger equation then for free particle boils down to this $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}]\psi(x)=E.\psi(x)$. Now, we are working in 1 dimension to start with, if we are working in 3 dimensions, if we said the particle is free in all directions, then I just have to add $\frac{d^2}{dy^2}+\frac{d^2}{dz^2}$ and Ψ would have been a function of x and y and z, not very difficult to extrapolate from here.

So, this is Schrödinger equation for a free particle in one dimensional space. And this here $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}]$, this is the kinetic energy operator. It is often called the T operator and here since it is along x direction, I will write $\widehat{T_x}$. This is the kinetic energy operator. So, this E of course, is going to be only kinetic energy for a free particle, as we said there is no potential energy anyway.

Now, this is a differential equation. And we are familiar with these differential equations, I hope. So, the trial solution that we can think of is $\psi(x) = A\ sinkx + B\ coskx$, we can think of another kind of trial function or solution as well, we will come to that.

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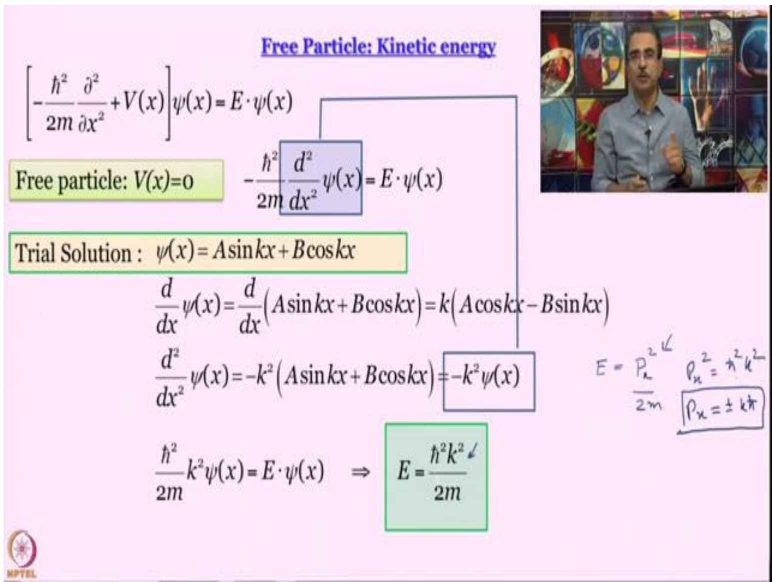

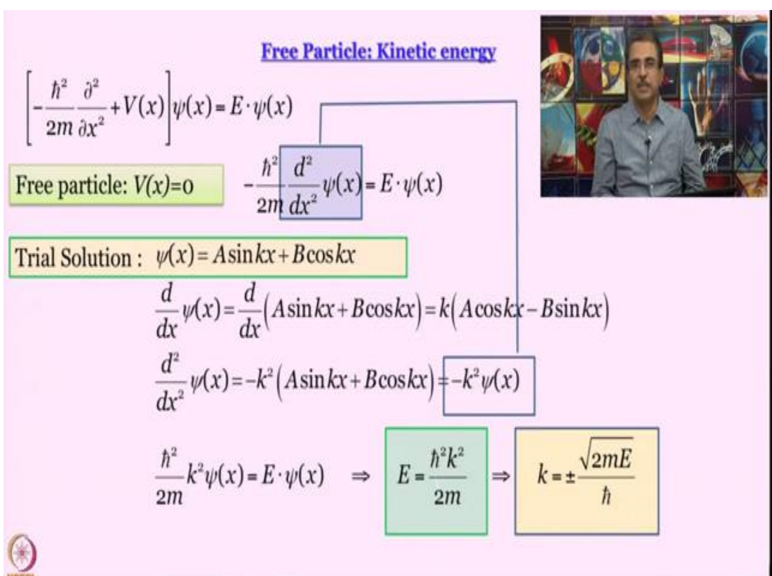

Now, here, is this a good trial solution? Well, to know that all we have to do is differentiate, differentiate once, this is what you get $\frac{d}{dx}\psi(x) = \frac{d}{dx}(A\ sinkx + B\ coskx) = k(A\ coskx -$

$B\ sinkx)$, differentiate twice this is what you get $\frac{d^2}{dx^2}\psi(x) = -k^2 \frac{d}{dx}(A\ sinkx + B\ coskx) = -k^2\ \psi(x)$. I am not going through the steps because it is very simple. This is the solution. I encourage you to just do it once yourself, and then you will be convinced.

Now, the question I want to ask is, what is this k? I have got $\frac{d^2}{dx^2}\psi(x) = -k^2\ \psi(x)$. What is k then? If I plug k back into the original Schrödinger equation, we see that if I replace $\frac{d^2}{dx^2}\psi(x)$ by a $-k^2\ \psi(x)$, then I get $\frac{\hbar^2}{2m}k^2\ \psi(x)$= $E.\psi(x)$.

Or in other words, I can write this energy as $\frac{\hbar^2 k^2}{2m}$, k is a measure of energy or rather k is a measure of energy. And remember that this energy is entirely kinetic energy. So, I can write another expression here, I know that if it is kinetic energy, then what is the relationship between kinetic energy and say linear momentum.

I will write Px here, because the motion is only along x. So, $E = \frac{P_x^2}{2m}$ we know that. So, if I compare this expression $E = \frac{\hbar^2 k^2}{2m}$ and this expression $E = \frac{P_x^2}{2m}$, then what will I get? 2m in the denominator, so, $P_x^2 = \hbar^2 k^2$ and so, well, what is Px then? That will be equal to $\pm k\hbar$.

So, what we see is that it appears that we are going to have a momentum of $k\hbar$ and the particle can move in this direction or in that direction. So, that is what seems to come out and we are going to arrive at it in another way also. So, $k = \pm\frac{\sqrt{2mE}}{\hbar}$

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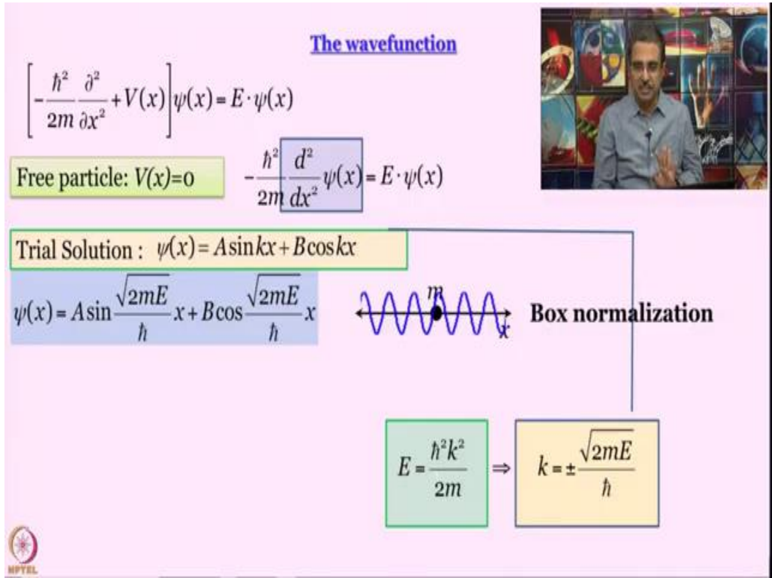

Plug it back into the trial solution, you get an expression $\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$. And if I plot it, this is the kind of function that I get. This looks like a cos function or a sin function, it is not, I actually multiplied sin x by some 3 or something and added it to cos x by 2 or something. So, this is what you get.

Now, is this a good wave function? Actually, it is not, because you can see clearly that it goes from plus ∞ to minus ∞, it does not become 0 anywhere, it is not normalizable. So, there is a little bit of a problem. So, to work with a free particle, what one does is, one uses the technique of box normalization, which means that if you say that you set some limits, you set long limits, 15 angstrom, 20 angstrom, something like that.

And you say that the particle exists within this limit and you normalize within that, of course, it is not a very, very rigid way of doing it, but that is the best you can do. So, be aware that the wave function for free particle is not really a perfect wave function.

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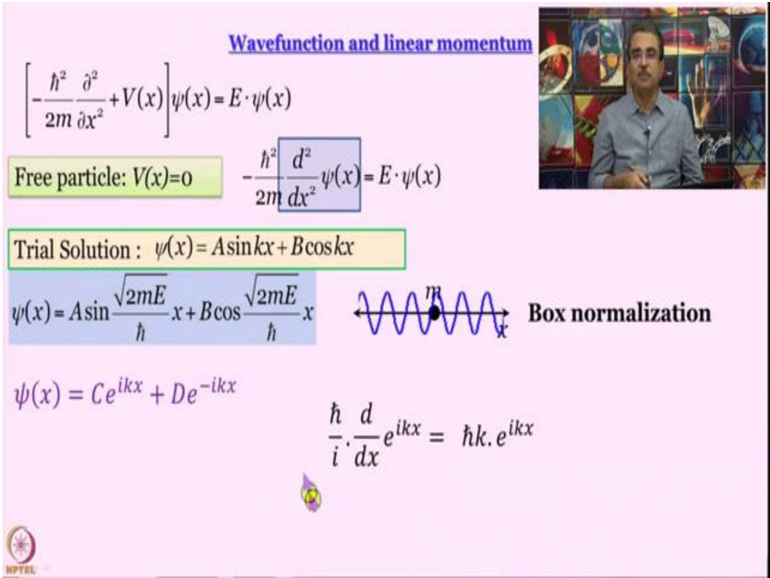

That being said, we can actually write the wave function in a different manner also, instead of writing the sin and cosine functions, I can write this kind of an exponential $\psi(x) = Ce^{ikx} + De^{-ikx}$, I leave it to you to differentiate it twice and convince yourself that this function also satisfies the Schrödinger equation for a free particle, you can arrive at it in another way, I think we all know that $e^{ikx} = \cos kx + i\, sinkx$, and $e^{-ikx} = \cos kx - i\, sinkx.$

Now, if you multiply e^{ikx} by C, multiply e^{-ikx} by D add them up, you are going to get something that will be a sum of a sin and cosine functions. But the reason, the good thing about writing the function in this particular form is that it starts making sense. Why does it start making sense?

Well, the momentum operator, what is momentum operator? I will come to that, before that let me just say this. I differentiate e^{ikx} let us say with respect to x, $\frac{d}{dx}e^{ikx}$, what do I get? I get $ik\, e^{ikx}$. So, this is actually an Eigen value equation. The only problem is that the Eigen value is imaginary. But it is not really a problem, because if you think of the linear momentum operator, linear momentum operator is actually $\frac{\hbar}{i}\frac{d}{dx}$.

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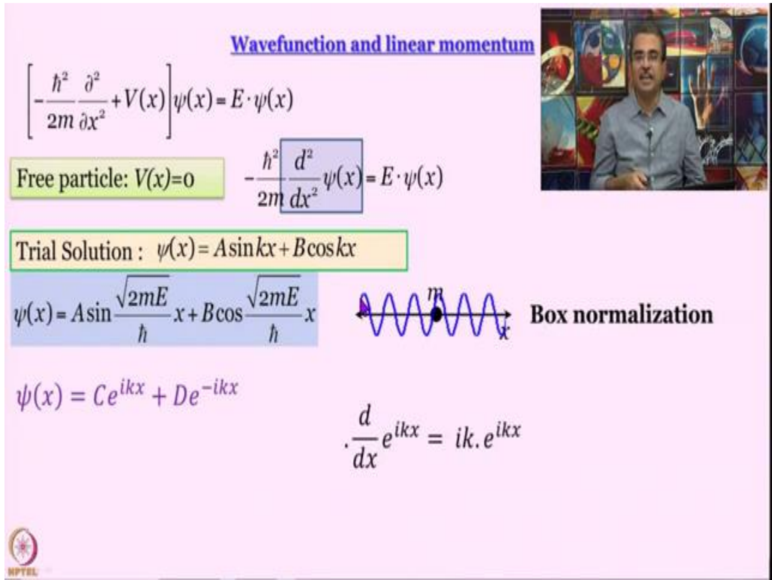

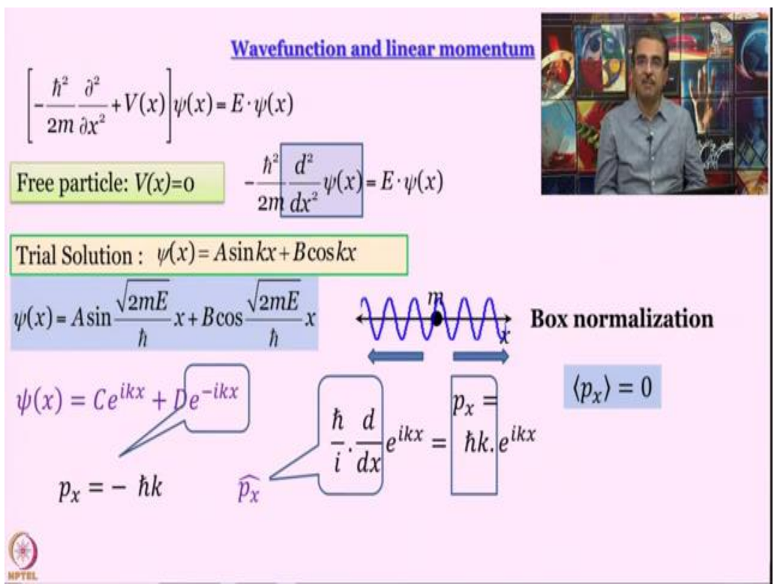

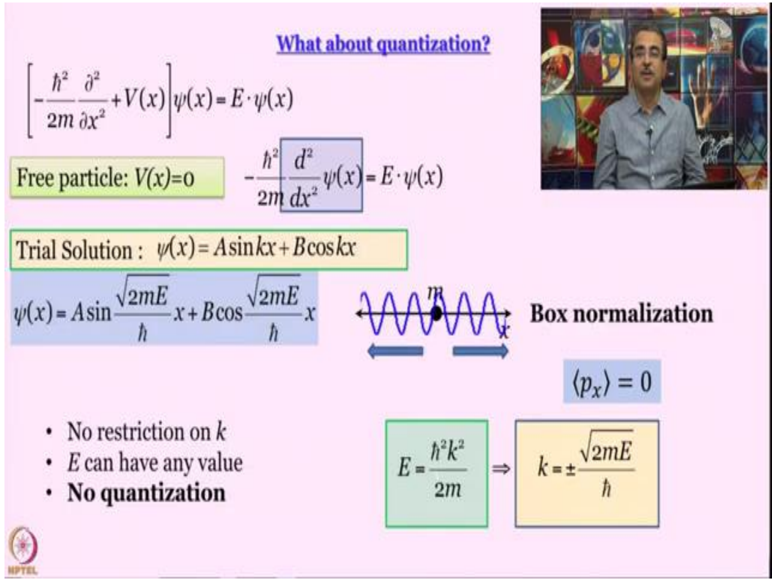

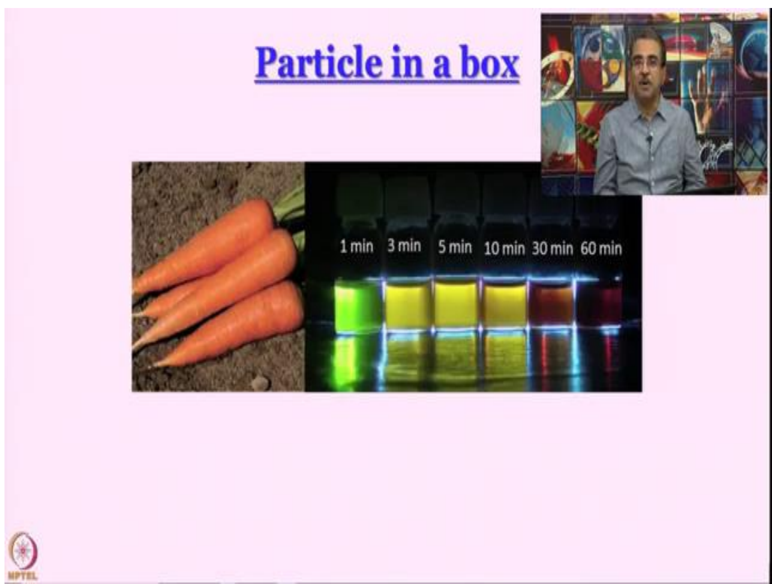

So, you multiply the previous result $ik\ e^{ikx}$ by $\frac{\hbar}{i}$, you end up getting $\hbar k$. What is $\hbar k$? $\hbar k$ then is the value of the linear momentum that you get if the linear momentum operates on the first term in the wave function. What would you get if the linear momentum operates on the second term of the wave function?

You are going to get $-\hbar k$. This is absolutely in line with the argument that we had proposed a little while ago, we had also obtained the values of $+\hbar k$ and for the momentum, even before using the operator. So, using the operator, it makes sense. That is why number 1, so we see that the particle can move in this direction, or in that direction.

What is the probability? Probability is equal, there is no bias for any direction. And probability being equal is given, will ensures that the coefficients also have to be such that their mod squares have to be same. This discussion that we just performed, I hope it rings a bell about the discussion that we performed maybe five, ten minutes ago, writing on the surface, remember what happened.

We perform a measurement; we are going to experience one of the Eigen functions of that particular operator that is what we see here. So, linear momentum can be either $+\hbar k$ or $-\hbar k$. That is what we learned. Average value of course has to be equal to 0. Again, I leave it to you to plug in this wave function into the expression for average value, of course, you will have to use this second form $\psi(x) = Ce^{ikx} + De^{-ikx}$ and you can work it out yourself.

But even without doing it, we can see from simple logic, that probability of moving either direction should be the same. So, this average value must be equal to 0. Average value of momentum is equal to 0, average value of energy is not equal to 0, because energy depends on k^2 and not k.

So, what have we got so far? Is there any restriction of k? No. So, there is no restriction of E as well. So, for a free particle, the first quantum mechanical system we have studied, there is no quantization. Where will quantization arise from? If we cannot find the particle, if we put it in a box, we will see in the next part, in the next class, that quantization arises nicely.