Introductory Quantum Chemistry

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Lecture - 8
Particle in a Box – part 2

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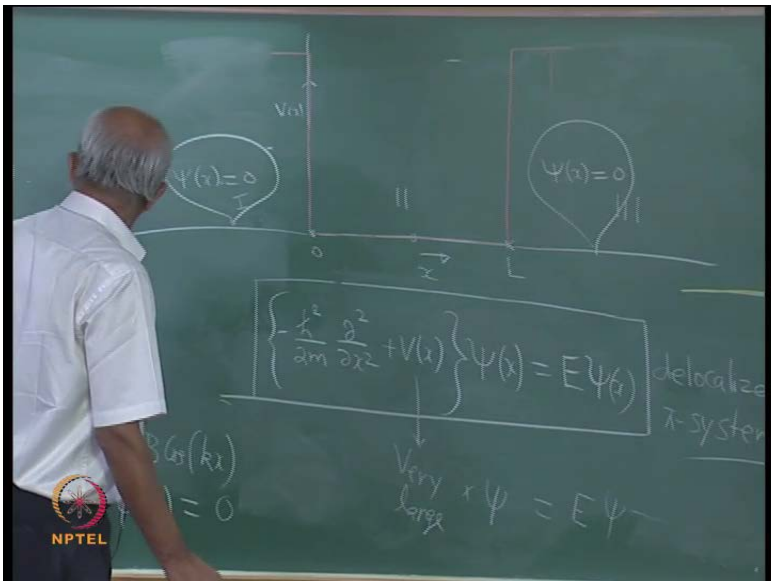

So, we now have to solve this equation. This was the equation that we obtained in this last lecture and we will try to solve this equation. And once they solve that equation we can get the solution of this equation because I will take that solution and calculate psi of x multiplied by E to the power of minus I E t by h cross, which is guaranteed to obey that equation and therefore, I would have a solution of this equation.

So, how do I solve this equation is the next question. For that I am going to divide my space into three regions. When I say space, you see, it means, all values x running from minus infinity to plus infinity. So, this region, which is to the left of the box is referred to as region one. We, to make it clearer I should remove this. This is the region one. What is region one? It is the region where x is less than 0. The particle, if it takes it there, it is outside the box.

And further this region, which is to the right side of the box, I shall refer to as region 3 while the region within the box itself I shall refer to as the region 2, and we are going to solve this equation. But then of course, you see outside the box, there is no probability of finding the particle. Why, because the potential energy is very large and we are saying, that some particle has amount of finite amount of energy, not an infinite number of energy. So, there is no way in which the particle is going to go into that region.

So, that itself tells me what the solution should be in this region because if I am going to say, that the probability of finding the particle outside the box is 0, that definitely, it should mean the wave function for the particle in region 1 as well as in region 3 must be 0 because only if the probability of wave function is 0 with the probability, which psi star psi will be equal to 0. So, I have ((Refer Time: 02:33)) the Schrodinger equation, I mean, if you want, you can kind of verify it by substituting the solution in here to just to make sure that everything is fine.

See, suppose you are in region 1, then what will happen is that the potential energy is very, very large in region 1, right. I said it is the infinity, but of course, I mean it is very, that means, it is a very huge quantity, very large quantity. So, here you have very large quantity and then what they say is that multiplied by psi must be equal to E. E is not a very large quantity, it is some finite number, finite value, multiplied by psi u. So, a very large quantity into psi must be equal to this equation, has the appearance, a very large quantity into psi must be equal to very small quantity into psi and the only possibility is that psi must be 0. So, therefore, equation is automatically satisfied if I say that psi is equal to 0. So, after having solved in this region as well as in the region 3, what is it the solution? I say, that psi of x is equal to 0 here in this region as well as in this region psi of x is actually equal to 0.

So, therefore, what is left is to solve it in region 2 and in region 2 what happens to this equation? Well, I will have to remove this also. Well, in that region I know, that this is the equation, but I know that in that region v of x is 0. So, therefore, what will happen? I will have minus h cross square upon 2 m dou square upon dou x square operating upon psi of x is equal to E psi of x. This is the equation.

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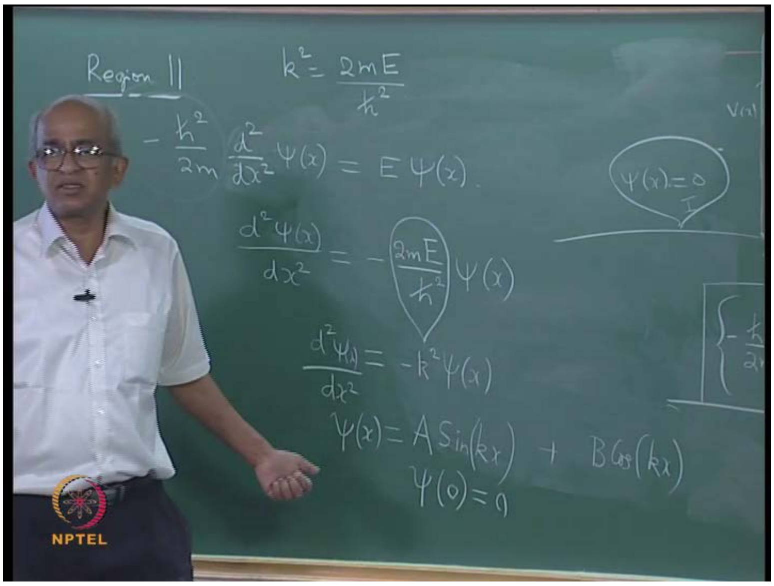

Now, here again if you look at this partial derivatives notation that I am using, strictly speaking this is not necessary because this partial derivative is going to operate upon psi, which is function of x alone. So, there is no another variable on which psi depends on, therefore there is no reason for me to use other partial derivative notation. So, I could have as well written d square upon d x square without making any error, so to say.

So, let me rearrange this equation slightly. Well, all that I am doing is I am multiplying throughout by the inverse of this. So, I take 2 m h cross square to the other side effectively, that is the equation, right. You rearrange this, this is the equation and we would like to save the trouble of writing this again and again and again. So, therefore, we are going to see, I am going to call this k square, this 2 m E by h cross square. I will refer to it as k, write it as k square and therefore, this is the nature of the equation.

So, I have defined k square and it is now very, very straight forward. You see, this is just an ordinary differential equation, which can be easily solved. You can actually verify, that a function of the form, a constant, which I will denote as A sine k x satisfies this differential equation. This is only a question of just differentiating this function two times. You will see that this equation is automatically satisfied by that function. So, A sine k x is the solution, but that is not the only solution, you can have another solution, which is of the form B cos k x. This is another possible solution.

This is not surprising because we have second order ordinary differential equation. There are two independent solutions and the most general solution would be a linear combinations of this two in which you add the first solution with the second and therefore, we will take the most general solution and say that that is my psi of x.

But then suppose I have find the solution, I mean, I have the solution and with the values of A and B at the moment they seem to be arbitrary. But suppose, I find the solution and make a plot of the solution, they, all these, all the things that I have obtained, what I mean is I am going make a plot of psi of x against x. See, this is the plot of B of x against x.

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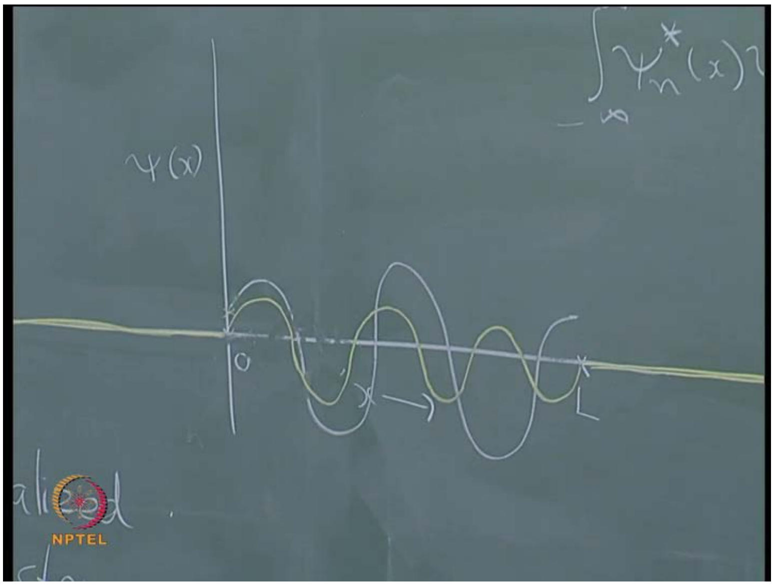

Now, I want to make a plot of psi of x against x and the box is of length L. So, therefore, the box extends from x is equal to 0, x is equal to L. So, if you think of plotting psi of x, what will, what is the result that you would obtain? Well, in this region, which is outside the box, I know psi of x has to be equal to 0. So, therefore, the plot is just a horizontal axis itself. So, that is the plot. And in the region where x is greater than 0 again the result is the same. So, this will be the plot.

But in this inside the box, the solution is of the form A sine k x and B cos k x. So, that is how it is, or if I want I can easily make a plot of this function because sine function and cosine function, they are oscillatory, I know that. So, may be what is going to happen is that I will have some such appearance because they are oscillatory, may be they will do that, correct. This is the kind of behavior that you will expect.

But then when you look at this you would feel little bit unhappy, why? Because you see, if you look at this function, you look at this point, x is equal to 0. At this point, if you are approaching from the left hand side what will happen? The wave function is always 0. And even close, very close to this point, the wave function is actually equal to 0. While on the other, on the other side, suppose you are approaching x is equal to 0 from the right hand side, from this side, what happens? The value of the function actually approaches that value in the way I have made this plot and therefore, what happens? The wave function actually changes in discontinuous fashion at x is equal to 0 and that is something that we do not want, right. This is something that I have described earlier. So, this is something that we want to avoid and in fact, we will consider this in more detail.

When we think of particle confined to a box of finite depth outside the, outside the box I will assume, that potential energy is not infinite, but finite. So, there it will be much more clearer. But at this point what I want to say is, that is, that here there is a discontinuity in the wave function. As it crosses the point x is equal to 0, the wave function suddenly jumps from value 0 to a finite value and we do not want that. So, in order that the wave function should be continuous, which means, that there should not be any sudden jump in the wave function when you cross the point x is equal to 0 what should happen? The wave functions plot will have to look like this, correct. This will be the correct wave functions plot, right.

The one that is shown in the yellow curve is, should be the correct curve, why? Because that satisfies the condition that wave function is continuous everywhere, continuous everywhere along the horizontal axis. And if that is the way it is, what the conditions that my wave function within this region should satisfy at x is equal to 0? Its value must be equal to how much in order that function is continuous? See, from the left hand side the wave function is 0 everywhere and in order that the function is continuous, the wave function value at x is equal to 0 must be 0. So, therefore, this function that I have found, it has to satisfy the condition, that x is equal to 0. The function, this function should satisfy the condition that it should be equal to 0. And not only that, when x is equal to L what should be its value? It again should be 0.

So, therefore, you have two conditions in the region 2. You have to solve this differential equation subject to two conditions. The conditions, notice they are at the boundaries of this region and therefore, these are referred to as boundary conditions that the wave function should satisfy because they are at the boundaries of the box. So, at boundaries what should happen? The wave function should be equal to 0, why? Because outside the boundary, outside the box the wave function is 0 everywhere. So, in order that the wave function is continuous even at the boundary, the wave function has to be equal to 0, correct. So, we now we will impose these two conditions on the wave function and see what the result is.

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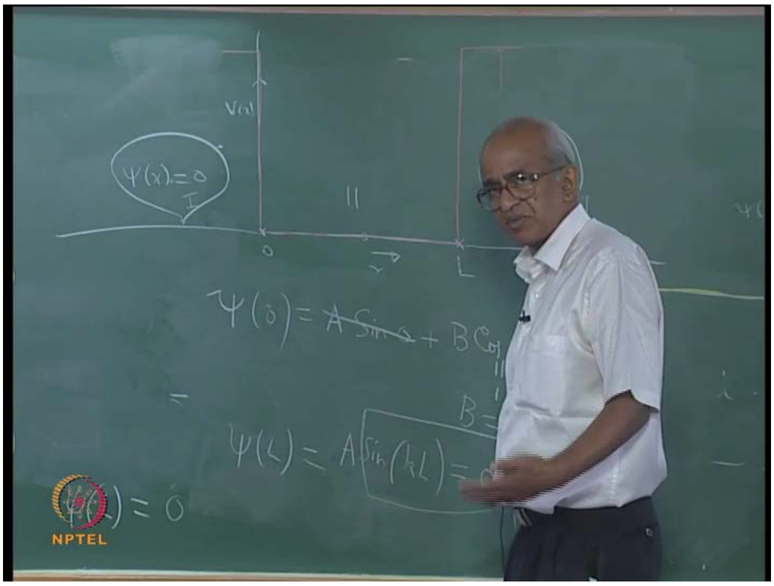

So, your general function is this one, psi of x is equal to A sine k x plus B cos k x. So, what I am going to do is I am going to take that general form and put x is equal to 0, right, and satisfy these conditions, psi at x is equal to 0 is equal to 0. So, if you, if you do that, psi at 0 will be equal to A sine 0 plus B cos 0 and that must be equal to 0, that is the result. And sine 0, I know, it is actually 0, so therefore, this term simply goes away and cos 0, I know, is equal to 1.

So, therefore, what does it mean? It means that in order to satisfy, by the first boundary condition B must be equal to 0, then psi at x equal to L, right. This is the general form of my function; this is the general function of my function. But now I have found that in order to satisfy my first boundary condition, B must be 0. So, let me put, that B equal to 0, this goes and so that is my function now.

And in there if I put psi is equal to L what will be my answer? The answer is going to be A sine k into L and this must be equal to 0. If you say, that product like A sine k L is equal to 0, then what are the possibilities? Well, one possibility is to say, ok, capital A must be. If you say product like A sine k L is equal to 0 there are two possibilities, either this can be 0 or A can be 0, these are the two possibilities. But suppose I say, A is equal to 0, I choose this possibility that A is equal to 0, then what will happen? You see, if A is equal to 0 you will have to put that value of A here. That means your psi will be 0 even within the box, correct.

See, but I, we started with the assumption, that the particles are inside the box and therefore, the wave function for the particle cannot be 0 within the box, correct. I, we are saying, that there is a particle in the box and if you cannot have a solution where if you find the particle is not within the box. In fact, the wave function if you said, that A is equal to 0, the wave function will be 0 within the box; not only within the box, even outside the wave function is 0. So, the particle will not be found anywhere that is actually nonsense. So, therefore, A is equal to 0 is not acceptable, we are not going to take as a solution. So, therefore, only possibility is that sine k L must be equal to 0 that means the value of k.

See, L is the length of the box that we cannot change. You have a box of given length, but this k is something that we can choose. So, we have to have sine k L equal to 0. Only if sine k is equal to 0 would I get an acceptable solution of my time independent Schrodinger equation.

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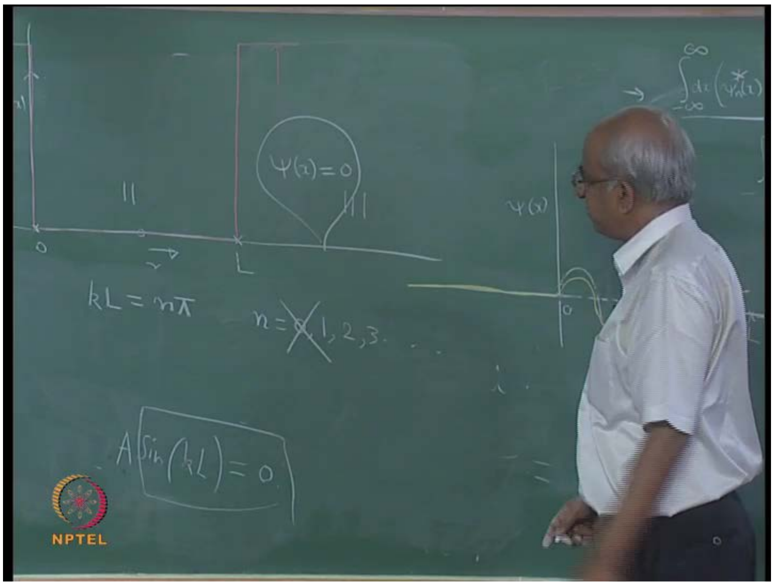

So, if k L is equal to, this is equal to, what would this be satisfied? Well, if k into L is equal to n pi, in order to satisfy the condition you will have to say, that k into L is equal to n pi. Only if this is the way, it is, will you able to get acceptable solutions. And this n is a number, you see it is an integer; it is constraint to be an integer. The moment it appears, that I can have n equal to 0, n equal to 1, n equal to 2, 3, 4 etcetera, ok. But suppose, I choose the case k with n is equal to 0, if you put n equal to 0 what will happen? You will have n equal to 0 here, you will have k into L equal to 0 that means, k must be equal to 0. And if you have k equal to 0 what will happen to this solution?

You will get 0 again, which is something that you do not want, I mean, that is not acceptable solutions. So, therefore, even these value n equal to 0 itself we are going to omit because it does not give me an acceptable solution, it does not give acceptable answer to my problem. So, therefore, all the, only possible values of n are 1, 2, 3, 4, 5, 6, etcetera and has to be an integer. In fact, taking the value 1, 2, 3, 4 etcetera and that actually means what? Well, remember this k is related to the energy. See, if you like you can write E in terms of k. This is the expression; this is the relationship between k and energy.

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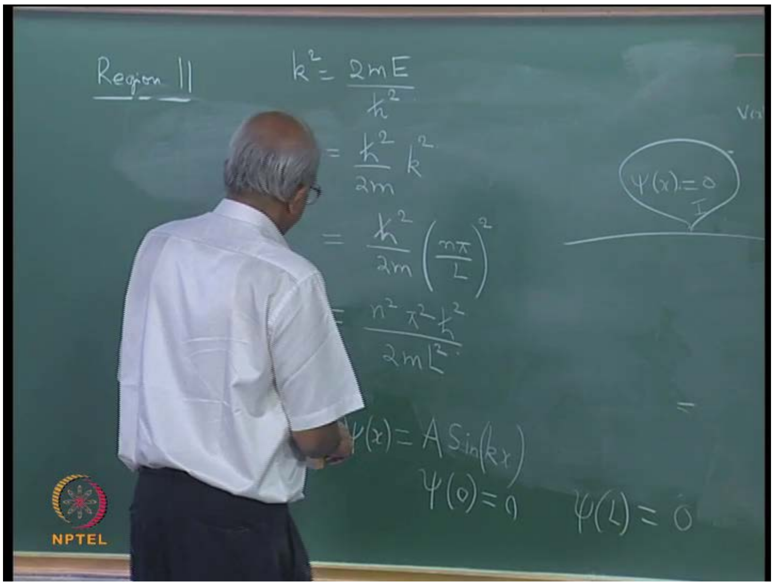

But now you find, that k is constraint, k has to be equal to how much from this equation? k has to be equal to n pi divided by l. That means, you see, if you have E equal to h cross square divided by 2 m times n pi by L the whole square, only if this is satisfied will you be able to get acceptable solutions. For no other values of E will you be able to get acceptable solutions of the time independent Schrodinger equation, right.

And what are these values actually? They are, I mean, I could write it in this fashion, n square pi square h cross square divided by 2 m L square. These are the values of energy for which you can get acceptable solutions and this n is referred to as a quantum number, n is referred to as a quantum number. And notice that it has come about automatically, all I did was I solved, tried to solve the Schrodinger equation satisfying the acceptability conditions. And once I impose these conditions I found, that suddenly in the solution there is this quantum number. Here it is come out from the process of solving the Schrodinger equation. This, you will find this in general situation when we discuss the hydrogen atom; again you are going to find similar things.

The three quantum numbers n, L and m that you would already know of, they actually arise automatically out of the solution of the Schrodinger equation when you impose the conditions that solution you get has to be acceptable, right. This will happen again and again. And further, what is this? This is the value of E and what is the wave function of itself? Psi of x, it is of the form A sine k into x, but we have found that k must be equal to n pi by L. So, therefore, it is of the form k sine n pi by L that is how the wave function is. And remember, that this is for the region within the box, outside box what will happen to psi? It will be equal to 0, right.

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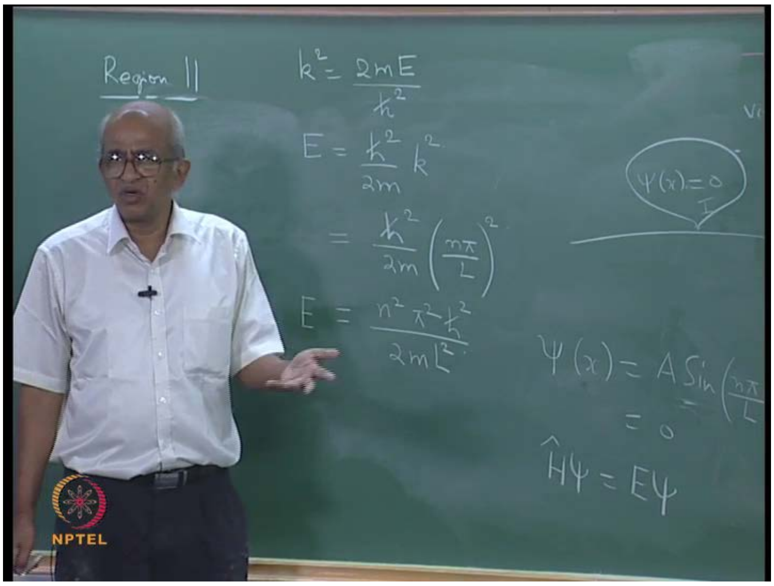

So, strictly speaking what I should do is, I should say that it is equal to ((Refer time: 23:53)) x is less than, sorry, x is greater than 0 and less than L and it is equal to 0 otherwise. Remember, you see the equations that we are solving was just this equation h psi is equal to E psi; this is a equation that we are analyzing.

In fact, we are asking what are the Eigen values of the Hamiltonian operator and what did we find? We find, that there are several different Eigen values, each value of n is going to give me a possible Eigen value. See, if you put n equal to 1, you will get one Eigen value; n equal to 2, 3, 4, etcetera, they are going to give you different Eigen values and each Eigen value has its own associated Eigen function.

And further, if you remember postulate three, suppose you make the measurement of the energy of the particle what will you find? You will find, that the answer will be of the form of n square pi square h cross square by 2 m L square with n having value 1 or 2 or 3 or whatever, right. So, let us look at this, these stages one by one, but maybe before doing that I should, I should determine that constant capital A.

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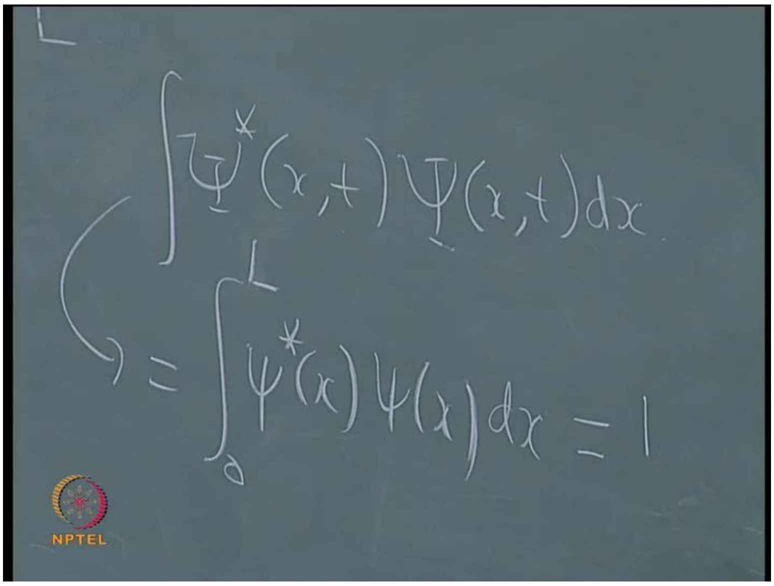

I told you, whenever we have a constant in front of the wave function how we would determine that. The answer is that we will use what is referred to as the normalization condition, which implies, that psi star psi, right, psi star psi dx integrated from minus, well maybe I should be little bit careful here, strictly speaking what I have to think of is capital psi. This object when integrated from minus infinity to plus infinity, the answer should be 1 that is the normalization condition.

But as far as, as far as these states are concerned, as far as the states, that we are thinking of are concerned, they are all stationary states, correct they are all stationary states. So, therefore, psi star psi will not depend upon time. So, the what is going to happen is that you would have psi star of x psi f x this product is nothing but psi star of x into psi of x into d x. And further, this psi, you see, they are out 0 outside of box, it is not necessary for me to integrate from minus infinity to plus infinity, but it is sufficient if I integrate from 0 to L, which is region of the box. So, this integral is, actually this is equal to integral 0 to L psi star psi dx and this must be equal to 1.

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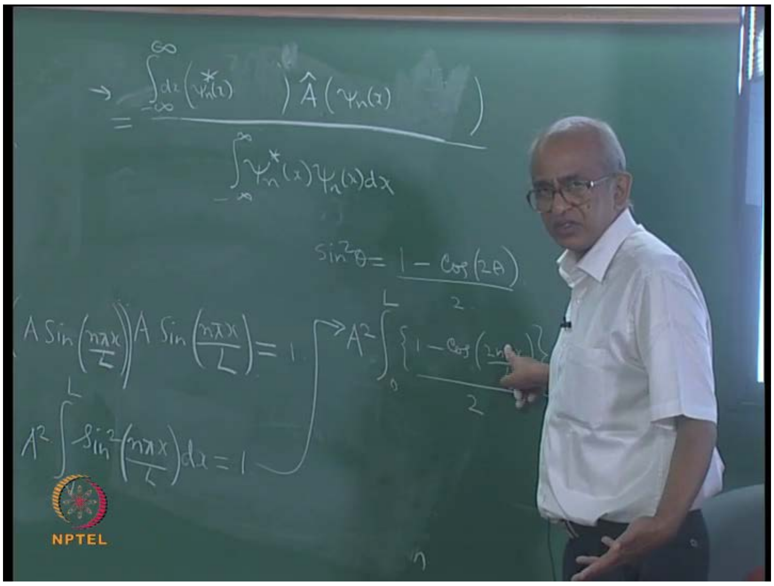

But now my function is actually psi of x is equal to A sine n pi x by L. So, I am going to use, that in this equation I will get A sine n pi x by L multiplied by psi star and dx and I will have to integrate from 0 to capital L. This must be equal to 1. But when I look at the function you do not find any square route of minus 1 anywhere. There is no i inside this, so therefore, star has no effect complex conjugates. Only if there is a minus square route of minus, once you think inside somewhere will have an effect. So, psi star is actually psi itself. So, effectively this will become A square integral 0 into L sine square n pi x divided by L into dx is equal to 1. So, this is a condition that will determine the value of capital A.

Now, how will you do this integral I will very quickly tell you because this is fairly straight forward. Recent trignometric identity, which says, that sine square theta is equal to 1 minus cos 2 theta; we divide it by 2. So, you can use that trignometric identity in here. So, what will happen is that you will get A square integral 0 to L into 1 minus cos 2 n pi x by L divided by 2 into dx is the result that you will get.

And then I, may be I will not evaluate this. What is going to happen is that this term when you do integral it will give you answer 0. This term and only in the first term, which is half will survive and so this is going to give you A square into integral 0 to L dx divided by 2 is equal to 1 and that is an integral that can be easily performed.

You will find that A square into L is equal to 1 imply, oh, A square into L is equal to 2 implying, that A must be equal to square root of 2 by L. So, therefore, we have to determine a value of capital A, the normalization factor and we can use that and write the solution. So, this A that is occurring in our expression, I can replace it with square root of 2 by n.

So, let us look at these different solutions. Well, before I look, I look at the solution, I notice, that you see, psi is dependent upon this quantum number n, so psi is the function of x. In addition, it depends upon this number n, which takes only integral values 1, 2, 3, etcetera. So, it is usual to put a subscript here to indicate, that it depends upon n, also the quantum number and similarly E will depends upon that number. So, therefore, this is going to have E subscript n. As we have seen, n can have any value starting from 1 to infinity.

So, therefore, how many Eigen function of Hamiltonian operator have you found? The answer is that for each value of n gives you one Eigen, Eigen function and other associated Eigen values, so I have found infinite number of Eigen values and associated Eigen functions.

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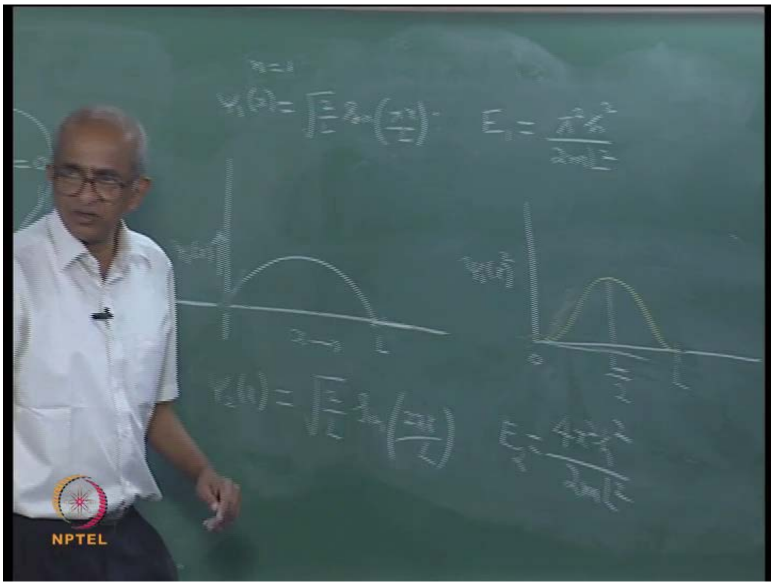

So, we look at the first Eigen function. The first Eigen function would have n equal to 1, ok. If n is equal to 1, I will have the function with this psi 1 of x, it will be given by square root of 2 by L sine pi x by L. The associated Eigen value will be E 1, which is equal to, what is the expression? In that expression, which is occurring there you will have pi square h cross square divided by 2 m L square.

If you think about it you will realize, that this is the stationary state that has the lowest value for E, right, because n is equal to 1. Any other solution will have a larger value of E and therefore, this is the lowest possible stationary state of the system. And its energy is equal to pi square h cross square by 2 m L square, and the wave function actually is square root of 2 by L sine pi x by L.

And if I, if I were to make a plot of this function how would it look like? Psi 1 of x is going to be plotted along the vertical axis and x along the horizontal axis, running from 0 to capital L. In this region it is not even necessary for me to plot the function because in this region, as well as in that region, I know that the function is 0. So, what is of interest is the value of the function within this box and sine functions we know, how they depend, they are actually sinusoidal, so to say they represent waves.

So, therefore, if you made this particular function, if you made a plot of it at this region where x, this point where x is equal to 0, the function will have the value 0. At x is equal to L, again, the function will have value 0. And if you think of the middle of the box, middle of the box is L by 2, if you put L by 2 in here what will happen? You will get sine pi by 2 and remember sine pi by 2 is equal to 1, right.

So, therefore, if you make a plot of this function the answer, that you are going to get is this. So, this is the way actually if you present a sinusoidal curve it would go like that, correct. This is how a sinusoidal function would look like, but all that is happening is that you do not have other parts, you have just this part. So, this is the wave function for the system. Psi 1 of x would have this behavior.

And of course, when you encounter such a wave function you will get, what is the information that you can get this wave function? This is the state, that has the lowest energy and for this function it will be very interesting to make a plot of psi 1 of x square. Why, because if you are calculating psi star psi, psi star psi is the probability density, but there is no i in this function. So, therefore, so therefore, psi 1 star psi 1 will be equal to psi 1 square. So, this is your probability density.

And if you made a plot of that against x, how would it look like? It would look roughly the same, but there are slight changes. What actually happens is, I mean, the way it behaves near x is equal to 0 is changed. The function, actually if you make a plot of it, it would look like this. So, that is how the function would look like, ok.

What is the difference actually? The difference between this plot and that plot is, see, here if you look at the slope of this curve, at x is equal to 0 slope is finite, it is non-zero. While the way I have drawn here, this slope has the value 0 that is the difference between the two curves, otherwise it is almost the same, I mean, they look the same.

And then if you have such a probability density and if I ask you what is the most probable position of the particle, answer is extremely simple. The most probable position for the particle is actually at the center of the box. So, the particle is most likely to found the middle of the box, which is L by 2.

Now, suppose if you think of next possible function, which is psi 2 of x, what will happen? The function will be square root of 2 by L sine 2 pi x by L. The associated Eigen value or associated energy will be 2 E 2, which will be equal to 4 pi square h cross square divided by 2 m L square. This will be the associated Eigen value; the energy is greater than the previous one, right.

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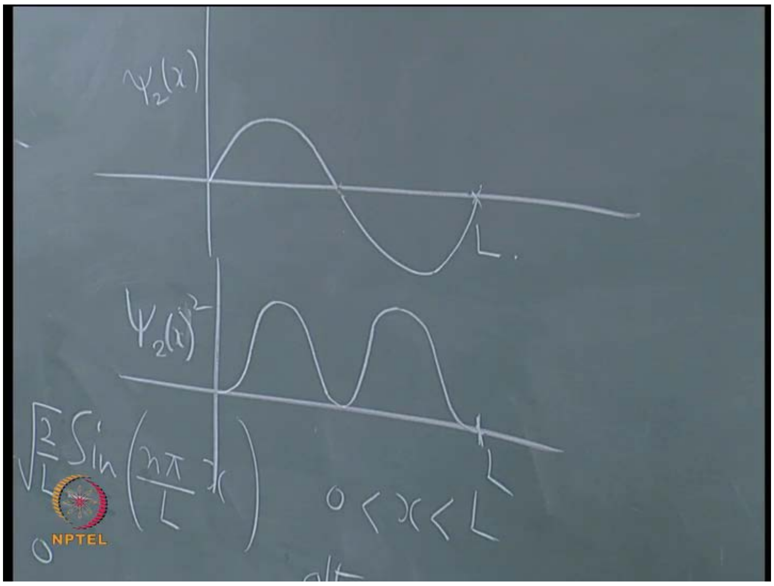

And if you made a plot of this function Eigen states how would it look like? Well, it is actually quite simple. At the boundaries of the box the function has to vanish, but in addition to boundaries, if you look at this function, where is my function? Where did I write it? Here is the function. Suppose you look at the function, at the middle of the box, at x is equal to L by 2, what will happen if you put L by 2 here? You are going to get sine of pi, which is actually 0. So, that means, at the middle of the box also the function is 0.

So, would you like to guess, actually we can make a plot, but we can make even a guess. What will happen is, that the function will start with the value 0, it will increase, reach some maximum value and then decrease and reach the minimum, not the minimum, reach the value 0 at the middle. And then how will it continue? Well, the way it continues is, goes down the function, becomes negative and then again at other boundary the function becomes 0.

So, what is happening is, that in this range the wave function is actually positive while in that range the wave function is negative. But as far as square of the wave function, which is actually the probability density, is concerned, square will always be positive. So, if you made a plot of the square, maybe I can make a plot just below this, psi 2 of x square, how would it look like? Well, the answer is, it will start from 0, then it will reach the maximum value, then become 0 at x is equal to L by 2 and again increase and again become 0 at x is equal to L.

This is the plot of psi 2 square, which is the probability density. And if you will ask the question what is the most probable position for the particle, you will say, well, in this case, there are two most probable positions. One is this point and the other is that point. This will be l by 4 and that will be 3 L by 4. And right at the middle of the box, the probability of finding the probability density for finding the particle is actually equal to 0.

Now, if you remember, this is, this very much resembles the standing wave patterns that we had in a string. Remember, that you see the simplest one. If you remember, there was no note, just in the same fashion the simplest possible wave function, you see, does not get its value 0 inside the box. The next one, remember, in that case there was one note and that is exactly what is happening here. There is one note, right.

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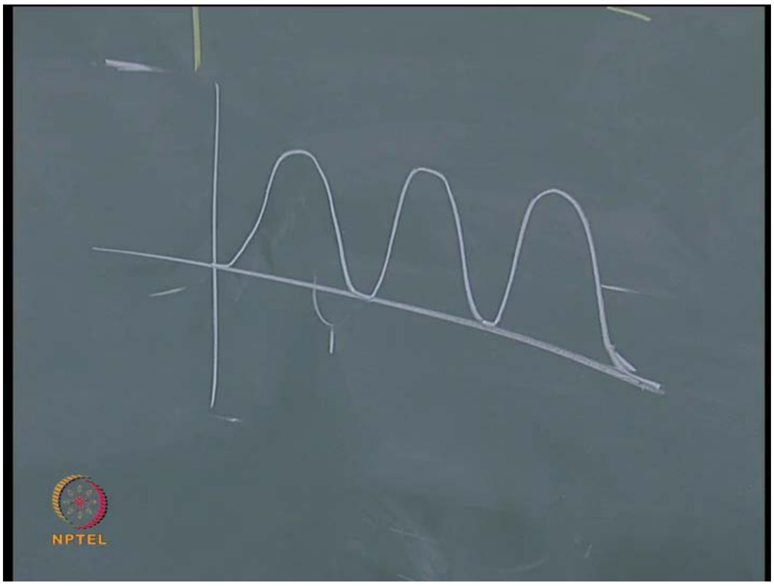

And then if you think of the next case, what will happen? You will have n equal to 3, I mean, it is not even necessary for me to look at the function, but I know what is going to happen, psi 3 of x, if you make a plot of it how will it look like? Answer is very, very simple; even without writing the function I can make a plot of it. It is going to have, I know, it is going to have two notes. So, this is the length L, I know that it will have two notes, right. So, how will it look like? It would look like this.

So, in this range the function will have the value, which is values, which are positive here; in this range it will have values, which are negative and then positive. That is how it is and there are two notes. You can make a plot of psi square in this precisely in the same fashion. It is very easy how will it look like; maybe I will just draw that also. So, that is how it looks like.

So, I can say, that if I have the wave function psi n, right, psi subscript n, n is the quantum number, then how many notes will it have? It will have n minus 1 notes, right. So, suppose the value of n was 10, what will happen? You will have 9 notes. And how it will look like? It is difficult to drew, but let me just try. This is L and they have to draw 9 n; wave function, which just have 9 notes.

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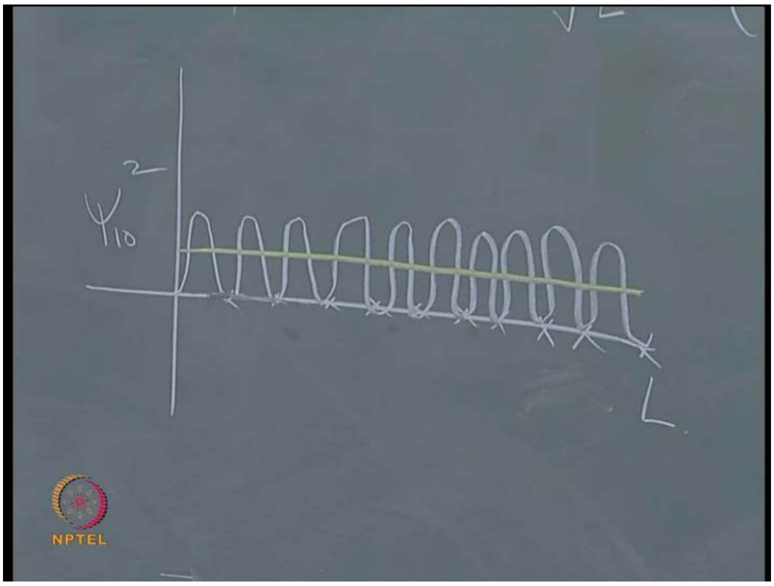

So, imagine I plot psi 10 square what is going to happen is I will have an appearance, well, I hope I have put 9 points. Well, I need one more and the final one. This is, this is L and then what will happen? My probability will look like this and they are all of equal height. You see, unfortunately we have drawn there, they do not appear to the same height, but they are all of equal height.

Now, this is a very large value of n, right. Suppose I said, that I have a particle, which is not obeying quantum mechanics, but it obeys classical mechanics and it is inside the box right and I do not know where it is. So, therefore, all positions within the box are equally likely and therefore, what is going to happen? If I am speaking in terms of probabilities the probability of finding the particle anywhere is the same.

So, if I plotted that classical probability as a function of position what would I get? What would I get? I will represent, in this, in this picture I would get a straight line something like that, correct, because the probability is same, it does not depend upon position. So, this is what you get.

And if you look at the quantum result, right, on an average it actually resembles ((Refer Time: 46:30)), is becoming almost the same everywhere, right. That is what is happening in the quantum results. So, as the value of n increases, the quantum mechanical result resembles more and more closely to the classical results. This is always the general situation whenever the value of the quantum number n is very large. The results that you obtain will be very close to what you would normally expect according to classical thinking.

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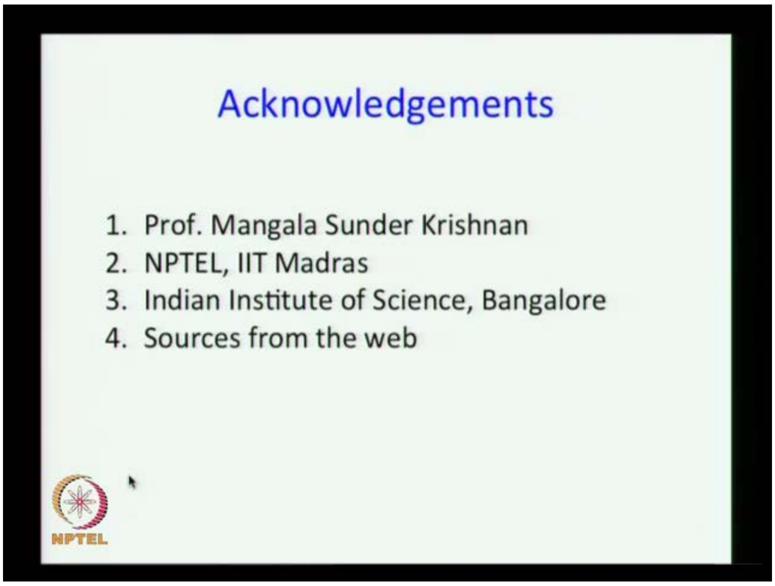

I think I can stop at this point.

Thank you for listening.