Introductory Quantum Chemistry
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Lecture - 13
Finite Well, Delta and Step Functions

You remember we were actually discussing the situation, where I have a potential well and the particle is confine to the potential well.

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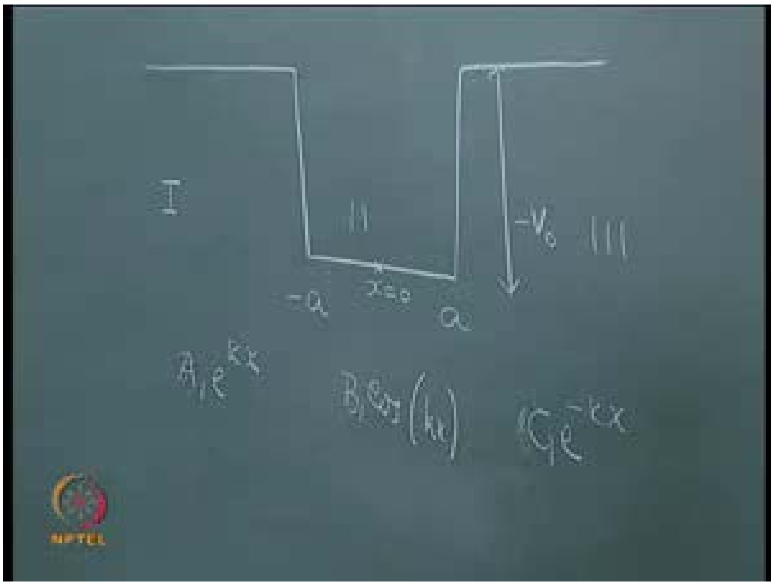

And, it is taken to be the potential values taken to be located between minus a and plus a. And in that region it has a depth of minus v 0 and the origin is taken to be at this point which is x is equal to 0. And as I told you yesterday what happens is that if the system obeyed classical mechanics; the particle can be trapped inside the potential well. And can in principle have an any of energy from minus v 0 to 0. And if its energy is greater than 0 than it would not be trapped to but it will go away that is how the system was. And then we have wrote down the wave function for the system in the 3 regions; this region the second region as well as the third region; region 1, region 2, region 3.

And, in this region we wrote the wave function as b 1 e to the power kappa x these are these said we already d 1. Now, I think it was A 1; here it was written as b 1 Cos k x while on the other side it was written as A 1 sorry c 1 e to the power of minus kappa x; that will actually regulates speaking I should say that this b 1 Cos k x plus b 2 sin k x.

But then we said that because the potential is symmetric; the wave functions may be symmetric or anti symmetric. That means, if I change the way the sin (x) the wave function may remain unchanged over it may at the most cos sin. And we decided that we will look at only and at least at first we will look at solutions which are symmetric. And therefore we had removed this b 2 sin k x that will be included when we analyze; the wave functions which are anti symmetric.

So, then we have also said that the wave functions have to be continuous everywhere. And not only that the derivative of the wave function also has to be continuous. Now, at this point I would introduce a little bit of mathematics which may not be familiar to you but this the really beautiful mathematics.

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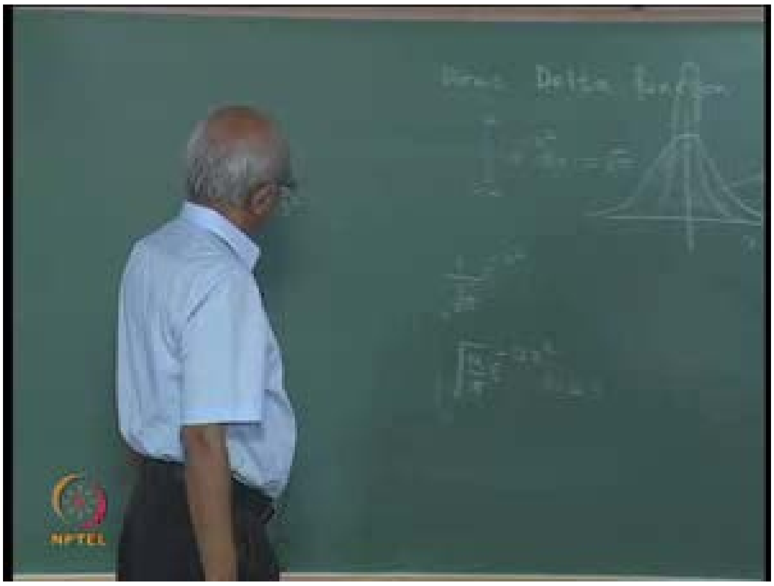

And, that constraints the subject of a Dirac delta function. Now, I am sure you would be familiar with a function like e to the power of minus x square; plot of e to the power of minus x square against x. How would it like actually it is very easy to visualize it. It is what is referred to as a Gaussian and the way it behaves is this at x is equal 0 it has it maximum value. And then I have say x increases either in the positive direction and a over decreases in the negative direction. Then, what will happen there? What are the functions simply goes on decreasing.

And, if I wanted to calculate the area under this curve what will you do? But this area if I wanted to calculate you will have to integrate this object from minus infinity to plus infinity; this a standard integral a difficult integral actually but the answer is known. And what happens is that the answer is actually square root of pi; this say very well known integral it can be evaluated, and therefore if I had through out of instead of e to the power of minus x square. I suppose I have through out of e to the power of minus x square by square root of pi; what will happen is that in this function if I plotted instead of e to the power of minus x square. If I plotted that function of what is going to happen is that the height of the that the function will look exact to the same. But the actual area under the function would be how much? It will be equal to unit a ok.

So, let me imagine this a this plot itself is in such a fashion that i am plotting e to the power minus x square by root pi. So, that this entire area let me now it is equal to 1 the total area. And now suppose I say I am going to modify this function a little bit. But I want to do is I want to say e to the power of minus a x square right. And I am going to multiplied by if I multiplied this by 1 by square root of pi they have already under the curve will not be even it there. But if I multiplied it by square root of a by pi; then what will happen is that the area under the curve will still be unit. So, you can easily show that that means if we integrated this answer is going to be 1. So, suppose I now say I have this functions square root of a by pi into e to the power of minus a x square. If a is equal to 1 it would have this appearance.

But suppose a is equal to 5 what would be the appearance of the function? If a is equal to 5 you can see 2 things happening; 1 first up all you will have a square root of a there if you put a is equal to pi this getting multiplied by square root of 5 correct. That means, the value of the function at the origin actually has increased by square root of 5 at the origin; at the origin you see x is 0. Therefore, what is happened this that the height of function at the origin has increased. But the area under the curve is still 1. And that obviously means that the width of this function has decreased right. So, if you think of a being 5 what would happen is that you would get another curve which would they look like this; its width has decreased. But its height has increased in such a fashion; that in such a fashion that the area under the curve still is equal to unit.

So, suppose I increase the value of a further 5 to may be 25 what would happen the function will become very narrow. But its height will be very large still the area under the curve will be unit; it will the same the area is not going to change. So, what I want to do is I imagine that this a becomes infinitely large. Then, what will happen? The function will have infinite height at origin and it its width will be extremely small. So, it will be just is 5; and that function is the 1 that is repeat as the Dirac delta function. So, how will I define that Dirac delta function?

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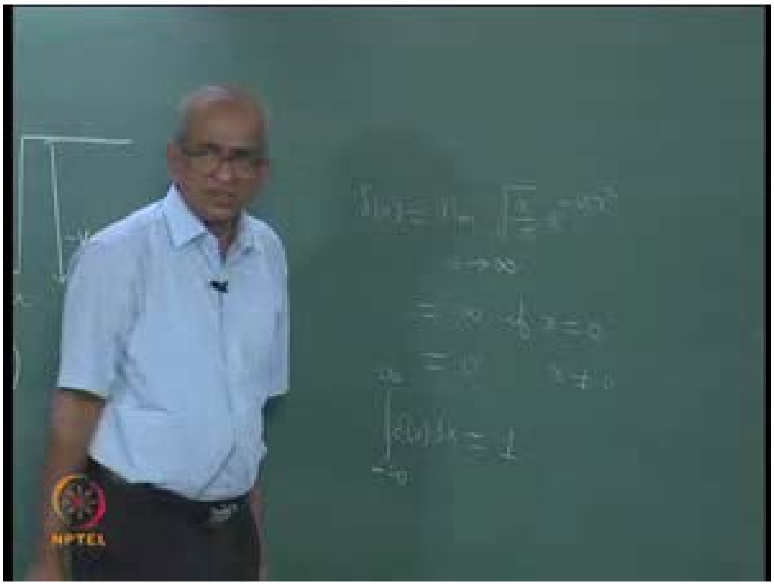

I will say delta of x is equal to limit I have take the limit where a this number a approaches what value; it has approach the value infinity. So, this my definition of the Dirac delta function and the way I have defined it you would realize that; this the function which has an infinity value at the origin. And they never else what is the value of the function because it is such a narrow spike anywhere else even close to 0. If you have a point close to 0 but not 0 then what will happen? The function will be having a negligible or a small or a value which is very small in fact 0 right.

So, another wave defining the same function is to say that delta is equal to infinity if x is equal to 0. And if x is not equal to 0 what will happen? Even at very points point is very close to x is equal to 0 what would happen is that the function is extremely narrow because I am taking the limit a turning to infinity. So, what will happen is that if x is not equal to 0 the function will actually have the value 0. So, that is another way of defining the function but not only that you can also notice that integral of delta x d x from minus infinity to plus infinity must be equal to unit a. The area under this curve is always unit a respect to that what is the value of a is; even if a is extremely large the area is still equal to unit a.

So, therefore this has to obeyed. So, this the rather peculiar function I mean when you think about physically there is nothing to this function actually it has a value only at 1 particular point. And that is infinitely large a very where else the function is 0. But this a mathematically peculiar function because this the finalize not a continuous function as we can see. Because as you go along the x axis what happens its value is a very where 0 until you hit the point x is equal to 0; and that point it has an infinite value. And then when you pass that point the value of the function is again back to 0. But now suppose I say I am going to take this function and I am going to integrate it.

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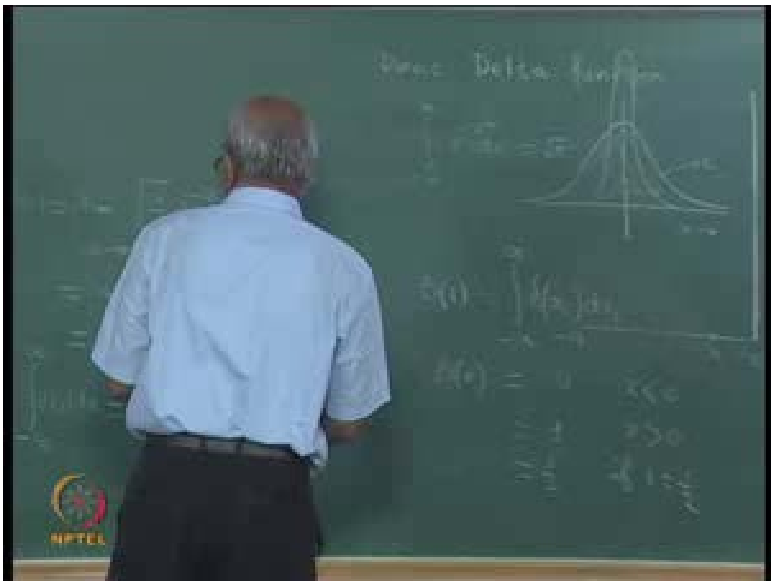

Let us say I take the function delta I will denote the variable of integration as x 1. I am going to multiplied by d x 1 and integrate from minus infinity to plus infinity I can integrate; I know what is the answer is going to be the answer will be unit a.

But suppose I now say I am not going to integrate up to plus infinity but I am going to integrate only up to a variable value which should I denote as x suppose. So, that means you see I have this very narrow, very peaked function that is my function it represent physically. This my function it is located at x is at 0 it will located at 0. And what you are doing is you are doing an integration from minus infinity up to this particular point up to that point let us say. What will be the answer the very where is a very where in the range of integration the function is 0. So, the integral will also be 0 correct. So, up to even if we are very close to 0 even if this x is very close to 0; what will happen the answer will still be 0? But suppose x was on the other side of 0 right. Suppose x was here just on the other side of the peak what will happen that the answer will be equal to unity right that the function will be 0. But the integral because when we are integrating we are actually calculating the area see if you are if you have integrate up to this point; the area total area of under the curve from minus infinity up to there is actually 0.

But once you have integrated up to this point you see that actually encompasses this peak; and because the peak is there the area of the peak is unity. So, the moment you say that your x is on the other side of 0 the functions will the integral will have the value unit. Therefore, you can say that this the function let may call this function theta (x). What is special about this function? Theta (x) is a function such that if x is less than 0 what is its value? It is 0 and if x is greater than 0 what is its value its 1 correct it is unit. And the way we have in defining it actually if you like you can ask I mean what is the value of the function when x is equal to 0 itself. You will take a very simple attitude you see this you think of this as a peak; peak is symmetric about the origin about x is equal to 0. So, if you are integrating up to x is equal to 0 what will happen you would have covered half of the peaked function.

And, therefore you will say if x is equal to 0 then it will have the value half; that is the simplest way in which i can think of this function. And if you made a plot of this function theta (x) what is the appearance that you are going to get? If you made a plot of theta (x) what would be the appearance? Well, it is a simple thing what happens is that that up to x is equal to 0 the value of the function is 0. So, the plot will coincide with the horizontal axis up to this point. And at that point itself of with our analysis tells may there its value is half. So, it is somewhere here; and beyond that when x is greater than 0 what happens the function is 1.

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Thank you, thank you when x is equal to 0 this equal to half ok

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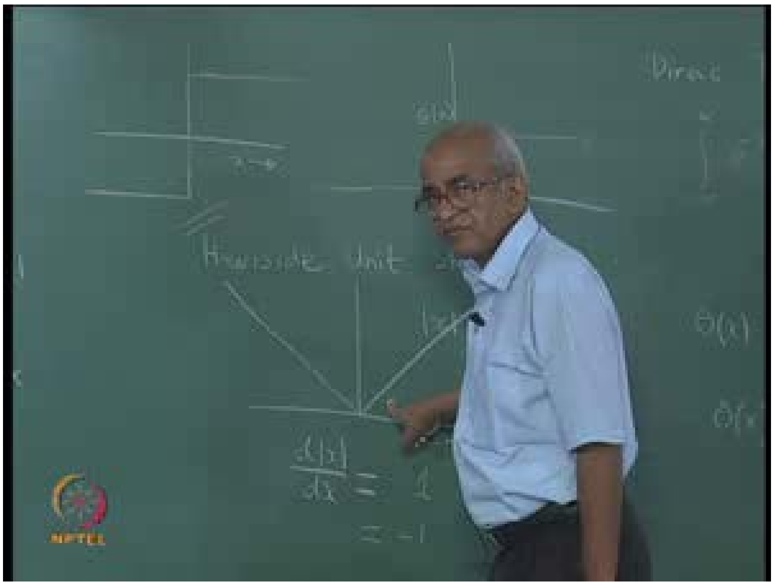

So, therefore beyond this point what will happen is that the value of the function is actually equal to unit right. Now, if you look at this actually I am in if you like you can throughout the functions something like this. And when you look at this I mean say what is happening is that if you are moving along this direction I up to here the function have the value 0; suddenly the function jumps it goes up by 1 unit it is like a step. And therefore this referred to as the step function. In fact the height of the step is unit is so this referred to as unit step function. You can think of step functions which have different heights if you want or that even a to do is you just multiplied this by that is say 4. You take this function multiplied by 4 than the height of the step will be equal to 4. And this was originally introduced by Heaviside. I think the name has an a in it I am not completely sure. So, Heaviside unit step function.

So, you look at this you see why did I introduce this function at this point the answer is that here I have a Dirac delta function which is which has the value infinity. This a very strange function its value in this range is 0; its value in that range is 0 at that point allow it has an infinite value a very ill behaved function. But you look at the integral of that function it is a step function. And it we said discontinuous function you can see that this function changes discontinuously right. I can make the argument in the reveres if I had a discontinuous function what will happen to the derivative? The derivative would be a Dirac delta function right. If I have a discontinuity in a function its derivative at that point will be a discontinuous function sorry will be a Dirac delta function ok.

Now, suppose I think of another function this the last function that shall discuss; as for as the mathematics is concerned. Suppose you think of this particular function magnitude of x. How will I plot of magnitude of x against to x looks like? It is a simple thing if x is greater than 0 magnitude of x is x itself. So, if I made a plot this the kind of appearance that you are going to get right x magnitude of x plotted again states would be just is straight line like this. That if x is negative what will happen? The plot will be actually somewhat similar it will be looking like that right magnitude of x if you plot again states if for negative values of x this the appearance. So, suppose I think of think of d magnitude of x by d x we will again you can take the symbol physical interpretation it is what is the derivative it is a slope. And what about the slope of this curve that over this 2 straight lines that I have drawn. You see when x is greater than 0, the slope is actually how much. How much will be the slope is 1 right.

So, therefore if x is greater than 0 this actually 1, and if x is less than 0 what is the value of the function? Again, you look at the this straight line you see if you look at this straight line you would realize that this as a negative slope. If the slope is minus 1 this slope is minus 1 therefore, what happens is that if x is less than 0 the answer is going to be equal to minus 1. So, what is this derivative? This derivative is an interesting function which has the value plus 1 if the x is greater than 0 while it has the value minus 1 if x is less than 0. So, if I made plot of this function this new function. How will it look like? Let me continue here.

X along the horizontal axis and the derivative of magnitude of x with respect to x is flow out at along the vertical axis. And obviously what happens is that if x is less than 0 the answer is minus 1 that is the plot. And if x is equal to plus 1 so if x is positive what will happen? The value has the function has the value plus 1. So, at x is equal to 0 itself what is happen the function has discontinuity correct. So, if you wanted to make a plot of the function and you will say it is goes like this; at x is equal to 0 itself it jumps it has a discontinuity. And the size of this discontinuity so much the height of the discontinuity this equal to 2 units, and so if I have to differentiate this function further what would have happens?

Suppose I want to take the derivative of that function well the function is a constant in this region. So, there the derivative 0 function is a constant in that region there again the derivative is 0; but at this point itself there is a jump discontinuity of 2 units. Therefore, the derivative of the function will actually be 2 times remember what happened with the delta function. If there was a delta function then there is a discontinuity of 1 unit in the function in the integral correct.

So, if this function has a discontinuity of 2 units its derivative is going to be 2 times the Dirac delta function correct. That is what happens. Now, let me again tell you the reason why I introduce to this function. Because you look at this function this the derivative of a function which is shown here. You see that the derivative of the function is discontinuous but the function itself the function is this the function itself is continuous correct. So, let make a summarize everything that I have told you. If the derivative is a delta function then the function will have discontinuity right. If the derivative is a delta function then the function will have a discontinuity. If the derivative is discontinuous then the function itself will be continuous. So, this is what we were using in the previous lecture; where did use it. We said that we have the Schrodinger equation.

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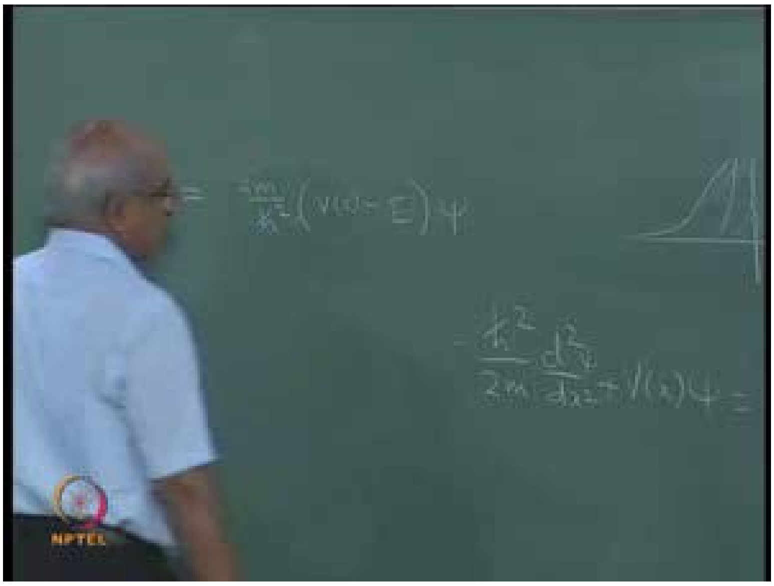

We said that we have Schrodinger equation which may be written as what was the equation d square psi by d x square is equal to right I mean the only way I can remember this. So, write the equation in the way I remember and then rearrange that is the equation. So, if I rearrange that what will I get for d square by d square psi by d x square? This the equation that I will get right. And the way the potential energy is in this problem what was happened is that the potential energy has a discontinuity. That is simply implies that the second derivate has a discontinuity. But even if the second derivative has a discontinuity, the first derivative is guaranty to be continuous. And not only the first derivative naturally if the first derivative is continuous then the function itself will be continuous. Therefore, that the fact that the wave function has to be a continuous function of position; that can be derived from the fact that the wave function obeys the Schrodinger equation ok.

The fact that the let me repeat wave function is a continuous function can be derived simply from the fact that the wave function obeys the Schrodinger equation, and if the potential is not equalizer; if it has only a finite discontinuity. Then, even the first derivative of the wave function will also be continuous right unless your potential is very peculiar. Even the first derivative will be continuous that is what we used in the last days lecture.

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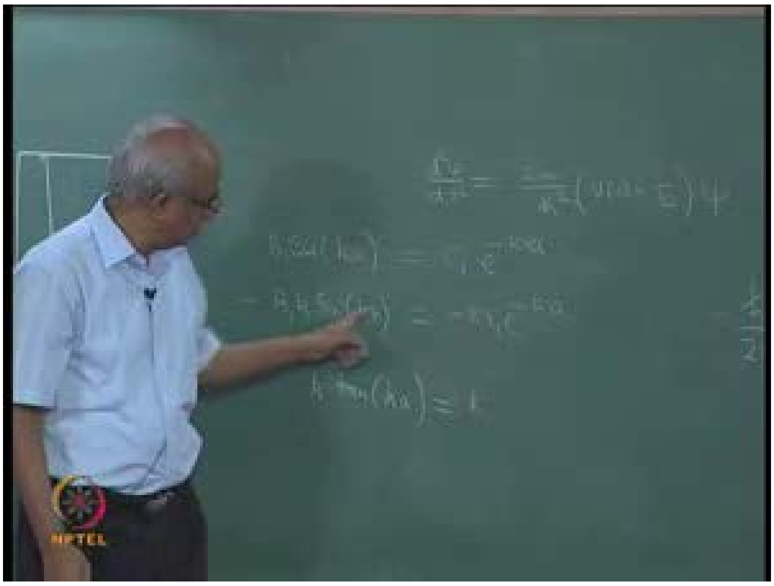

So, let us now do that or let me just remind you what happens with this with this particular function. We impose the condition that the wave function at this point should be continuous. And we also impose the condition there its derivative must also be continuous and we arrived at an equation. Now, strictly speaking what I should do is I should impose the same condition at the other side at the other end also. So, let me just do that today right just let me just impose the condition that the wave form should be continuous at this point which is x is equal to a. So, the wave function on the left hand side is given by this function while the wave the right hand side is given by that function. So, how will you impose the condition you will say that b 1 cos k x must be equal to c 1 e to the power of minus kappa x when x is equal to the when x is at the boundary. That means, I have to put x is equal to a. Therefore, I will put a here. And I will put a there not only that the derivative of the function should be continuous. So, what is derivative of this function? The derivative of that function is minus b 1 k sin k x but you have to evaluate this derivative at a at x is equal to a.

So, derivative at that point is going to have an a inside it right you will have to put a. And then what is the derivative of this function? The derivative is actually minus kappa c 1 e to the power of minus kappa x but you then have to put x is equal to a. So, you are going to get a here and these 2 have to be equal. And just as we did in the last days lecture actually we can divide this equation by that equation. And what is the result? You will find the result k tan k a; this equal to kappa right. This the result that you will find. If you we just divided you see this equation by that equation which actually means that you divided this by that and you divide that by that, and because these 2 are equal because this side is equal to that side. Then, what will happen? If you took the ratio again they have to be equal. And if you look back any 1 notes you will find that it is precisely the same equation.

If you look into your notes if you will find that it is precisely of the same equation; that has obtained by applying these conditions at the other boundary same equation we obtain, when we impose the condition that the wave function and its derivative should be continuous at the other boundary. So, we do not get a new equation that is the same equation. And the question now is how do we solve this equation and let me tell you how to solve it.

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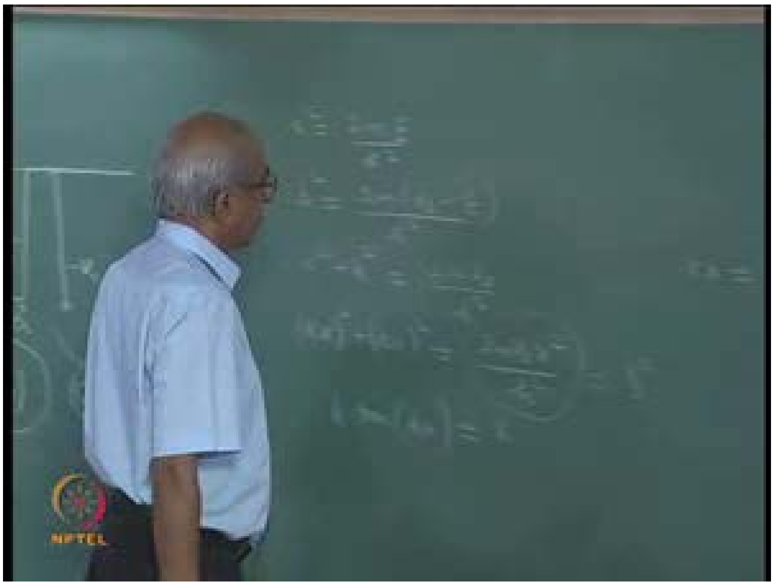

So, let me remind you of the definitions of k and kappa? Kappa was defined to be 2 m epsilon by h cross square correct me if I make a mistake. And k was defined to be 2 m well there is a mistake already this kappa square. And k square is 2 m v 0 minus epsilon divided by h cross square right this from the previous day.

Again, what was epsilon? Again, let me remind you I am imagining that that the particle has an energy which is that much right. It is just the energy of the particle i am assuming is less than 0 and this height I have taken to be epsilon. So, that the energy of the particle is equal to minus epsilon right that was the notation. So, obviously if you added k square and kappa square what would be the answer? Clearly, the answer is going to be 2 m v 0 divided by h cross square. That obviously implies that I can write kappa in terms of k; kappa must be equal to well before I do that let me just multiply throughout by the parameter a, which is occurring in the problem. You see this parameter is actually determines a determines the width; 2 a actually is the width of the potential well.

So, what I will do is I will just multiply this by a square. So, that you will have kappa a square plus k a square is equal to 2 m v 0 a square by h cross square. You may wonder why I did that; answer is actually is very simple see this kappa is occurring in the exponent correct it is occurring in the exponent that it is occurring with x. Now, in a physical problem x has dimensions what is the dimension of x length right x has the dimension of length. Therefore, what happens is that kappa has dimensions of length in waves. Because if kappa x is occurring in the exponent anything that occurs n the exponent has to be dimension less. So, this implies that kappa has dimensions of invades of lengths. And so if I multiplied by something which has dimensions of length the result that I get will be dimensionless.

And, we always prefer to work with dimension less things. So, that is the reason why I have taken kappa into a. Why because kappa into a is going to be dimensionless, and obviously k into a will also be dimensionless. And this right hand side this whole thing itself will be dimensionless; it is always nicer to work with dimensionless things. And so let me say that this entire thing I will denote by the symbol zeta square, this simply because I do not want to be writing that whole thing again and again and again. So, I just write zeta square instead of that.

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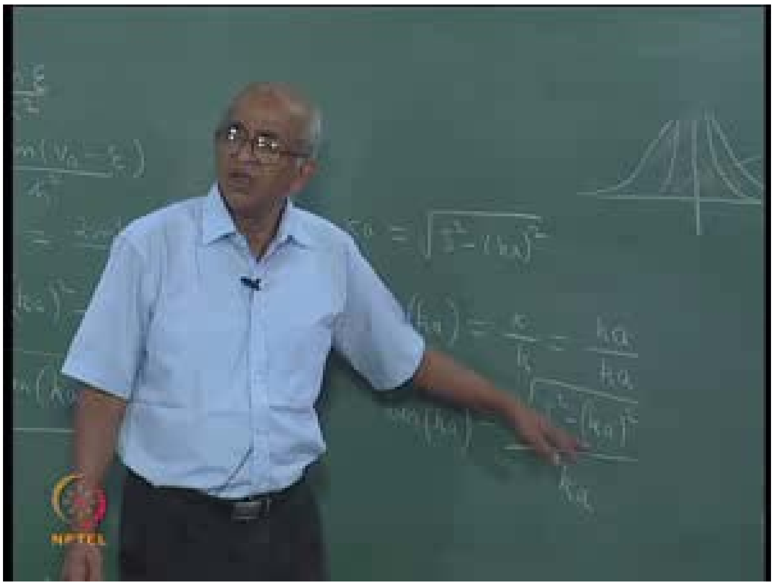

So that means actually I can write kappa in into a as zeta square minus k a the whole square with a square root sign. So, there is a relationship between kappa and k and that relationship I am writing in this fashion that is all. And now I know that this equation is to be satisfied. And I have also mentioned you yesterday that kappa and k are both dependent up on epsilon. So, this an equation that will actually determine epsilon; which means that this the equation that will determine the energy of the system.

So, I want to solve this equation and that is why I am doing this manipulations. So, in this equation I can make a slight rearrangement and say that tan k a is equal to kappa divided by k over I can add an a to both numerator and denominator. And write this as kappa a divided by k a right I have into modified anything. And then I can say kappa a is what kappa a is given by this expression. So, I could write this as zeta square minus k a the whole square divided by k a.

Now, it thus look a little bit complex but what is the answer that I get the answer that tan k a has to be equal to that. So, this a condition has to be obeyed. It has to be obeyed to have an acceptable state of the system. But you look at k what is k? K is related to the energy of the particle right. Energy of the particle is minus epsilon.

So, only k which satisfies this condition are allowed. And that implies that only those values of e which correspond to that k are allowed only those values of e will satisfy right; only those values of e which lead to a k which satisfy this equation are the 1s which are allowed. Therefore, what should I do? I have to find k in such a fashion that this equation is obeyed. And once I get that value of k what will I do? I will put the value of k here and evaluate the energy of the system. So, this the procedure and I am forcedly receiving this equation it is a little bit complex. But we can actually find solutions in a fairly simple fashion we cannot find a analytic solution unfortunately. So we have to reserve to what is the effect was it graphical procedure for solving this equation. So, how do you solve this equation?

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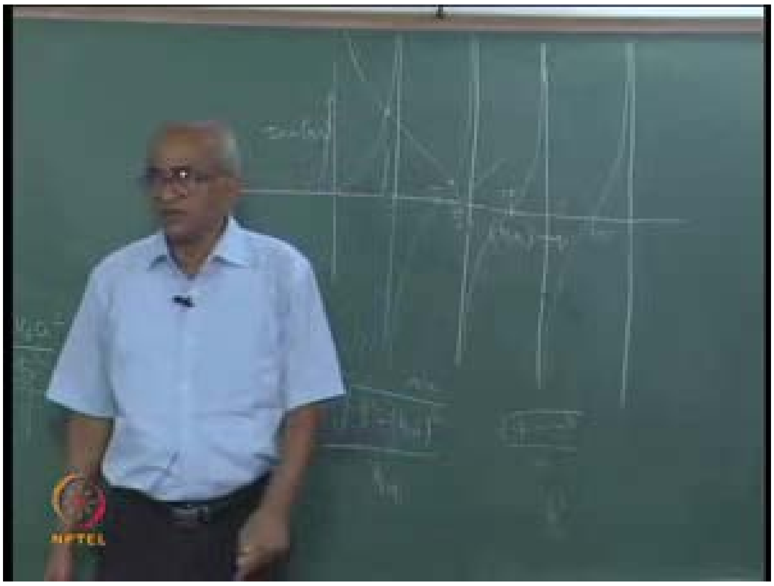

And, this again is a very interesting thing say you have on the left hand side you have a function; on the right hand side you have a function both are functions of k. And I want to find the solution? So, how will I do that the answer is I will make a plot of the left hand side right; against k. I will also make a plot of the right hand side against k. Let us see what they results are. So, the left hand side I will draw with some color the left hand side tan k a. So, the horizontal axis going to be taken to be k a, so the variable now is k a and I want to plot tan k a on the vertical direction. I hope you remember how a plot of tan x against x would look like at least roughly. So, the weight which would look is you see when x is equal to 0 tan x actually is 0. So, it would start at 0 right like that P; and as you increase the value of x it will actually increase.

But when x is equal to pi by 2 right tan x well instead of k a I am just saying x. So, tan x when x is equal to pi by 2 what is its value it is infinitely large. Therefore, the plot would look like this. I have to be little bit careful this the point x is equal to pi by 2 correct. But what will what about the plot beyond this point well; it is interesting that the plot starts at minus infinity something like that. And when it goes to 0 here and then it goes to plus infinity again. And that will happen this next infinity will happen when x is equal to 3 pi by 2. And again the plot will continue. And you will have another infinity at what value would you say? The next infinity will happen when the value of x is or when k a is 5 pi by 2. And then I will draw 1 more. This goes on repeating because this tan of course it is composed by sin and cosine which are periodic. So, tan also will be periodic correct.

And, not only that these points; what is this point? It is actually pi this pi and this point will be 2 pi, this will be 3 pi and so on. So, that is the appearance you say the green curve is the appearance of the function tan. Now, what would be the appearance of the right hand side if I made a plot of it? This function what is the function you have a constant I mean if you want if you want to get an idea I can say this something like this a constant. So, maybe I will say 4 this the variable x. Let me say so 4 minus x square is of this from 4 minus x square divided by x with a square root on top. This the kind of function that you have to think of plotting; obviously you see the function is imaginary if x is greater than 2 right. So, we will worry only about the region where x is less than 2 ok.

So, and further when x is close to 0 what will happen to this function it is going to be infinitely large. So, as a result what will happen is that when I am going to make the plot here. When you are very close to the origin the value of the function is very large. So, it starts at infinity then as you go on increasing the value of x. What will happen this function wills actually if you think about it you would realize that it will decrease? So, if it decreases what will happen it will go on decreasing something like that? And then what will happens is that finally when k into a is equal to zeta the function will become 0. And beyond that the function is imaginary correct. Therefore, this the point where k into a is equal to zeta right.

So, this how the plot of the second function is that; the first function is shown with the green curve the second function is shown with the brown curve. And where is it will sit that the first function is equal to the second function. All you want to solve this equation you have made a plot of this function you have made a plot of this function. And you now ask where is it that the function is equal to the second function and the answer is that the 2 are equal at points where the 2 curves intersect right. Those are the points that you want. So, where are these 2 curves intersecting I did have yellow color somewhere this point number 1 and that is point number 2.

So, how many solutions would I have if this the way the 2 curves were the answer is that there are only 2 values of k. The first value is given by this point which actually makes this corresponds to a k value which is somewhere here this the corresponding k value. And the second point is there and the corresponding k value is somewhere here. And what should I do now I have to find these 2 values of k put those 2 values of k into this equation. And find out the corresponding values of epsilon? And therefore there are 2 allowed energy levels. And there is nothing more only 2 allowed energy levels because you see there are only 2 points where the 2 curves intersect. I think I will stop and then continue in the next lecture.

Thank you for listening.