Introductory Quantum Chemistry

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Lecture - 12

Particle in a Well of Finite depth

So, we were discussing the wave functions for a particle in a 3 dimensional box.

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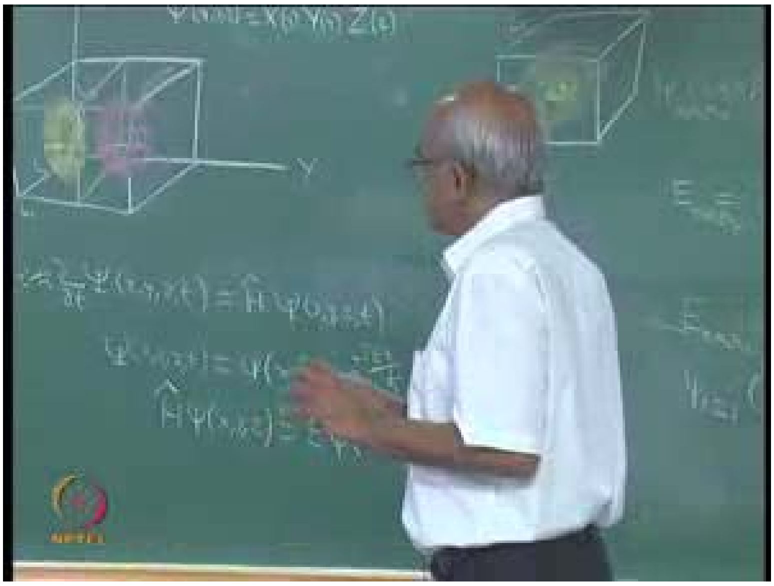

We show that the simplest as no nodes; while the next possible 1 has 1 node. In this particular case where I thought of psi 1 to 1 it has a node in the y equal to L by 2 plane or if you had total psi 2 to 1 obviously what is going ((Refer Time: 00:52)) 2 1 1. What will happened is there it would node which is at x equal to L by 2. And, where will that be it will be actually a plane perpendicular to this plane; the earlier node plane node right, nodal plane actually. Now, I do have a mathematical program which can show you all these things.

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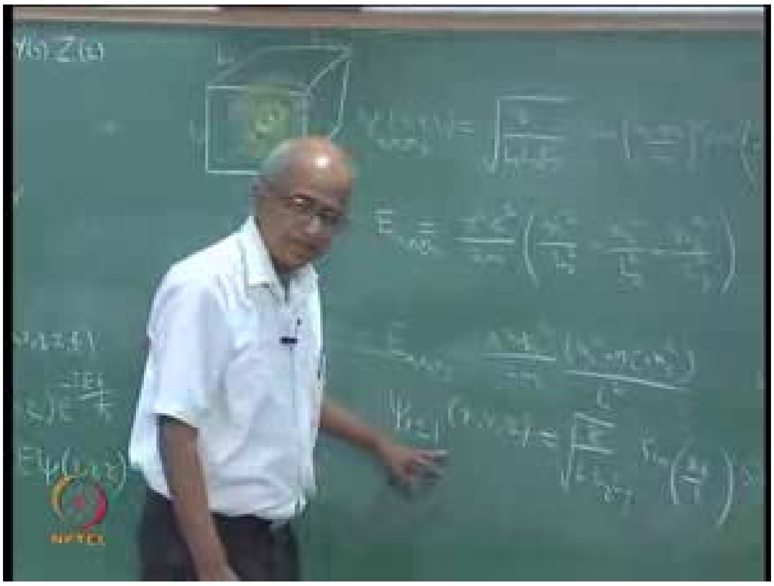

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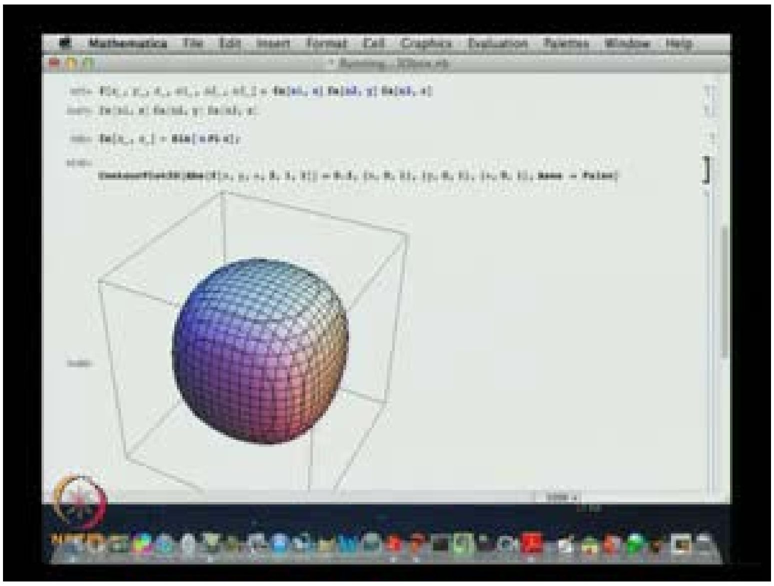

If you look at this figure; the way of this figure is construct is as follows you take the wave function for the ground stage right as I said it has no node. So, what is going to happen is that it will have its maximum value at the center. And, it is go away from the center at the value of the function will go on steadily decreasing right. At the center, let us say it has a value of 1 just to illustrate. Then, what I can do is as I go away in each the direction its value will decrease; there will be a particular point in that direction at which the value will have will be equal to 0.5 right. In each direction, you will have a point where the value is equal to 0.5. You can join together all these points to get a surface and that is a surface that is plotted in this figure.

So, these again if you look at picture; it so very clear that it resembles the lowest possible function resembles an automatic orbital. The automatic orbital is nothing but the s orbital; I can draw pictures of other orbital sources in the same fashion. For example, if you think of 1 which one I should well let me just plot this it will take a little bit of term because it is not a small calculation; it is a fairly lengthy calculation. And, the computer will do the calculation I will show you how the plot looks like. As I told you, these things are plotted using the software mathematic ((Refer Time: 03:07)) which is extremely powerful they still doing the calculations.

So, I have put one of the 3 quantum number equal to 2 there these are still equal to 1.

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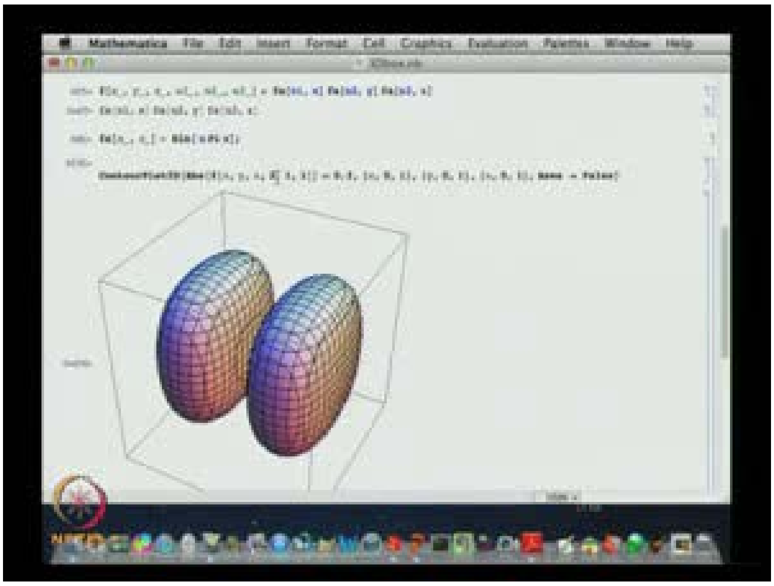

So, obviously it is this 1; that I have put I can plot other thing also but suppose I said n 1 is 1, n 2, sorry I suppose I say all of them are 2; what would the appearance? Let us see that or maybe what I will do is; I will say 2 of them are equal to 2 and so the last 1 is equal to 1. So I am actually not looking at 2 2 2 but 2 2 1.

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As I said the calculation thus take a little bit of term it has to be find the surface; and then plot it.

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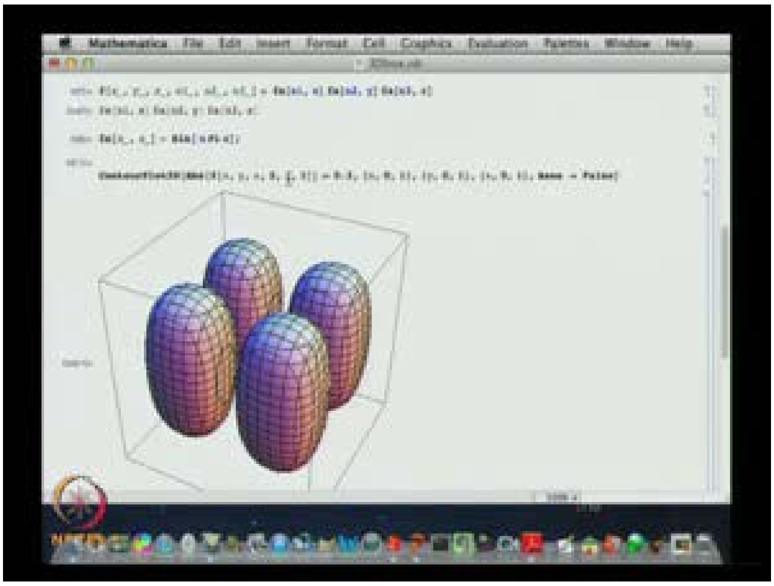

This is how the function looks like; if you want I can even rotate it but I even rotation may take a little bit of term; it is taking term. So, I do not think I should try to do that. Let us look at the other function which I take about psi 2 2 2 this will have 3 nodal planes; and 3 nodal plane will all be perpendicular to each other. So, look at that function. Now, this 1 for example, it does resemble 1 of the atomic orbital ((Refer Time: 05:48)) resemble d x, d x y or something like that.

Now, I if think about it I can tell you. It actually resembles d x y this particular plot which is there now; while it is plotting let us think of something else. See here I was assumed that the box is completely symmetric; all the 3 sides are equal right. So, if you are familiar with symmetry you will say that it has octahedral symmetry, cubic. But suppose I now say I am going to distort this. I am to going to distort the yeah you look figure right.

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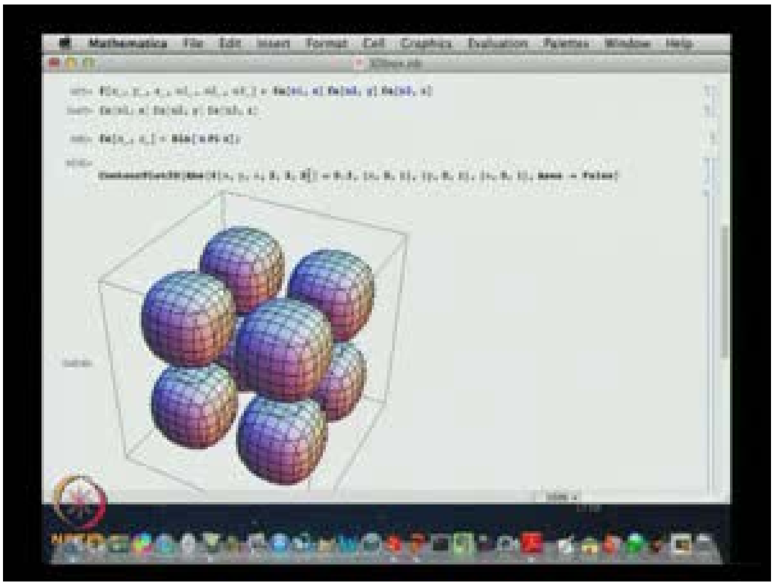

This box I have assumed that they all the side are equal but now suppose I say the length of the box in sub direction is increased. Let us say the length of the box in the sub direction is increased a little bit. Then, what will happened your expression for energy? What we are saying is that these is our general expression L 1 is equal to L 2, right that is what we are saying but L 3 is a little bit different. So, therefore L 3 actually slightly larger than L by an amount which I shall donate as delta L. So, this is L square, that is L square and this is L plus delta L square.

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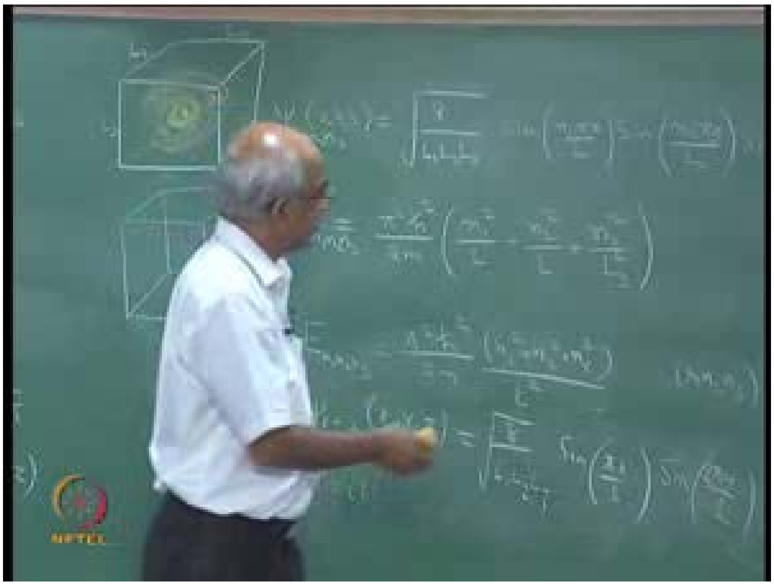

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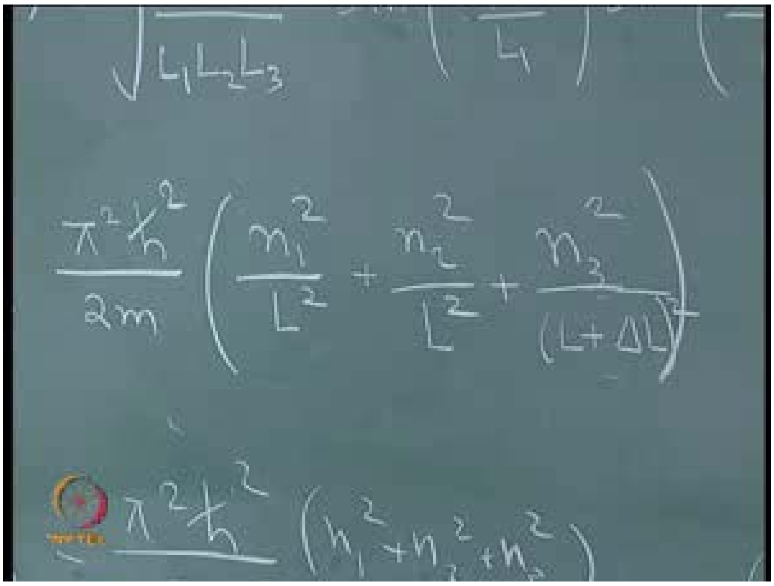

So, what will happen to the l energy levels? The pictures that I have drawn here is for the perfect cube; but suppose I decrease the symmetry of the system by stretching the box. Then, what will happen the energy levels?

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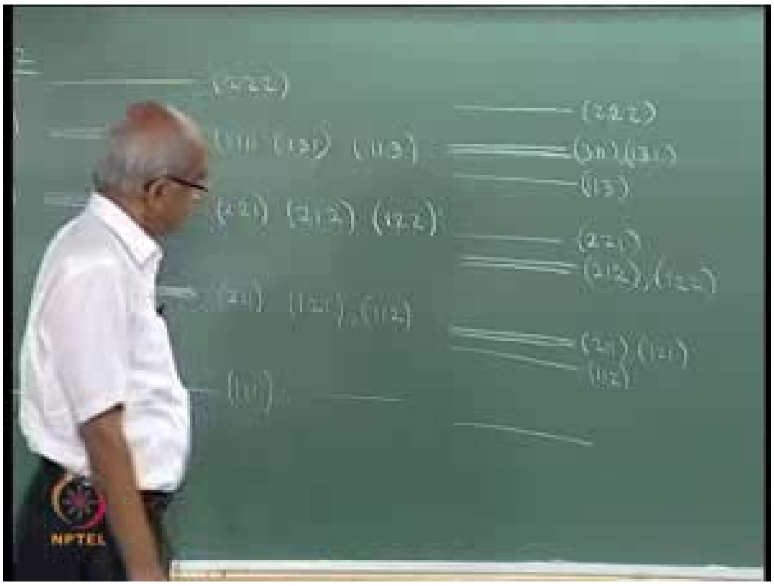

Of course, you say this energy level of course, you say this energy level 1 1 1 will get lowered a little bit and then, what will happen 2 1 1, 1 2 1 and 1 1 2. You will find that these also 2 1 1 and 1 2 1 also will get lower but by exactly the same amount. So, I can represent them here, they are lower than in this earlier figure this is 2 1 1 and 1 2 1. But if you think of 1 1 2 actually 1 1 2 will get lowered by a larger amount. And, that means you see these 3 states are no longer degenerates. And, so as a result of lowering of symmetry what has happened is that an energy level which has triply degenerate has a split up into 2 energy levels; one of them is doubly degenerate and the other is single degenerate.

Now, in a similar fashion the same kind of think will happen with this; there what will happen is that 2 1 1 will be lowered sorry 2 2 1 will be lowered. But 2 1 2 and 1 2 2 will be lowered even more; and therefore they will remain degenerates. So, again the degeneracy of the original energy level is lifted it splits up into non degenerate and doubly degenerate levels. Similarly, here too 1 1 3 would have an energy that is lower than either 3 1 1 over 1 3 1. And, finally of course, 2 2 2 is lowered but there is only one energy 1 straight; and therefore there is no spitting it. So, essentially the idea is this you see if you had cubic symmetry; you would have triply hold degenerate energy levels. And, if you distorted cube to form a rectangular parallelepiped then what happens? Then energy levels are actually split up to give you energy levels of lower degeneracy.

Now, you will pass on to the next interesting problem we will go back to a 1 dimensional problem. And, we will now say that I have a particle it is within a box but that and that box as a length equal to may be L; earlier with or we said that outside the potential energy is infinitely large but we will remove that. And, we will say that the potential energy outside is not infinitely large but finite and see what happens?

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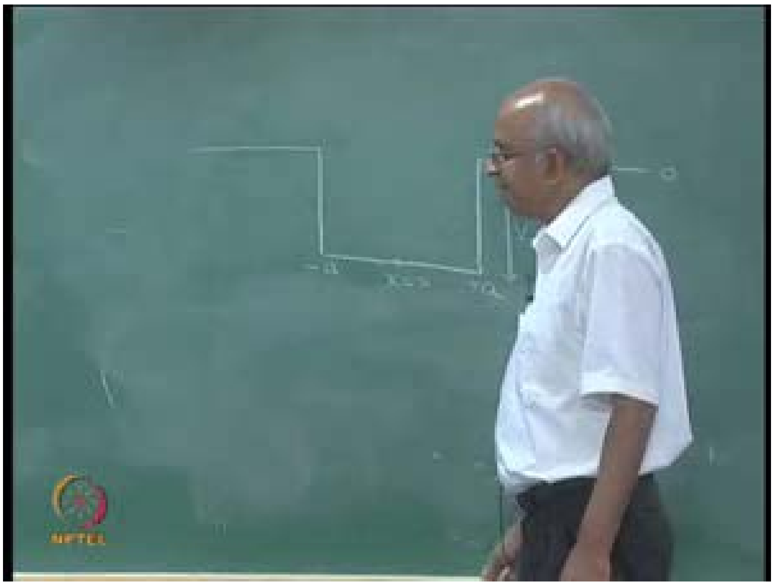

So, to make thinks clear let me imagine that I have a box which extends from may be here to there; in that region the potential energy is low while outside the potential energy is different and large right. In fact, I will imagine it this way. Let me say outside the potential energy is 0 just for the take of convenience outside I am going to say the potential energy is 0. And, if I put it like that then what will happen if you think box the potential energy is actually negative right. And, I will say that this height is equal to v 0. So, if the particle is inside the box its energy, potential energy will be minus v 0. Because it is the box, within the box the potential energy is low.

If it is outside I will say the potential energy everywhere is 0. And, also it is convenient to say that I will have my coordinate system in such a fashion that the origin is right at the middle of the box. And, the box will let may extend from minus a to plus a. So that the total length of the box is now 2 a right. Why do I do that well the answer is actually quite simple I have already told you that; if I choose the potential to be symmetric. Then, I have big advantages I can classify my wave function as being symmetric or anti symmetric. And, then I am going to use that makes thinks extremely simple. If you make use of symmetry then calculations become very easy. I want to use that is region why I choose the coordinate system to be in such a fashion that x equal to 0 is this point.

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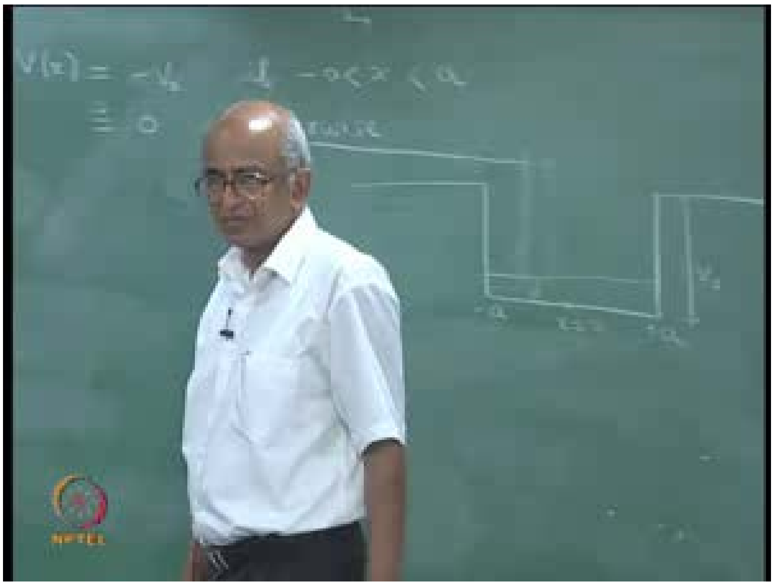

So, let me now define the potential energy of the system V(x). How will you define it if it is equal to minus v 0 right v 0 is assumed to be positive right; so minus v is 0 negative. When if x is less than minus a sorry mistake minus a is less than x; and x is less than plus a; that means the particle within the box. And, outside the box what will happen? I will say that the potential energy is 0. Now, before we go in to the quantum mechanical description this imagine I have a classical particle what will happen to a classical particle? You say classical particle can be within the box then it potential energy will be minus v 0 and it is not moving.

So, therefore the total energy will be minus v 0 correct. So, the lowest possible energy for a classical particle if it was subjected this kind of potential will be minus v 0 or then maybe I can push the particle within one direction giving it some kinetic energy. And, then what will happen it will suppose I gave it that much kinetic energy then it will go heater than come back and go and oscillate in within this box. And, the amount of energy that I can give it can be anything.

So, therefore you see the particle can have any energy starting from the bottom from minus v 0 onwards; if it obeys classical mechanics it can have any energy. But then of course if it is total energy greater than 0 then what will happen? If you push the particle in this direction it will go off to infinity. This is what will happen classically, so, classically speaking you say this is the particle can have the any energy from minus v 0 to plus infinity; stat 2 in quantum mechanics is the question that we will answer.

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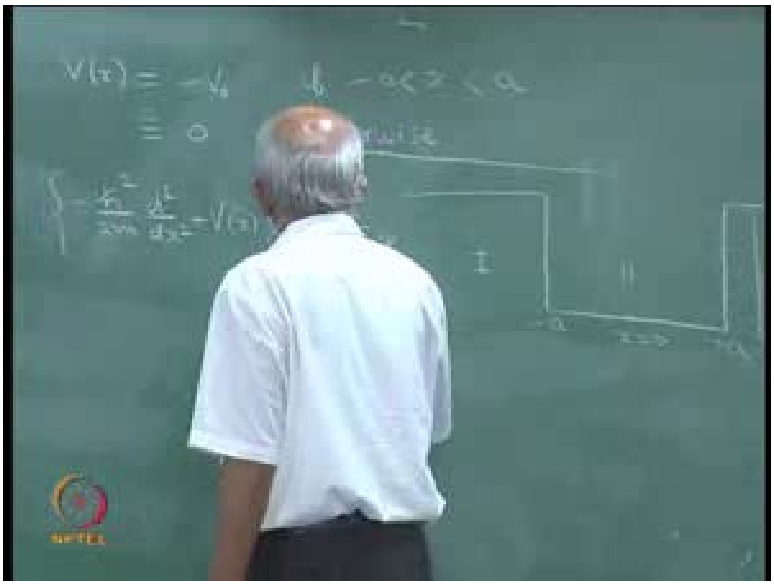

Therefore, I will write the Schrodinger equation take the I only write the term independent Schrodinger equation; because we are looking for these stationary states of the system. And, so I will have the Hamiltonian operative containing its kinetic energy and if the potential energy. And, this is going to operate upon psi with an the answer as to be equal to E psi, right.

As I told you classical speaking the energy of the particle can be anywhere between minus v 0 to plus infinity. And, classically what will happen is that if the total energy of the particle is greater than 0; if it is greater than 0 what will happen to particle will go away; while if it is less than 0 it means, the total energy is less than 0. Therefore, the total energy is negative. Then, what will happen the particle will actually go back in forth; so it is bound within box if such a particle is going to be bound within box.

So, what we want know is quantum mechanically will the particle remain bound within the box. Therefore, what I am going to do is I am going say that I am thinking of a situation where the energy of the particle is less than 0 right. I will first look at situations where the energy of particle is less than 0. And, then after that I will worry about situation where the total energy of particle is greater than 0 correct. So, let us try to write down this differential equation in 3 different regions, which are the regions; this is region 1, this is region 2 and that is region 3.

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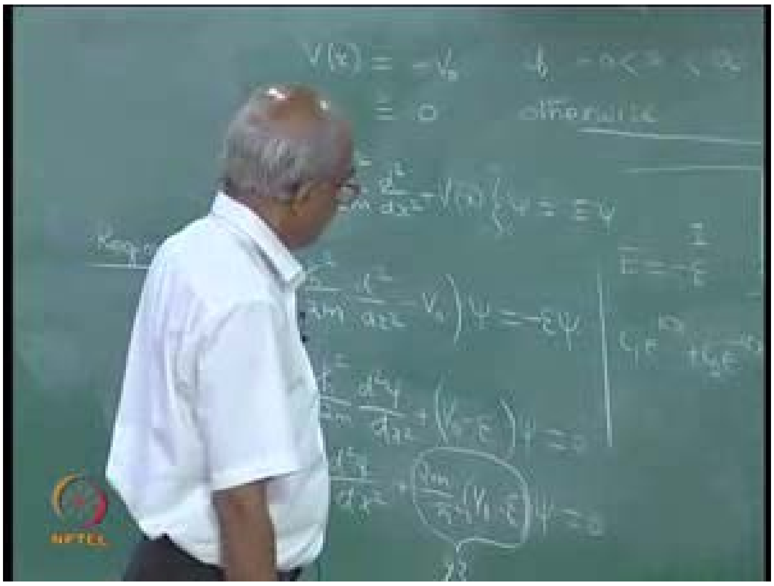

I will first think of region 1. In region 1, what is going to happen to this differential equation I will have minus h cross square by 2 m d square upon d x square in region 1; what is the region 1? Region 1 is the region where the value of x is less than minus a and in that region what is the potential energy of the system it is 0. So, therefore this plus 0 operating upon psi (x) is equal to the energy of the particle; sorry the energy of the particle, multiplied by the wave function. But I told you that I am interested in the situation where the total energy of particle is less than 0. Therefore, what I will do is I will adopt this notation I will say that E is equal to minus epsilon; where why do we adopt this notation simply because I want the epsilon to be positive right.

So, I would write the energy of particle as E is equal to minus epsilon where I know that I am interest in situations where epsilon is a positive number. So, then what will happen this is actually minus epsilon terms psi. And, what this effectively means is h cross square by 2 m d square psi by d x square is equal to epsilon psi; where epsilon remember is a positive number or you can rearrange these and write this d square psi by d x square is equal to 2 m epsilon divided by h cross square psi; epsilon is a constant because it is related to the total energy of the particle.

And, at this point you say as usual we do not want to be writing this object again and again and again it is very inconvenient. So, introduce something which I am refer to as kappa; such that square of kappa is equal to 2 m epsilon by h cross square right this is equal to kappa square. So, therefore d square psi by d x square is equal to kappa square psi; kappa is a constant. So, second derivative of a function is equal to the function multiplied by kappa square. So, what is a solution of that equation? If you want to solve this, it is extremely simple. Well, there are 2 possible solutions; the first one is e to the power of plus kappa into x. In fact, I can put a constant what is the well let me not put a constant I will do that in a few seconds.

So, you have one solution which is of the form e to the power of plus kappa x; you have another solution which is of the form e to the power of minus kappa x. And, you can multiply this by any constant that you like so maybe you can say C 1 e to the power of kappa x and C 2 e to the power minus kappa x; these are possible solutions as we can verify very easy to verify. Because if it just took the second derivative of this. You will find that is equal to these functions getting multiplied by kappa square. What if you took the second derivative of this you will find that, that is equivalent to multiplying this function itself by kappa square? Therefore, it satisfies that differential equation.

So, you can say the mass general solution will be a linear combination of these 2, because you see if you have 2 particular solutions you can always add them up; and answer will always be a solution of the original equation. So, therefore in this region; in region 1 was what is a solution that we have found; C 1 e to the power of kappa x plus C 2 e to the power of minus kappa x is the solution, fine. So, what will be the solution in this region? Well, there also the potential energy is 0. Now, the equation is just the same it is not any different, it is the same equation; and if the equation is just the same what will happen? The solutions are going to be similar. So, how will you arrive the way the solution in this region; the answer is going to be while I will have some A 1 into e to power of minus kappa x plus A 2 e to the power of plus kappa x; where A 1 and A 2 are some arbitrary constants, right. And, now you have to look at the solution in region 2. So, what will happen in region 2?

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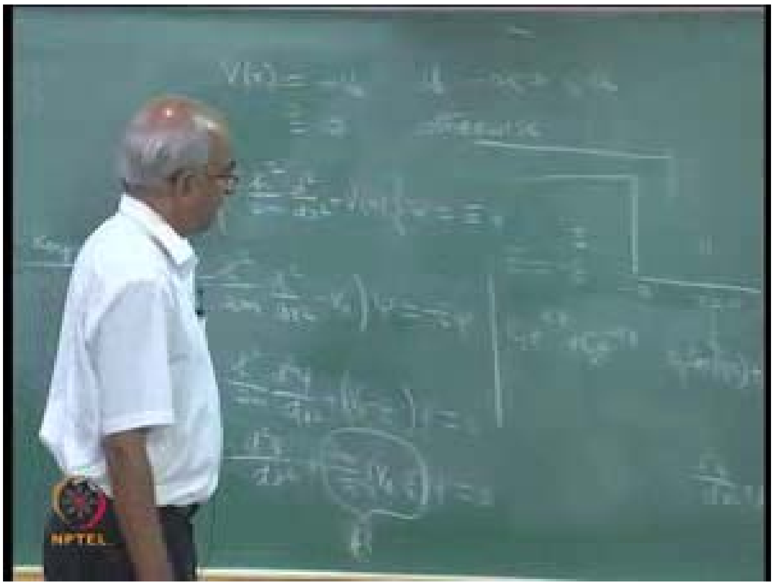

In region 2, this differential equation becomes minus h cross square by 2 m. Now, I am thinking of region 2; d square upon d x square what is the potential energy of the system? If the particle is in that region then it is this is minus v 0, psi is equal to minus epsilon psi this is the differential equation. You can easily rearrange this equation what is going to happen is you are going to get h cross square by 2 m d square psi by d x square plus v 0 minus epsilon into psi is equal to 0 right. Now, just multiply throughout by minus sign and then take this term to the left hand side; you are going to get this equation or if you like you can rearrange I mean like this as d square psi by d x square plus 2 m by h cross square v 0 minus epsilon psi is equal to 0.

Now, v 0 is a constant, epsilon also is a constant right. Therefore, this whole thing is a constant then it is perhaps convenient that I introduce another constant which I will define to be such that; the new constant that I am introducing is q. And, they introduced it in such a fashion that q square is equal to this number. So, therefore in this region the differential equation has the form d square psi by d x square plus q square psi is equal to 0; that is in region 2. So, what is this solution in that region? This is slight particle in a 1 dimensional box; that we have already discussed the solution is actually this possible to for you to write the solution as may be some v 1 cos k not k but q x plus some v 2 sin k x.

I hope we do not mind if we change notation a slightly because what comes to be naturally is k. So, what I will do is I will say instead of calling this q let me just call it k; k square is define to be equal to that. So, therefore here you are going to get k square and naturally the solution will be B 1 cos k x and B 2 sin k x; where k square is defined to be equal to 2 m by h cross square into v 0 minus v. So, these are the solutions in different regions but it is not enough to get solutions in these different regions; you have to ensure that the solution that we are getting is acceptable.

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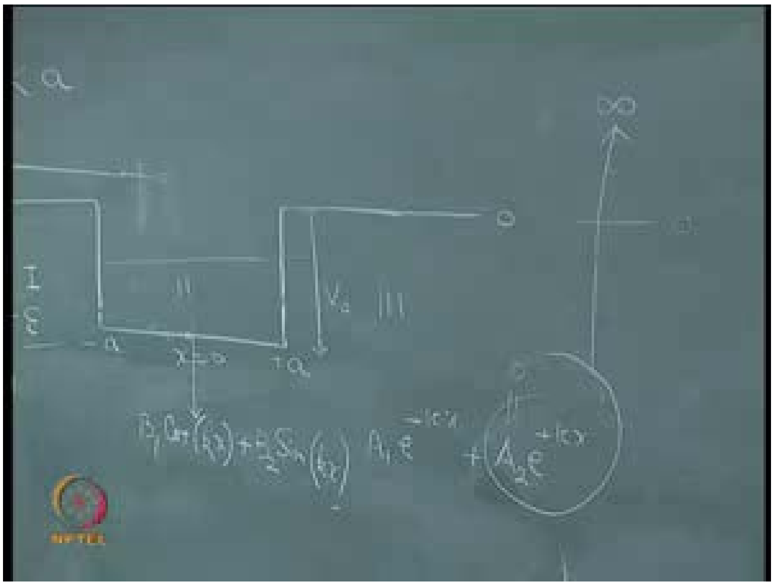

So, let us look at the solution that have in these region I have A 1 a e to the power of minus kappa x plus A 2 e to the power of plus kappa x. Now, suppose we allow x to go to infinity what will happen? This term I would expect will decrease because it is a to the power of minus kappa x but what about this term? This term will increase to infinity. So, if you said that this is your wave function; you are actually saying that the particle as you go way from the box, the particle is more and more likely to be found.

In fact, the probability that will be found they very large difference is extremely large because this will tend to infinity; as x becomes infinity large. And, that behavior is not acceptable then there is no physical reason for that to happen. And, therefore the only way in which I can get out of this difficulty is to say that A 2 must be equal to 0 otherwise, I am not going to get an acceptable solution. So, therefore straight away here I can say A 2 must be equal to 0. If you think of this other parts right look at this part here imagine x is going to minus infinity. Then, what will happen to these 2 terms? You have e to the C 1 e 2 the power of kappa x; x is going to minus infinity. So, what will happen this same actually will decrease to 0 while what about the other term? It will increase to infinity. And, therefore this term is going to give me problems. And, therefore, to have an acceptable solution I am push to put C 2 equal to 0.

So, therefore in this region the solution has to be simply C 1 e 2 to the power of kappa x, right; the other part I have to it to throughout. Now, you have to be very clear as to why this is done, say I am saying that the total energy of the particle is less than 0. Therefore, what do I expect; I expect that the particle will be trapped within this potential well it has no possibility of going away right. And, therefore the probability of finding it at a large distance as to be vanishingly small, right; that is what we are doing. Now, as for as this part is concerned what do we do with this part? Well, I have this very interesting possibilities say I know that my solution to the Schrodinger equation; for this problem it has to be either symmetric it has to be an even solution or an odd solution; this is what we have proved in the morning right. So, suppose I am interested in the even solution. Even solution means, it the symmetric solution you replaced x with minus x the solution will remain the same, it will remain unchanged right.

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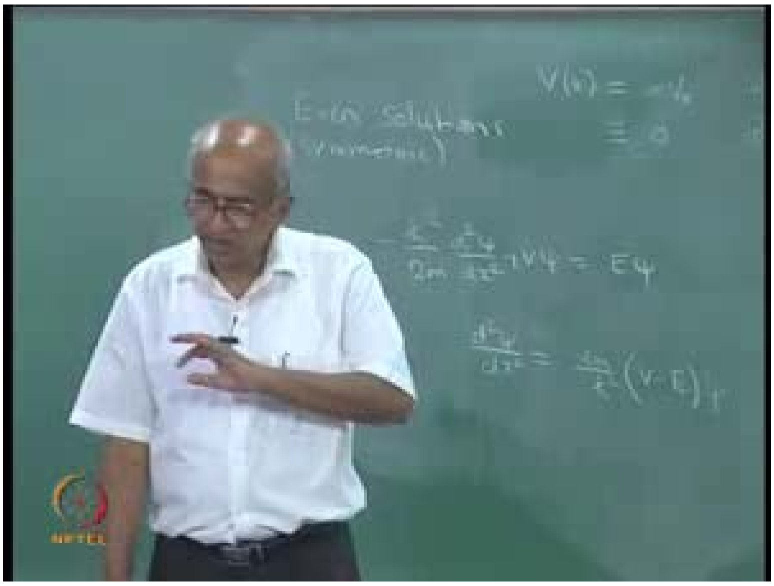

And, if you look at the functions that you have here of course k x and sin k x; we know that cos k x is an even function, while sin k x is an odd function. So, if I am looking at even solution. So, what is going to happen I am going to have only cos k x, I will not have sin k x. And, if I am looking only at word solutions then I will have only the sin functions; I am not going to have the cos function and that is the enormous simplification.

So, let me imagine that the I am going to look only at the even solutions of this Schrodinger equation at the moment; later on I will have to look at the odd solutions, right. It is a symmetric; what this means is that if you replace x with minus x the solution remains unchanged. And, if that is to happen what is the condition; the condition is that the function should contain only B 1 cos k x, it should not it should not contain B2 sin k x. So that actually implies that B 2 which has occurring there must be equal to 0.

So, now we have the next problem is a we have to determine C 1 B 1 and the constant there are is actually A 1. So, we have to determine these 3 constants A1, B 1 and C 1. How do I determine this? Well, let me tell you the way in which I will determine them; see you look at the potential. The potential actually at this point it has a finite step; it value as you as you cross this point the value of the potential changes by a finite amount. So, the strictly speaking the potential is discontinuous at this point, at the point x is equal to minus either potential is discontinuous.

So, if you look at this Schrodinger equation; what does the Schrodinger equation say in general it says that that minus h cross square by 2 m; here I am telling you something that is very general. This is the Schrodinger equation. And, you can rearrange this and say this means that d psi by d x square is equal to how much? We just rearrange, you are going to say it is going to be 2 m by h cross square v minus E in the psi is that ok; if I rearrange this I will yeah this is ok. Now, if we look at this equation I mean you can say of trial what is this it tells me how much is the second derivative of the wave function that solve that it does. And, if you had a situation where the potential is discontinuous. That means, second derivative of that function is discontinuous that is all that it means.

See, if v is discontinuous that means the second derivative of the function is discontinuous that is all that it means. But if the second derivative is discontinuous all that it means is that the first derivative will be continuous. And, if the first derivative is continuous what will happen the wave function will also be continuous. Therefore, by looking at the Schrodinger equation itself I can say that if even if I had a discontinuity in the potential. If the potential changes even if the potential changes discontinuously, what will happen to the wave function the wave function will not change discontinuous; like this argument can be made rigorous and mathematical?

So, therefore the conclusion is that even if you had a discontinuity in v the wave function will not change discontinuously; its second derivative will change discontinuously. But that means the first derivative will be continuous and if the wave function itself will be continuous. So, therefore what happens is that at this point at x is equal to minus a you have a discontinuity in the potential; but that does not mean that the wave function is discontinuous; the derivative of the wave function as well as the wave function itself is continuous at this point. So, what does that mean?

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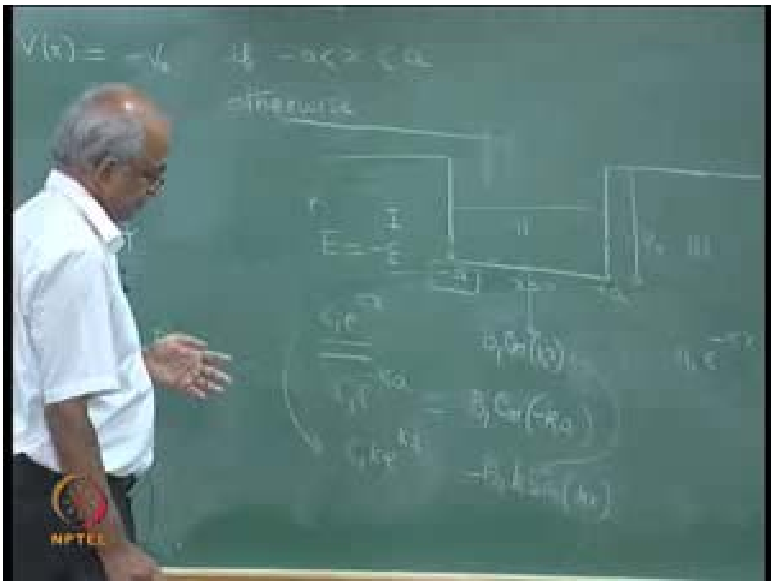

It means that the if I evaluated the wave function at this point using this formula, right, this is the wave function that is a appropriate for the for this region. So, even at this point it is valid and I can evaluate its value at that point using this formula I can also a value at the value of the wave function at this point. Using this formula I can evaluate the value of the wave function at this point using that formula.

If the function is continuous what should happen? The answer that evaluates using this must be equal to the answer that I get using this; otherwise, the function will not be continuous. So, therefore what is the thing that I am going to have here I will put x is equal to minus a. So, the answer will be C 1 e to the power of minus kappa a right; that is the value of the wave function at minus a evaluated using this expression. And, what is the value of the wave function at this point using evaluated using that expression. It will be equal to B 1 cos minus k a and that 2 have to be equal right. And, so what happens you get this equal to that.

See, why do I do that the answer is actually extremely simple, I want to find out relationships between C 1 and v 1. How do I do that they have to find to impose the condition that the wave function and its derivative are both continuous. That is the way which I will determine the constants C 1 and v 1; not only the wave function its derivative also should be continuous right. So, how will you calculate the derivative? Well, the derivative of this function with respect will be C 1 kappa e 2 the power of kappa x let be the derivative. And, the derivative of this function will be what? It is going to be B 1 derivate of cosine k x what is the derivative answer is k sin kappa x with the negative that is the derivative. So, a derivative of the first function is so much the second function is so much. And, that the boundaries you see this 2 have to be equal; so if you put x is equal to minus a this and that have to be equal.

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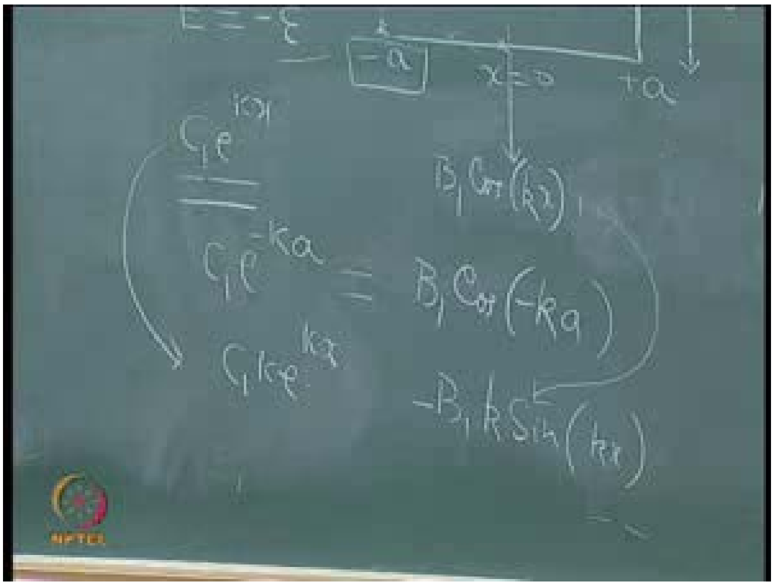

So, let us put x is equal to minus a and what is the answer that you get you get C 1 kappa e to the power of minus kappa a is equal to minus B 1 k sin minus k a.

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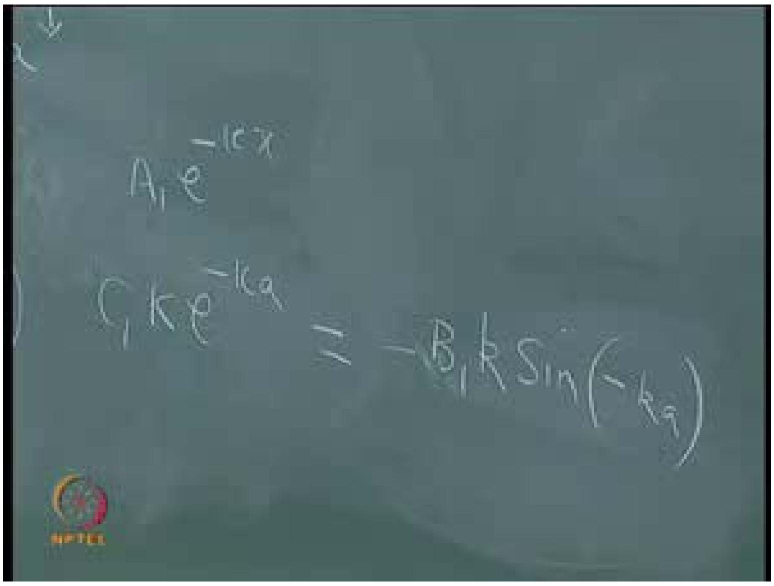

So, you see that we have obtained 2 equations; one by saying that the wave function is continuous. And, the other one by saying that derivative of the wave function has to be continuous.

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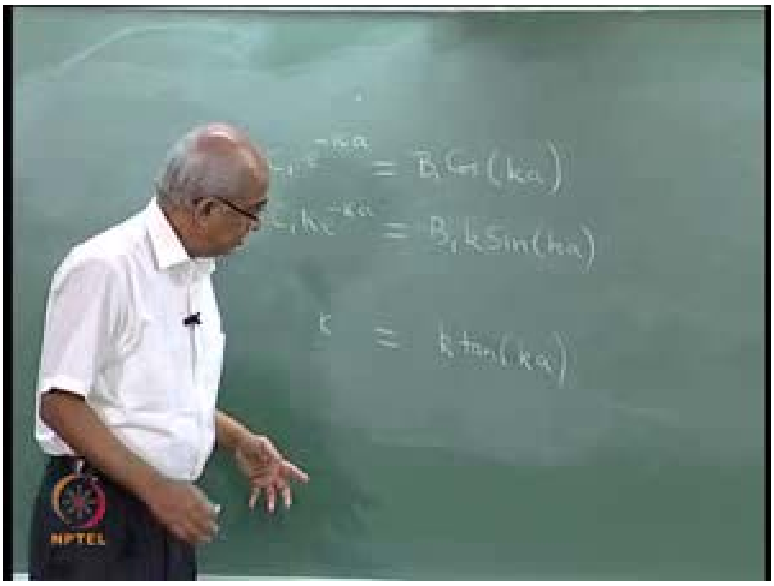

So, what are the 2 equations let me write them neatly somewhere; first equation says C1 e to the power of minus kappa a must be equal to B 1 cos k a well, cos of minus k a but as per as cosine is concerned; this minus sign is not important because cosine function is an even function. Therefore, this is actually equal to B 1 cos k a. What about this second equation? The second equation is written here and how does it treat; it says that C 1 kappa e to the power of minus kappa a is equal to minus B 1 k sin minus k a but sin function as we know is in odd function. So, this negative sin you can take it out side and cancel this negative which already exits. And, therefore this is going to B 1 k sin k a. So, these are the 2 equations that we arrived. And, the first this 2 equation contained the unknown quantities B 1 and C 1 but it is very easy to get rid of this unknown quantities B 1 and c 1.

The way to get rid of this them is simple what you do is you take this second equation divided by the first equation. That means, you see the left hand side of the second equation I shall divide by the left hand side of the first equation. What is the result the result is actually kappa. And, the right hand side of the second equation I will divide by the right hand side of the first equation, the answer is going to be k tan k a. And, this is a somewhat complicate equation which we have to solve to find the allowed energy levels of the system. This is the equation this ensures that both the wave functions and its derivatives actually are continuous.

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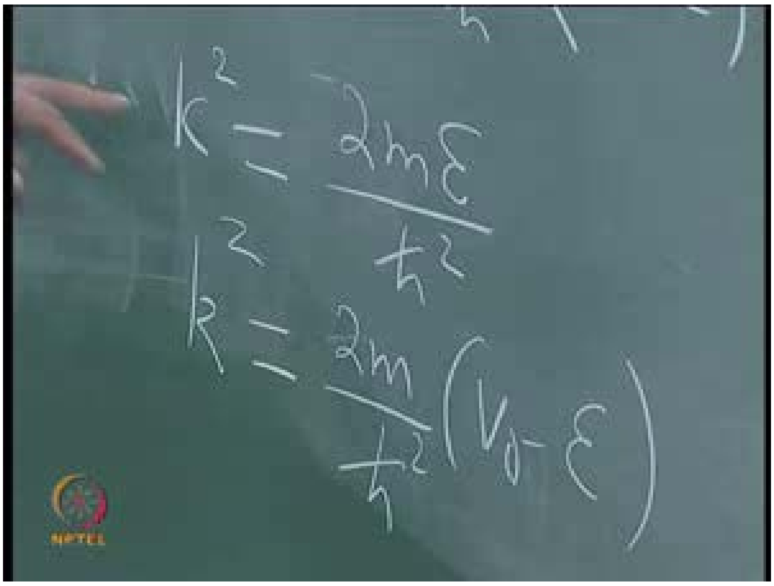

But you look at the expression see kappa where is our expression for kappa I think I have probably removed it. But I should have kept it; kappa was defined to be something and k was defined to be something else; kappa was defined to be 2 m epsilon divided by h cross square with a square root or kappa square was defined to be 2 m E epsilon by h cross square right. This is our definition while k square was defined to be 2 m divided by h cross square v 0 minus epsilon; this was the definition of a square. So, the point is that kappa and k r actually dependent on epsilon right; they are both depending on epsilon and this is an equation that is to be satisfied. You see, you have epsilon inside this kappa; you also have epsilon inside that k right. And, if you are able to solve this equation see this is equation that has to be obeyed after getting an acceptable derivation; then, this equation has to be obeyed.

It is clear that this will not be satisfied for any arbitrary value of epsilon. There are only certain values of epsilon which will satisfy that condition. What does that mean in terms of our earlier discussion this means that it is not possible for the particle within this potential well you have any energy; the energy is that it can have or which they are discrete or as we say they are quantized right. So, the energies are such that they will satisfy the situation but unfortunately this equation is a rather complicated looking equation. And, it seems very difficult to solve this equation.

If you solve this equation, then you will be able to find the values of epsilon which will give you the allowed energy levels for the particle. In fact, what one can adopt is a graphical solution of this equation. I will tell you how this equation may be solved graphically; and you can get very interesting results. But before well before I close it I will tell you what actually is the final result.

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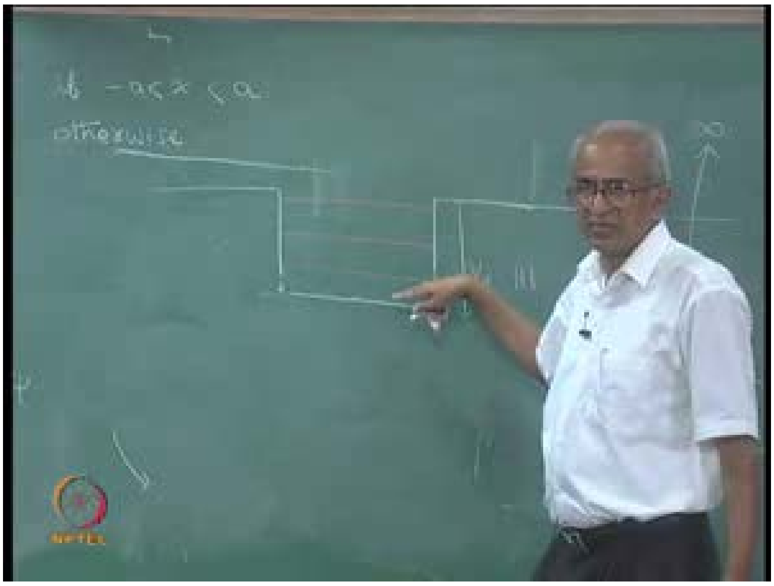

The final result is that it is not possible for the particle with in this potential. Well, they have any energy there are only certain allowed energy levels that it can have; and the maybe I can represent this allowed energy levels in this same picture. This is what we will discuss in the next lecture. So, it will have may be 1 energy level there, another energy level may be somewhere here, and the third under the level may be very close to 0; may this something like that it would have 3 energy levels so or may be 4. I mean the allowed in the box is actually 5; only a given number allowed energy levels are there.

So, this system may remain in any 1 of this 3 and if the system remains there then what happens is that the system is bound. It is trapped in the potential well. And, then we can also ask what will happen if the energy of the particle is greater than 0. Then, just as in classical mechanic the particle has an energy which is above 0 what happens is that it is not bound here; but it can go away. Therefore, that it will represent it in unbound state of the particle while these 3 will represent the bound state of the particle. I think we will stop here. Thank you, for your attention.