Introductory Quantum Chemistry
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Lecture - 11
Particle in a Three Dimensional Box

So, we had seen this simple model for a conjugated system. Simple model was that you have a particle which is moving in L dimension in a, and it is confined to a region of length l; but now suppose I have a piece of metal.

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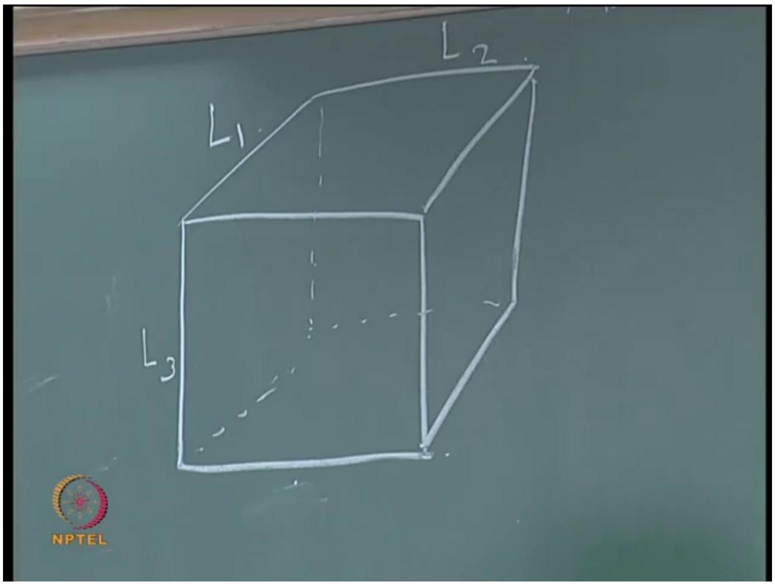

Let us say I have a piece of metal which is nicely shaped something like that. And, just to make things simple will say that this piece of metal is having the shape of a box rectangular box. So, to say and I can say of course this heights of the box are L 1. I will call this side L l, I this side L 2 and that side is L 3. We know that in a metal there are conduction electrons and just the way the electron in a conjugated system can move from one end to the other end. The conduction electrons in this piece of metal can move anywhere within this piece of metal. And, so the simplest approximation that you can have for these electrons is to say that; they are free to anywhere within this 3 dimensional box right.

If they are inside the metal then of course their potential energy is low. If they are inside this piece of metal then potential energy is low while outside the potential energy is large. Therefore, we can say that I have a situation where I have a particle I mean there are of course say large number of electrons in the metal. But we are only going to look at 1 electron in fact this involves so many approximations. One if you think of 1 electron that electron actually interacts with the other electrons; and it also interacts with the nuclei. Therefore, the potential is actually quite complex but we imagine that we are not worried about any of these things. We will just say that if the electron is within this rectangular box its potential energy may be taken to be a constant everywhere. And, that constant it is convenient to take it to be equal to 0; while if the electron comes out then you see that does not feel the presence of the nuclei. Because it is outside the piece of metal and its potential energy is very large, and again as before we will take it to be infinitely large. So, let us have a coordinate system.

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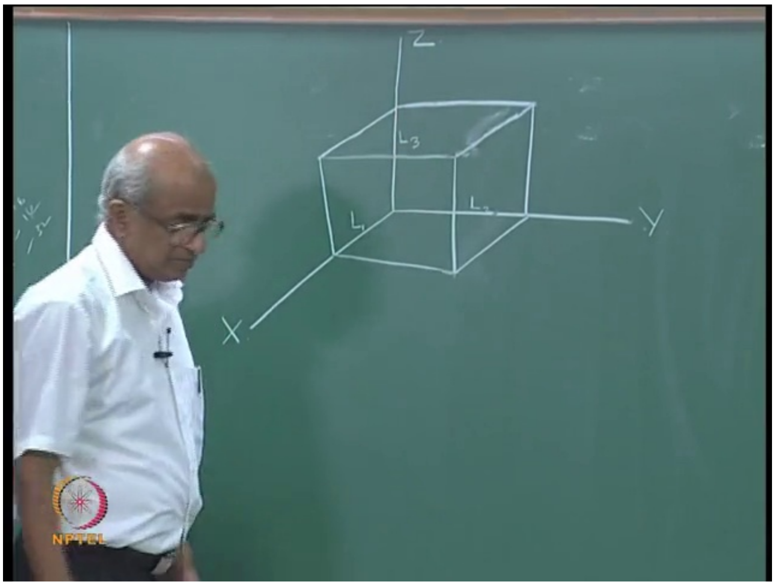

So, this is my coordinate system; this will be my x axis, this will be my y axis and that will be my z axis. And, let me put that piece of metal here in such a fashion that which would occupy this region. So, this is the piece of metal and as I said the sides are L 1 that means this length is L 1; this side is L 2 and the height of the box is L 3. Now, normally when you think of a piece of metal it is microscopic; in size its size is maybe 2 centimeters, 4 centimeters whatever you want. But these days you know that people have lots of interest in nano technology; and it is actually possible to make various tiny small pieces of metals nano particles. And, so you can have ever various small sized particles; they are straight may not be exactly this kind of shape but may be this is something like a sphere or some other shape. So, this actually even though it is a simple model; it can have applications in even in nano technology. And, now what do I say? I say that I have a particle moving in 3 dimensions.

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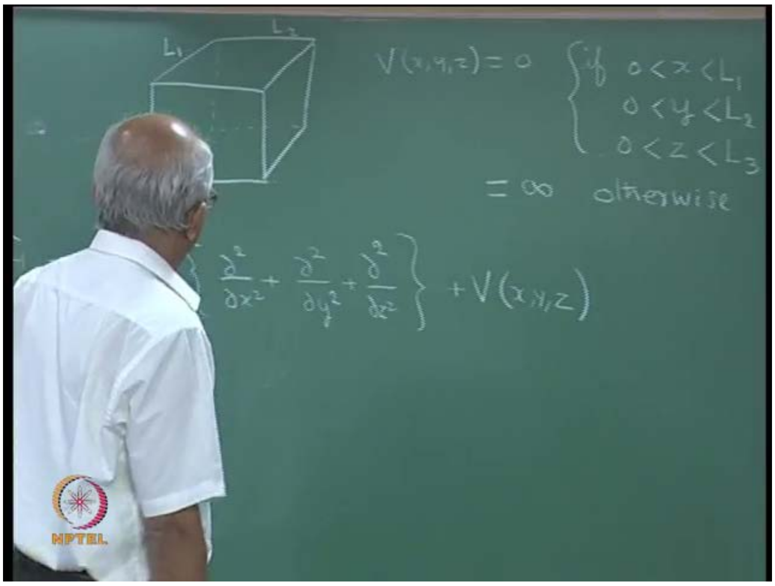

So naturally I am going to find out the solutions of the Schrodinger equation. So, I should write the Hamiltonian for the system because a particular electron in this piece metal they can move anywhere in the inside it. It is actually moving in 3 directions. Therefore, what is going to happen is the Hamiltonian will have definitely contribution from the potential energy minus h cross square by sorry I another mistake contribution from the kinetic energy which would be minus h cross square by 2 m into you will have dou square up on dou x square this comes from motion in the x direction; dou square up on dou y square coming from motion in the y direction and dou square up on dou z square coming from motion in the z direction. And, in addition what should I do I will have a potential V (x, y, z). But I have already told you what the potential is going to be if the particle is inside the box; we will be taking to be equal to 0.

So, let me write it here V (x, y, z) is equal to 0 when the particle is inside the box. So, what does it mean as for as x y and z are concerned? Well, you look at the coordinate system you see your box extends you see this point is the origin that has x equal to 0.

And, if you moved along this direction this is the point with x is equal to L1. So, if the particle is within the box its x coordinate has to be between 0 and L 1. What about its y coordinate if the particle is within the box; in a similar fashion its y coordinate has to be between 0 and L 2. Its z coordinate has to be between 0 and L 3. Even if one of these conditions is not satisfied then the particle is outside the box right. And, therefore I say if all these conditions are satisfied the potential energy is 0 otherwise it is equal to infinity. Now, I want to solve this Schrodinger equation of course I should actually write down the time dependent Schrodinger equation. But it is not necessary for us to analyze that because we have already done this analysis earlier.

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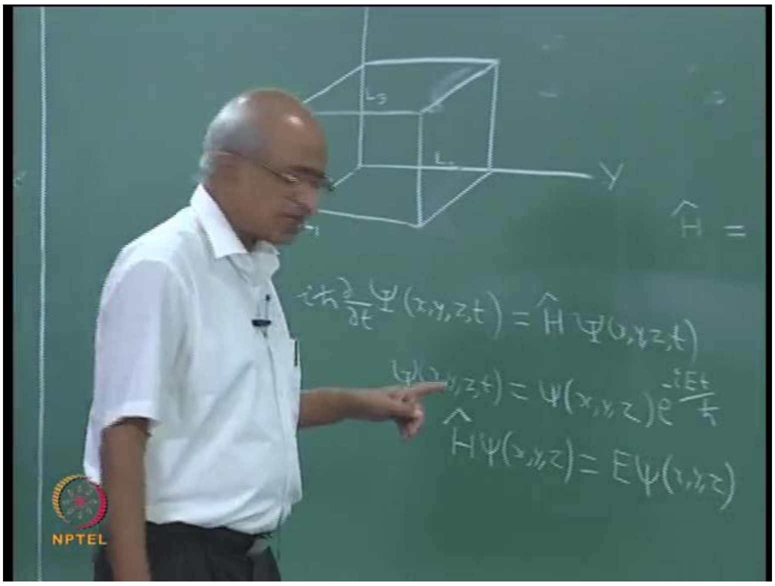

But just for the sake of completeness let me write it here psi will be a function of x, y, z and in addition to that it will depend up on time; and this is equal to that Hamiltonian which is written there too long to write. So, let me just write H operating upon psi x y z and t. So, this is the equation that we are basically interested in but then I you can say this capital psi (x, y, z, t) may be separated as a product of 2 functions. The first one depending only up on the spacial coordinates and the second part and we know what it is it is E to the power of minus i E t by h cross. Here, psi will depend up on x, y, z all the position coordinates. So, this is what it is this. This kind of thing we have already analyzed. And, so how will you determine this psi? The answer is that you have to look at the simpler equation the time independent Schrodinger equation which will says that H psi must be equal to E psi.

So if you can find the solutions of this equation which essentially means that you have to find the Eigen values of the Hamiltonian operator; and the corresponding Eigen functions. So, if you can find these things then any given Eigen function of the Hamiltonian operator may be put in here and you will get the solution of the time dependent Schrodinger equation; that is what we have learnt till now. Therefore, we will worry about this equation H psi is equal to E psi and you want to solve it. So, let us look at this equation but then the moment you look at this equation you realize that it is a partial differential equation. And, partial differential equations are difficult to solve. So, what we are going to do is we are going to use the method that we have already used; the method of separation of variables that is the method that we are going to use. But before I do that I want to point out something to you.

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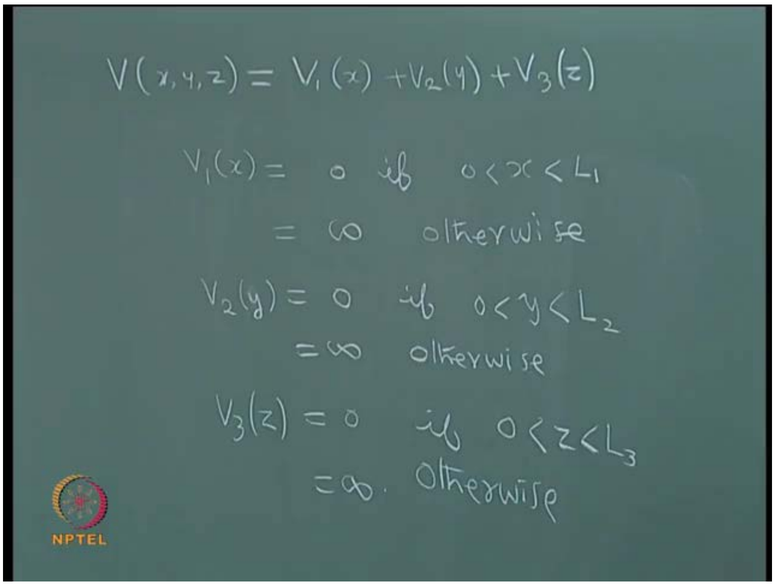

The potential as it is defined V (x, y, z). What I am going to do is I am going to claim that it neither it masses some v 1(x), like some v 2 (y) plus another v 3 (z). I am going to claim that it may be written like this where I will define v 1 (x) x to be equal to 0. If x is between 0 and L 1, right. Look at what I am doing you see I have defined v 1 (x) to be like this. So that if the particle is particles x coordinate is outside this limit what should I do I will say that v 1 (x) is infinity right. So, if we if the x coordinate is in this limits then the potential v 1(x) will be 0; while if the x coordinate is outside this range the potential v 1 (x) will be infinity. Similarly, how will I define v 2 (x) not v 2 (x) but v 2 (y) it will be defined to be 0, if y is between 0 and L 2 and it will be equal to infinity otherwise and v 3 (z) will again be defined to be 0, if 0 less than z 0 sorry less than L 3 and equal to infinity otherwise. So, what that I am saying is that the original potential may be written as if it is a sum of 3 separate terms which are defined like this.

Suppose, the particle happens to be inside the box, then what will happen x will be between these limits and v 1 will be 0; y will be between these limits v 2 will be 0 and z will be between these limits and v 3 will be 0, so that the potential will be actually 0 right. But suppose the particle is outside the box then at least one of these variables x, y or z will not satisfy this condition. And, then what will happen the corresponding v will be infinity right.

And, just to illustrate suppose I say x is not in this range but y and z are in that range; then what will happen v 2 and v 3 will be 0 but v 1 will be infinity. And. therefore the net answer that you are going to get for the total potential will be infinity. Therefore, it is possible for me to write the potential in this other simple fashion and that is very useful; because see I mean the potential has been separated into 3 separate terms. The potential is written as if it is sum of 3 separate terms one depending only up on x, the other depending only on y and the third depending only on z.

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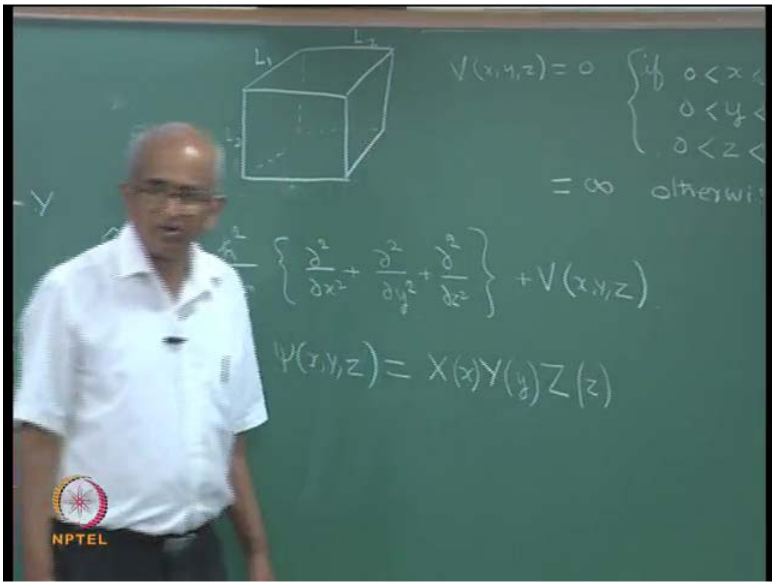

Now, what we will do is we will take our psi which is a function of x, y, z and try to find a solution which will be written as X into Y into Z . I hope you will not confuse between that X and this X; this is just labeling the coordinate while this is a function X is a function. And, it is going to be a function of x alone, Y will be assumed to be a function of small y alone and Z will be assumed to be a function of z alone. So, definitely we are using the method of separation of variables. I have a function size which depends up on x, y, z; I assume that it may be written as a product of 3 separate functions each one depending only on one variable; as I told you earlier this is a policy of divide and conquer. Now, what is it that I want to do? I want to determine X Y and Z in such a fashion that the product satisfies the equation. So, let me take this product and substitute that into this equation.

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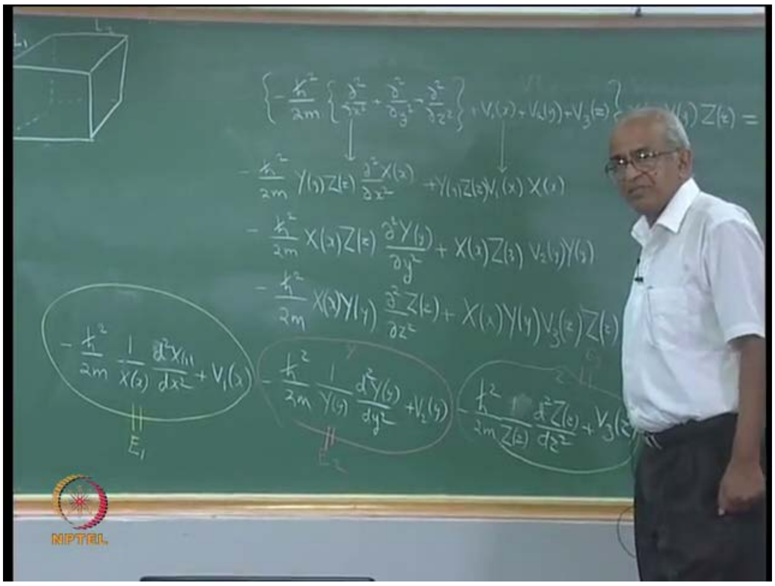

So, the equation actually is minus h cross square by 2 m that is your kinetic energy part then you have v 1 (x) plus v 2 (y) plus v 3 (z) operating up on X (x), Y (y), Z (z). And, the answer must be equal to capital E into X (x), Y (y), Z (z). Now, if you look at dou square up on dou x square you see we are going to it is going to operate up on this product. But in that product only X depends up on x; Y and Z does not depend up on x. Therefore, this operator is going to affect only the only the first part of this function of this product; while second derivative with respect to y it is going to affect only that. And, second derivative with respect to z is going to affect only the last term Z right.

So, therefore let us let us rewrite this equation. So, you are going to get minus h cross square by 2 m dou square up on dou x square operating up on X (x); just writing the term arising from here it will be that. And, then of course you have Y and Z but they are unaffected. So, I will put them here Y (y) Z (z). So, this is this term is actually giving me that. Then, there is also a term v 1 (x) multiplying X, Y, Z. So, let me just write that term also v 1 (x) multiplying X (x) but that also would have I mean v1 (x) is multiplying all the 3. Therefore, I would have Y (y) Z (z) this term is coming from this one right. If that is the case then I can write the term coming from y; what is it going to be minus h cross square by 2 m X (x) Z (z) dou square Y (y) by dou y square plus x(x) z(z) v 2(y) Y (y) correct.

This is similar except that here we are concerned with dou square up on dou y square; well I will make this. So, let me keep it somewhere psi(x, y, z) is equal to X into Y into Z . And, then the next term is going to be minus h cross square by 2 m you will have dou square up on dou z square operating up on Z that we said multiplied by x (x) y (y) plus x(x) y(y) v3 (z) Z (z). And, this whole thing must be equal to the right hand side which actually is equal to E X (x) Y (y) Z (z) right. Now, I should also tell you that this really not necessary to use partial derivative notation in here; because X actually depends only up on small x there is no other variable to be kept constant. Therefore, if you like you can even you can write this as d square x by d x square.

Now, having seen this I want to simplify this it looks quite messy. So, what I am going to do is I am going to divide throughout by this expression divide throughout by that. And, then what will be the answer well on the right hand side I am going to get E. If you look at this term right or these 2 terms; what will happen you see I am diving throughout by X into Y into Z. So, this Y and Z will go away but I will have a one by X sitting here. And, so well here actually this symbol everything X Y and Z will go off. Therefore, let me derive those 2 terms we are going to have minus h cross square divided by 2 m 1 by X (x) d square X (x) divided by d x square that is coming from this 1 plus the next term actually happens to be v 1 (x) right; that is also it will have from the first 2 terms. Similarly, from the second 2 terms you are going to get minus h cross square up on 2 m very easy to write this actually simple.

Well, that is equal to E. So, this is the result. Then, if you look at this result you notice something interesting; if you look at this part, these 2 terms what do you find they depend up on x; while if you look at these 2 they depend only up on y. And, if you look at those 2 they depend only up on z. And, if you added the 3 together the answer is going to be a constants correct. Now, if I want actually I can take these 2 times to the other sides. And, then what will you have you want the left hand side you will have something which depends only up on x, on the right hand side you have something which depends up on y and z; but remember x y and z are independent variables. And, therefore what is the conclusion this something that is occurring on the left which will be this term fine it is a equal to a function of y and z; if such an equation should be satisfied this term must be a constant.

This is the method of separation of variables if you have an equation which is that a function of x l 11 equal to a function of y and z. Then, that function of x alone should be equal to a constants and the other part also should be equal to a constant. Therefore, what is the conclusion the conclusion is that this must be equal to constants. And, I am going to code this constant E 1 this must be equal to a constant. But then if you are taking this 2 terms to the other side they are giving this. Then, I mean why should I take those two terms I could have taken this and that also to the other side. And, repeated the argument and it would imply that this also must be equal to a constant. And, therefore this is equal to some E 2. And, the third one also must in a similar fashion be equal to a constant which you will call E 3.

And, the and further these constants must be a such that E1 plus E2 plus E3 must be equal to the total energy of the system. That is how it should be. So, look at what has happened? You see had a partial differential equation rolling 3 variables but now I have 3 separate equations right. What are the 3 separate equations? This must be equal to a constant which I call E1, this must be equal to another constant E2 and this must be equal to a third constant E3. And, the some of these 3 constant must be equal to the total energy of the system. So, let us look at these equations.

If you look at the first equation what is it say minus h cross square by 2 m X (x) d square X (x) by d x square plus v 1 (x) is equal to E 1 that is what this equation says this equation correct. But if we if we want we can multiply throughout by this X (x). And, if you multiplied throughout by X (x) what will happen? You will get minus h cross square by 2 m d square X (x) by d x square plus v 1 (x) in to X (x) is E 1 could be E 1 X (x). So, this is a an ordinary differential equation for X, which I will try to solve. But before I try to solve it I want to remind you what v 1 (x) is there in your notes at v 1 (x) is defined to be equal to 0; if x is between 0 and L1 and it is equal to be infinity otherwise right.

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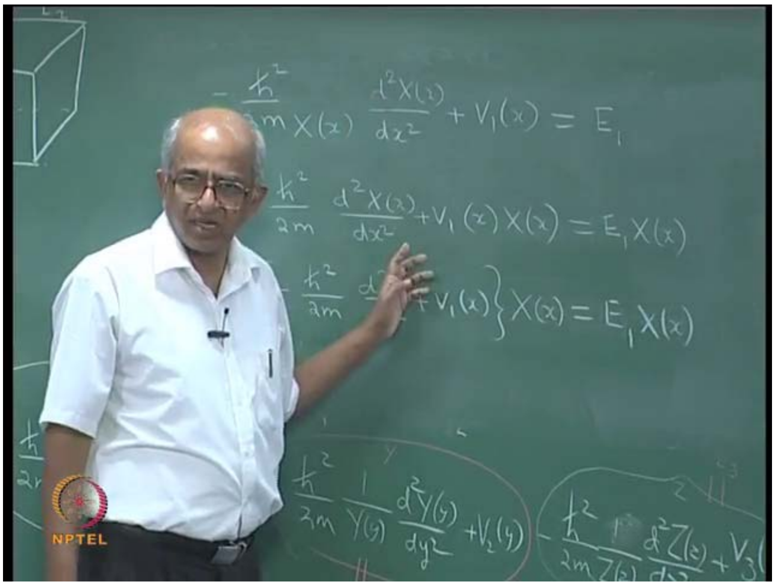

Now, if you look at this equation what is thing is to not that it may be written as minus h cross square by 2 m d square up on d x square plus v 1 (x) operating up on X (x) is equal to E 1 x (x) right. This equation if you like you can write it in this fashion. You may wonder why I did there the answer is extremely simple. Say this actually this operator is what this is the operator for kinetic energy and v 1 is a potential energy. And, therefore if you look at this equation this actually describes particle in a 1 dimensional box right; this equation is the just the equation for particle in a 1 dimensional box. The for the box extends from 0 to L l the length of the box is L 1 and this is a problem that we already have solved right. So, what is a solution?

The solution obviously can be obtained only if the solution can be obtained only if E 1has the value some number n square pi square h cross square divided by 2 m L 1 square right; the length of the box is now L 1. So, when I solve this equation what you are going to get is a quantum number right. And, that quantum number cannot have the values 0 but it can have the values 1, 2, 3, 4 etcetera. And, what will be the corresponding a function X (x) we know there it is going to be square root of 2 by L 1 sin n pi x by L 1.

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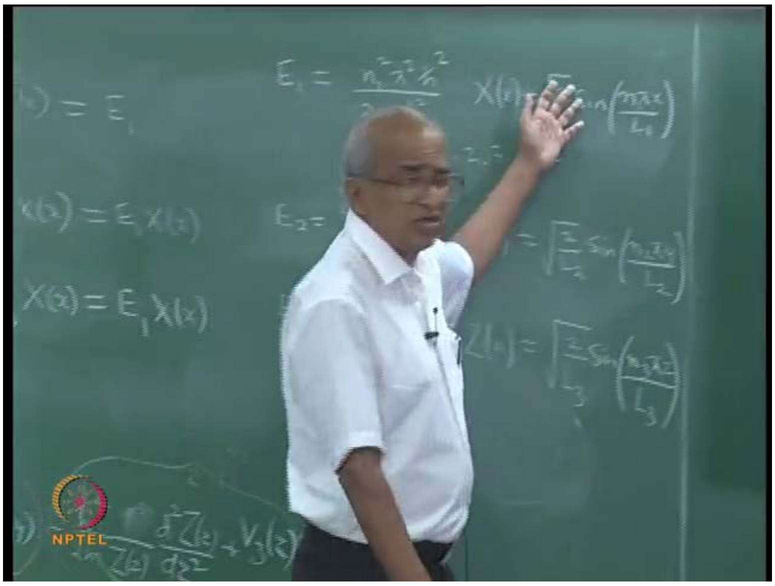

I will change my notation a little bit because you see this is associated at the I am I have told only the first equation. Similarly, I have to worry about the second equation the third equation because this quantum number has arise an out of the solution of the first equation. I will not call it n but I will call it n 1 and what about n 1? n 1 can take the values is 1, 2, 3, 4 etcetera we cannot take the value 0.

Similarly, if you rewrote this equation and solved it you are going to get another quantum number which will be n 2; which we will take the value is 1, 2, 3 etcetera. And, you will find that E 2 must be n 2 square pi square h cross square divided 2 m L 2 square right the length of the box in that case is difference. And, Y (y) will be given by square root of 2 by L 2 sin n 2 pi y divided by L 2. And, finally if you think of E 3 this going to be given by n 3 square by 2 m L 3 square pi square h cross square and Z of e z will be given by square root of 2 by L 3 sin. So, we have solve the problem completely right we have found the Eigen values of the systems; we have also found the Eigen functions. And, in fact these function we have chosen them to be normalized that is the x y this constant square root of 2 by L 1. So, square root of 2 by L 2. So, what is the complete solution that I have obtains now? The complete solution is actually a product of x X Y and Z.

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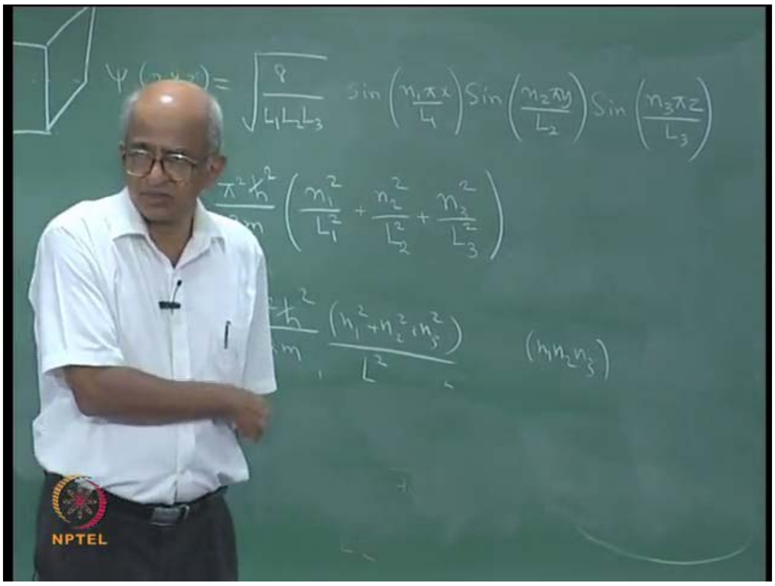

So, I am going to now say that my psi which is a function of x, y and the z is the product of these 3 functions. So, let me multiply those 3 functions. So, if you multiply these 3 functions you see you have a square root of 2 here, square root of 2 here, square root 2 there if you combine the role of the are going to get square root of 8 divided by L 1, L 2, L 3 right. And, it is going to be sin n 1 pi x by L 1 sin n 2 pi y by L 2. So, this is the answer. And, what is the energy associate with this it will be the sum of E 1 plan E 1, E 2 E 3 is so you add them up; you will find that there are gives energies are of the from pi square h cross square divided by 2 m in to n 1 square by L 1 square is comes from motion in the z direction actually then n plus n 2 square by L2 square plus n 3 square by L 3 square.

And, also it is obvious that the wave function depends up on 3 quantum numbers n 1 n 2 and n 3. So, I am going to put n 1 n 2 n 3 here. And, the energy also depends up on the exactly there is 3 numbers. So, E is a function of for E is depend in up on n 1 n 2 n 3. What is the lowest possible state of the system it is clear that you will get that by putting n 1 equal to 1 n 2 equal to 1 at n 3 equal to1 correct? Well, what will do is I will confine myself at least for a few minutes at least to a situation where the box is actually having the shape of a cube. It has a shape of a cube what will happen? The L 1 is equal to L 2 and that is equal to L 3. And, so I will have pi square h cross square by 2 m n 1 square plus n 2 square plus n 3 square divided by capital L square; where capital L is equal to L 1 equal to L 2 equal to L 3. So, this will be the energy of the system. So, the lowest possible stage happens when n 1 is equal to 1, n 2 is equal to 1, n 3 is equal to 1. So, in fact any particular state of the system may be specified by specifying the values of these 3 quantum numbers. If you give me these 3 quantum numbers then I can tell you what the wave function is I can also tell you how the energy is. So, what I will do is I will write these 3 numbers with in brackets n 1, n 2, n 3. And, that specifies in which state the system is or the particle is.

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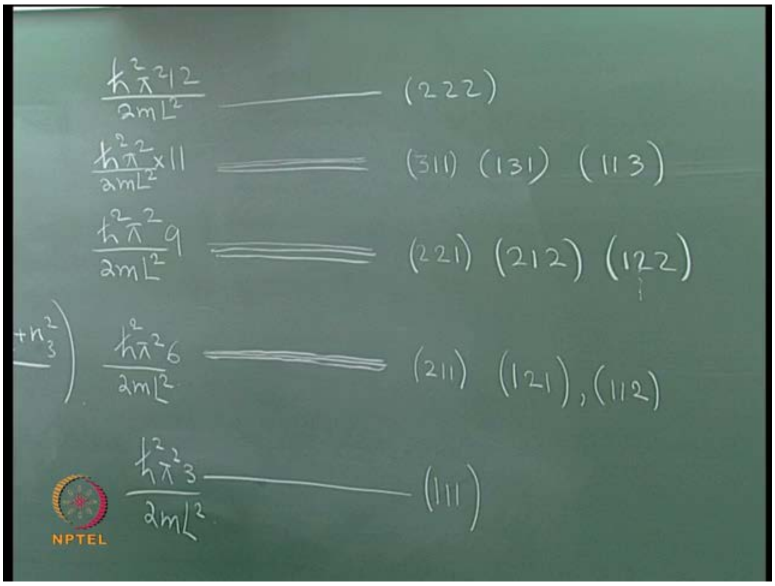

And, therefore the lowest possible state of the system would correspond to having n 1 equal to 1, n 2 equal to 1 and n 3 equal to 1. So, what we will do is we will label the status 111 and you can actually calculate the energy of this state. And, you will find that if you put n 1 equal to 1, n 2 equal to 1, n 3 equal to 1; the energy will be given by h cross square pi square in to 3 divided by 2 m L square.

And, then we one can ask what will be the next energy of the next possible stage to get that what you would have to do is you will have to put n 1 equal to 2, n 2 equal to 1, n 3 equal to 1. So, such a state I will write as 2 1 1 as the energy of that can be easily calculated what will you find? You will find that it is given by h cross square pi square divided by 2 m L square in to 6. And, therefore I can represent that by a horizontal line this represents the allowed energy level. Then, if you think about it for a minute you see there is a another possible stage which may be written as 1 2 1. And, if you calculate the energy of that you will find that it is exactly equal to this energy. Therefore, it is this state also having the exactly the same energy; but not only that you also have a straight like 1 1 2; this also has presides the same energy. And, therefore one says that this energy level actually has 3 8 associates with it not 1. This one has only 1 state associated with it.

And, therefore we would say that the this energy level is known degenerates; meaning that there is only 1 stage. This energy level we will say it is triple degenerates; there are 3 states. And, usually what we do is we indicate that by drawing 3 lines close to each other. Then, what will be the next allowed energy level it is would be as that it can be obtained by putting let us say 2 of the quantum numbers equal to 2. So, for example we can 2 2 1 then 2 1 2, 4 1 2 2 whole of them will have presides the at the same energy.

How much will be the energy it will be equal to h cross square pi square divided by 2 m L square multiplied by 9. And, obviously this energy level also is triple degenerates; as I said it is indicated by drawing 3 lines very close to each other. The next energy level you can think about it you will find that it is this actually obtained by putting the quantum numbers equal to 3 1 1 over 1 3 1 over 1 1 3; this also is triple degenerates. The energy will be given by h cross square pi square divided by 2 m L square in to 11. And, interestingly the next possible allowed energy level is non degenerates. It is obtained by putting 2 2 2 and the energy will be h cross square pi square in to 12 divided by 2 m L square of course, I may you can go on doing this within we can calculate the L energies of the allowed states further. But we will now do that but the important thing notice is that the ground state that is lowest possible state is non degenerates. The next 3 levels are triple degenerate and the following one is again non degenerates. Now, let us think of the wave function for the lowest possible state.

How would the wave function for the lowest possible state decline? When this is not a question that is difficult to answer because for the lowest possible state; you know that the you will have n 1 equal 1, n 2 equal to 1, n 3 equal to 1 right. And, this part see if n 3 is 1 sorry n 1 is 1 you will have sin pi x by L 1. It was just the wave function for the particle in a 1 dimensional box; the ground state wave function for the particle in a 1 dimensional box and it has no nodes right. So, if n 1 is 1 this will not give me any nodes. Now, point where the function is 0 in fact the maximum will be while of this function will be at the middle of the box in 1 dimension. Similarly, if you are thinking of this one again the as a 1 dimensional as a wave function for a 1 dimensional box what is going to happen is that the, we 0 at the 2 ends and its maximum value will be at the middle. We write at L 1 by 2 and this one will have its maximum value at L 3 by 2. Therefore, if you think of the product of all these where will it have its maximum value write at the center of the box? Therefore, if you wanted to represent this wave function how will you represent it?

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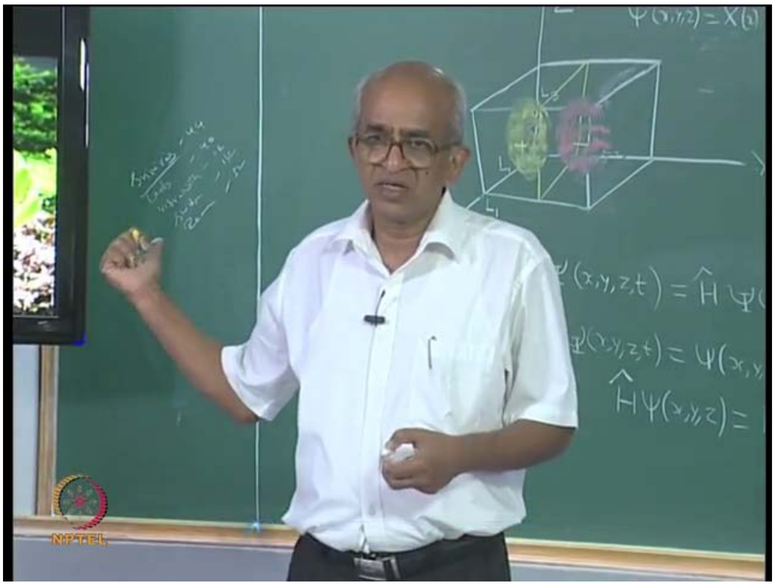

Well, is the way in which I can represent this function is to use shading right see the maximum value of the function is right at the center of the box; where it will have the largest value. And, then as we go away from the center what will happen? The function will go on the decreasing eventually at the surface of the box the function will become 0. That is how this function will be. Now, suppose you are thinking out psi 1 to 1 x, y, z explicitly written it is going to be 8 by L 1, L 2, L 3 square root sin pi x by L 1; there it is not really necessary to put L 1 there because we are assuming that the box dimensions are all the same.

So, a instead of L 1 actually it will be L sin pi y by L sin pi z by L I have made a mistake because I assumed that n 2 is equated to 2. Therefore, I should put a 2 here. Now, as far as this function is concerned as you vary x from 0 to L; the function always remains positive. This also remains positive if you remember it is the ground state wave function for a 1 dimension box. But this one it is not the ground state wave function for a one dimensional box but it is the first excide state. The first excided state has a node. And, this function will vanish when y is equal to what value L by 2. When y is equal to L by 2 what will happen? When you will have L by 2 here and so you will have sin pi and sin pi is actually 0, therefore whenever y is equal to L by 2 this function is going to be equal to 0 right. So, where is y is equal to L by 2 in the box if you say y is equal to L by 2 where is it that y is equal to L by 2?

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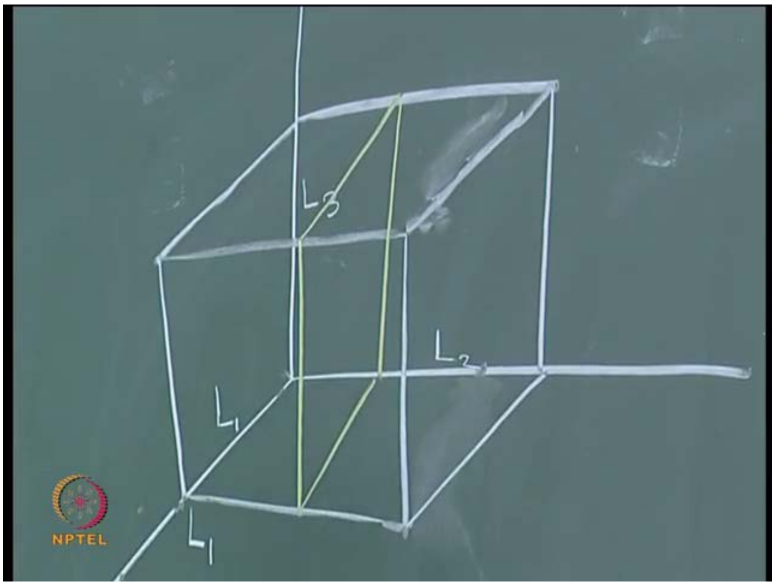

Well, you think of a plane like this cutting the box into 2 halves right imagine this is your rectangular box. This is the y direction imagine a plane like this that anywhere on that plane you know that y is going to be equal to L by right. And, on that plane you will realize that this wave function has to be 0 and to the to this side of that plane the wave function you know will be positive on the plane the function will be 0. That means, one the other side the function is going to be negative, and therefore if I represented this function by shading. How would it look like? Well, I would have a density for the function here that means the value of the function is large in this region. Again, on the surface of this surface of this box if the function has to vanish; on the beyond this plane itself the function will vanish.

On this side of the plane what will happen inside the function will have a value that is going to be negative right? On the plane it is i mean the let me just repeat this. this is the plane on the plane the function is 0 this is by box. So, on the plane the function is 0. It with this side the function is positive; to the other side the function is negative. And, therefore the way to represent this function will be by shading and to say that this is the positively region and that is the negative region. Now, when you look at this actually resembles something that you already know this side. This resembles one of you were atomic orbital. If you look at this it resembles one of your atomic orbital which atomic orbital is that? E type atomic orbit in fact it resembles p y.

Thank you for listening.