Micro and Nanoscale Energy Transport
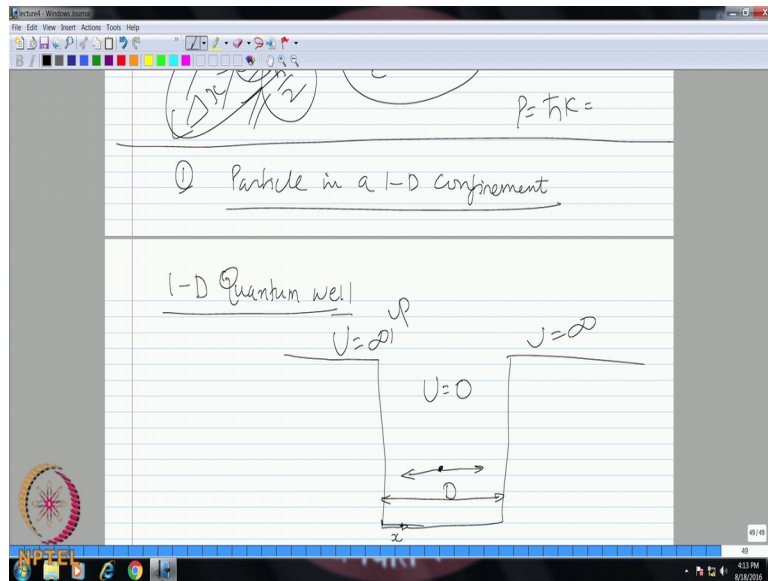**Dr. Arvind Pattamatta**
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Lecture – 09
Fundamentals of Quantum Mechanics Part 3

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Good evening. So, today's class we will start applying the Heisenberg's Uncertainty Principle. Whatever we have discussed yesterday we will see how the uncertainty in the momentum and displacement becomes more evident, if you look at a confinement. So, we took the example of a free particle in space solve the Schrodinger's equation and found that still in this case; you have uncertainty which is spanning or tending to infinity or locating the particle position in space. But the momentum is nearly precisely described and therefore, there is a satisfaction of the Heisenberg's and certainty principle.

Now, let us extend this to the case where we confine this electron wave to a small width. So, sometimes they also refer this kind of a confinement to quantum well just like you have a physical well. Where you dig deep and put something inside and you cannot expect this object an or a person, who is inside the well to climb out unless you have a sufficient energy to overcome this potential head of this well the similarly a particle which you put in a potential well or a quantum well should have enough sufficient energy to overcome the potential energy constraint on this particular particle. So, in this
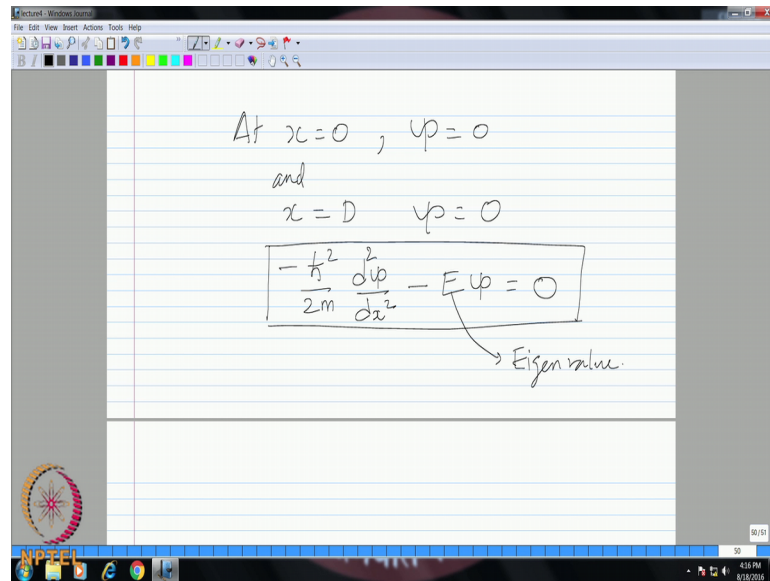
case let us say that we have a well something like this it looks rectangular and you have particle inside this well.

So, inside this well the particle is free to move around in one dimensional space of course; that means it can move this way or this way. So, there is no constraint on this part particle inside the well. So, the potential energy constraint within the well is 0. Now outside the well we will put a constraint that the particle cannot is keep this well. So, this is particle is always trapped. So, this is what we want we want to make a confinement such that the part particle is only within the well and cannot move out.

So, therefore, the potential energy outside the well the potential energy constraint is infinity; that means, the particle should have infinite amount of energy to overcome this barrier and climbed across this and then go out which is not possible. So, in terms of the wave function therefore, you cannot have any wave function outside this potential well; that means, a probability of finding the particle outside the potential well is 0. So, therefore, this becomes the kind of boundary condition for us. So, just at the point let us say the coordinate system.

Let us start from this is a 1 dimensional system. So, our x starts from the left end of the potential well and the total width of this potential well is described by capital d. So, it could be nanometers. It could be microns it could be millimeters we have already see in that if, your confinement is of the order of millimeters the energy jump between successive levels is actually very less and cannot be resolved right much lower than, your value of KBT, where as if the confinement becomes the order of nanometers this energy jump or the discretization of energy or the quantization of energy becomes more evident and magnitude wise it is comparable to the energy at room temperature.

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So, it could be any value d, but let us make a general derivation and therefore, the boundary conditions that can be written are at x equal to 0 and at x equal to capital d.

So, since the potential energy constraint is infinity outside the well. So, the wave function will be 0; that means, you cannot find or there is no probability of finding a particle outside this potential well it is confined well within the well. So, therefore, we will be solving this Schrodingers equation only within the well right. So, outside the well there is no wave function existing. So, we will solve this within the well, with these boundary conditions and therefore, when we do the separation of variables we have a function of time o D is a function time which is an exponential function the other being a function of space that is the Eigen function problem and what is this Eigen function problem for this case.

So, you have minus h bar square by two m D square psi the Laplacian operator in one dimensional space and your potential energy constraint inside the well is 0. So, therefore, that term drops out and you have E psi. So, this becomes your Eigen function problem. So, the Eigen value for this is this is your Eigen value this is your n h. So, once you apply the boundary condition you will be therefore, able to find out an expression for the Eigen value which is the energy which is also the expected value of the Hamiltonian right.

So, let us do this. So, I will give you some time, in the similar lines that we did the solution for a free standing particle. Now you try to solve this with these boundary conditions the earlier case freestanding particle did not have any boundary conditions. Now, the same solution you apply the boundary condition try to find out the constants and the Eigen value capital E might be easier, if you work with the trigonometric functions in this case.

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So, you can assume that your psi which is the function of x is a cos K x plus B sin K x and what is K here square root of 2 h bar h bar square upon h bar so.

Student: (Refer Time: 08:01).

Yea, it should be 2 m capital E by h bar square. Now, you assume rather than the exponential functions in this case take this to be trigonometric functions the boundary conditions may be easier if you apply to the trigonometric functions the first boundary condition gives you what.

Student: a is 0.

A is 0. So, therefore, your psi now becomes sinusoidal function in space right and application of the second condition at x is equal to capital d. So, you are in this case.

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Student: (Refer Time: 09:39).

So, you have K D is equal to n phi and n going from one to infinity, 0 again gives a trivial solution. Therefore, K becomes n phi by d. So, now, with this can actually express the solution for capital e. So, you can substitute for K from let us say call this is equation number 1 here. So, into, let us say this is 1 and the second one is 2 substituting 2 into 1. So, what do you get for E?

Student: (Refer Time: 10:44).

So I am just going to rewrite it like this you have phi h bar n by capital D the whole square that. So, this is your energy and now, you see the difference compare to now if you go back the way we have derived it before for a standing wave right.

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Before we started the Schrodingers equation this was the derivation that we have. So, we have h square; now you convert this to h bar I think you will get the same similar expression. So, the earlier case what we have derived was just a standing wave from wave assuming a wave nature and we just started from there we showed the energy of this standing wave will be function of n, for each value of n.

So, you have different modes of waves and then corresponding values of energy now the same thing through the Schrodinger's wave equation. We can also arrive at the same conclusion that. So, the given wave whichever is trapped inside the electron wave or whatever which is trapped inside this quantum well is now quantized.

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And you have therefore, different values of. So, wave functions corresponding to this quantization. So, psi of x will therefore, be equal to what B sin K x. So, where K is nothing, but now n phi by; so, this I just use the subscript n to indicate that, now the wave function is also quantized for different values of n from 1 2 infinity.

So, these are the discrete wave functions or quantized wave functions corresponding to the value n and we have also plotted these. How these waves looks n equal to 1 how it looks n equal to 2 in the standing wave problem we have plotted this. So, exactly this is how they are quantized inside the well now, the corresponding energy levels are also functions of these discrete levels. So, n equal to 1 will have a particular value of E n equal to 2 and so on.

So, now the energy levels are also quantized. So, therefore, now the remaining problem is how do we find out this constant B? So, how are we going to find this out? So, we will now use the normalization criteria right. So, we have seen that as per the interpretation of bond you have psi star psi from minus infinity to infinity, this gives you the probability of locating the particle somewhere in free space. So, in this case now the particle is confined within the quantum well. So, it has to be somewhere from x equal to 0 to capital D and you having to locate it somewhere from x equals to 0 to D. So, this should be equal to 1. So, therefore, if you substitute maybe you can try this.

Let me see how have worked out. So, the value of B should turn out to be imaginary number i by into square root of 1 by 2 times D. So, this is how turns out. So, you can just do this as homework use the properties of trigonometric functions and check whether you get this value of B.

So, the next step is to find out what is the exact location of this electron wave. Now what is the likelihood of finding this particles and what location can we find it where we can find it.

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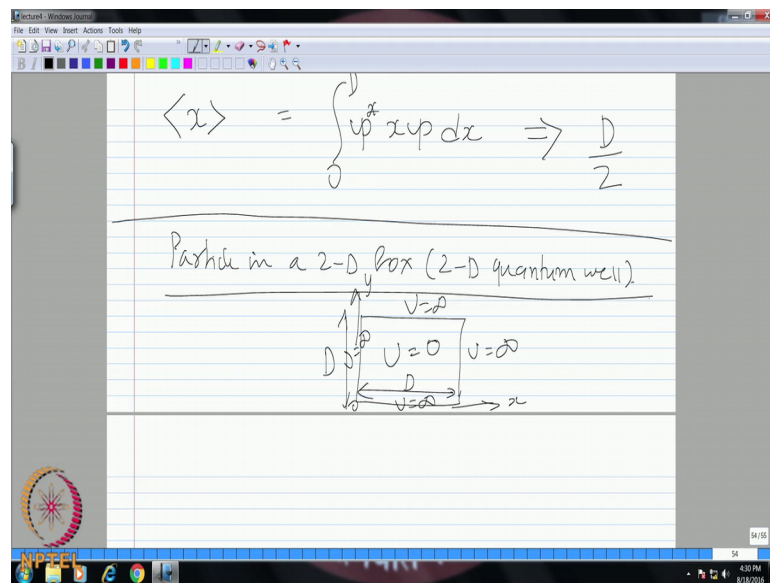
So, therefore, now we start looking at the expected value of position which will be 0 to D psi star into x into psi into D x and if you evaluate this the solution should come out to be D by 2. So this tells you that in this particular case your likelihood of finding the particle of is most likely in the center which makes sense, if you just have a quantum well of width D more likely will be at the center there is no reason. Why it should go to towards x is equal to 0 or x equal to D you have electron waves propagating has left running waves and right running waves. But mostly with the known the particle located at the center of this particular quantum well. So, this is with respect to finding the likelihood or expected value of the position.

So, similarly we can also do other things, but in this case we will just stop with this exercise. So, this is just to give you in one dimensional confinement, how you can use the solution of Schrodinger's wave equation get the wave function energy and also the

positions. So, you could also do the Hamiltonian operation. But finally, that will give you the expected value of the Hamiltonian is the nothing, but energy E which is already determine as the Eigen value. So, you can also apply the same thing for getting the momentum Expected value of momentum as well.

Now, the next thing what we will do is go from 1 D to 2 D. So, we will talk about particle in a 2 D box or quantum well this is a 2 dimensional quantum well. So, the previous case was a 1 dimensional well, where the particle can only move in the plus x or minus x. Now this can move along the y as well. So, to just show you looks like our conduction problem where we consider a slab a rectangular or square slab. So, let us consider a square well now. So, this is your x coordinate and this is your y and the width in the respective x and y are equal the coordinates origin starts from here, and inside the well your potential energy constraint is 0 and at just at the boundaries of the well you start infinite potential energy constraints. So, in this case the particle cannot escape from this two dimensional well.

So, just it is similar to what we have done in the 1 d. Now we have to extend this problem to two dimensions. So, the same equation that we have written here has to be written in two dimensional space and the same separation of variables this is the starting point then we have a Laplacian or Laplacian operator becomes two dimensional and we have to therefore, we will have another partial differential equation. Here we have D square psi by D x square plus D square psi by D y square. So, again that has to be separated into 2 o d's 1 as a function of x 1 as a y.

So, we will introduce another separation of variables there and separate the Laplacian into 2 o d's 1 as a function of x and y and then, we will find the solution in each direction. So, so this is the procedure for first can you write down the equation into two dimensions and then approach this with the separation of variables in x and y space.

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So, what do you get for the Schrödinger's equation in space by 2 m into some connection is gone? How does it happen, I did not do anything? So, d square psi by d x square plus d square this is a partial differential equation and you also have minus E psi equal to 0. Now, the assumption is we have to again separate. So, we assume that we can separate your psi which is a function of x and y as sum capital x which is a function only x and capital y function of y and now you can substitute this into let us say equation number one and divide throughout by capital x and capital y we have 1 by x d square x by d x square plus 1 by y d square y by d y square plus you have two m E by h bar square equal to 0. So, everybody could get this.

So, now if you again look at this particular let us call this as equation number 2. So, you see this first term is a function of x second term is a function of y and what is this constant.

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So, therefore, each term has to be equal to a constant right. So, therefore, we can say 1 by x d square x by d x square has to be equal to another constant, we will say this is K x square. Now, we should also put a minus sign here we will see that y in a brief time. So, you have also similarly 1 by y d square y by d y square should be another constant, I am just distinguishing this constant from this constant by using subscript x and y. So, you have a different constant in the x direction from the y direction you can you can also use l and m as to separate constants here, and why we put a minus sign here because the energy value should always be magnitude should be positive.

So, if therefore, take. So, if you equate this to the energy. So, you have 2 m E by h bar square will turn out to be K x square plus K y square. If you do not have this negative sign here, they can become negative and this tells you nonphysical values of energies. So, which is not possible and therefore, these constants have to be here explicitly negative and that is why we say minus K x square K x turns out to be negative again, this will become possible. So, in order to make this explicitly negative, we depict this as minus K x square and minus K y square. So, now, these are like 2 od's for which you can find out the solution individually 4.

So, please solve 3 and 4, I think trigonometric functions is better.

Student: (Refer Time: 28:54)

Yeah. So, what do you have it is similar to the earlier case in the one dimensional case.

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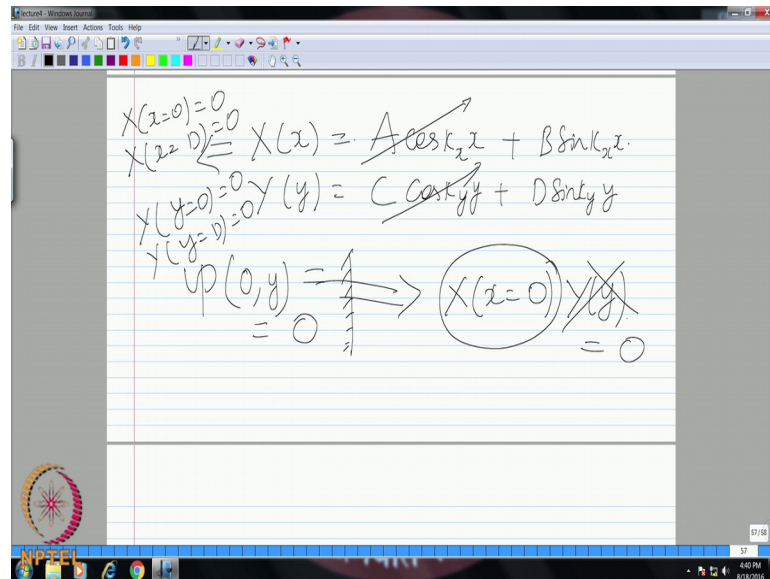
So, x of x will be again yeah let us say a cos K x of x plus B sin K x of x similarly y of y let us say something like c cos K y of y plus d sin K y of y. So, I think you can use the boundary conditions which we have proposed earlier for 1 d, we can do the same thing now in 2 d space. So, your psi value for example, at x is equal to 0 for example, and for any given value of y right. So, that is at the left boundary. So, this should be equal to 0 because the potential energy constraint is infinity.

So, then what will happen to a corresponding value of x at x equal to 0. So, this is equal to x at x equal to 0 times y of y right. So, this should be equal to 0. So, y of y if it is 0 the entire solution is trivial. So, therefore, we have to explicitly say that x of x equal to 0 is equal to 0 and that becomes the condition to 1 of the boundary condition to solve this. So, you have for this particular solution boundary condition is x at x equal to 0 is equal to 0 and similarly you have x at x equal to d also should be 0 and similarly for y. So, all these boundary conditions are linear and hence; I mean whenever we separation of variables the respective directions also we will get the same boundary conditions.

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So, therefore, if you solve apply the boundary conditions. So, what do you see that directly this term gets out this term also goes out we have only sin functions in x and y and what about the corresponding Eigen values. So, we will have the condition that K x d is equal to let us say n phi n is equal to one to infinity similarly we will have K y d will be let us use m l here l phi along the y direction. So, where l is also from 1 to infinity, therefore, finally, how do we determine E? So, 2 m E by h bar square is equal to K x square plus K y square. So, you can now substitute for K x as n phi by d and K one as l phi by d and therefore, what do we have for E is that.

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So, similarly what about the wave function psi? So, we will have the product of the x and y which gives you the wave function in space right because we assume for separation of variables that psi is equal to x of x equal to y of y. So, the resulting solution therefore, now since we knocked of the cause term, we have only the sin terms B times of d is another constant. So, therefore, we can just write this as on global constants we will call this a c which is the function of l n and we have sin what do we have?

So, we can have n phi x by d and the other sin which is a function of l phi y by d this is the corresponding expression for the wave function and this is the corresponding expression for the energy of possessed by the waves. Now we know that in all cases your l will go from one two to infinity similarly n also will go from 1 2 to infinity. So, now, if you look at for example, compare this to the 1 d case. So, what do you have? So, you have an additional quantization due to the second dimension.

So, earlier 1 d case you had only quantization in the x direction which gave to one particular a mode. So, l square phi square h square by 2 m d square, Now on top of that you also have a secondary confinement or quantization in the y direction which gives rise to this in the phi direction as well which is n square. So, now, if you substitute these values say l equal to 1 and n equal to 1. So, the values of energy irrespective of whether l equal to 1 or n equal to 1 or l equal to 2 n equal to 1 or n equal to 2 l equal to 1 whether you flip the values of l and n the values of the energy is going to be the same whereas, the values of wave functions are going to be different right.

So, in one case you have function of x the other case you have function of y. So, when you say for example, l equal to one and n equal to 2 in 1 case and the other case you have n equal to 1 and l equal to 2. So, in terms of energy this is not going to make any difference right where as in terms of wave function this will make a different because your n is also associated with x and l is associated with y. So, this is called degeneracy. So, this term will bring in now or people refer this to as degenerate energy states energy states or energy levels this is a very common term in quantum mechanics peoples talk about degeneracy.

So, what is degeneracy degeneracy is nothing, but you have different modes of waves, but the same value of energy. So, they will have different wave functions, but the same possessing the same value of energy. So, if you look at the energy state they will be

occupying the same energy level, but they are 2 different wave functions. So, in terms of just only looking at the energy levels it looks like they are degenerate; that means, they occupy the same energy level whereas, while from the wave function point of view they are 2 distinct wave functions. So, this is a very common thing that happens especially in two dimensional confinements.

In one dimensional confinements you have no degeneracy each particular wave function occupies a given energy level where as in 2 dimensions you can have more than one wave function which is occupying a given energy in 3 dimensions you can have more you have more degenerate states in 3 dimensions. So, therefore, this is very. So, you see a how we have progressed starting from 1 d. We have free standing wave where there is no confinement there is no discrete waves it is all continuous. Now then we put a confinement then we see that there is a principle called quantization happening you have discrete energy levels you have wave functions and again the 1 d confinement is different from 2 od's in case of 2 d. Now you have secondary confinement happening in the y direction and because of this we have introduced this concept called degeneracy.

So, this is a very important concept we do not have to now go to 3 d because in 3 d you will just expand this to third dimension you will have a another K square and similarly you will have another sin function there, but never the less you will have additional degenerate states.

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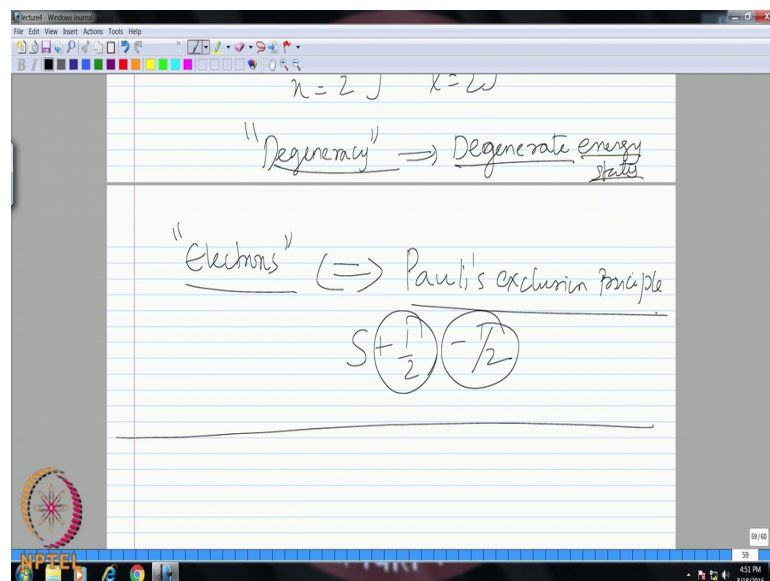
So, now how this degeneracy for example, applies to electrons are somewhat special because they have to obey what is called as Pauli's exclusion principle.

So, what happens is, if you apply only the Schrodinger's equation for the one dimensional quantum well it tells you that each electron with the given wave function will occupy a particular energy level. But; however, that is not the complete picture. So, you have to also apply the Pauli's exclusion principle which states that you have electron which is spin which is plus half and spin of minus half and these 2, are 2 different electrons.

So, therefore, there is a degeneracy already coming in because of the application of policy exclusion principle they make occupy the same energy level, but they are too distinct not wave function because a Schrodinger's equation cannot predicted unless you apply the Pauli's exclusion principle and you have to put this as an additional constraints. So, this is something that you have to remember, I am not going to go into lot of details why the policy exclusion principle came about and all that, but you should just apply this as an additional constraint then you deal with the electrons.

So far, whatever energies that we have dealt with they were all your transitional kinetic energies right. So, they were all dealing with particle motion either in one dimensional space or two dimensional spaces. So, when we started this we looked at the contribution of different energies to the microscopic energies. So, just to give a review we will go back to that. So, that is the same order that we are following here as well yeah. So, we talked about the different energy contributions in micro scale and then; of course, we had classified this into classical picture the other is a wave picture for particle picture is classical nutronian mechanics which already what are the contributions to transitional energy rotational and vibrational.

Now, we are trying to do the same with using the Schrodinger's equation in the quantum level. So, we have now already are that time I stated that the transitional energy is given by h bar K square by 2 m and now we have derived this particular expression and stated what is K x K y case if you have 3 dimensions, you have confinement in all the 3. So, therefore, the transitional energy is already been derived.

Now, the next step is to look at the other one; energies 2 is a vibrational energy and the other is the rotational energy. So, with the purview of Schrodinger's wave equation how

we consider these 2 now, I will give you overview of first looking at vibrationl energy and then will go to the rotational energy little bit more complex.

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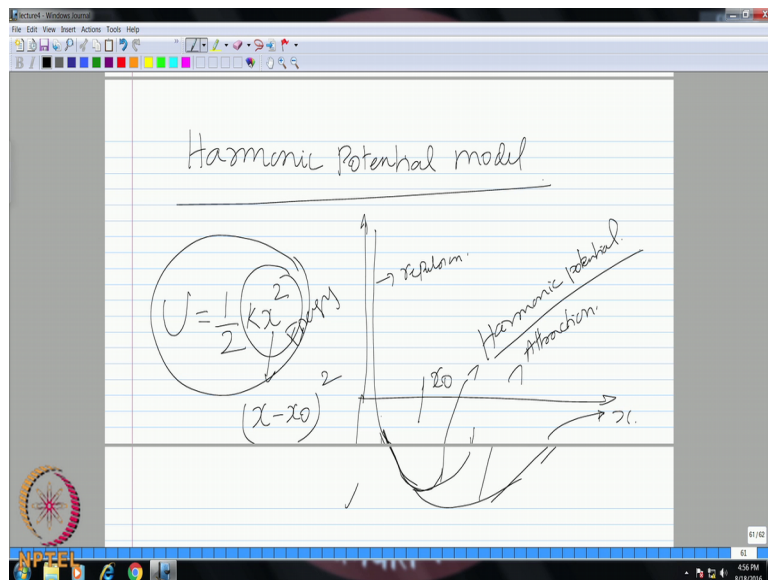
So, we will look at the derivation of quantum vibrational energy I will give an introduction and stop, we do not have enough time. So in the case of quantum vibrational energy how does we what kinds of a model do we apply in the case of macro scale? We applied a spring mass system and then, we said that a overall energy is equal to the vibrational energy the vibrational energy is nothing, but both the kinetic and potential energy is together we are going to do something similar, but using the Schrodinger's equation. So, we will use the harmonic potential model and this was also described the very beginning under the introduction.

So, I talked about inter atomic potential this is a molecular dynamic calls it is Lennard Jones potential. So, when the 2 atoms are sufficiently close you have repulsion force too far away then they have attraction force. Therefore, if you flout this kind of a potential diagram. So, you have the energies interaction energy plotted on the y axis you have plus and minus and you have the distance, if they are too close to have repulsion force. So, this is your repulsion potential here and then they are separated then, you have attraction potential and then this goes exponentially. So, this is your attraction potential and if you are just taking it away and away the attraction potential goes to 0 asymptotically.

So, how do we take into account? So, this is your actual potential constraints that you have to put in the Schrodingers equation, but how are you see this is a very complex potential right. So, you have power law dependence and that is different for the repulsion different for the attraction. So, in order to make it simple we use the harmonic potential model which makes an approximation that, you have a parabolic variation of this potential with x so; that means, you can say about some position x naught this is your equilibrium separation between the atoms.

So, less than that there is going to be repulsion more than this it is going to be an attraction a very simple model which describes this in a parabolic fashion and if you plot this harmonic potential and top of the actual potential this will how it will look. So, this is your harmonic just a parabola about the mean or equilibrium position x naught. So, this is your harmonic potential.

So, since we are not looking at know numerical stimulation, but simple analytical solution we always represent this inter atomic potential by means of this harmonic model. Therefore, in the case of harmonic model what will be the potential energy constraint half of K times x square. So, this is just like in your macro scale spring mass system this is your potential energy associated with the spring mass system.

Similarly, we assume that. So, here you can replace this as if you want x minus x naught the whole stuff the whole square. So, about the equilibrium if you are x, x is less than x naught. So, you have a potential like this and if your x is greater than x naught, you have potential symmetric about x naught. So, now, we make a harmonic model assumption we also assume this kind of potential will work well parabolic potential we will just substitute this into the Schrodinger's equation.

But now the Schrodinger's equation will become difficult to solve because, now we will have an additional term which will be function of x and therefore, the coefficients will become non constant, but a function of x. So, then this has to be the resulting we can still use the separation of variables, but the resulting o d has to be numerically solved in the next class I will give the procedure and I will give you the solution also all right and then, we will see how the energy levels look for this problem and then we will go to the rotation problem all right.

Thank you.