Micro and Nanoscale Energy Transport
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Lecture - 10
Fundamentals of Quantum Mechanics Part 4

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So, the wave vector is primarily an indication of you can say the momentum and finally also the energy. The energy is related to the wave vector. So, we will see that in the say, case of simple particles you have a very simple relationship. So, h bar into k square. h bar square k square is what? We have with energy and wave vector. Therefore, if you are looking at wave vector itself, how do you interpret it? So, we will, when we look at the real solids then we will understand this more, you know. We will use this concept of wave vector to define several other quantities such as such as density of sates so on. And then we will use that in statistical thermodynamics but your question is whether it has a magnitude. Yes, it has a magnitude. It is also directional.

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I think if, you go back to our single particle system, here. So, we were looking at right here. So, in this case you have just one single wave vector in a along x and your e is related to your wave vector. And your wave vector, what it says here is, it is quantised because your n is now becoming discreet. Whereas if you take a particle which is completely free, which is not confined, completely free particle, free standing particle you have continuous wave vectors. So, whereas now when you put a confinement, you see this wave vector along the x direction is quantised. It is no more continuous in this direction.

And it is quantised such that it takes discreet values, multiples of pi by d and correspondingly the energy is related to the wave vector. Finally, you know what is the purpose of these waves vector is too finally calculate the energy. So, we are relating the energy and wave vector and then we are now finding how the wave vector behaves in a in a quantise system. Now if you go to a two dimensional case the wave vector is quantised in both directions, both x and y. So, this is what we are getting here and finally,

when you substitute this k square k x square plus k y square into h bar square by 2 m. So, for k x and k y you substitute as pi into l by d.

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And similarly, k y is now pi into n by d. That means, wave vector is now quantised in both the, you know x and y directions because of this confinement in both directions. So, what it means physically is that now the energy levels are also becoming discreet. So, when you have continuous waves, you have continuous values of wave vector. The energy values are also continuous, now, because of the quantum confinement, the wave vectors become discreet and also the corresponding energy values.

Whereas if you don t confined net in the z direction, still there it will be continues. So, and then in the quantum mechanics, we describe the wave function. Why we describe wave function is from this way, you get the probability of deriving other quantities. The expected values of position, momentum, and energy all this comes from this wave function. So, correspondingly, we have to know the wave function in order to solve the other quantities but primarily the energy is directly obtained here from the wave vector. Is it clear?

So, now as we proceed, you will understand more and more, what is the function of this wave vector? So, but right now, you should understand that wave vector is basically deciding energy and if you are confining it, it becomes discreet. If you do not confine it, it is continuous. So, so far the last class we did all this. Then we started looking at the

quantum vibrational energies. So, we looked at translational energy that is particle in quantum well and then particle in a box. So, they are all infinite wells that are one step particle is strapped that cannot come out.

So, you can also have finite wells with the finite potential height, potential energy constraint. So, in that case what happens is up to certain energy levels, the particle is confined beyond that it becomes continuous. Once it comes out, once the particle can escape this potential energy constraint then it becomes continuous. So, within the potential energy constraint, it becomes quantised. So, I will give some one or two problems related to this kind of finite quantum wells in the assignment. You should be able to do it.

So, now the other mode is the vibrational mode. In the case of classical, you know vibrational energies, we have already taken the example of the spring mass system and we have derived theses vibrational energies, is the sum of kinetic plus potential energy. So, in the case of quantum microscope, microscopic modal, so, how do we account for the vibrational energy? So, once again, so, as I said, you know you have a very complex representation of the forces of attraction between two atoms, if, you consider two atoms and you know the force between them to be approximated by a spring with spring constant k. So, you can talk about forces of repulsion when they come close to each other and when they are separated they there is an attractive force. So, this is actually your Lenard Johns potential which includes both the repulsive and attractive forces.

Now, this is more difficult to directly plug in this kind of potential into the Schrodinger's wave equation and solve. So, therefore, we are going to use an approximation. So, we use what is called as a simple Harmonic modal.

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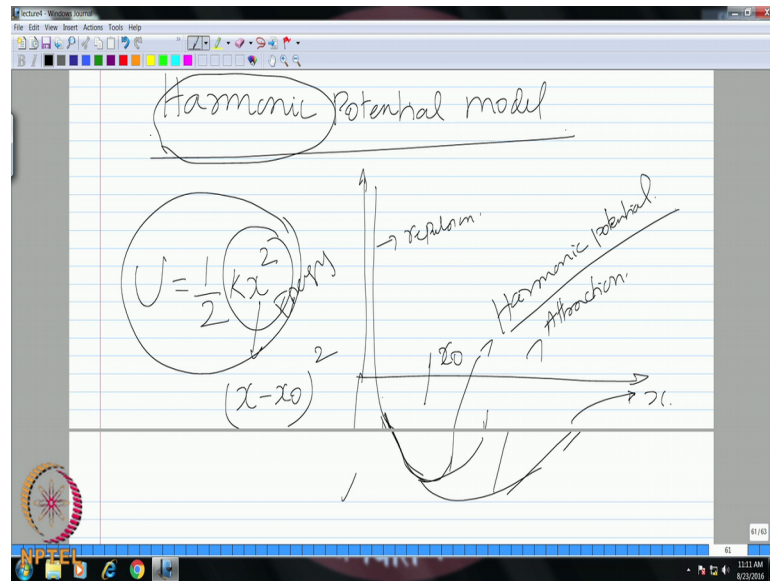
A simple harmonic modal assumes a parabolic kind of a potential, about a mean or about an equilibrium location. So, let this equilibrium location be x naught. So, about this equilibrium location, you have a parabolic potential which says that if you are distance is more than this equilibrium value, now there is going to be an attractive force what is less. There is going to be repulsive force and that is it is very simple approximation which is fairly accurate.

So, now, so this is your potential energy constraint that has to be plugged into your Schrodinge's wave equation.

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So, therefore, so, in this case the Schrodinger's equation will be minus. So, we are going to write this only in the spatial derivative. So, we have d square psi by d x square. We have now emotion of these atoms in the x direction. They can either come close or they can go far. So, we are describing the corresponding motion by means of waves, writing the Schrodinger's equation plus. Now, in the original equation, we have potential energy constraint minus e time's psi. So, now, we are going to substitute for this potential energy constraint as half k x square minus e times psi equal to 0.

So, this is your o d in space. We are now interested mostly in this cases, the o d in space because this is the one which will be give you the Eigen value which in turn, gives your energy. Whereas the one in time, it is standard behaviour, so, we are not too much concerned about bringing the time behaviour. Now, we are mostly concerned about finding the relationship between energy and the wave vector. So, in this case k is not wave vector you please do not confuse. This is spring constant.

Now, to solve this again we need two conditions. So, what do we do? Now, this potential energy constraint says that whatever particle is basically trapped within this potential well described by this parabolic potential. So, very far away from this, so, x going to minus infinity or plus infinity. This practical cannot exist there because these partials are essentially governed by this potential constraint by this particular parabolic potential. So,

we will impose the condition that psi at either x tending to minus infinity or tending to infinity wave function cease to exist.

So, now we can solve this particular o d but if you look at the structure now, compared to the particle in a quantum well. So, there, we didn't have any potential energy in the quantum well, we had this directly. You are expressing this in terms of sine and cosine that was the Eigen function. That is the wave function but now, we have k x square. Now, this becomes a function of x, so, we have non constant coefficients.

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So, we have an o d with Non constant coefficients. So, we cannot find very simple analytical functions in terms of trigonometric functions. So, therefore, we can use some numerical methods to solve this to solve this o d which is giving straight forward results. So, originally this was attempted to be solved using series expansion by Landau and Lifshitz in 1997. This is not so old.

So, there were the first two attempts, this though series expansion technique and I will directly give you what is the corresponding Eigen value that they obtained. They get e subscript and because now it becomes quantised, we can write this in function of this number. This can be you know 0 1 2 or whatever. So, we have h nu time's n plus half where your frequency nu is 1 by 2 pi square root of k by m. So, this is the solution after applying the series expansion and solving, let us say this equation 1. Kind of this looks little bit familiar but not so much.

So, if you put for example, if you do not have this n plus half. So, E is equal to h nu is a common expression that is used to relate for a wave frequency with the energy. Now for the vibrational, quantised vibrational energies, we have this factor n plus half coming into picture. And n, now can take the values from 0 1 to till infinity, the particle which is basically trapped into this kind of a potential energy constraint, even by this parabolic potential will have energies quantise, like this.

So, you can imagine this particular potential like this and you can have multiple modes, multiple wave functions. So, each can take, you know different values of n, so, n equal to 0 1 2 and so on. So, essentially this potential energy constraint is quantising these energies to these discreet values and why, what is the physical significance?

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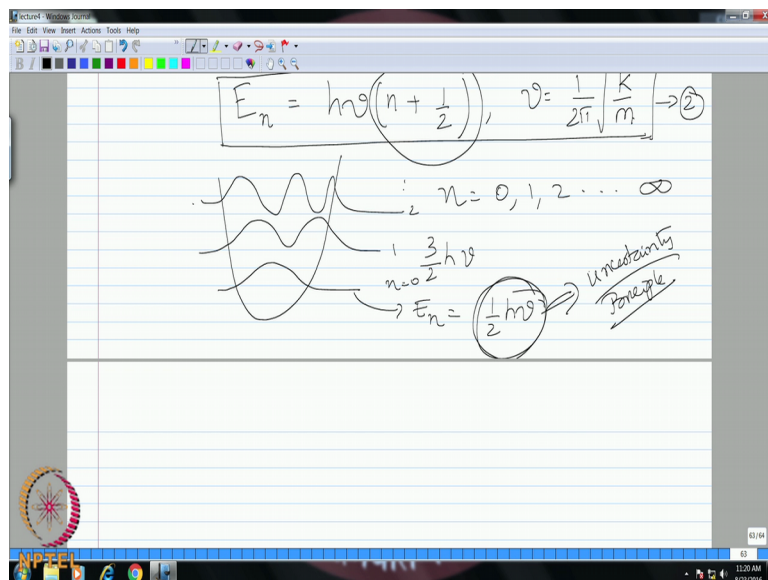
If you put n equal to 0, you have the first energy corresponding energy for this wave function will be half of h nu. Similarly, then this becomes, you have 3 by 2 h nu and so on. So, what does this half h nu here mean? At n equal to 0, so, this is the ground state. At the ground state, you still have some value of vibrational energy. That means, even if you don't basically disturb, this spring mass system, the quantum mechanics predicts that still this will have some kind of a vibrational energy given by half h nu. And this has to be some finite value because again it has to satisfy the Heisenberg's uncertainty principle.

So, according to the uncertainty even at your ground state some quantum of energy still there, present to satisfy the Heisenbergs uncertainty principle. So, so this is basically what we have to understand about the vibrational energy in quantum mechanics. So, I am not going though all the detailed derivation here. But if somebody is interested, how this o d is actually solved, you can refer to some text books related to quantum mechanics and they will be able to provide all the details.

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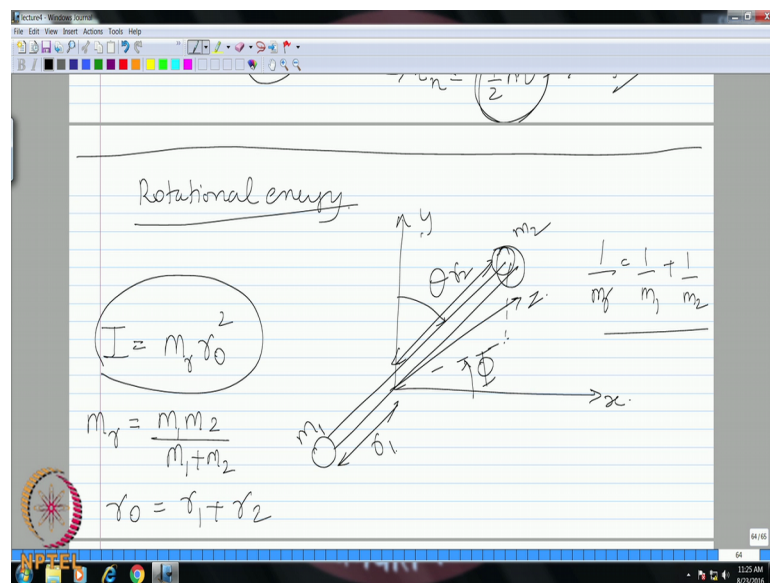
So, let us move on to the other kind of potentials. So we have covered vibrational energy, we have covered translation energy, what else is left?

Rotational energy, so, we can now look at, what quantum mechanics tells us about applying potential energy constraint with rotation. So, now, let us look at the case where we again consider two atoms like this. But now, instead of vibrating, they are rotating because for monatomic system there is no rotational energy, you should have considered at least diatomic molecule, so, in, if you take two atoms. So, let us represent this in x y z. So, let us say that you have one atom here, you have another atom. Let us consider this as a rigid body rotation.

So, we are linking this to two atoms, like they are rigid, you know there is no relative motion while rotating. So, this entire body will be a rigid body which is consisting of two atoms here and they will be rotating. Now, when they rotate, they rotate in a spherical coordinate system. That means, they can make an angle of theta with the vertical access.

So, they can rotate like this and they can also rotate in the x z plane above the y access, above the y access also, they can rotate. So, that is the azimuthal angle. So, there you can imagine, that the projection of this particular object in the x z plane is now making an angle - phi. So, this phi can go all the way from 0 to 360 degrees.

So, then this will make a sphere, so, theta going from 0 to 180 and phi going from 0 to 360 will make the rotation completely in a spherical coordination system. So, let the mass of one atom m1. The other one is m 2, in diatomic molecule, you do not have to have same equal masses for the 2 atoms. So, accordingly the moment of inertia will change, if they are equal masses then you have perfect balance but here, now you can, the movement of inertia can shift depending on the higher mass. So, the distance of this from the origin let us say, it is r 1 and from the second atom to the origin let it to be, r 2.

This is basically the system under consideration and the corresponding movement of inertia for this rigid body system will be m subscript r in to r naught square, where m r is called the reduced mass because now you have two masses m 1 and m 2. We have to write equivalent reduced mass which is kind of a harmonic mean between the 2 masses m 1 plus m 2.

So, that means we, how do we write harmonic mean? 1 by m r is equal to 1 by m 1 plus 1 by m 2 this is your harmonic mean. So, it will always harmonic mean, will be bias towards the smaller value. The lesser mass and the corresponding moment of inertia is this where what is the r naught r 1 plus r 2. So, this is the moment of inertia. Now, why do we have this moment of inertia?

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Now let us expand the Schrodinger's wave equation. Now, Schrodinger's wave equation in a generic coordinate system will be what laplacian psi is equal to e psi. So, we will not put any potential energy constraint on this. It is just rotating just like. We have a free electron which is translating. This can just simply rotate in space without any potential energy constraints. So that means u is equal to 0.

So, now if you expand this in a spherical coordinate system. So, the laplacian now has to be written in a spherical coordinate system. So, your del square will be 1 by r square d by d r r square d by d r. Plus you have 1 by r square sin theta d by d theta into sin theta d by d theta. Plus we have variation with respect to the azimuthal angle, phi. So, that should be d square by d phi square, and you have 1 by r square sin square times theta. So, here I am going to use instead of m, the reduced mass m r because we are considering in equivalent particle with the mass reduced, mass and m r.

So, this is my equation and expands the del square. Now, if you look at the variation with respect to r. So, we are only looking at variation with respect to theta and phi rotation to describe the sphere. So, therefore, there is no variation with the respect to r, so, this term can be cancelled. So, essentially we have variation with respect to theta and phi.

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If you write this, you have sin 1 by sin theta. So, I am going to multiply throughout by r square in fact, here. So, I will multiply throughout by r square; so, have d by d theta sin theta into d psi by d theta plus 1 by sin square theta d square by d phi square. So, on this side, so, then I am going to so, multiply throughout by r square. So, you should have we can write minus 2 into e i by h bar square into psi. So, I am dividing throughout by h, h bar square and multiplying throughout by 2 times m r into r square 2 m r into r r naught not square. I am writing as moment of inertia i.

So, if you want you can just do that step, I skipped the step here, so, basically in this equation, if I multiplied by 2 times m r. So, this becomes del square psi minus e times c by h time square into 2 times m r psi and then I am also going to multiply throughout by r naught square. So, I have m r into r naught square, r naught square here, so, this am writing as my, I and in the expansion of laplacian, I have 1 by r naught square that gets cancelled. So, here r can be written in terms of r naught. So, we can replace r with the r naught anyway so that is not varies with r.

So, you can E plus r with the r naught. So, this is your Schrodinger's equation with the respect to variation in theta and phi. We have again a partial differential equation in two dimensions. So, we have to again use separation of variables to separate derivative of theta and phi, try 2 independent ods and try to solve them.

We will therefore, assume psi of theta comma phi to be something likes p of theta and psi of phi, you can use whatever variable you want but this is what I am using here. So, this convention now I suggest you to plug into this p d e. So, let us call this as 1 try to separate it into two ods.

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So, if you substitute this, can write this as psi of c 1 by sin theta d by d d theta sin theta into d p by d theta because psi is constant now. Differentiating with respect to theta, so, plus you have 1 by sin square theta p of theta you have d square psi by d phi square because psi is now function of only phi.

On the other side you have minus 2 E I psi by r square. So, let us divide throughout by psi. So, this psi here, what I have written here is the function of theta and phi, so, we can divide throughout by psi function of theta and phi. Therefore, you will have 1 by p sin theta d by d theta sin theta d p by d theta plus 1 by psi which is the function of phi sin square theta and we have d square psi by d phi square. This is equal to minus 2 E e I by bar square. This is everybody got this? So, just like we have the 2 d quantum well, so, we have derivative with the respect to x y and you have the Eigen values on the other side. So, this is the constant the moment of inertia constant for the system is constants. So, therefore, so, you have to have a, so, this is the function of theta, this is the function of phi. So, this should be equal to constant that means independently they have to be constants.

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But we will assume in this case now, in simplest solution that you can get is if you have this entire term Constance. This entire term constant then you will have another constant, so, what we will do is now, just like we did the two quantum well, we will break this into two Eigen, further Eigen value problem.

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So, one which is 1 by p sin theta d by d theta sin theta d p by d theta which is equal to some Eigen value which is k theta square minus k theta square, there in the 2 d quantum well, we used some something like minus l square or minus n square. That means this has to be again a positive, a negative quantity here. So, this side, so, if you look at it so, you have a positive value of Eigen function e. So, this two has to be summed up than you negative sin will cancel off and will have a positive value. So, therefore, this has to be a negative value. Here, similarly which you look at 1 by psi of phi sin square theta d square psi by d phi square will assume this is some other constant minus m square.

Therefore, essence this means minus k theta square minus m square is equal to minus 2 E I by square. So, you will have positive values of E from this, so, therefore, if you write the second. So, let us call this as 3 and this as 4. So, we have to solve now d square psi by d phi square is equal to minus m square sin square theta psi. This let us call this as equation 5. So, this is the od that we have to solve and from this, once we get these Eigen values m, we can actually find the solution for 3 also because we can relate.

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We can write this k theta square as basically minus 2 E I plus 2 minus m square. So, therefore, we can directly substitute for, let me put this view, so, we can directly put this k theta square into equation 3 in terms of m. So, we can write equation 3 in terms of m. So, once we solve the equation 5 and get the m square values we can actually find the solution to the other od as well have d by d theta of sin theta d p by plus. Now, I am writing my k theta square as 2 E I by h bar square minus m square times p equal to 0. So, I am just substituting let us say 6 into 3, so, that I can rewrite my 3 in terms of m.

Therefore, I let me call this as 7. So, we can solve first equation 5, obtain m, the Eigen values m and then put this into equation 7, put this into equation 7 and then what? Solve for what? E the actual energy E, so, again the way you solve it is not as straight forward as the one that you did it in Cartesian system. You can do this by series expansion or numerically. So, I will only give the final solution for E, so, the energy Eigen values, so, we have multiple Eigen values here.

We have m which is not an Energy Eigen value, but the actual Energy Eigen value is E. So, the Energy Eigen value solution will be h bar square by 2 times I, I is the moment is inertia that we have defined. We have that I here in the equation 7 and multiplied by numbers l into l plus 1, you hang on to this, I will come back and say what is l. Now l is the function of m. So, the m that we have Eigen values that we obtain here is actually rewritten in terms of l and how they are related?

So, your l should be greater than or equal to mod of this number m, the other Eigen value m is related to this l like this and your l, m can take the values 0 plus or minus 1 plus or minus 2 and so on and a condition for this l. You can say this wave number these are again in terms of wave numbers. You can express them. So, you can say wave number l should be greater than or equal to modules of m. So, this is the constraint and depending on that you can calculate the energy of this particular wave function.

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So, that means, if you talk about let us say m equal to 0, so, when you solve this equation number 5. So, you will be constraining. Now you will be quantising it so, will have discreet values of m, so, it could be starting from 0 1 2 3 and so on. So, if m equal to 0 what happens? l should be greater than or equal to modal we will see that now m, if m equal to 0. So, what are the values of l that can take greater than or equal to, so, it can take 0 and then it can also take 1 2 and so on.

In fact, the way it is written, slightly different. So, let me clarify that the way it is written, let me, we can just rewrite it as mod m less than or equal to l and l can take the values 0 1 2. So, in this case therefore, if you are l equal to 0. So, the m has to be 0 and if l equal to 1 the m should be less than or equal to l. So, it can be plus or minus 1 right or 0 understand so, if l equal to 2 so, m can be plus or minus 2 plus or minus 1 0. So, this is the way it is written. So, you have to start from the lower energy levels and then go to higher energy level.

So, if you do write it the other way, l is greater than or equal to m. So, for m equal to 0, l can go all the way up to infinity you know. So, usually we start with the lowest energy level and then build up on this, so, the way it is the written is mod m less than or equal to l. So, for l equal to 0, we have m equal to 0 that is the lowest energy level and then for l equal to 1 m should be equal to plus or minus 1 or 0 and then l equal to. So, this is the

way you basically fill the energy levels in the rotational system right. So, depending on the value of l so, this, so, you have two numbers here 1 is l the other is m ok.

And now, again we have this concept of degeneracy here, so, what it means is that if you look at say m equal to 0 l can be 0. So, you have basically in this case two energy levels, we will having the same value of energy or two wave functions one for m equal to 0 1 for l equal to 0, but energy is dependent to only on l. So, there is a degeneracy coming again, when you go to m equal to plus or minus 1 0. So, for l equal to 1, you have only one value of energy, but m can be plus by 1 minus 1 or 0. Again you have degeneracy there, you understand you can have three different wave functions, one for plus 1 minus 1 0, but all of them having the same value of energy for the rotation system.

Similarly, if you go to l equal to 2 what is the degeneracy there 5. So, in general the degeneracy as a function of l will be what? 2 l plus 1, so, for l equal to 0 the degeneracy is 1, l equal to 1, degeneracy is 3, l equal to 2, the degeneracy is 5. That means, for each of these numbers 0 1 2, you have different values of degenerate energies states that means they are different wave functions governed by these numbers but they have the same value of energy because energy is only a function of l or not m here.

So, this is another good example of degeneracy the other one that we saw in a two dimensional quantum well. So, there again the energy is l square plus n square, so, for values of l equal to 1, n equal to 2 and n equal to 2, l equal to 1, you can have the same energy. Here you have a different way so, here your energy is function of only one wave number or quantum number that quantum number is only l, but actually the o d is governed by two quantum numbers l and m, but it does not the energy does not recognise that. So, that is why, again there is the degeneracy in this problem. We have although different wave functions; you have the same value of energy. So, same energy level is being occupied by multiple wave functions, so, this is another example, good example of degeneracy in the rotational system understand?

Student: (Refer Time: 45:47) momentum quantum magnetic quantum number.

No, it is somewhat similar to that but this is only rotational system that we are considering. In rotational system, you have quantum number with respect to theta direction we have one quantum number with respect to phi direction, but the energy is function of only one quantum number. So, this kind of concept of degeneracy is only

typical to the quantum mechanical systems, so, let us quickly do the last part of the quantum mechanics which is these are the fundamental quantum mechanics that we are talking about.

So, these are for what we called as electronic energy levels, so, what whatever we have done there also for mechanical energies talking about translation, rotation and vibration. You can talk about filling of electrons that that is what you are asking about the orbital concept. So, they start with the lowest orbit, go to the highest over. What is basically causing this to do? So, basically filling of electrons in the lowest energy level to the highest energy level and that is also predicted by quantum mechanics.

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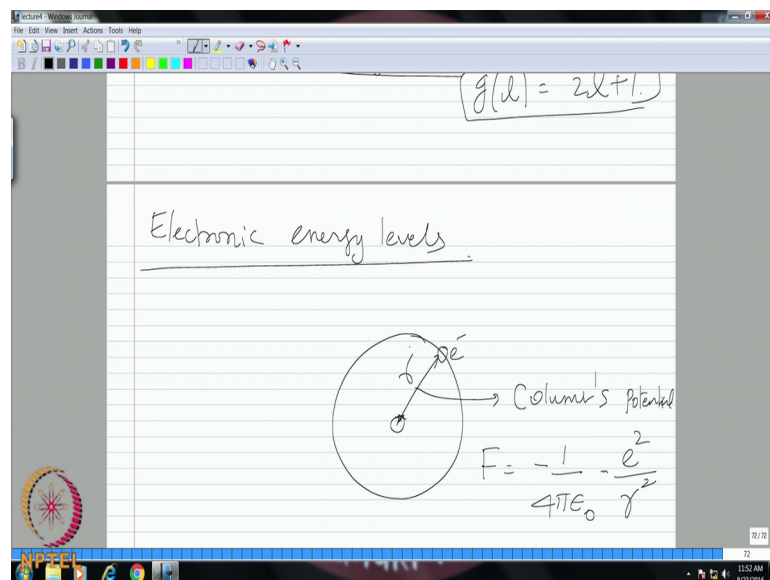
So, we will therefore, look at this very briefly this is not very important for heat transfer, but just to also complete it so, Electronic energy levels.

So, here we take a very simple example of hydrogen atoms. So, you have. How many electrons are there in a hydrogen atom? One so, you have the nucleus and this is the simple modal where you have n electron orbiting the nucleus. So, we are going to expand this modal, simplistic modal to other atoms also we will assume even other atoms we can predict it by assuming. Electrons keep rotating around this particular nucleus as a centre and therefore, we have to consider the force of attraction between the nucleus and the electron as the potential energy constraint, in the case of electronic energy level. So, this is given by your coulombs potential. So, this is your standard potential, the coulombs

force says that if you have an electron separated from the nucleus at a radius r to the force is 1 by 4 pi times the permittivity of free space into the charge of the electron square divided by r square.

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So, therefore, the potential energy can be determined as f is equal to d u by d r so, we can integrate F as a function of r so, therefore, u of r will be what? Minus e square by 4 phi epsilon naught into r. This becomes your potential energy constraint so; you can substitute this into the Schrodinger's equation again as a new potential energy constraint. Now, this is again a spherical system this electron orbiting, then nucleus. So, therefore, however, we are not interested in variation with theta and phi now, only with the radial direction.

So, we are interested in energy quantisation only in the radial direction and therefore, whereas, in the rotational energies we discarded the derivative of r. Now in the case of electronic energy, we will discard the other two directions. So, this two can be neglected and will have only the derivative with the respect to r and you can substitute the coulombs potential energy as the potential energy constraint and if you solve this once again by the separation of variables which is not as straight forward.

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So, we will get an expression for the Eigen values of the electron filling so, which is minus capital m. So, the m now becomes the mass of the electron in the Schrodinger's equation that I am writing as M here c 1 square by 2 h bar square n square.

Now, this c 1 is the constant. Basically e square, I think it should be e squares by 4 pi epsilon naught, so for the case of electron, if you substitute the mass of electron then find out this constant and therefore, you are modified planes constant. Then, this becomes minus 13.6 electron volts divided by n square and what is n? So, n is greater than or equal to 1 and we have other quantum numbers coming into picture which is not in the energy but while you solve the equation, you will have quantum numbers.

So, that is l plus 1 and modulus of m should be less than or equal to l and your l can be 0 1 2 and so on. So, the energy is a function of only n but n is dependent on the quantum number l and again you have another quantum number m, for which know you can take the values depending on l is equal to 0 1 2 and so on . So, you have multiple quantum numbers, but finally, we energy is the function of only one quantum number n ok.

So, again you have degeneracy here so, therefore, now depending on the value of n you can start filling the electrons in an atom. So, for n equal to 1 so, this is the first electron occupying the in - our first orbital. So, the corresponding energy of this electron is minus 13.6 electron volts.

Student: Sir if.

And as you keep increasing your n, so, let us this value keeps reducing.

Student: (Refer Time: 53:01).

That is a good question I think when you are solving them. So, I think we should also use the so, it should also be a function of theta and phi you are right because we also consider the rotation of this electron around the nucleus. So, finally, you are right so, I think we cannot neglect the theta and phi dependent. So, when we do the separation of variables, I think we should have psi, should be something like some r which is the function of r and will have another y which is the function of theta and phi. Now, this will have the quantum numbers l and m and this r will have the quantum number n you are absolutely right.

So, that the wave function now become function of both, of all the three wave number, quantum numbers n l n. You are right. In the case of rotation system, you have only two wave numbers, two quantum numbers. In the case of electronic energy, you have to consider it is a three dimensional system now. We cannot therefore neglect the variation with respect to theta and phi so, the separation of variables therefore, will have quantum numbers appearing for theta and phi which are l and m and for r, and you have quantum number n, so that that is why, now you have additional level of degeneracy coming.

So, we will stop here. Tomorrow, I will just talk little bit about this filling of the electrons and how these orbital have come. So, very briefly and then we will slowly conclude the quantum mechanics, and then go to the next topic.