Micro and Nanoscale Energy Transport
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Lecture – 11
Fundamentals of Quantum Mechanics Part – 5

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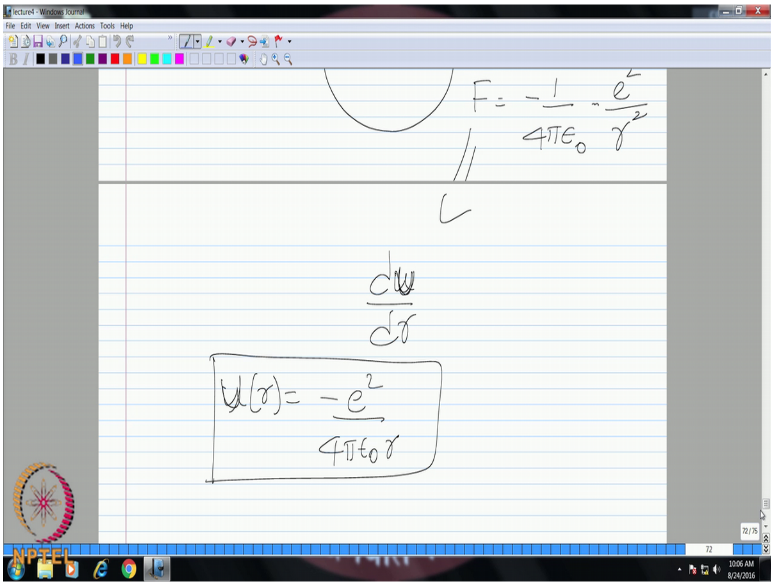

$$F = -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2}$$

$$\frac{dU}{dr}$$

$$\boxed{U(r) = \frac{-e^2}{4\pi\epsilon_0 r}}$$

Energy states for the vibration mode rotational mode and have same this is the fundamental one. So, from basic level to the next level change in the energy and then you have to equate to the energy of the emission, proton emission H nu. So that should give the corresponding wavelength. This is how the, what you can say the corresponding emissions set are coming out certain gases, are actually fundamentally happening.

Basically, what they do is there is, when you have certain energy which is incident. So these can actually observe this energy and can get exited to higher energy levels and after sometime they again jump back to lower energy levels resulting in emissions. This emission will happen in a certain frequency band for certain gases and that is actually calculated like this, from the quantum mechanics.

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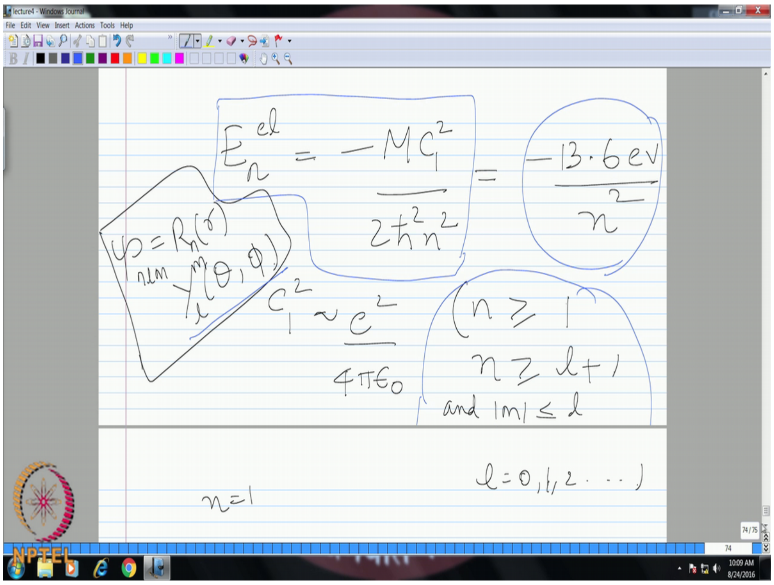

$$E_n^{el} = -\frac{Mc_1^2}{2\hbar^2 n^2} = \frac{-13.6\,eV}{n^2}$$

$$\psi_{nlm} = R_n(r)\,Y_l^m(\theta,\phi)$$

$$c_1^2 \sim \frac{e^2}{4\pi\epsilon_0}$$

$(n \geq 1$

$n \geq l+1$

and $|m| \leq l$

$n=1$

$l = 0, 1, 2 \ldots)$

Good Morning. Today we will continue our discussion related to the electronic energy levels that we had started yesterday. We had use the columns, potential energy constraint and showed that the corresponding values of the electron energy from the quantum mechanics by solving the Schrodinger's equation is obtain like this, where M is the mass of the electron, C is a constraint.

If you plug in all the constraints for electron, you get the resulting expressions as minus 13.6 by N Square, where N is the quantum number now, I mean as correctly pointed out yesterday. So this becomes a 3 dimensional problems. We have to solve the Schrodinger's equation theta phi and R. The corresponding quantum numbers, the theta and phi direction will be L and M and the corresponding quantum number in the R direction is N and the energy level here, the value of magnitude of energy is found to be a function of only N. You find again D gene racy.

Now which is little bit on the higher level of you know D gene racy that you saw in the rotational problem. In rotational problem you had only 2 quantum numbers, now you have an additional quantum number, an additional level of D gene racy. These are the constraints on the quantum numbers, so that means, N should be greater than or equal to 1, N should be greater or equal to. These are the N is related to the quantum number L through this expression. Here and the quantum number L is related to M through this expression. So, therefore, let us workout, what are all the different quantum state starting from for the case N equals to 1. So, for N equal to 1.

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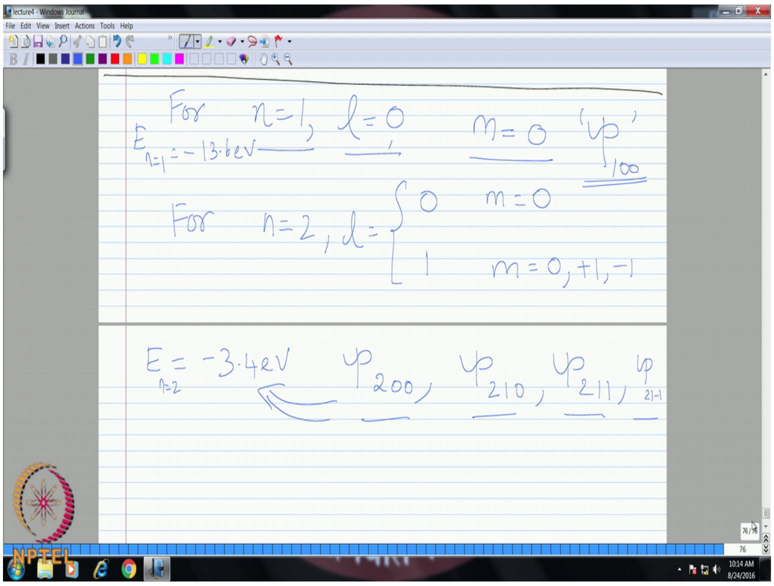

For $n=1,\ l=0 \quad m=0 \quad \psi_{100}$

$E_{n=1} = -13.6\,eV$

For $n=2,\ l = \begin{cases} 0 & m=0 \\ 1 & m=0,+1,-1 \end{cases}$

$E_{n=2} = -3.4\,eV \quad \psi_{200},\ \psi_{210},\ \psi_{211},\ \psi_{21-1}$

Now, let us look at all the D generates states possible. So, what is the value of L? And what is, what are the values of L and M are? M magnitude of M should be less than or equal to L. So, in this case, if N equals to 1, the value of M L should be 0. So, N should be greater than or equal to L plus 1. If L equals to 0 then N is greater than or equal to 1, which satisfying the condition, and if L equal to 0, what is the value of M? Should be 0, therefore, the D generates state for N equal to 1 is basically L equal to 0, M equal to 0. So, this is 1 quantum state. So, we will call this corresponding wave function corresponding to the value of N, L and M will designated as 1 0 0. This gives a particular quantum state and for this, the particular energy if you substitute N equal to 1 will be minus 13.6 electron volts.

So, this is 1 quantum state. Now you can just expand this for N equals to 2. So, for this case, what are the values of L? So, if L equal to 0, N is greater than or equal to 1. You have 0 is possible and L can be also 1 because N can be greater than or equal to 2 in this case N equal to 2. So, L equal to 1 is also a possibility, correct? We can have also 1 again for L equal to 0, now we have values of M, that is 0 and for L equal to 1, 0 plus 1 minus 1. So M, magnitude of M can be less than or equal to L. So, L 0 is also possibility.

Therefore, in this case how many quantum states to you have, 1, 2, 3, 4; so 4 quantum states having the same value of energy.

So, what is the value of energy for this case? Minus 13.6 by 4, 3 point 3 point 4 electron volts for N equal to 2 and for N equal to 1 minus 13.6. Therefore, the possible quantum states for this. So, this shows D gene racy, if N equal to 2. We have 2 0 0 corresponding to N equal to 2 L equal to 0 M equal to 0 then we have 2 what are the possibilities 1 0 we have 2 1 1 we have 2 1 minus 1.

So, you have basically 4 wave functions with the same value of energy. This is a again showing classical D gene racy. So, like this you can keep writing the quantum states for other values of N n equal to 3 4 5. So what I am going to give you is a convention that people are using in filling electrons according to the orbitals. I will just give you, what will be the quantum number and what is the corresponding convention people use or denote this as orbitals.

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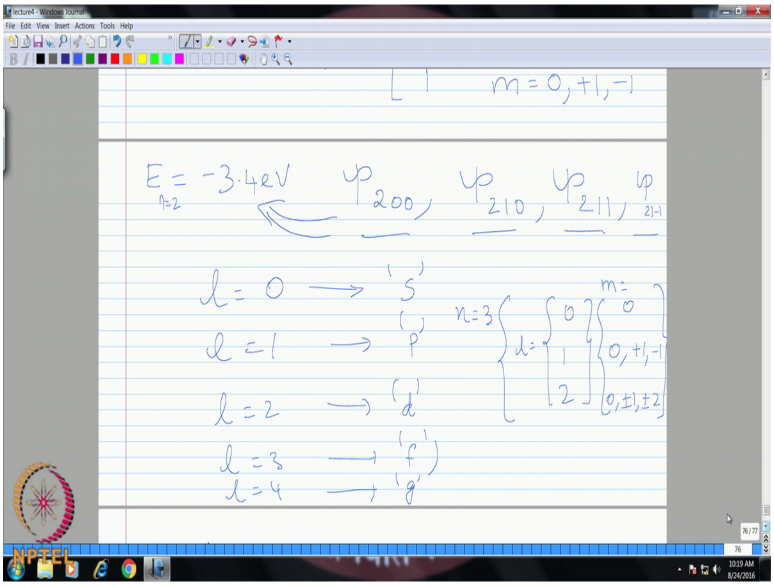

If you are talking about L equal to 0, this corresponds to what we call as orbital S, L equal to 1 is the orbital P. We have ‘S’ ‘P’‘D’ ‘F’. So, we have L equal to 2 L equal to 3 D F and then what else? G, we have an orbital G also ‘S’ ‘P’ ‘D’ ‘F’ ‘G’.

What these convention means that, each denote a particular value of quantum number L, starting from L equal to 0 to L equal to 4. Therefore, now you can looking at the this quantum states you can clearly understand how these orbitals are filled for case of N equal to 1, L equal to 0, M equal to 0, so what is this orbital?

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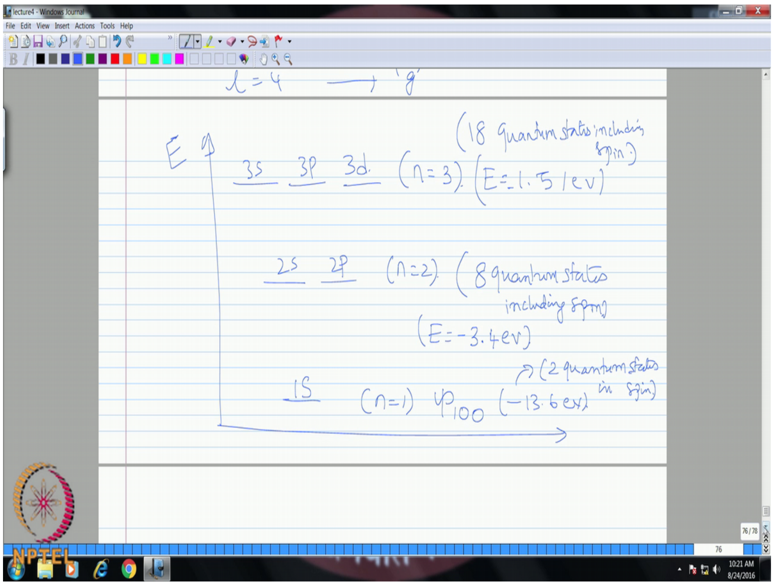

I will just draw the corresponding energy. So we have N equal to 1, which is denoted by the wave function 1 0 0. L equals to 0 is what? S orbital, we have therefore, 1 S. This quantum state denoted by N equal to 1, basically as only 1 wave function. So which is called the 1 S orbital?

Next, this has the energy of minus 13.6 electron volts. Electron occupying this particular quantum state is denoted by 1 S electron. If you go to N equal to 2, we have in this case 4, but we have how many L quantum numbers? 0 and 1, basically we have 2 orbitals here. 1 is the S orbital, the other is P orbital. We call this as therefore, 2 S, 2 P because this 2 comes from the value of N. Therefore, we have 3 quantum states corresponding to 2 P and 1 quantum state corresponding to 2 S or in other words you can have 3 electrons occupying 2 P and 1 electron occupying 2 S.

In fact, if you are including the spin, plus of half minus half, we have additional D gene racy. In 2 P instead of 3 you can say 6 electrons can occupy and 2 electrons can occupy the S orbital because we have plus half, minus half spin is also there. Actually speaking you have in this case 8 quantum states, including spin. In this case we were talking about two quantum states including spin and then if you go to the N equal to 3, now you can do some calculation and tell me, what are all the possibilities for N equals to 3? What are all the values of L 0 1 2 and corresponding values of M? This is 0, this is 0, plus 1, minus 1 and for 2, 0 plus or minus 1 plus minus 2. Therefore, what are all the orbitals that we have? 3 S, 3 P and 3 D and what is a corresponding value of E? 13.6 divided by 9, 1.1.5 1 minus 1.51 electron volts, for N equal to 2 we have minus 3. How much 4 electron volts?

How many quantum states are possible for N equal to 3; 1, 2, 3, 4, 5, 6, 7, 8, and 9 into 2 for the spin. We have 18 quantum states, including spin. This is to just give you an idea you know, when you do chemistry you are not dealing with quantum mechanics, you are just directly taught the orbitals, how they occupy, but the orbitals is only convention coming from the quantum mechanical states and I mean you asked, 1 of you asked the question about the emissions.

Now how can we talk about emissions in the case of the electronic energy level? What happens when the electron from higher energy state from higher quantum state jumps to a lower quantum state? This results in the emission of a photon H nu and there for how do we calculate H nu? H nu is basically equal to delta E from higher quantum state to the lower quantum state.

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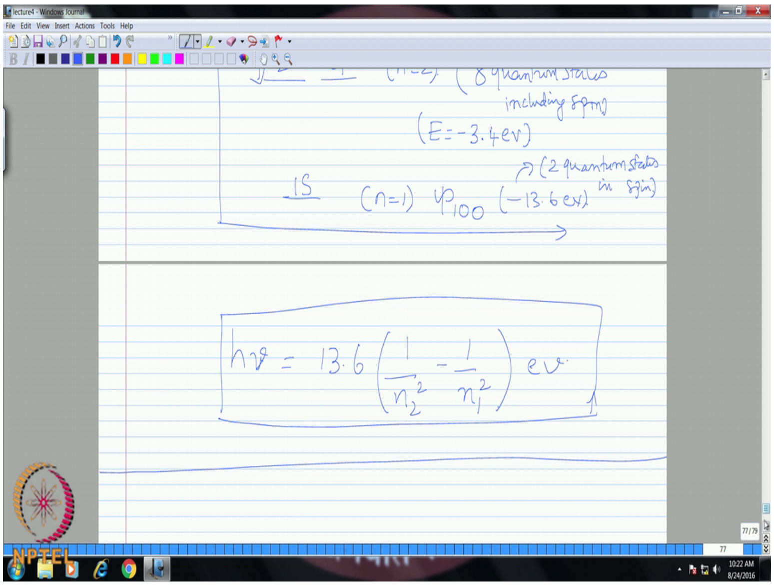

(8 quantum states including spin)

$(E = -3.4 eV)$

1S $(n=1)$ ψ_{100} $(-13.6 eV)$ → (2 quantum states in spin)

$$\boxed{h\nu = 13.6\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) eV}$$

Therefore, in general the emission of photon can happen when you have 13.6 1 by N 2 square minus N 1 square, electron volts. Therefore, you can calculate, what is the frequency? Or wave length of the photon emitted depending on which state from to which state the electron is actually coming down. This kind of you know summarizes all the basics you know whatever just need to understand before we go to the next topic.

What I will do now? Just before I stop the quantum mechanics, I will give a small exercise, where we again go back to our quantum well.

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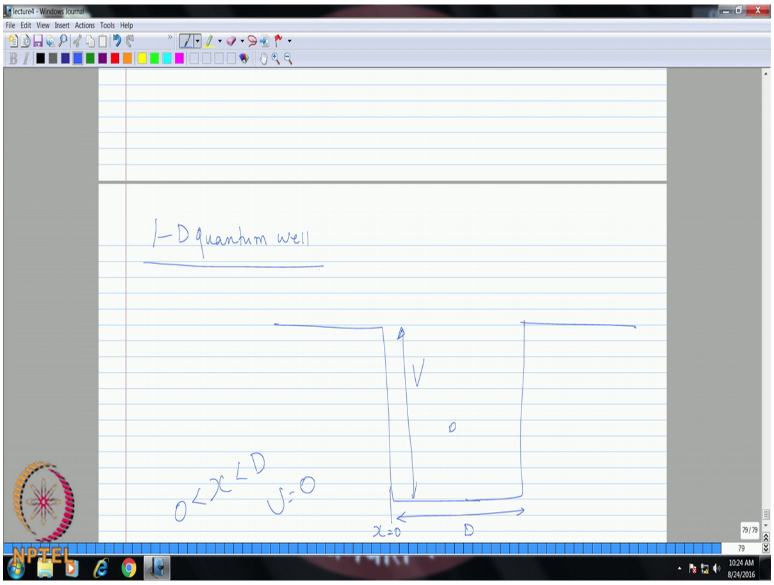

1-D quantum well

Let us consider again the 1 D quantum well, but now the differences instead of having an infinite well, let us look at a well which is having a finite potential barrier height. That means in the 1 dimension our coordinates starts from X equal to 0, the width of this well is D and you can talk about say an electron trapped within this well, but this well is not infinitely deep. Deep means this is not coordinates, this is just energy or potential energy required to escape this constraint.

In this case let us assume that the height or potential barrier, width potential barrier height is V. We is not infinity, it is finite. Inside this well, that is between X greater than 0, less than D, there is no potential energy constraint on this particle or electron. This can freely move about inside the well.

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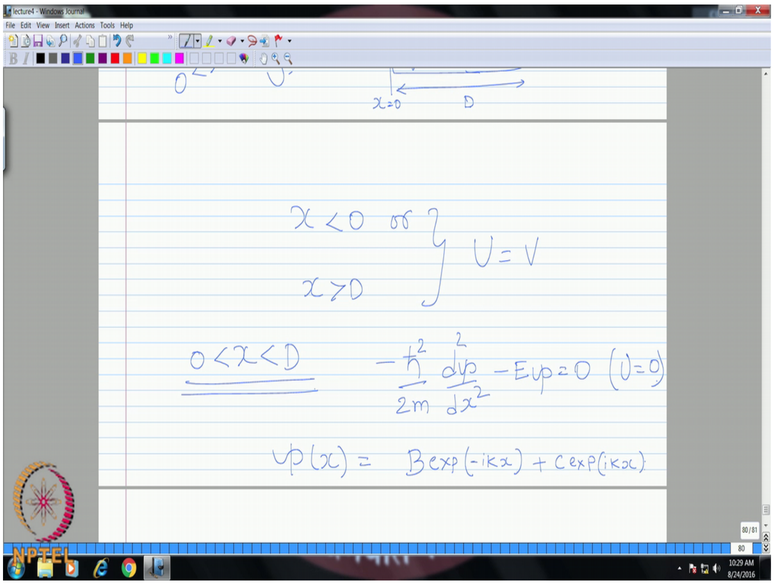

$$\left.\begin{array}{l} x<0 \text{ or} \\ x>D \end{array}\right\} U=V$$

$\underline{\underline{0<x<D}}$ $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}-E\psi=0 \quad (U=0)$$

$$\psi(x)=B\exp(-ikx)+C\exp(ikx)$$

Whereas, if we are talking about X less than 0, or X greater than D, your potential energy constraints is finite equal to V, for this case write down the Schrodinger's equation, view separation of variables, only in the special direction write down the solution. Now, how many solutions you will have. For the case of infinite potential well how many solutions you had? You considered only the domain X 0 to D, outside the wave function is 0 because it cannot get out the well. You did not considered domain outside you considered only within the well. You had 1 solution.

Now there is also a possibility, the electron can come out of the potential well and they can therefore exist for the other dimension so that means, you have to also find a solution for X less than 0 and X greater than D. We will have 2 more solutions. Therefore, 3 solutions you will have. Let us first write down the equation for X greater than 0, less than D. In this case the special equation, the O D will be D square psi by D X square, and then what do you have? Minus E psi equal to 0 because, you equal to 0, the solution for this, if you write in terms of exponential function.

You can also write in trigonometric function or exponential function. This will be something like let us use the constraints B; I will use B exponential. What do you have? You have a right running wave; you have a left running wave. Right running wave, we have an imaginary number I. What do we have? Plus I K X or minus I K X for the right running wave, please state whether Minus I K X or plus I K X?

Right running wave is minus I K X.

We will write it as minus I K X plus C exponential, left running wave, I K X. I think it has to be other way plus should be for right. Plus should be for the right running wave and minus should be for the left running wave. That means, inside the potential well, you can have electrons running to the right or left constraint by this potential well. We have still not come to the boundary conditions, will do that.

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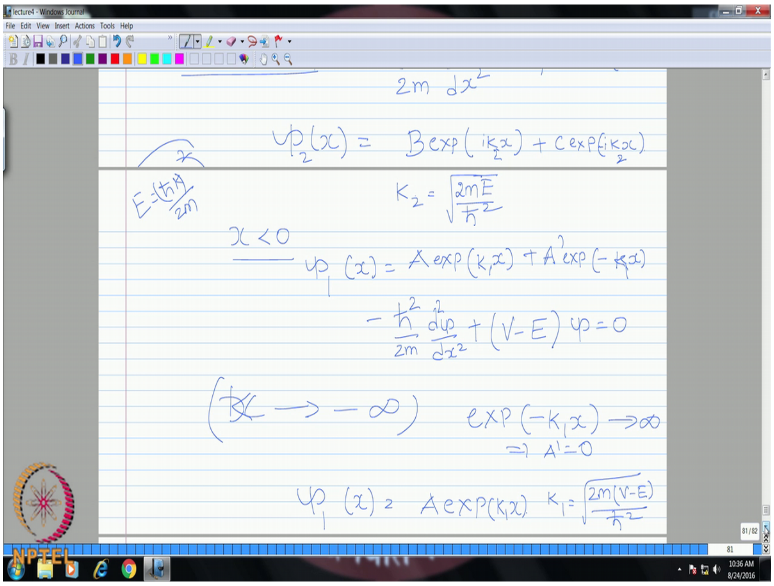

$$2m \; dx^2$$

$$\psi_2(x) = B\exp(ik_2x) + C\exp(-ik_2x)$$

$$E = \frac{(\hbar k)^2}{2m}$$

$$k_2 = \sqrt{\frac{2mE}{\hbar^2}}$$

$x < 0$

$$\psi_1(x) = A\exp(k_1x) + A'\exp(-k_1x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (V-E)\psi = 0$$

$$(x \to -\infty) \qquad \exp(-k_1x) \to \infty$$

$$\Rightarrow A' = 0$$

$$\psi_1(x) = A\exp(k_1x) \quad k_1 = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

Now, X less than 0, let us call this solution first solution as psi 1, subscript 1, because this wave function is going to be different from less than 0, on greater than d.

For less than 0, you can again write down solution some A exponential I K X plus something like A prime exponential minus I K X. Now, we have to careful to differentiate this K and this K because now the Schrodinger's equation for this case will be what? We will have also the potential minus V minus what is the sign? If you minus of E minus V, psi. This is the correct representation here. Therefore the difference here, let us say this is K, let us say this is K 1, this is K 2. We can also write in a slight a different form, you know I am just giving making you aware so that you are not all the time doing the same thing. You can also write this as plus V minus E.

In the case, what will happen to the solution? It will be still exponential, but the imaginary number will not be there or in other words, in terms of trigonometric function it becomes hyperbolic sign plus hyperbolic cause, will be the solution, or in terms of exponential function we will not have this I. Rather you will have just real part, yeah I mean, but we are just writing it in a form like this so that we are dealing with real part, not imaginary part why because we will just apply a condition now.

A condition is that, if you are considering X less than 0, a wave which basically exists on this part and if you are talking about X going to minus infinite. What will happen to 1 of these terms? This is X minus infinity. This will be exponential of infinity minus infinity whereas, this will become exponential of minus of minus infinity plus infinity. Exponential of infinity is what? Infinity, in order to make this finite therefore, A prime has to be 0.

This is why we want to work with the real values here. That is why we have just re written the equation such that we will have the real routes and then, we will apply this condition that is going to minus infinity, exponential minus K 1 X goes to infinity which gives a prime equal to 0, in order to make the solution finite. Therefore, what we get here is psi 2 of X is equal to A exponential K 1 X.

Now how is K 1 related to E and how is K 2 related to E here? How do we relate? For example, here if you recollect E is equal to H bar K the whole square by 2 M. When there is no potential energy constraint, U equals 0, this is what we got for relation between E and K. Therefore, K essentially is what? Square route of E by 2 M, E by (Refer Time: 29:32) whereas, in this case X less than 0. Your K 1 will be square route of 2 M instead of V, we will have V minus E. Let us also, we consistent with the, we will use this as 1 for X less than 0 because we have used K 1 here and let us do this as 2. This becomes 1, X less than 0. Similarly we have to do this for X greater than D.

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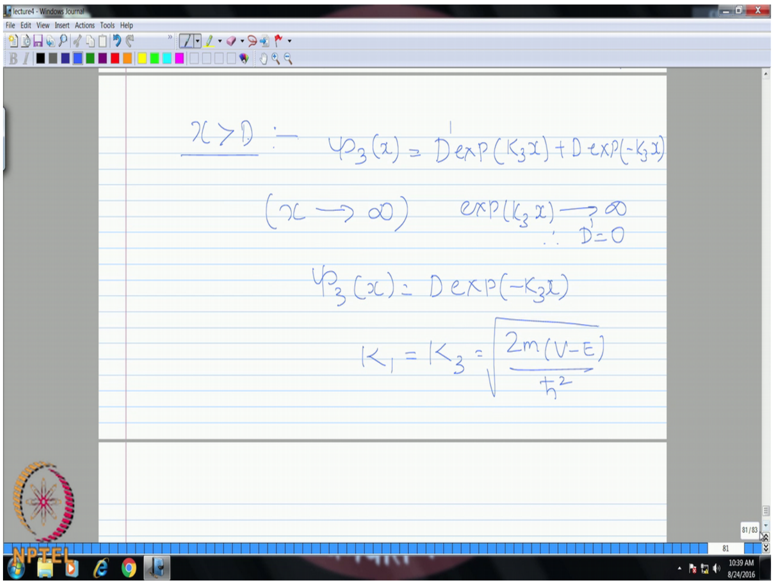

$\underline{x > D}$:– $\psi_3(x) = D' \exp(K_3 x) + D \exp(-K_3 x)$

$(x \rightarrow \infty)$ $\exp(K_3 x) \rightarrow \infty$

$\therefore D' = 0$

$\psi_3(x) = D \exp(-K_3 x)$

$$K_1 = K_3 = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

Let us write this as psi 3 X. So, in this case, we will have the same Schrodinger's equation as represented by this form and the solution we will write this as some D K 3 X plus D prime X 3 X. Once again we can put the condition X going to infinity. Your exponential K 3 X goes to infinity and therefore, D equals to 0. Therefore, you are a let me call this as D prime and D so that, the D prime part gets eliminated, D prime goes to 0 therefore, psi 3 X will be D exponential minus K 3 X and what is K 3 here? Once again 2 M V minus E, Therefore, you can replace K 3 with K 1. Both are same.

Now how many unknowns are there? Psi 1, we have A is the unknown constraint, psi 2 we have 2 constraints B and C and psi 3 we have constraints D. Totally we have 4 constraints, 4 unknowns. Now we have to look at the boundary conditions.

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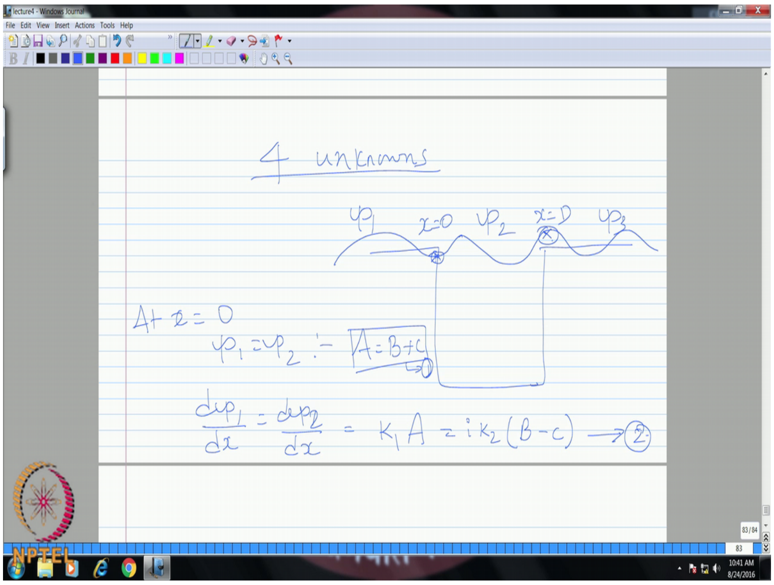

4 unknowns

At $x = 0$

$$\psi_1 = \psi_2 :- \boxed{A = B + C} \rightarrow ①$$

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} = K_1 A = i K_2 (B - C) \longrightarrow ②$$

For the case of infinite quantum well, we simply put at X equal to 0 and X equal to D, the wave function is 0, but in this case we have continue to have wave functions for X less than 0 and X greater than D. So, you were talking about a wave for X less than 0. You may have a wave and this now can continue like this and keep going. For X less than 0, we have a wave now X between 0 and D, this wave has continue and then X greater than D, again has to continue. Therefore, there has to be a continuity of the wave function coming from solution psi 1 with psi 2 and psi 3 especially at the boundaries.

At X is equal to 0 and X equal to D the wave function psi 1 and psi 2 has to be continuous, they have to be same and similarly at X is equal to D, psi 2 and psi 3 have to be same and not only the value, but also the slope. The slope also has to be equal. Now, therefore, will have four conditions, 1 on the wave function, and 1 on the slope at X equal to 0 the other at X equals to D.

We will have 4 equations to solve for 4 unknowns. Therefore, if you put the condition at A X equals to 0 psi 1 equals to psi 2. This will give you A equal to B plus C, you can check this later, but I am directly giving you boundary conditions. This is your condition 1 then the fact that the slope also should be equal at X equal to 0 gives you that K K 1 A should be equal to I times K 2 into B minus C. Please check this later.

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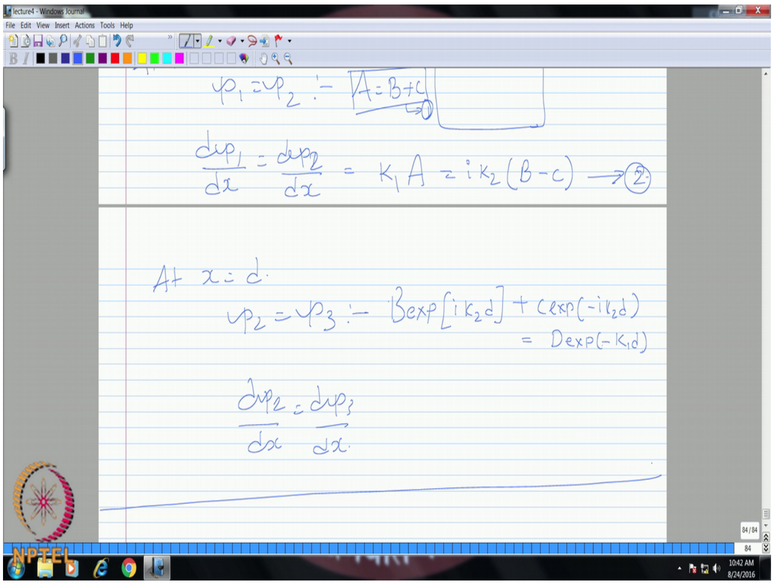

$$\psi_1 = \psi_2 :- \boxed{A = B + C} \rightarrow ①$$

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} = K_1 A = i k_2 (B - C) \longrightarrow ②$$

At $x = d$.

$$\psi_2 = \psi_3 :- B\exp[i k_2 d] + C\exp(-i k_2 d) = D\exp(-K_1 d)$$

$$\frac{d\psi_2}{dx} = \frac{d\psi_3}{dx}.$$

Similarly, at X equals to D, psi 2 equal to psi 3 should give you B exponential I K 2 D plus C exponential minus I K 2 D, should be equal to D exponential minus K K 1 and K 3 are same. We can use K 1 times D. Similarly the slopes, D psi 2 by D X should be equal to D psi 3 by D X.

You can continue this exercise, find the constants and therefore, we can find out the actual quantize energy states, the energies, the energy, the magnitude of these energies are related to these numbers K K 1 and K 2. By solving these equations we should be able to therefore, find out the required values of energy. So just I am giving you little bit more complex problem compared to what we have done previously. You can do all kinds of things because now we are dealing with wave effects.

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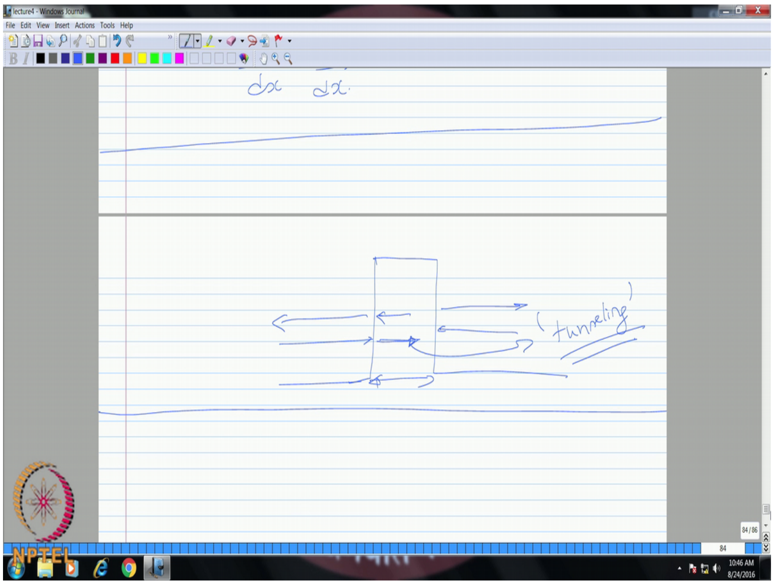

For example; there could be another configuration, where you have what is called as a barrier instead of a well. You can have a potential barrier and you can have a wave which is coming you know this way. It faces this barrier now what happens is you can also have a reflection of this wave from this barrier, some portion can be transmitted. Similarly inside you have right running and left running waves and again on this side you can have incoming and outgoing waves.

You can apply Schrodinger's equation for this kind of barrier problems also and you can actually see that there is a finite wave which is actually transmitted across the barrier and you solve this equation. Although there is a barrier, there is a boundary, the wave actually go straight through. This is this effect is called tunneling effect. This is a very important phenomenon in quantum mechanics. When you keep a barrier of a finite width and you will I will you will also see that the transmission of this wave through the barrier depends on the width of the barrier. If the barrier is too wide, it cannot tunnel through. Very tin width, it can tunnel through, why this tunneling happening? It is purely described by quantum mechanics.

You can extent the problems to include also a barrier and you can also see how these tunneling happens so on. We will not have much time to going to all these details, but never the less, I hope now you have some basic idea about how to use the Schrodinger's equations, solve simple problems and what I would like to do is then move on to the next topic, the incoming wave should be a right running wave, the reflected wave is a left running wave and similarly inside and the other side also. Now, that yeah exactly, now, that you know the convention for the right running and left running waves you do not even have to again start from starch. You already know the right running wave should be have you know plus I K X. Left running wave is minus I K X. Directly use only those waves that you are consider yeah then it becomes much easier for you. I think if you take any fundamental book on to quantum mechanics, this kind of barrier problems and finite potential well problem should be were doubts. Then you will be able to easily understand.

So, the next part, what I would like to cover is look at extension of this quantum mechanics to a more practical system. Therefore, we will may be in the next 3 class or So, look at little bit of solid state physics.

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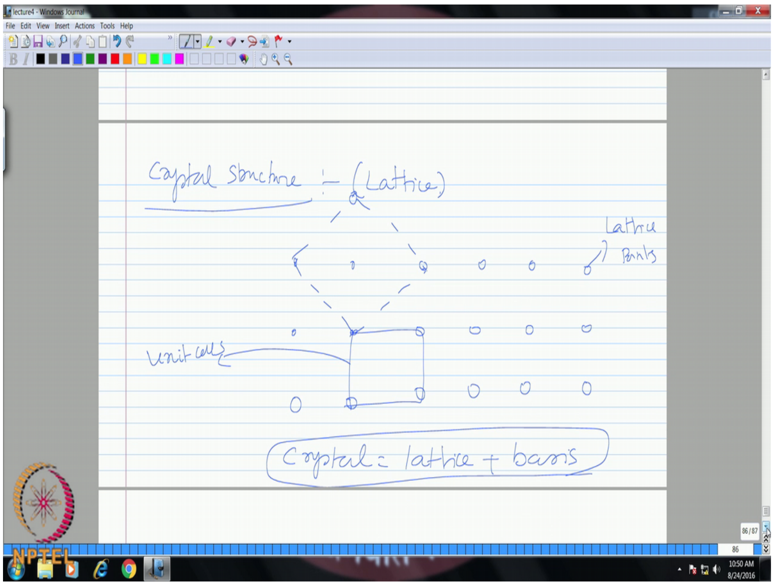

We have considered you know in the previous case I mean electron waves which are subjected to some simple potential and how the wave function looks, how the energies states get quantize and how to calculate them, but I mean for us for heat transfer, how does this affect our heat transfer problems? We have to look at a more practical configuration were electrons are confined in crystals, in solids. How does the quantum mechanics decide these quantum states in the more conflux configuration? I will, what I will do is I will not be able to solve the equations for more complex cases, but I will introduce you to the problem and then I will give the solution and mainly to let you know the real scenario.

Therefore, when you extend this the free electron model which is what we have a quantum well to a solid crystal structure. We have a crystal or crystalline solids. We described by what is called as a lattice. How do we define this kind of a lattice is just regular arrangement, you can have some fixed points in space and fixed separation and then you can just put some points and now you can arrange atoms on this on to these point. Depending on the kind of arrangement that you have, you have different crystals.

You can now start building therefore, units cells based on this. Some simple cells could be something like this, where you arrange atoms in the corners of this particular unit cell. You can have a simple structure; you can also basically have more complex arrangements. You can include something like this and you can have another 1. So, you can connect like this you know. These are all called unit cells.

These fixed points are called lattices, lattice points and if you put the atoms to the lattice points. This is called basis. If you put the atoms to these fixed that is points this is called basis. Therefore, your crystal is actually nothing, but lattice plus basis. When you arrange the atoms on to these lattice points, then you define form a crystal and this crystal will have a periodically repeating structure. We actually look at a unit cell of a crystal and then for we can apply periodicity principle.

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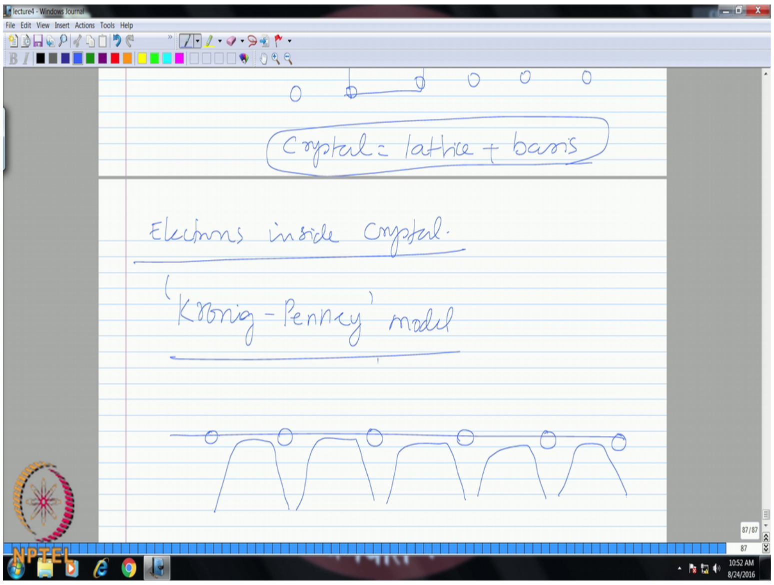

Now I do not thing will have much time to, but let me give you a brief idea about what happens to electrons inside such a crystal structure. We are now moving from free electrons subject to some arbitrary potential to real scenario. In this case, you can model, a very popular model called the Kronig Penny model. To describe the electrons in a crystal so; that means, you have atoms and these atoms interaction between the atoms now we have we know that there is potential. We use the harmonic potential or whatever it is, but never the less the interaction potential between the atoms is now the potential constraints. Between these atoms you have this kind of potentials and this is now going to be periodic and repeating.

Therefore, we can consider a unit cell to model the electron motion. Now the electron could be confined within these potentials. The electron that you have in a crystal now is actually constrained by the potential due to the interaction between to atoms.

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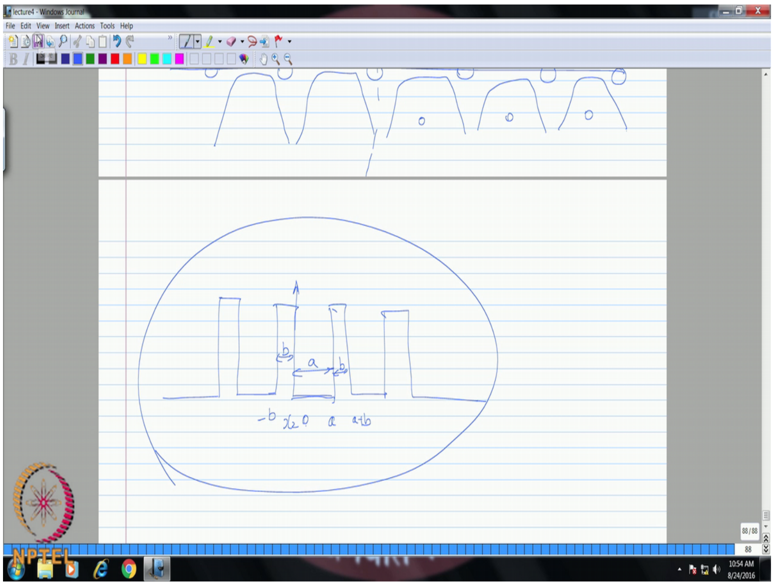

And that is described by the Kronig Penny model. Now the Kronig Penny model simplifies this kind of interaction potential that which you have is a more complex on to a simple potential like this rectangular potentials. You can have a coordinate say X equal to 0 and let us say this is X equal to minus B, the width of this potential in the negative X direction and this width between the potentials or spacing between the potentials could be X equal to A. This is then a plus B. This is B here. This could be like a quantum well, which is of width A and this is again B.

Therefore, now it becomes a repeating. As you go from 0 to A plus B, you can work out periodic, solve the Schrodinger's equation for this periodic potential and that becomes repeating so on and so forth. This is the simplification, what Kronig Penny model does to the actual electrons inside a periodic crystal structure.

So, then the Schrodinger's equation for this system is solved. We will, may be look at the solution tomorrow because now we do not have enough time. Now, as where the less, we will do this tomorrow and then we will also look at therefore, the electron energy level in an actual crystal, how they look from what we have as simple free electrons, how the how the energy levels are modified by means of crystal structure. Then we will look at also the vibrational energy levels of not electrons, but due to the vibration of these atoms inside the crystal structures. That is the phonon energy levels.

So, these 2 we will study, we will look at we will study, how their energy levels are actually looking inside the crystal structure. That is the starting point for our E transfer calculations, where we, you statistical thermo dynamics, first we have to understand the basic energy levels of electrons and phonons in solids. Then we apply the statistical thermo dynamics to converts these micro states to a macro macroscopic properties.

In the next, I would say about 6 to 9 classes slowly we will transition from the microscopic state to the classical state.

Thank you.