Spectroscopic Techniques for Pharmaceutical
and
Biopharmaceutical Industries
by
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Lecture-09
Vibrational Spectroscopy Theory and Application-I

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Vibrational, Rotational-
Vibrational, Raman
Spectroscopy

(Theory and application)
First Lecture

During last 2 lecture, we have discussed about Rotational Spectroscopy. Now, we will go to Vibrational Spectroscopy, where we will look at how to calculate energy of different vibrational level and what is different characteristics of Vibrational Spectroscopy and finally, we will look at its application. Apart from that we will also discuss Rotational Vibrational Spectroscopy and Raman Spectroscopy.

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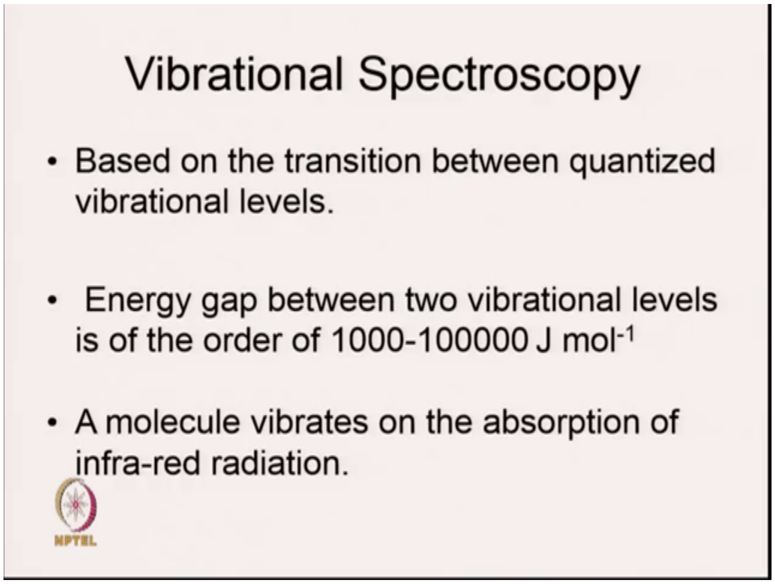

Vibrational Spectroscopy

- Based on the transition between quantized vibrational levels.
- Energy gap between two vibrational levels is of the order of 1000-100000 J mol^{-1}
- A molecule vibrates on the absorption of infra-red radiation.

So, Vibrational Spectroscopy as the name suggests, it is based on the transition between quantized vibrational level. Generally, the gap between two vibrational levels is of the order of 1000 to 100000 Joule per mole and if molecule or species absorbs energy of radiation of this order a molecule start vibrating. So, basically your molecule vibrates on the absorption of IR radiation.

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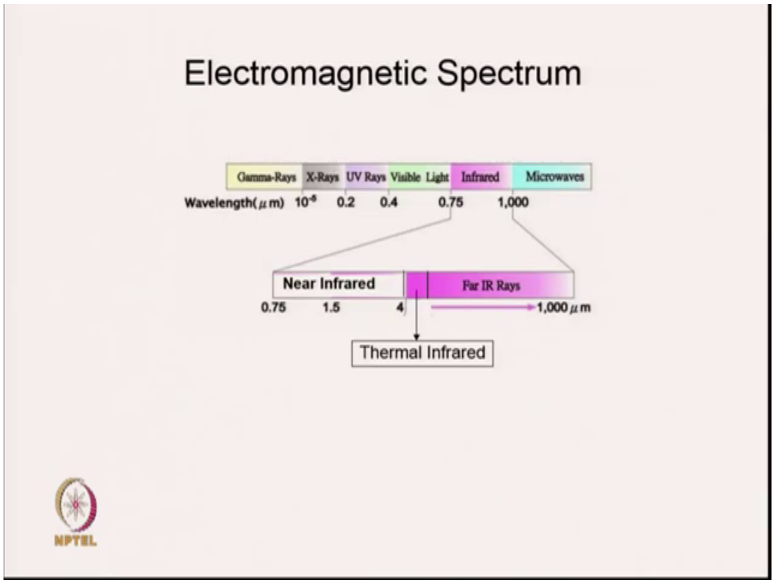

Electromagnetic Spectrum

So, this is your electromagnetic spectrum and you can see that highest energy is of gamma rays and then your X ray. IR comes between wavelength of 0.75 micro meter to 1000 micrometer.

Infrared is divided into 3 different regions 1 is near infrared, which goes from 0.75 micro meter to 4 micro-meter and your thermal infrared which is around 4 to 50 micrometer and after that you have far infrared, IR. So, that is goes till 1000 micrometer.

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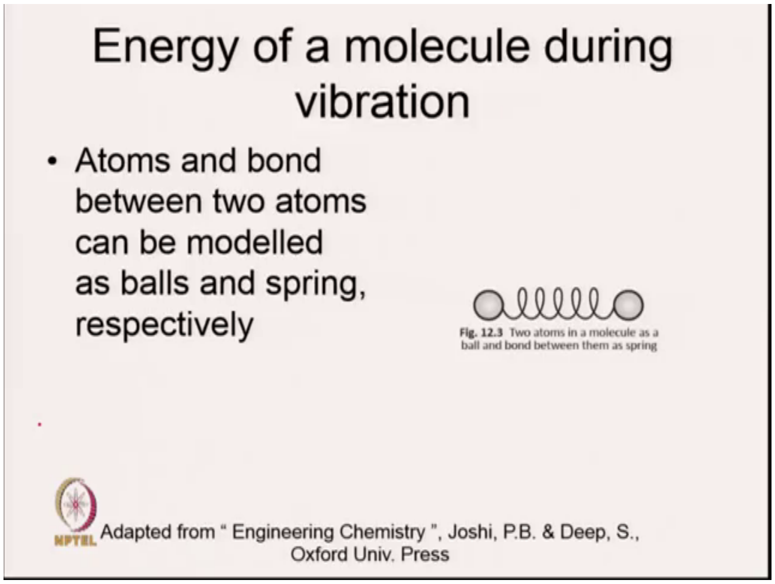

Energy of a molecule during vibration

- Atoms and bond between two atoms can be modelled as balls and spring, respectively

Fig. 12.3 Two atoms in a molecule as a ball and bond between them as spring

Adapted from " Engineering Chemistry ", Joshi, P.B. & Deep, S., Oxford Univ. Press

So, your energy of molecule during vibration. So, first thing when we deal with Vibrational Spectroscopy to know what is the energy of molecule during vibration. So, 2 atoms as a 2 balls and bond between this can be taken as a spring and what happened during vibrational it is going like this. So, some time it is getting stress, sometime compressed extension and comparison and that is what you can associate with vibration of a molecule.

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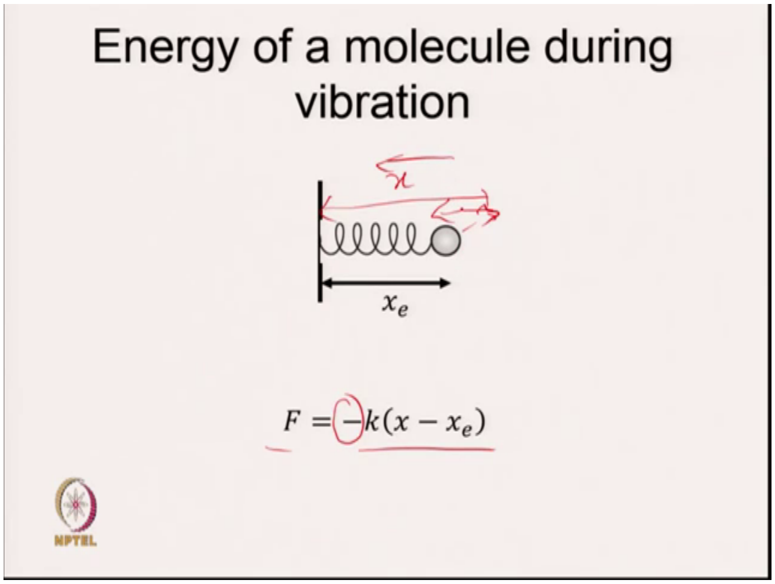

Energy of a molecule during vibration

$$F = -k(x - x_e)$$

So, let us think about how to calculate energy. So, suppose an atom is here and then it is bound to a wall and this is your equilibrium distance from the wall. So, here equilibrium distance, then if suppose, if you extend it, then what will happen? So, suppose you extend by this much amount, so, this distance is your, this total distance is your X and this distance is Xe. So what will happen that if displacement is towards right hand side, then a force will act just oppose it to this force will act opposite to the direction of displacement.

And that is why force is your proportional to this displacement, proportional to this displacement and this negative sign tells you that direction of displacement and force will be just opposite to each other. And your this displacement is basically your X minus Xe, displacement is your X minus Xe. So, if we want to know how this system changes its energy, we need to solve your Newton's law of motion.

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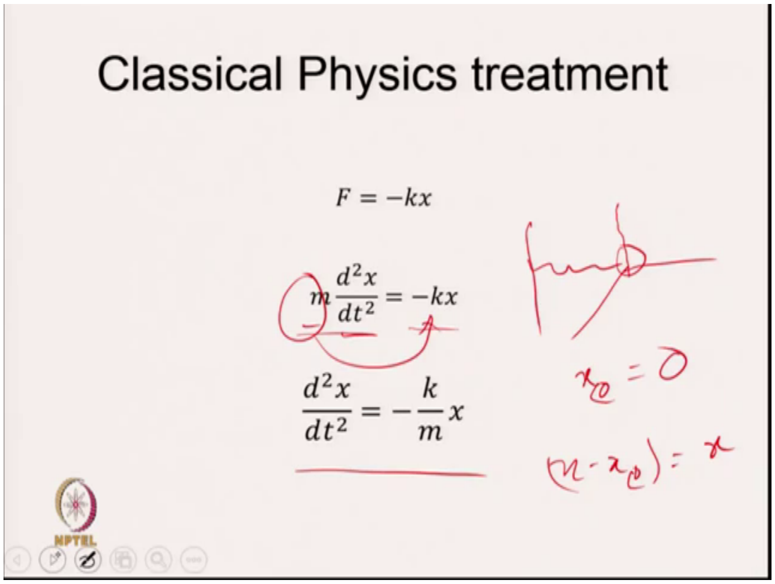

Classical Physics treatment

$$F = -kx$$

$$m\frac{d^2x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

$x_e = 0$

$(x - x_e) = x$

So, Classical Physics Treatment what we are going to discuss is classical physics treatment. Here we know that force is minus KX. So, what we now taking as that just think about this. So, we have this system and now what I did is, I put my axis at the atom. So in that case your Xe will be 0, Xe will be 0 and then X minus Xe will be equal to X. And in that case force will be given by simply minus K into X. We know that, force is equal to mass into acceleration, so, this is your mass and this is your acceleration, acceleration nothing but second derivative of position with respect to time or displacement with respect to time, is, so, this is ma I is equal to minus KX.

And now, we can just simply put this m here, we can bring it here. So, now you have this equation, which is your differential equation, second order differential equation. Now, if you will be able to solve this you can get your frequency of vibration or energy of vibration.

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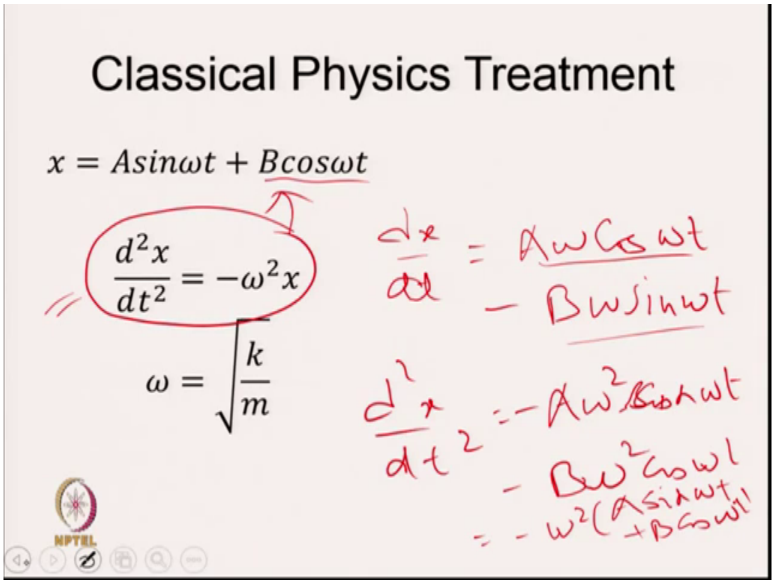

Classical Physics Treatment

$$x = A sin\omega t + B cos\omega t$$

$$\boxed{\frac{d^2x}{dt^2} = -\omega^2 x}$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$\frac{dx}{dt} = A\omega \cos\omega t - B\omega \sin\omega t$$

$$\frac{d^2x}{dt^2} = -A\omega^2 \sin\omega t - B\omega^2 \cos\omega t = -\omega^2(A\sin\omega t + B\cos\omega t)$$

So, again we will go for Classical Physics Treatment. So, solution of that differential equation is your X is equal to A sin omega t plus b cos omega T. So, suppose if you do dx by dt what you are going to get is your A omega cos omega t minus B omega sin omega t. And if you do double differential of this, what you are going to get is for cos omega will be minus so, minus A omega square sin omega t minus B omega square into cos omega t. So, you can see that your, it is basically simply minus omega square A sin omega t plus B cos omega t and this is nothing but X.

So, you have d2x by dt square is equal to minus omega square X, minus omega square X. So, for this kind of differential equation, for this kind of differential equation your solution is X is equal to A sin omega t plus B cos omega t again you can look at dx by dt is equal to, if you take differential of sin omega t with respect to t, you will get omega into cos omega t. So, that is what we have written A omega cos omega t for this differential will be minus B omega sin omega t.

And when you do double differential, differential of cos omega t with respect to t is minus sin omega t multiplied by omega. So, what you are going to get is A omega square with minus sign into sin your omega t and for this you will get minus B omega square cos omega t. So, this is basically minus omega square. If you take common, then you will get A sin omega t plus cos omega t.

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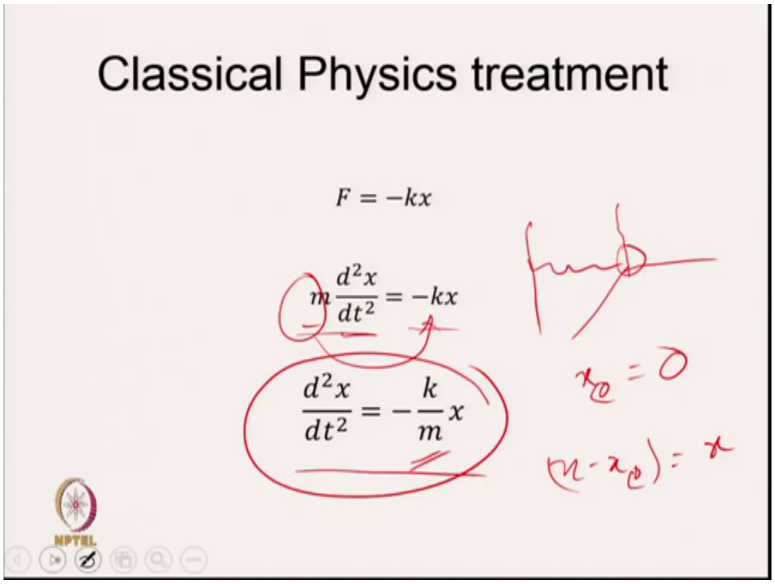

Classical Physics treatment

$$F = -kx$$

$$m\frac{d^2x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

$x_0 = 0$

$(x - x_0) = x$

So, you have this equation and if you remember, the last equation for this vibrating system is your this. So, if I put K by m is equal to omega square and I can get the solution and that is what we have done this. We have taken omega A square is equal to K by m and so, our solution is this, A X is equal to A sin omega t plus B cos omega t. And now your omega which is angular frequency will be equal to root k by m and your frequency or vibration will be equal to 1 by 2 pi root under k by m, root under K by m. So, you can get the solution for energy.

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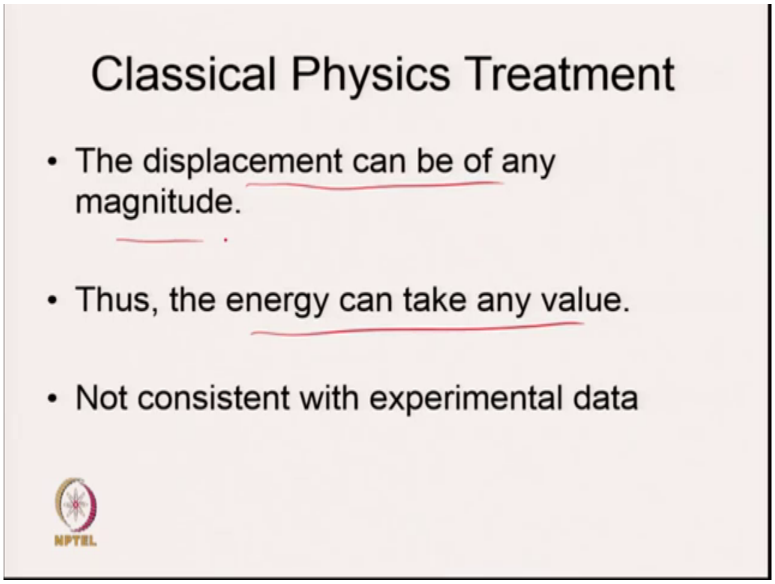

Classical Physics Treatment

- The displacement can be of any magnitude.
- Thus, the energy can take any value.
- Not consistent with experimental data

Unfortunately, what this Classical Physics Treatment tells you that energy can take any value, energy can take any value and its value will depend on displacement, displacement. Since, displacement can take any value and energy can also take any value, which is not consistent with experimental data. Because, what we know from the experimental data that energy is quantized, energy is quantized.

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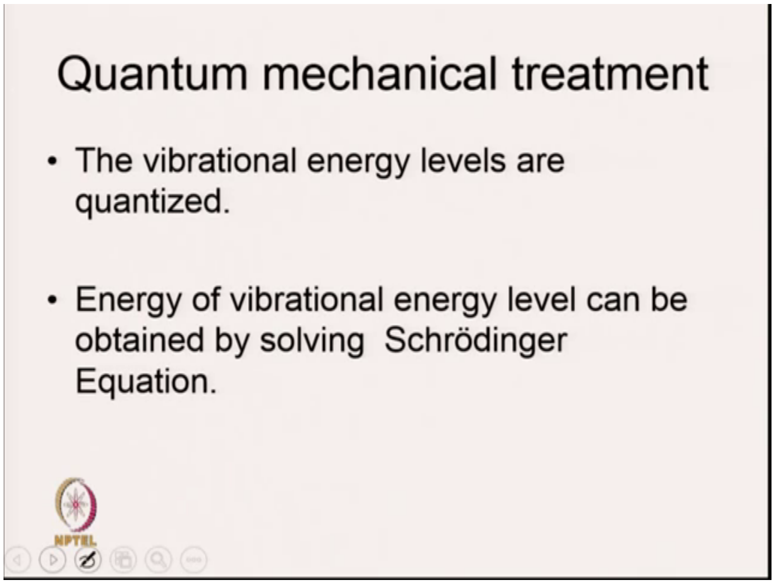

Quantum mechanical treatment

- The vibrational energy levels are quantized.
- Energy of vibrational energy level can be obtained by solving Schrödinger Equation.

And, so, Classical Physics Treatment is not enough. What we need to do is Quantum Mechanical Treatment, it is important because the vibrational energy levels are quantized and the way we can get the energy, energy of different energy levels is by solving Schrödinger equation.

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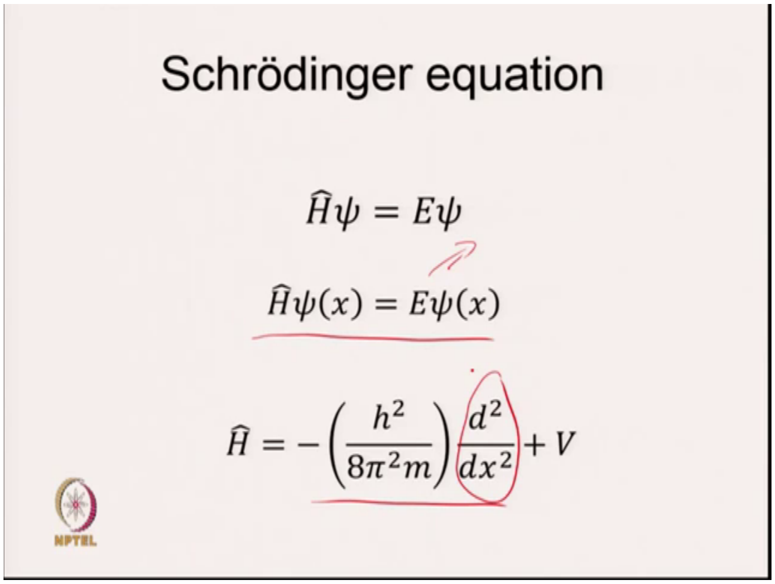

Schrödinger equation

$$\hat{H}\psi = E\psi$$

$$\underline{\hat{H}\psi(x) = E\psi(x)}$$

$$\hat{H} = -\underline{\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2}{dx^2}} + V$$

And we already note that Schrödinger equation is basically in Schrödinger equation you apply Hamiltonian operator on the wave function to get the energy as Eigen value. So, just we saw that in the, this kind of model, your psi is a function of X. We are going to apply Hamiltonian on our this wave function, vibrational wave function and then what we expect that will get the energy value. Again Hamiltonian operator has 2 different part, 1 is your kinetic energy operator and your potential energy operator and kinetic energy operator will be given by this differential. Since psi is only function of X here, so, we have only one term, where your you have a differential with respect to X. So, next step is to calculate potential energy.

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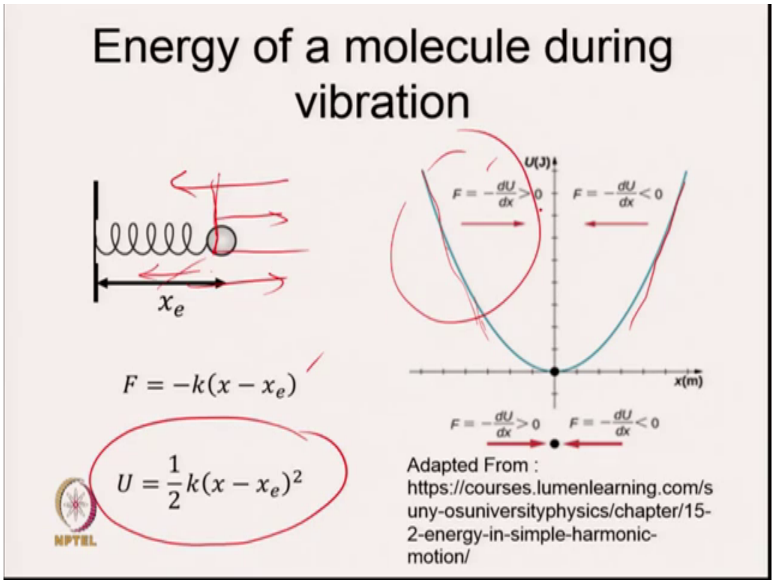

Energy of a molecule during vibration

$F = -k(x - x_e)$

$U = \frac{1}{2}k(x - x_e)^2$

Adapted From :
https://courses.lumenlearning.com/suny-osuniversityphysics/chapter/15-2-energy-in-simple-harmonic-motion/

So, we know force, force is given by minus K X minus Xe for this system. Now, we can calculate the potential energy by integrating this and integrating this with respect to X. So, your potential energy is integral minus FdX, integral minus FdX, or F is your force is basically minus dU by dX. So, dU is equal to minus FdX. So, if now you see that again here, so, what you will get is when you integrate that you will get the potential, potential energy is given by this equation U is equal to half K X minus Xe whole square.

Now, you see if I put my coordinate system such that our atom is at origin, then your Xe will be 0 and F is minus KX and your U is equal to half KX square. So, this is equation of parabola. So, if we plot U versus X you will get something like this. So, your plot of U versus X and its slope will give you F because F is equal to minus dU by dX. So, slope with negative sign will be equal to force. So, now see this if you are in this direction, your slope is positive.

So, here you are talking what X is positive, X is positive means there is like you are extending this and force will be towards left hand side So, force will be like this, ok. So, if we take slope here and you see this slope is positive and your F direction will be negative, F direction will be negative. So, this will be this side. Now, second case you can take of when you are compressing this whole system, what will happen that your since displacement is towards left hand side, your displacement is negative, displacement is negative.

So, you are dealing with, with this region, here, force will be, since displacement is in this direction your force will be in this direction, force will be different. And, if you look at the slope here, your slope is negative. And so, F is going to be positive, positive means towards the right hand direction. So, this basically tells you how potential energy changes with your displacement.

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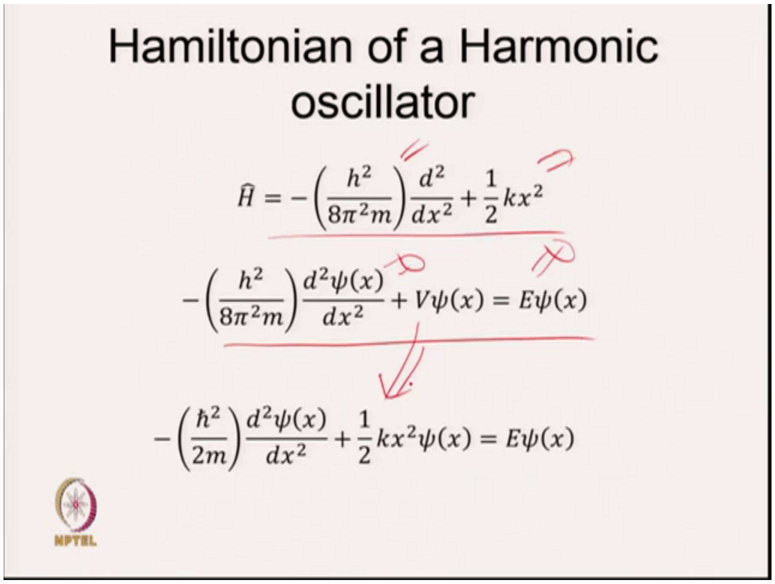

Hamiltonian of a Harmonic oscillator

$$\hat{H} = -\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi(x)}{dx^2} + V\psi(x) = E\psi(x)$$

$$-\left(\frac{\hbar^2}{2m}\right)\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

So, now we know kinetic energy operator, we know potential energy operator, now we are going to get Hamiltonian operator and finally we will apply to wave function to get the value of E. So, this is your Hamiltonian. This is kinetic energy part and this is potential energy part. When we apply to the wave function of vibrating system, we have Schrödinger equation. And if we are able to solve this we can get the energy value for different vibrational levels. So, we just put the value of potential energy half KX square and now, we need to solve this.

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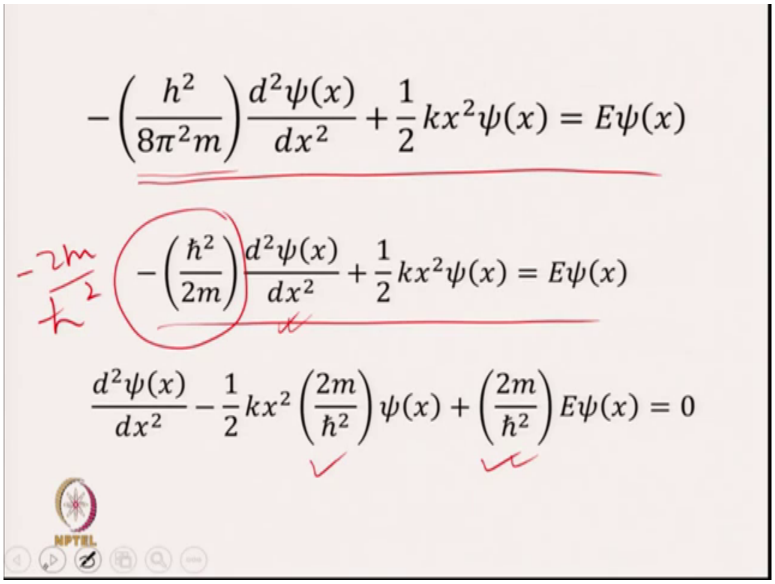

$$-\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}kx^2\psi(x)=E\psi(x)$$

$$-\frac{2m}{\hbar^2}$$

$$-\left(\frac{\hbar^2}{2m}\right)\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}kx^2\psi(x)=E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2}-\frac{1}{2}kx^2\left(\frac{2m}{\hbar^2}\right)\psi(x)+\left(\frac{2m}{\hbar^2}\right)E\psi(x)=0$$

So, this is your Schrödinger equation and the way we start solving this is to make it in the form of a known differential equation which solution is known. And the way we do it is to simplify a bit. So, what we did is here this can be h by 2 pi is h bar and so, we express this in terms of h bar to just simplify it. So, this is another form of your same Schrödinger equation. And now what we will do is we want to remove this coefficient from this double differences. So, the way we can do is simply multiply this by minus 2m by h bar square, minus 2m by h bar square and when you do that, this becomes 1 and here again you are multiplying by 2m by h bar square.

And if you bring this, this side there will be again 2m by h bar square. So, now we have a differential equation which is a bit more simplified. And now we will look for its solution, ok.

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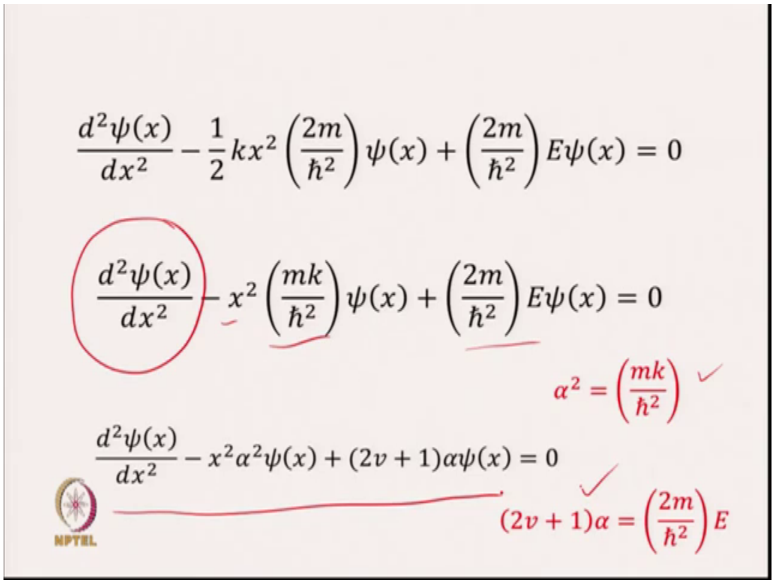

$$\frac{d^2\psi(x)}{dx^2} - \frac{1}{2}kx^2\left(\frac{2m}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\left(\frac{mk}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\alpha^2 = \left(\frac{mk}{\hbar^2}\right) \checkmark$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\alpha^2\psi(x) + (2v+1)\alpha\psi(x) = 0$$

$$\checkmark$$

$$(2v+1)\alpha = \left(\frac{2m}{\hbar^2}\right)E$$

So, the second simplification which we can do is, is simply this. So, this is the second order differential and then you can take X square terms here and the rest is mk by h bar square and similarly, you have 2m by h bar square E.

Now, if suppose we take this mk by h bar square is equal to alpha square and 2 m by h bar square is equal to v, 2 v plus 1 alpha. We will get equation. Now, question why we are doing this? Because solution of this is already known, solution of this kind of differential equation is known. By assuming that alpha square is mk by h bar square and 2v plus 1 alpha is 2m by h bar square into E. So, using this 2 we can calculate the energy.

So, first we will calculate energy and then we will get to solution of this the Schrödinger equation.

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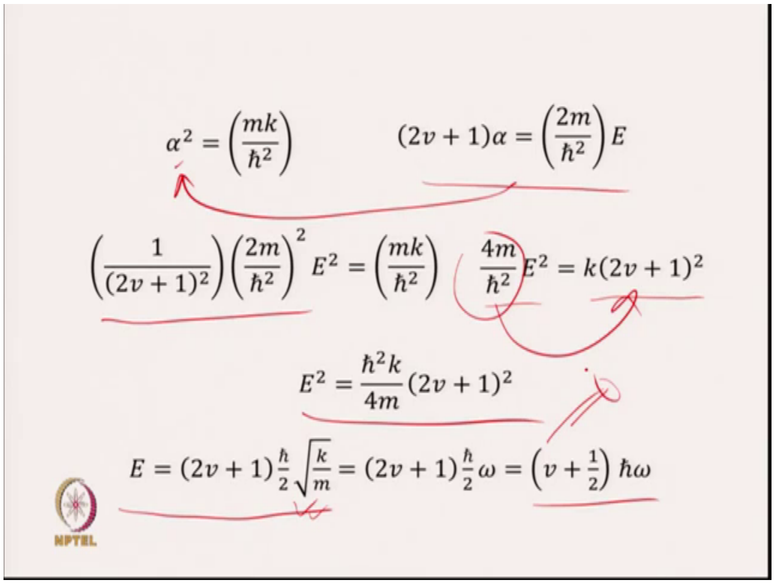

$$\alpha^2 = \left(\frac{mk}{\hbar^2}\right) \qquad (2v+1)\alpha = \left(\frac{2m}{\hbar^2}\right)E$$

$$\left(\frac{1}{(2v+1)^2}\right)\left(\frac{2m}{\hbar^2}\right)^2 E^2 = \left(\frac{mk}{\hbar^2}\right) \qquad \frac{4m}{\hbar^2}E^2 = k(2v+1)^2$$

$$E^2 = \frac{\hbar^2 k}{4m}(2v+1)^2$$

$$E = (2v+1)\frac{\hbar}{2}\sqrt{\frac{k}{m}} = (2v+1)\frac{\hbar}{2}\omega = \left(v+\frac{1}{2}\right)\hbar\omega$$

So, alpha square is mk by h bar square. And this is the second assumption which we took, 2v plus 1 alpha is 2m by h bar square into E. Now, just put in this 1. So, alpha square will be 2m by h bar square, E square divided by 2 v plus 1 square. So, this is from the second assumption is equal to mk by h bar Square. And if we cancel both side, there are some terms which are common if we cancel then what you will get is 4m by, 4m by h bar square from this term, 4 m by h bar square into E square is equal to k, 2v plus 1 square, k 2v plus 1 square and now, we can get E square.

So, E square is simply you just take to this side and you will get E square and if you just take a square root, you can get the energy and since we know that this is h bar 2 root under, root under k by m is omega. So, we can simply write 2 v plus 1 h bar by 2 omega and then your, you can also write like this v plus half h bar omega. So, this is your energy for vibrational level and v is your new quantum number, v is your new quantum number.

So, now, you can see that now energy is quantized, we can only take integer value, we can only take integer value and so, energy is quantized and this is quite different from energy which we obtained in classical physics treatment. So, this is your 1 of the advantage of quantum mechanics.

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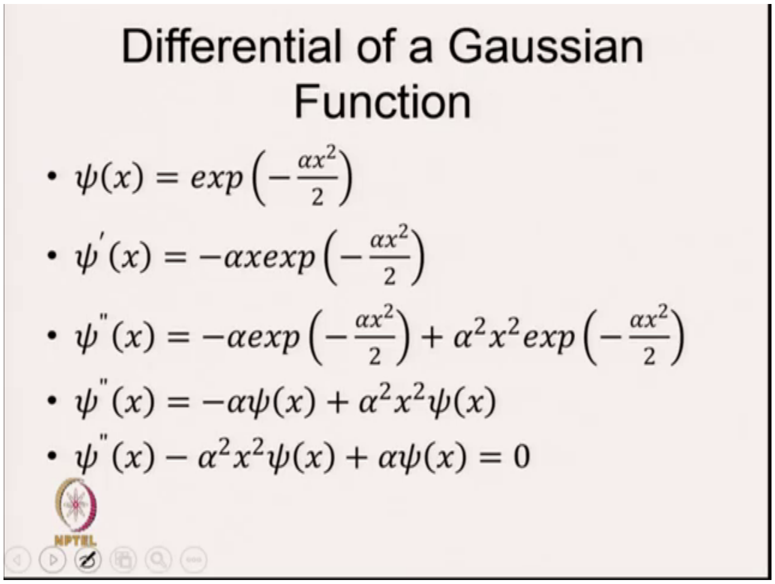

Differential of a Gaussian Function

- $\psi(x) = exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi'(x) = -\alpha x exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha exp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha\psi(x) + \alpha^2 x^2\psi(x)$
- $\psi''(x) - \alpha^2 x^2\psi(x) + \alpha\psi(x) = 0$

Now, solution of the differential equation which is just written in simplified form the solution is a Gaussian Function. So, now you can recall why we are trying to simplify it because for that differential equation already solution is known, that differential equation is basically differential of a Gaussian Function, differential of a Gaussian Function. So, let us take the first case and we are trying to solve the differential equation for v is equals 0.

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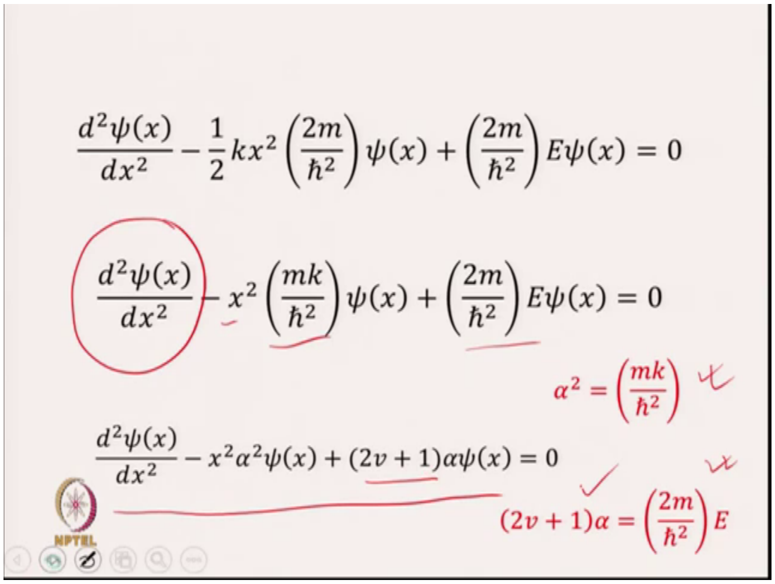

$$\frac{d^2\psi(x)}{dx^2} - \frac{1}{2}kx^2\left(\frac{2m}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\left(\frac{mk}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\alpha^2 = \left(\frac{mk}{\hbar^2}\right)$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\alpha^2\psi(x) + (2v+1)\alpha\psi(x) = 0$$

$$(2v+1)\alpha = \left(\frac{2m}{\hbar^2}\right)E$$

So, v is equal to 0 this differential equation will be, simply this will become 1, simply this will become 1.

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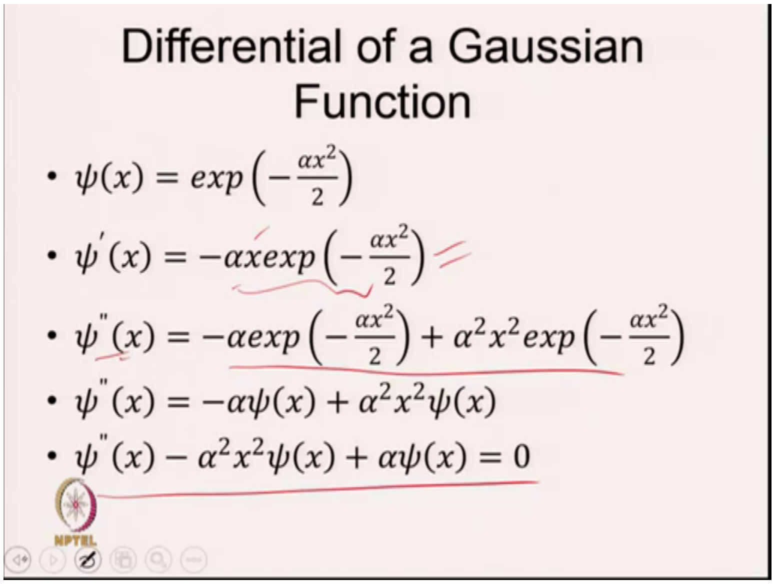

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- $\psi'(x) = -\alpha x exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha exp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha\psi(x) + \alpha^2 x^2\psi(x)$
- $\psi''(x) - \alpha^2 x^2\psi(x) + \alpha\psi(x) = 0$

Now, we can see the solution of this. So, suppose we started with psi x is equal to exponential minus alpha x square by 2. If we take the first differential, that is what we are going to get because differential of minus alpha x square by 2 is minus alpha x.

So, we will (got) get first differential is minus alpha x exponential minus alpha x square by 2. If we differentiate again with respect to x, what we are going to get is simply this. So, here first x is differentiated, taking other constant and then your x is taken as constant and then differential of this and so, you get this equation. And what you do get is the double differential is minus alpha and this is psi X, that is what we assumed here psi X plus alpha square X square psi X and this is your differential equation (())(20:29) but this is the exact differential equation when v is equal to 0, ok.

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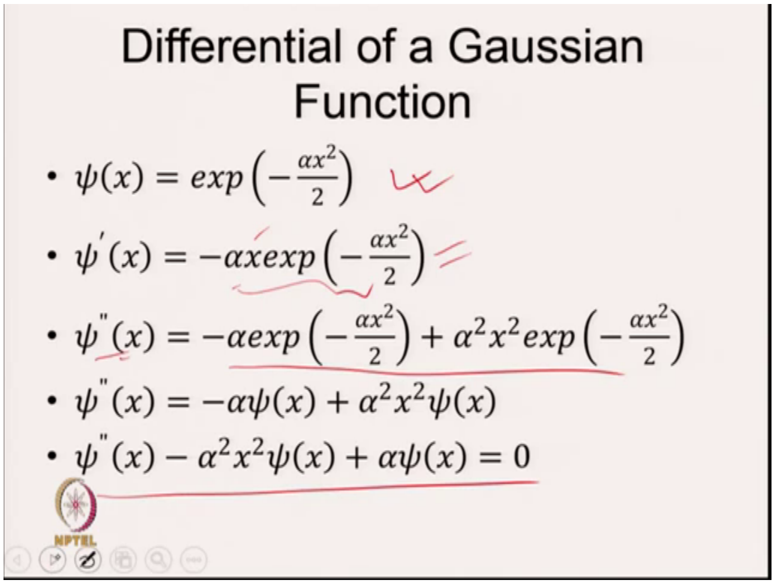

Differential of a Gaussian Function

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- $\psi''(x) = -\alpha\psi(x) + \alpha^2 x^2 \psi(x)$
- $\psi''(x) - \alpha^2 x^2 \psi(x) + \alpha\psi(x) = 0$

So, for v is equals 0, the solution is exponential minus alpha x square by 2. Now, we know what is the wave function for your ground energy level, ground or v is equal to 0.

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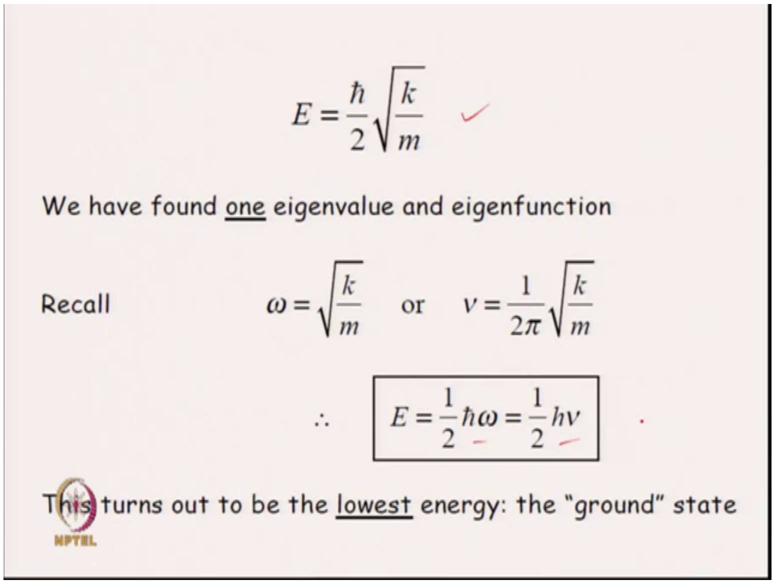

$$E = \frac{\hbar}{2}\sqrt{\frac{k}{m}}$$

We have found one eigenvalue and eigenfunction

Recall $\omega = \sqrt{\frac{k}{m}}$ or $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

$$\therefore \boxed{E = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu}$$

This turns out to be the lowest energy: the "ground" state

So, let us think about what is the energy of that. Energy is simply h bar by 2 pi k by m. So, now we have found 1 Eigen value and 1 Eigen function, omega is equal to root k by m. So, we can simply write E is equal to half h bar omega or half h nu and this is your ground state energy.

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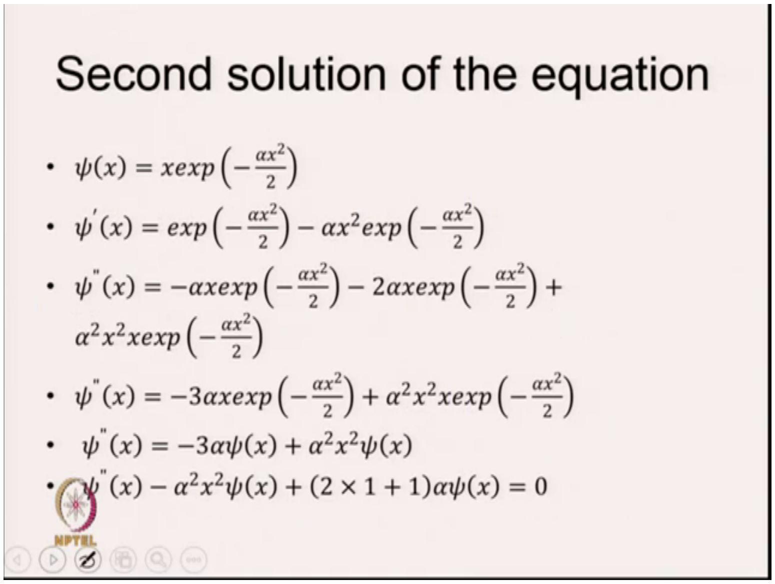
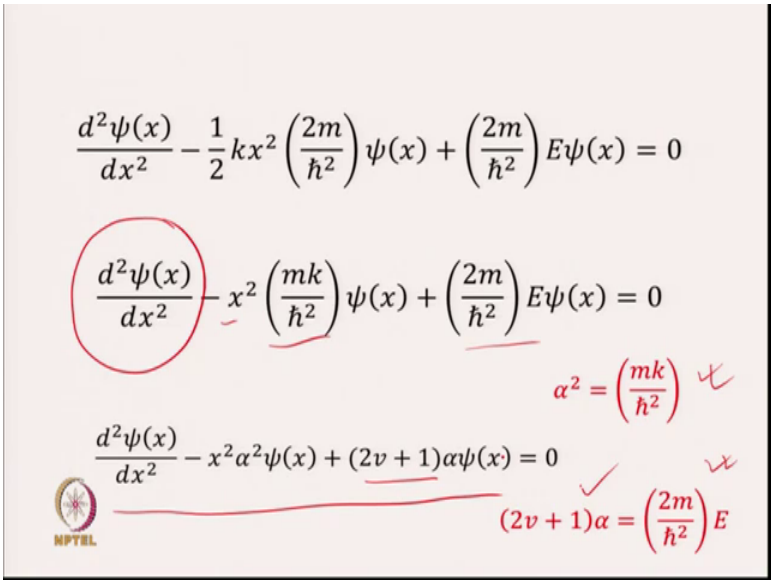


Second solution of the equation

- $\psi(x) = x\exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi'(x) = \exp\left(-\frac{\alpha x^2}{2}\right) - \alpha x^2\exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha x\exp\left(-\frac{\alpha x^2}{2}\right) - 2\alpha x\exp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 x\exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -3\alpha x\exp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 x\exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -3\alpha\psi(x) + \alpha^2 x^2\psi(x)$
- $\psi''(x) - \alpha^2 x^2\psi(x) + (2\times 1 + 1)\alpha\psi(x) = 0$



$$\frac{d^2\psi(x)}{dx^2} - \frac{1}{2}kx^2\left(\frac{2m}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\left(\frac{mk}{\hbar^2}\right)\psi(x) + \left(\frac{2m}{\hbar^2}\right)E\psi(x) = 0$$

$$\alpha^2 = \left(\frac{mk}{\hbar^2}\right)$$

$$\frac{d^2\psi(x)}{dx^2} - x^2\alpha^2\psi(x) + (2v+1)\alpha\psi(x) = 0$$

✓

$$(2v+1)\alpha = \left(\frac{2m}{\hbar^2}\right)E$$

Now, we will go to V is equal to 1 and try to see what will be the solution. So, if you remember that this is your differential equation. If I take V is equal to 1 what I am going to get is 2 into 1 plus 1 means 3 alpha psi X and now we are trying to look at the solution of this, ok.

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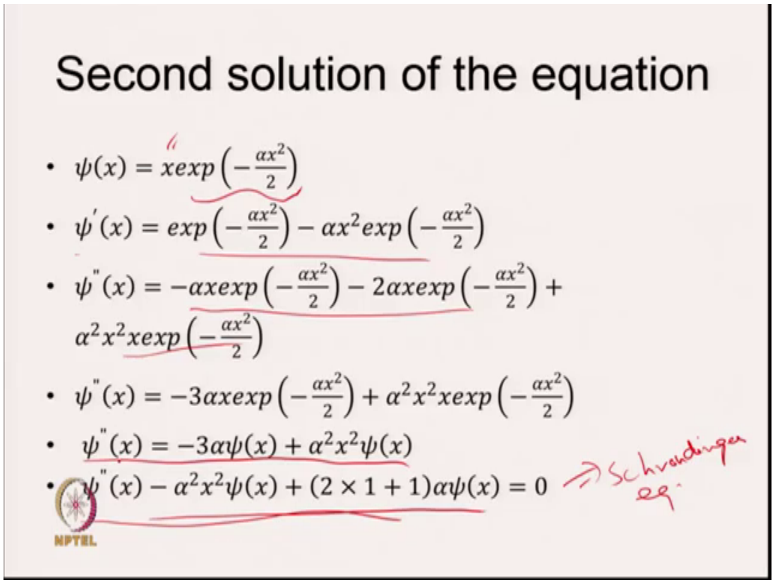

Second solution of the equation

- $\psi(x) = xexp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi'(x) = exp\left(-\frac{\alpha x^2}{2}\right) - \alpha x^2 exp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -\alpha xexp\left(-\frac{\alpha x^2}{2}\right) - 2\alpha xexp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 xexp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -3\alpha xexp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 xexp\left(-\frac{\alpha x^2}{2}\right)$
- $\psi''(x) = -3\alpha\psi(x) + \alpha^2 x^2 \psi(x)$
- $\psi''(x) - \alpha^2 x^2 \psi(x) + (2 \times 1 + 1)\alpha\psi(x) = 0$ → Schrodinger eq.

So, solution of this is again known and this is your x multiplied by exponential minus alpha X square by 2. So, it is different then e the solution for the solution, wave function of the ground state, wave function of the V is equal to 0 level was simply exponential into minus alpha x square by 2.

But, here we have another term differentiate it in the similar way, what we did for a ground state, so psi dash X, which is the first differential will be given by this equation, the double differential will be given by this. And if you simplify this, what you are going to get is psi double dash X is equal to minus 3 alpha psi X plus alpha square X square psi X and this is nothing but the differential equation for V is equal to 1, differential equation for V is equal to 1 when I put V is equal to 1 I get this.

So, this is your Schrödinger equation for vibrational level, Schrödinger equation when V is equal to 1. So, what we saw that if we have a wave function is equal X into exponential minus alpha X square by 2, we can get the solution of the wave function for V is equal to 1. Similarly, we can get solution for each of V, for example, if V is equal to 2 and you can simply write 2 into 2 plus 1 and then you solve it and solution of these things are already known.

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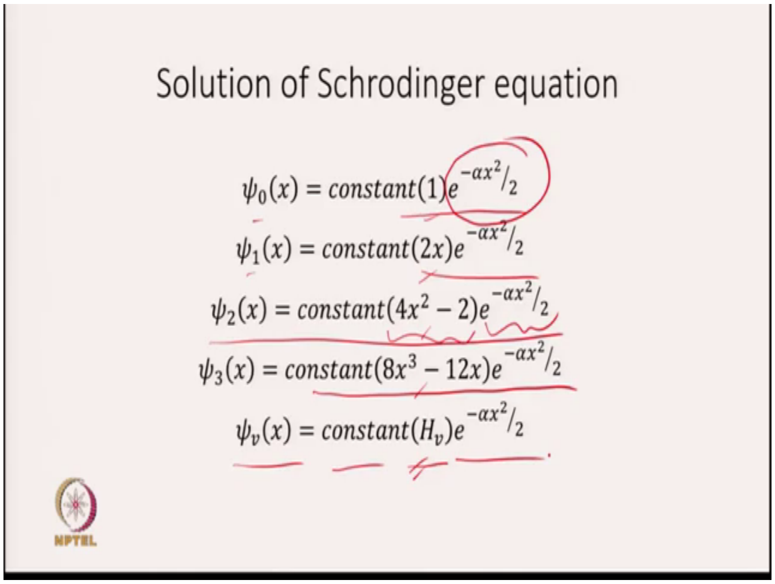

Solution of Schrodinger equation

$$\psi_0(x) = constant(1)e^{-\alpha x^2/2}$$

$$\psi_1(x) = constant(2x)e^{-\alpha x^2/2}$$

$$\psi_2(x) = constant(4x^2 - 2)e^{-\alpha x^2/2}$$

$$\psi_3(x) = constant(8x^3 - 12x)e^{-\alpha x^2/2}$$

$$\psi_v(x) = constant(H_v)e^{-\alpha x^2/2}$$

So, what we have seen is the solution of Schrödinger equation for different value of V and for V is equal to 0, it is simply constant multiplied by exponential minus alpha X square by 2. If V is equal to 1. Then, wave function is your 2 X multiplied by exponential minus alpha X square by 2. And similarly, we also looked at solution when V is equal to 2 and what we we found out is that solution is your 4 X square minus 2 multiplied by exponential minus alpha X square by 2.

Similarly, if we look at solution for V is equal to 3, your solution is constant multiplied by 8 X cube minus 12X multiplied by exponential minus alpha X square by 2. So, if you look at all solutions, for different vibrational level what you will find it that exponential minus alpha square by 2 is common, what is changing is your of function of X. So, in this case, it is simply 1. And when V is equal to 1, this is 2 X and when V is equal to 2, that is your to 4 X square minus 2 and when V is equal to 3 this function is 8 X cube minus 12X and your this function is denoted by your Hv, where H is known as Hermite Polynomial.

So, in 1 equation you can give, a 1 equation you can give the solution of wave function for level V and that will be psi VX is equal to constant multiplied by Hermite Polynomial into exponential minus alpha X square by 2. So, this Hermite Polynomial is a function of X, which will be different for different value of V, different value of V.

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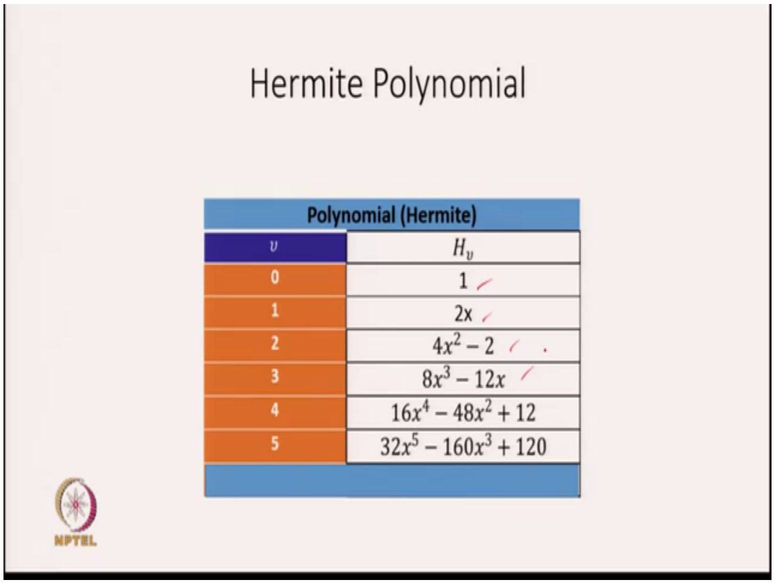

Hermite Polynomial

Polynomial (Hermite)	
v	H_v
0	1
1	2x
2	$4x^2 - 2$
3	$8x^3 - 12x$
4	$16x^4 - 48x^2 + 12$
5	$32x^5 - 160x^3 + 120$

So, when V equal to 0, Hermite Polynomial is 1 and V is equal to 1 Hermite Polynomial is 2 X, when V is equal to 2 Hermite Polynomial is 4X square minus 2 and when V is equal to 3 your Hermite Polynomial is 8 X cube minus 12X and similarly, you have different Hermite Polynomial for different value of V.

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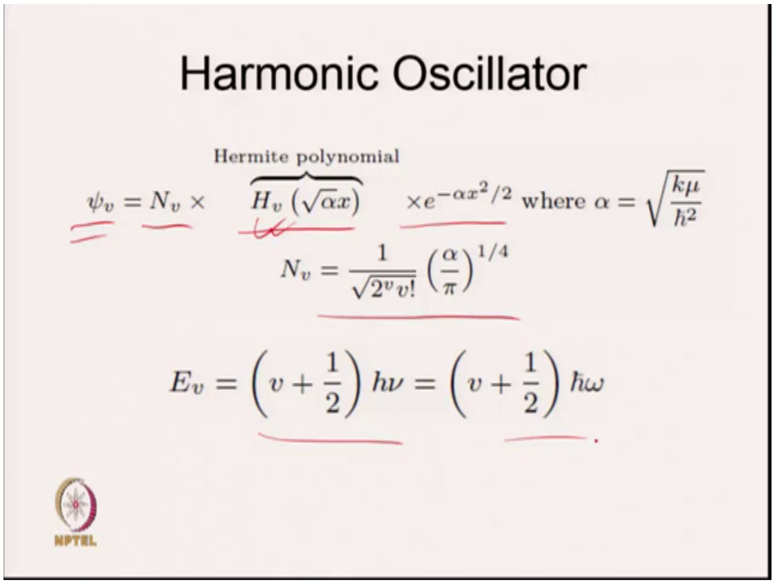

Harmonic Oscillator

$$\psi_v = N_v \times \overbrace{H_v\left(\sqrt{\alpha}x\right)}^{\text{Hermite polynomial}} \times e^{-\alpha x^2/2} \text{ where } \alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

$$N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$E_v = \left(v + \frac{1}{2}\right)h\nu = \left(v + \frac{1}{2}\right)\hbar\omega$$

So, what we have seen right now is your psi, the solution of the Schrödinger equation for vibrating system is given by Nv into Hv into exponential minus alpha x square by 2, that is what I just talked about this is called your Hermite Polynomial and Nv is equal to, your this is your normalization factor and Ev will be given V plus half h nu, V plus half h nu or V plus half h bar omega h bar omega. So, for different value of V there will be different solution, but, those solutions is related to Hermite Polynomial and energy for those vibrational level can be given V plus half h nu.

So, and V is your vibrational quantum number and again you can see that since we can only take integer values. So, energy your vibrational levels are quantized.

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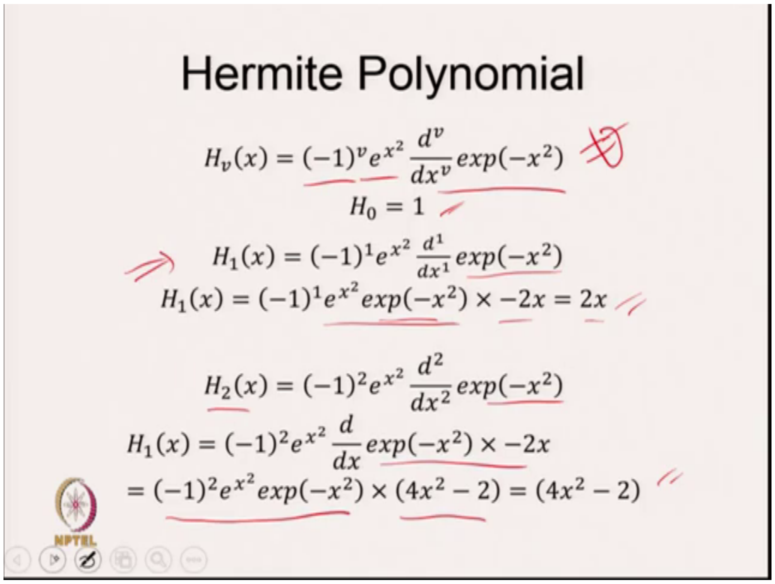

Hermite Polynomial

$$H_v(x) = (-1)^v e^{x^2} \frac{d^v}{dx^v} exp(-x^2)$$

$$H_0 = 1$$

$$H_1(x) = (-1)^1 e^{x^2} \frac{d^1}{dx^1} exp(-x^2)$$

$$H_1(x) = (-1)^1 e^{x^2} exp(-x^2) \times -2x = 2x$$

$$H_2(x) = (-1)^2 e^{x^2} \frac{d^2}{dx^2} exp(-x^2)$$

$$H_1(x) = (-1)^2 e^{x^2} \frac{d}{dx} exp(-x^2) \times -2x$$

$$= (-1)^2 e^{x^2} exp(-x^2) \times (4x^2 - 2) = (4x^2 - 2)$$

Now, we will discuss about Hermite Polynomial a little bit. So, Hermite Polynomial is basically given by 1 single equation and that is written here. What is that, it is simply minus 1 power V and then exponential X square multiplied by this differential. Now, you can think of if V is equal to 0 then what will happen this will be 1 and this whole thing, this will be 1 and so, everything will be 1 and what get is 1, when we solved the Schrödinger equation and for V is equal to 0 Hermite Polynomial was 1.

For the V is equal to 1 you can again solve this and this is minus 1 power 1 ex square d by dx exponential minus x square. And if you differentiate this, what you will get i exponential minus Xsquare into minus 2X and minus 1 power 1 and this 2 becomes 1, these are exponential multiple of 2 exponential and this becomes 1. So, what you get is simply 2X.

Similarly, we can get Hermite Polynomial for second vibrational level by again solving this equation, so minus 1 square ex square d 2 by dx square exponential minus X square. So, first you will get same term. So, this is the exponential minus X square into minus 2 X and now you have to differentiate again and what you will again get is this terms multiplied by 4 X square minus 2 and this comes out to be 1, so, you have 4 X square minus 2. And so, if you remember that Hermite Polynomial which we solved was for V is equal to 0 it was 1 and for V is equal to 1 it was 2 X and for V is equal to 2 plus 4 X square minus 2. So, Hermite Polynomial can be given by 1 simple equation, which is shown here, shown here, ok.

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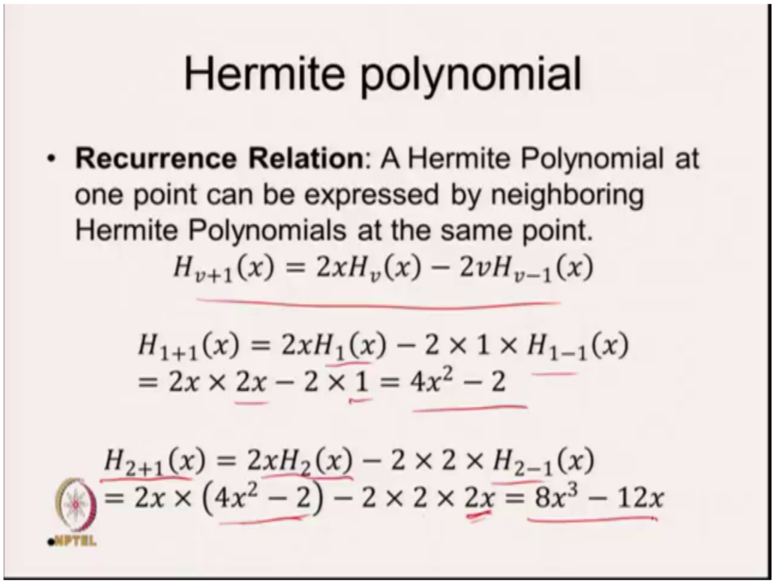

Hermite polynomial

- **Recurrence Relation**: A Hermite Polynomial at one point can be expressed by neighboring Hermite Polynomials at the same point.

$$H_{v+1}(x) = 2xH_v(x) - 2vH_{v-1}(x)$$

$$H_{1+1}(x) = 2xH_1(x) - 2 \times 1 \times H_{1-1}(x)$$
$$= 2x \times 2x - 2 \times 1 = 4x^2 - 2$$

$$H_{2+1}(x) = 2xH_2(x) - 2 \times 2 \times H_{2-1}(x)$$
$$= 2x \times (4x^2 - 2) - 2 \times 2 \times 2x = 8x^3 - 12x$$

There is another property of this Hermite Polynomials and they have a Recurrence Relationship. What does that mean? That if you know 2 previous Hermite Polynomial then you can get the next Hermite Polynomial. So for example, if you know Hermite Polynomial for V is equal to V and for V is equal to V minus 1, then you can get Hermite Polynomial for the V plus 1 level and the equation is here.

So, Hermite Polynomial for V plus 1 level is given by 2 X into Hermite Polynomial for level V minus 2 V Hermite Polynomial for a level V minus 1. So, for example, if I want to calculate Hermite Polynomial for V is equal to 2, then we can take help of Hermite Polynomial for level 1 and for level 0 and we know that Hermite Polynomial for level 0 is 1 and Hermite Polynomial for level 1 is 2 X. So, we can calculate Hermite Polynomial for level 2.

So, now see here that, we are calculating here for the level 2. So, 2 X into Hermite Polynomial for level 1 minus 2 into 1 into Hermite Polynomial for level 0 and now put Hermite Polynomial for level 1. We know that the value is 2 X, and Hermite Polynomial for level 0 is 1, so, you just put it here and what you can be able to get is Hermite Polynomial for level 2. And this is for X square minus 2. Similarly, by using Hermite Polynomial for level 1 and Hermite Polynomial for level 2, you will be able to get the Hermite Polynomial for level 3.

And that is what we have done here that we are calculating Hermite Polynomial for level 3. And this is, this can be expressed in terms of Hermite Polynomial for level 2 and Hermite Polynomial for level 1. We know Hermite Polynomial for level 2 is 4 X square minus 2 and Hermite Polynomial for level 1 is 2 X, so we simply multiply 2 X into Hermite Polynomial for level 2 minus 2 into the V into Hermite Polynomial for level 1 and when we do that, we can get Hermite Polynomial for level 3 and that is equal to 8 X cube minus 12 X, 8 X cube minus 12 X.

So, this kind of, this, Polynomial has some very important features which we need to keep into mind. But, by solving the differential equation coming out from Schrodinger equation, we can calculate what will be the wave function corresponding to a particular vibrational level and what can be the energy for the, for that vibrational level. And, we can calculate energy of transition.

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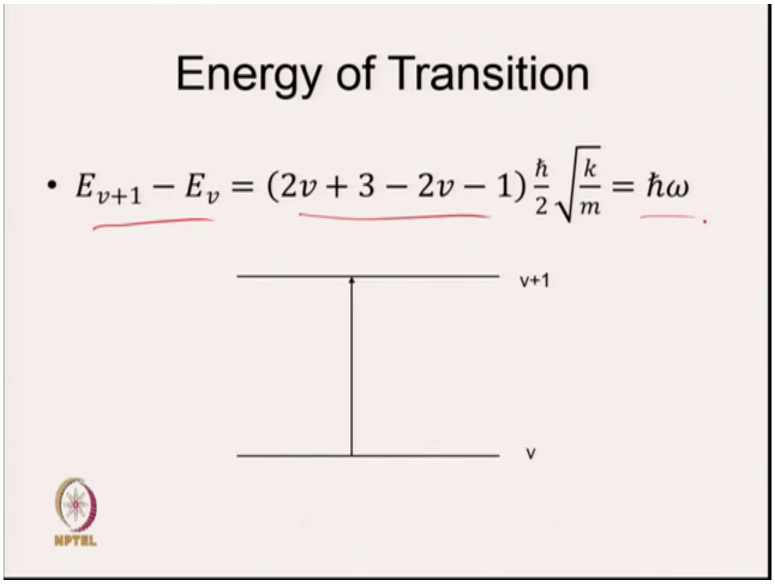

Energy of Transition

- $\underline{E_{v+1} - E_v} = (\underline{2v + 3 - 2v - 1})\frac{\hbar}{2}\sqrt{\frac{k}{m}} = \underline{\hbar\omega}$

And that is equal to your; if suppose you are going from the transition is from the level V to level V plus 1 then we can simply get Ev plus 1 minus Ev and if you do that, this comes out to 2v, we will see that 2v 2v cancels out 3 minus 1 will give you 2.

So, 2 2 cancels out, so this is simply h bar and under root k by m, where your (k) root under k by m is omega. So, your delta E will be equal to h bar omega, h bar omega.

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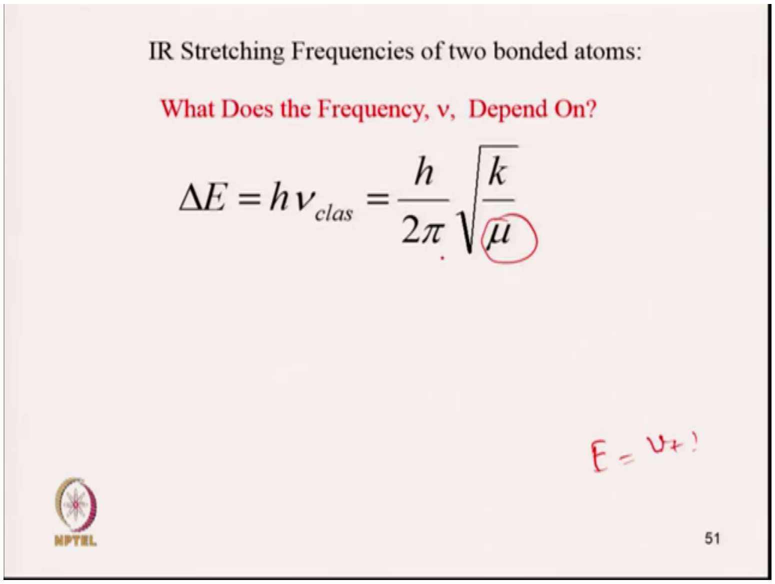

IR Stretching Frequencies of two bonded atoms:

What Does the Frequency, ν, Depend On?

$$\Delta E = h\nu_{clas} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$E = v+1$

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So, for transition between 2 allowed levels, your delta E is going to be h by 2 pi root under k by mu. Here we have replaced m by mu because we are dealing with more than 1 atom and here mu is reduced mass and k is again force constant so, h by 2 pi root under k by mu. So, frequency of transition is going to depend on mu and k.

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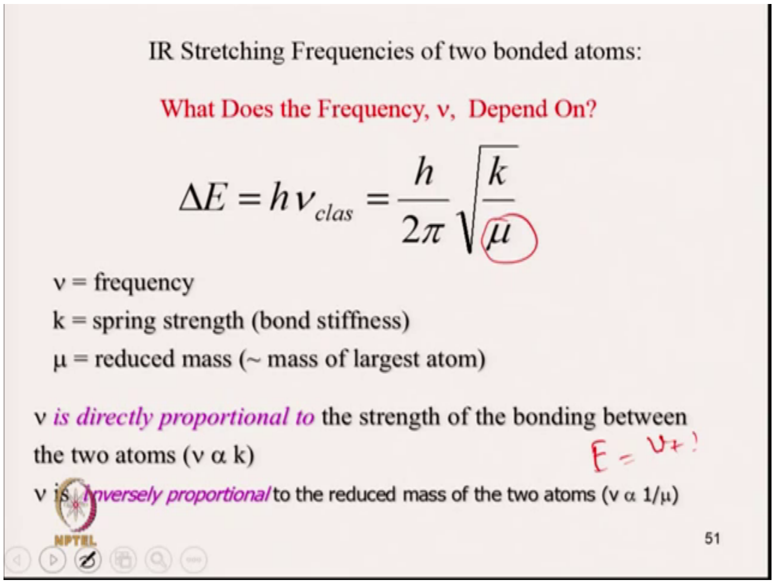

IR Stretching Frequencies of two bonded atoms:

What Does the Frequency, ν, Depend On?

$$\Delta E = h\nu_{clas} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

ν = frequency
k = spring strength (bond stiffness)
μ = reduced mass (~ mass of largest atom)

ν *is directly proportional to* the strength of the bonding between the two atoms (ν α k)

$E = \nu +$!

ν is *inversely proportional* to the reduced mass of the two atoms (ν α 1/μ)

So, nu is equal to frequency, mu is equal to reduced mass, k is equal to spring strength and here we can relate it to bond stiffness. So, if bond is stiffness is high what does that mean k is high and so nu will be high. And if mu is greater, then your nu is going to be low. So, nu is directly proportional to the strength of bonding between 2 atoms where nu is inversely proportional to reduced mass of two atoms. This is very important because this explains why frequency is high, why frequency is low.

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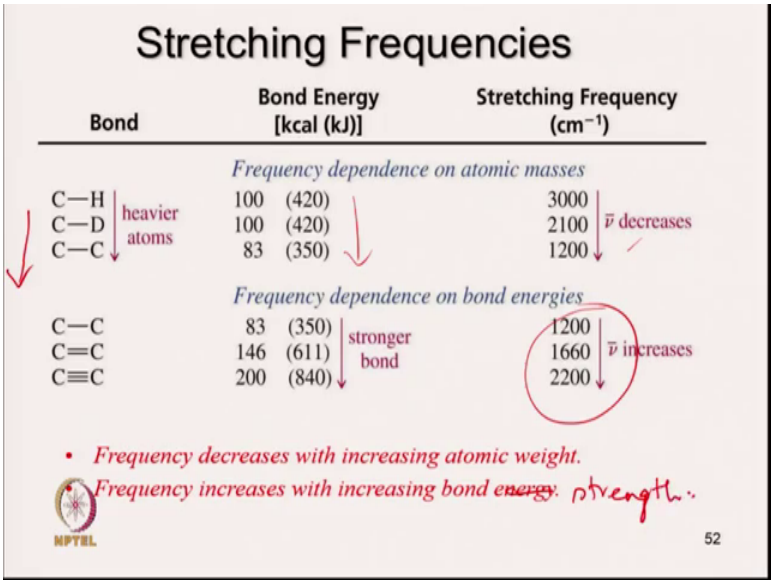

Stretching Frequencies

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm^{-1})
	Frequency dependence on atomic masses	
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
	Frequency dependence on bond energies	
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200

- *Frequency decreases with increasing atomic weight.*
- *Frequency increases with increasing bond ~~energy~~.* strength..

So, let us discuss some example. So, here we are talking about a Stretching Frequency. So, let us think about stretching frequency of CH bond, CD bond and CC bond. And as we know that your atomic weight of C is higher than deuterium, which is higher than hydrogen. So, as we go down from CH to CC, from CH to CC your mu value is going to increase and if mu value is going to increase, what you expect that, nu will decrease, ok.

So, nu will decrease or delta E will decrease. So, here you see that delta E value in kilo cal and this is the the second value and parentheses in kilo Joule. So, this is decreasing with increase in value of reduced mass. And that is why your wave number is also decreasing, wave number is also decreasing and this is in centimeter inverse, so you are going from 3000 to 1200, ok. We will look at the effect of K, it is Bond stiffness and as we know that bond stiffness is going to be higher, if you move from single to triple bond.

So, triple bond is more is stronger compared to double bond and double bond is more stronger compared to single bond and so, energy is going to increase with increase in k value. Because if you remember energy is proportional to root under k and your wave number is again going to increase with increase in the stiffness, increase in the stiffness. So, there are 2 very important factor, first is your k which relates to Bond stiffness, where second is your nu which relates to atomic mass of an atom, ok and mu is basically your reduced mass.

So, frequency decreases with increasing atomic weight and frequency increases with increasing bond strength, increasing bond strength. So, here it is bond strength. Since, frequency in IR spectroscopy is dependent on k and mu, this can be utilized to know the functional group up the compound, given compound and that can help you in the structure determination of unknown compound.

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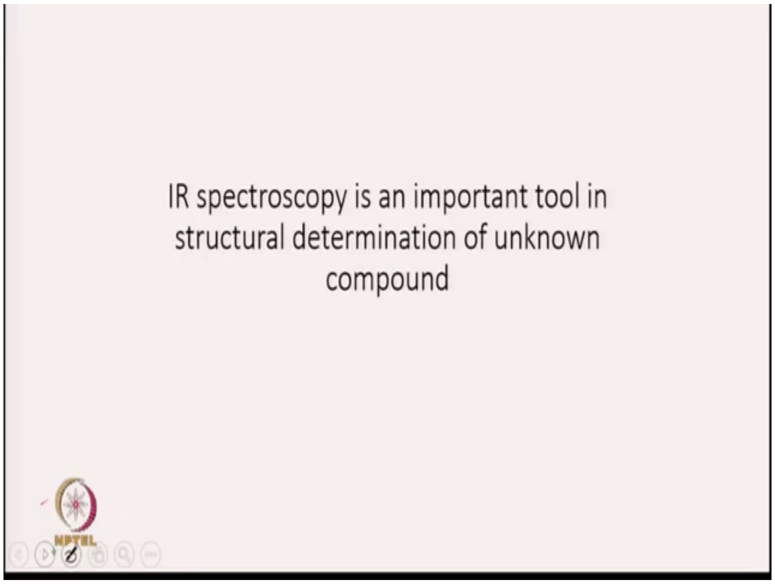
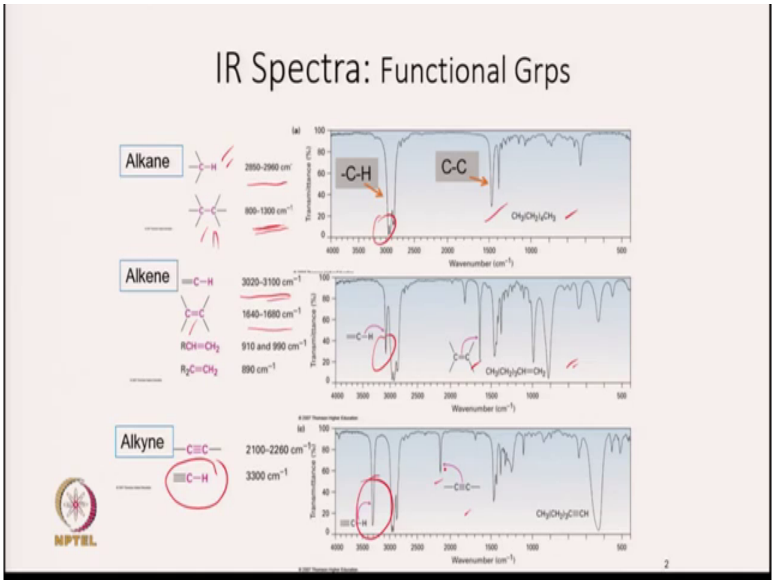


IR spectroscopy is an important tool in structural determination of unknown compound



IR Spectra: Functional Grps

We will see some of the examples. So, here we have IR spectra of alkane, alkene and alkyne and we have your hexane, 1 hexene and 1 hexyne. And now, you can see that in case of alkane, we can look at 2 different frequencies, 1 corresponding to CH bond and other corresponding to CC bond. CC bond. And now, you see that when you go from CH bond to CC you are basically replacing 1 hydrogen by another carbon. And so, what you expect is nu is going to be higher in case of CC bond, nu is going to be higher in case of CC bond and thus frequency is going to be lower for the CC bond compared to CH bond, compared to CH bond. Since, your frequency is inversely proportional to your reduced mass, reduced mass and reduced mass is higher for CC bond in comparison to CH bond.

Now, if we go from alkane to alkene, what we can see is that this CH frequency is moving to higher wave number, moving to higher wave number and this is related to the fact that if k increases for a bond, then frequency will increase, k is related to bond strength, k related to bond strength and CH bond strength is higher when H is attached to SP2 carbon, comparison to when H is attached to SP3 carbon, H is attached to SP3 carbon.

So, CH bond strength is higher and thus higher in alkene and so, your wave number is going to be at higher number. Same is the case when you move from CC bond in alkane to CC bond in alkene, CC bond in alkene. So, here there is a double bond between C and C in case of alkene and so, bond strength between C and C will be higher in case of alkene in comparison to alkane and so, your wave number is going to be higher and that is why you can see that CC bond in alkane is that frequency 800 to 1300 centimeter inverse, where C double bond C in alkene comes at 1640 to 1680 centimeter inverse.

Similarly, if you move towards alkyne, C triple bond C is certainly going to be of higher bond strength comparison to C double bond C and which is higher, which is higher in bond strength in comparison to CC single bond. And so, when we move from CC bond, when we move from CC bond of alkane to CC bond of alkyne, there is increase in the wave number. And similarly the case with hydrogen attached to your SP carbon, so, hydrogen attached, when hydrogen is attached to SP carbon, the bond is strength of CH bond is going to be higher in comparison to when hydrogen is attached to your SP2 carbon or SP3 carbon.

Since, SP carbon, in SP carbon your percentage, (())(41:52) strength is higher in case of your SP carbon and so SP carbon is more electronegative and thus, electro negativity difference between SP carbon and hydrogen is highest and your bond strength is higher. Now, you see in the spectroscopy, this is your CH for alkane and that comes out to be within this range. And then if you go to alkene it is moving towards left hand side which is towards higher wave number.

You see it is here, here and then in alkyne CH frequency is at higher number. So, there is a shift of CH frequency from lower to higher when we move from alkane to alkene and to alkyne and similarly the case of CC and you will see this is CC for alkane, this is CC for your alkene and this is CC bond for alkyne. And you see this is going towards higher wave number side. So, just by looking at your CH frequency and CC frequency, you can distinguish between 3 different kind of hydrocarbons.

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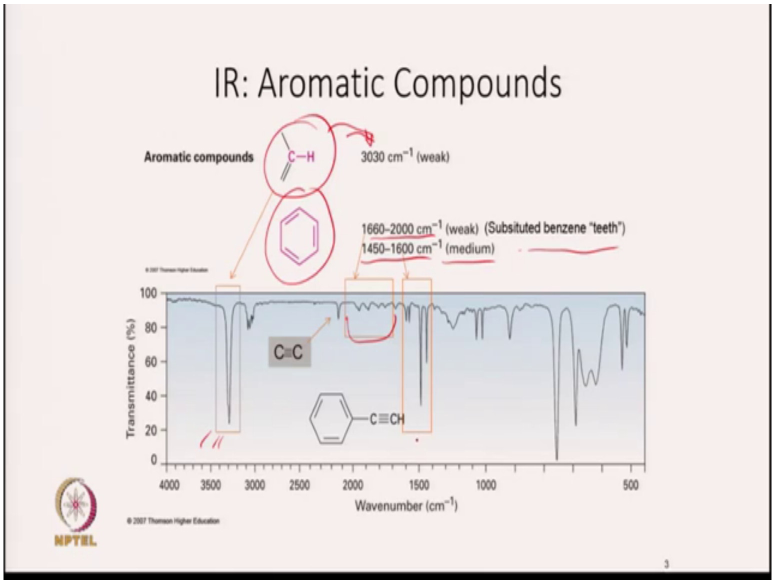

IR: Aromatic Compounds

Aromatic compounds has benzene ring and benzene ring has some characteristic features which you can see in the IR spectra and so, to know that where the compound or whether the molecule has benzene ring or not IR can be utilized, IR can be utilized. And if you look at the benzene, so, there will be like this kind of bond and this comes around your 30 30 centimeter inverse, 30 30 centimeter inverse which is here. So, this is characteristic of your benzene ring, this is characteristic of benzene ring.

What you are looking at is phenyl acetylene, phenyl acetylene has benzene ring and so, you will get 1 peak around 30 30 centimeter inverse. And then you have like some peaks between 1660 to 2000 centimeter inverse and that is that are quite big and they are called when 'benzene teeth', benzene teeth and you can see this these are those peaks, these are those peaks and this is typical of substituted benzene and then you have some medium range peaks or peaks with medium intensity which comes between 1450 to 1600 centimeter inverse and that you can see here.

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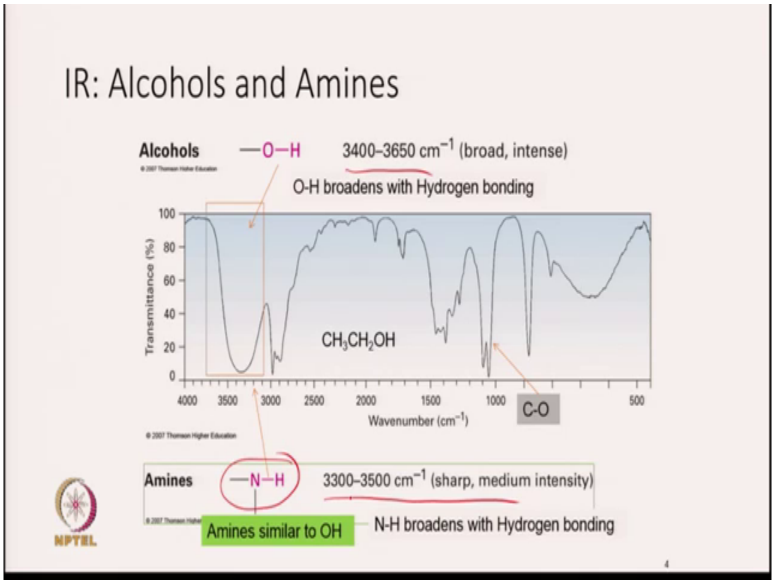

IR: Alcohols and Amines

Alcohols —O—H 3400–3650 cm^{-1} (broad, intense)

O-H broadens with Hydrogen bonding

Amines —N—H 3300–3500 cm^{-1} (sharp, medium intensity)

Amines similar to OH

N-H broadens with Hydrogen bonding

Alcohol, (ami) amines has characteristic peak which can be observed in IR spectroscopy. So, for alcohol, you will get a peak around 3400 to 3650 centimeter inverse and they typically broaden with hydrogen bonding. So, a broaden peak, a very broaden peak around this 3400 to 3650 centimeter inverse indicates not only OH bonding but, but also OH undergoing hydrogen bonding, undergoing hydrogen bonding. Similarly, NH can be seen by your sharp medium intensity peak around 3300 to 3500 centimeter inverse. So, as very sharp peak at 3300 to 3500 centimeter can indicate towards amine functional group in the compound.

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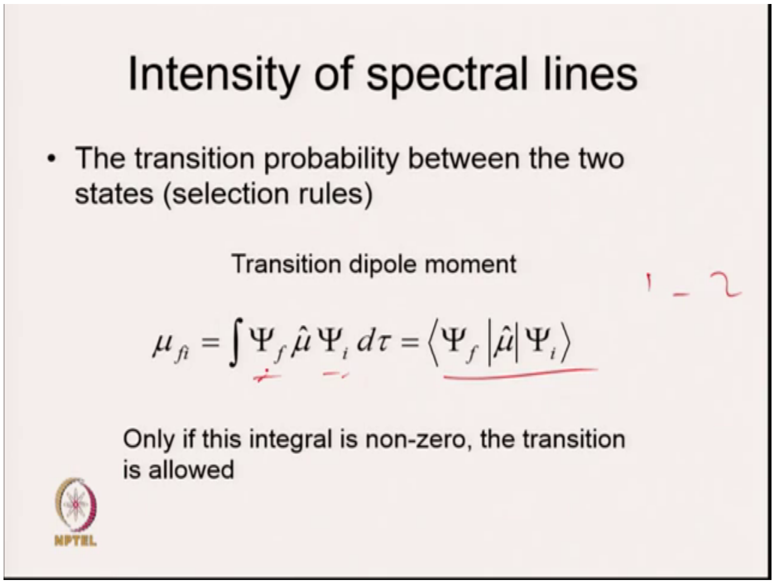

Intensity of spectral lines

- The transition probability between the two states (selection rules)

Transition dipole moment

1 – 2

$$\mu_{fi} = \int \Psi_f \hat{\mu} \Psi_i \, d\tau = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle$$

Only if this integral is non-zero, the transition is allowed

Now, on what factor intensity of a spectral lines depend? We have already discussed that what are the different factor on which intensity can depend. One is your based on transition dipole moment and second is based on your Boltzmann distribution. So, here we will just discuss your transition dipole moment for vibrational transition, but transition probability between 2 state is given by your phi final to initial state.

So, here function of final state and function of your initial state multiplied by your what is known as Transition dipole moment, ok and this is also shown by this notation. If this integral in non-zero then transition is allowed, if it is 0 then that is not allowed. So, here we will use vibrational wave function. So, suppose we are going from V is equal to 1 to V is equal to 2 then you have to take wave function of the second vibrational state and first vibrational state. So, you are going from 1 to 2. So, then this will be psi 1 and this will be psi 2. So, psi 2 into mu operator multiplied by psi 1 d tau, if this is non-zero then your transitions are allowed, ok.

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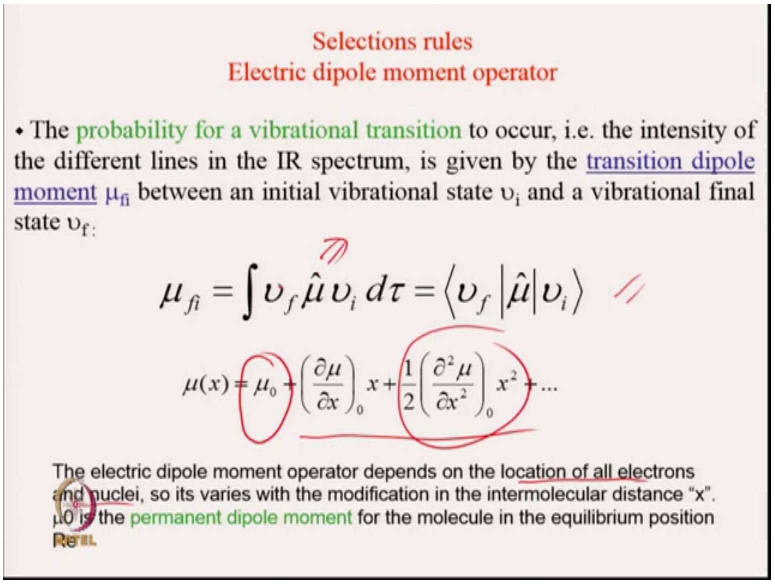

Selections rules
Electric dipole moment operator

- The probability for a vibrational transition to occur, i.e. the intensity of the different lines in the IR spectrum, is given by the transition dipole moment μ_{fi} between an initial vibrational state υ_i and a vibrational final state υ_f:

$$\mu_{fi} = \int \upsilon_f \hat{\mu} \upsilon_i \, d\tau = \langle \upsilon_f | \hat{\mu} | \upsilon_i \rangle$$

$$\mu(x) = \mu_0 + \left(\frac{\partial \mu}{\partial x}\right)_0 x + \frac{1}{2}\left(\frac{\partial^2 \mu}{\partial x^2}\right)_0 x^2 + \dots$$

The electric dipole moment operator depends on the location of all electrons and nuclei, so its varies with the modification in the intermolecular distance "x". μ0 is the permanent dipole moment for the molecule in the equilibrium position

So, again transition dipole moment is given by this. I already discuss about that. Now, here transition dipole moment is a function of x, function of x. So, it depends on location of all electron and nuclei when it is inter molecular distance or we can say that if it is in equilibrium position then mu is given by mu naught which is basically permanent dipole moment, but this is when it deviates from the equilibrium position. So, your mu is equal to mu naught plus del mu by del x this is first derivative of mu with respect to x, multiply by x and then this is the second term. We will just put it here and see what happens.

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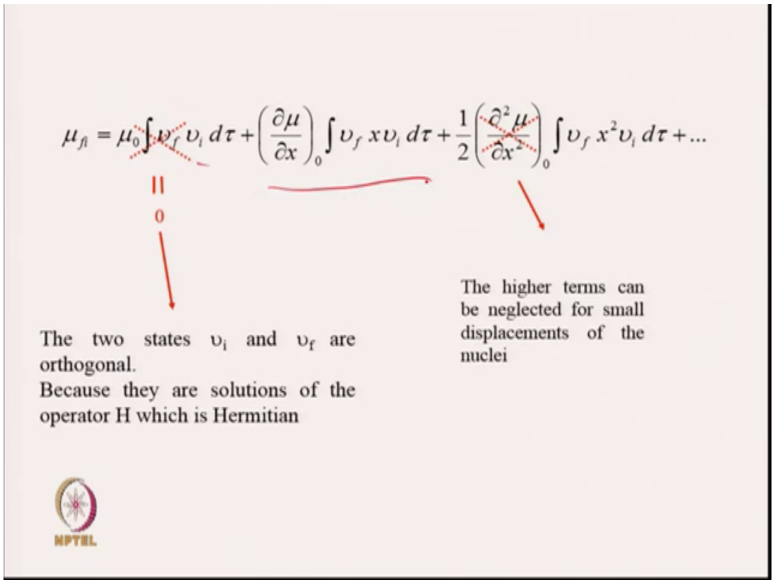

$$\mu_{fi} = \underbrace{\mu_0 \cancel{\int \upsilon_f} \upsilon_i \, d\tau}_{= 0} + \underline{\left(\frac{\partial \mu}{\partial x}\right)_0 \int \upsilon_f \, x \, \upsilon_i \, d\tau} + \frac{1}{2}\left(\cancel{\frac{\partial^2 \mu}{\partial x^2}}\right)_0 \int \upsilon_f \, x^2 \upsilon_i \, d\tau + \ldots$$

The two states υ_i and υ_f are orthogonal.
Because they are solutions of the operator H which is Hermitian

The higher terms can be neglected for small displacements of the nuclei

So, if you do that, again, we replaced psi F by VF just denote wave function of vibrational state and this is your I initial state. So, let us go back. And you see here, if I put this mu naught mu naught is constant it will come out and you left with VF Vi d tau, VF Vi d tau. So, that is what we are getting mu naught VF Vi d tau plus del mu by del x 0 VF X VI d tau. This is the second term and the third term which we are going to neglect. If we assume that there is small displacement from equilibrium position then we can neglect the higher terms, ok.

Now, we know that the 2 wave function, vibrational wave function are orthogonal, so, they are integral of VF Vi which is basically wave function of final vibrational state is VF and VI is the wave function of initial vibrational state. So, this is going to be 0 and if this is going to be 0 so you are left with 1 term and this should not be 0 if the transition is allowed, ok.

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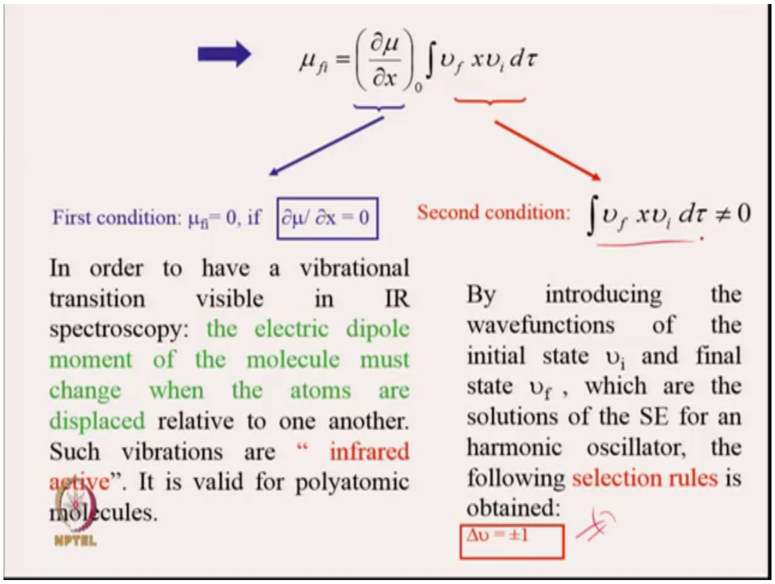

$$\mu_{fi} = \underbrace{\left(\frac{\partial \mu}{\partial x}\right)_0} \underbrace{\int \upsilon_f x \upsilon_i d\tau}$$

First condition: $\mu_{fi} = 0$, if $\boxed{\partial\mu/\partial x = 0}$

In order to have a vibrational transition visible in IR spectroscopy: the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are " infrared active". It is valid for polyatomic molecules.

Second condition: $\int \upsilon_f x \upsilon_i d\tau \neq 0$

By introducing the wavefunctions of the initial state υ_i and final state υ_f, which are the solutions of the SE for an harmonic oscillator, the following selection rules is obtained:

$\boxed{\Delta\upsilon = \pm 1}$

So, this is your the second term and what I told you that this should not be 0. If transition is allowed. This can be 0 del mu by del x are (())(49:44) is 0. What does that mean is if suppose this is 0, then everything is going to be 0. So, this should not be 0. What does that mean? What does this represent?

This represent that if x changes mu is not changing, x changes mu is not changing. So, if it is not changing it means del mu by del x is equal to 0. If it is changing, then it will not be 0. So, first selection rule is that electric dipole moment of molecule must change and the atoms are displaced related to 1 another and that is called your if it happens then such vibration are known as ‘infrared active’, ok, it is valid for polyatomic molecule, certainly.

The second thing is now, the second term mu can be 0 if second term is 0 so, this should not be 0. And if we solve this what selection will we get is delta V is equal to plus minus 1. For delta V is equal to plus minus 1 this integral is not going to be 0, this integral which I am talking about is not going to be 0 and that is why this is another selection. So, there are 2 part of the selection rule,1 is your electric dipole moment of the molecule must change during vibration and the second is delta v is plus minus 1.

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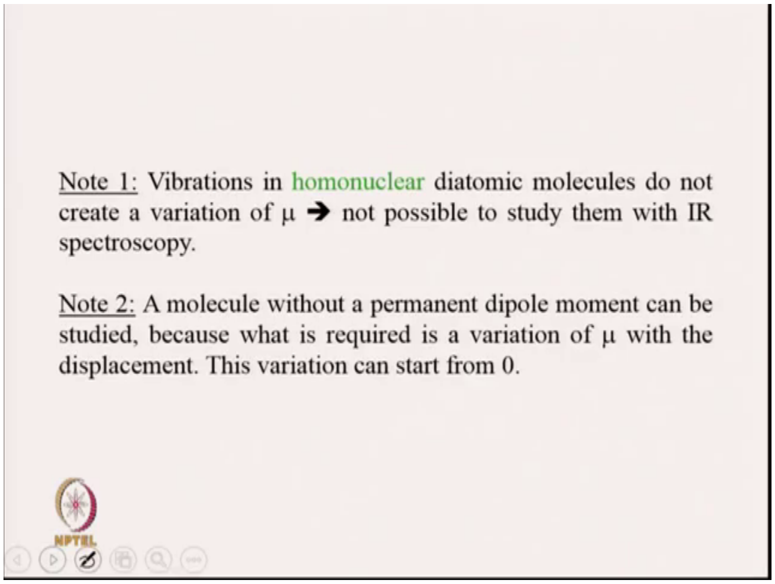

Note 1: Vibrations in homonuclear diatomic molecules do not create a variation of μ ➔ not possible to study them with IR spectroscopy.

Note 2: A molecule without a permanent dipole moment can be studied, because what is required is a variation of μ with the displacement. This variation can start from 0.

So, that is what is well known selection rule for vibrational spectroscopy that vibration in homo-nuclear diatomic molecule generally does not create variation in mu. So, you cannot study them with IR spectroscopy, Ok. For homo-nuclear diatomic molecule, because what selection rules tells that it, must your dipole moment must change during vibration then only you can see, then only that transition is allowed.

So, a molecule without a permanent dipole moment can be studied. So, it does not mean that we cannot study any molecule, which does not have permanent dipole moment. What matters is that your dipole moment must change during vibration, during vibration. So, for example in the case of carbon dioxide if you take anti stretching, where one is going extended and other is getting compressed then there will be change in dipole moment during vibration, although it does not have a permanent dipole moment and so this can be study through IR spectroscopy.

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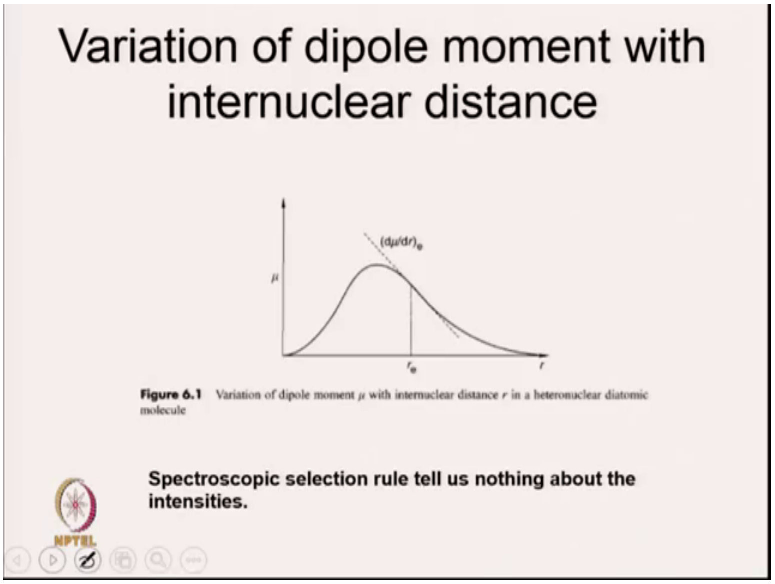
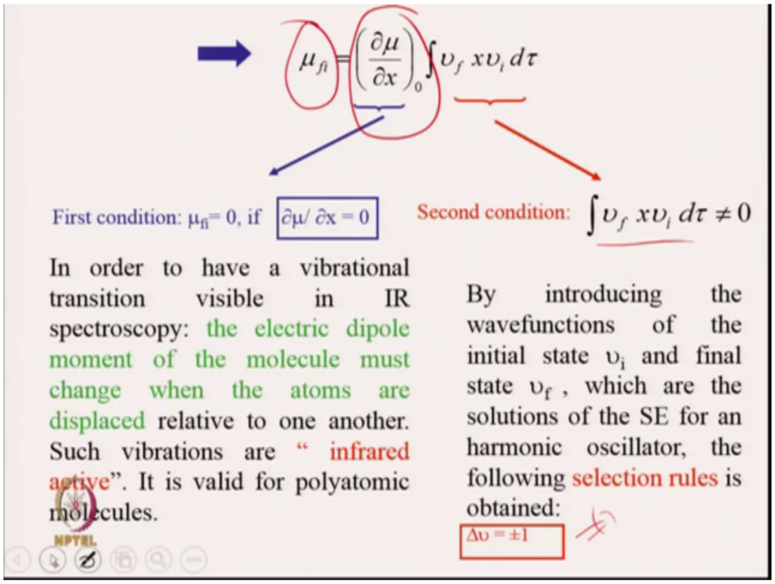


Variation of dipole moment with internuclear distance

Figure 6.1 Variation of dipole moment μ with internuclear distance r in a heteronuclear diatomic molecule

Spectroscopic selection rule tell us nothing about the intensities.



$$\Rightarrow \mu_{fi} = \underbrace{\left(\frac{\partial \mu}{\partial x}\right)_0}\underbrace{\int \upsilon_f x \upsilon_i \, d\tau}$$

First condition: $\mu_{fi} = 0$, if $\boxed{\partial\mu / \partial x = 0}$

In order to have a vibrational transition visible in IR spectroscopy: the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are " infrared active". It is valid for polyatomic molecules.

Second condition: $\int \upsilon_f x \upsilon_i \, d\tau \neq 0$

By introducing the wavefunctions of the initial state υ_i and final state υ_f, which are the solutions of the SE for an harmonic oscillator, the following selection rules is obtained:

$\boxed{\Delta\upsilon = \pm 1}$

Now, again 1 thing we must keep in mind that your intensity is proportional to, let me see here, intensity is proportional to this intensity is proportional to this quantity. Okay, mu Fi Square, ok and mu Fi square is basically if you do a square, so, your intensity will depend on square of this. So, what does that mean is, it is not always true that if, if the selection rule is satisfied, it means it is the most intense peak because what I told you that it also will depend on how mu changes with R.

So, mu changes with R in this fashion, mu changes with R in this fashion. It is not constant at every distance. So, for example, if distance between 2 atoms is 0, means you are like 2 molecules are upon each other and there is no dipole moment and if they are very far apart then again there is no dipole moment. And so, you see here, it is at very low distance and very high distance, R is equal to 0 and R is equal to infinity is going to be 0 okay.

So, and in between there is going to be maximum dipole moment in between this 2 value, R is equal to 0to R is equal to infinity. If you look at this that at maxima, at maxima, your d mu by dR is going to be 0. So, again dipole moment will not change at the this R value, at this R value where the there is maxima., but again if you go to this side or that side mu value is changing with R and that is how; So, again your intensity will depend on where is your, how does mu changes with R rather than just only on selection rule.

So, if suppose Re is here, this Re is at the maximum then at this position your dipole moment will also not change. So, spectroscopic selection rule does not tell us about intensity at least in vibrational case and, and you have to look at how dipole moment changes with inter-nuclear distance, ok.

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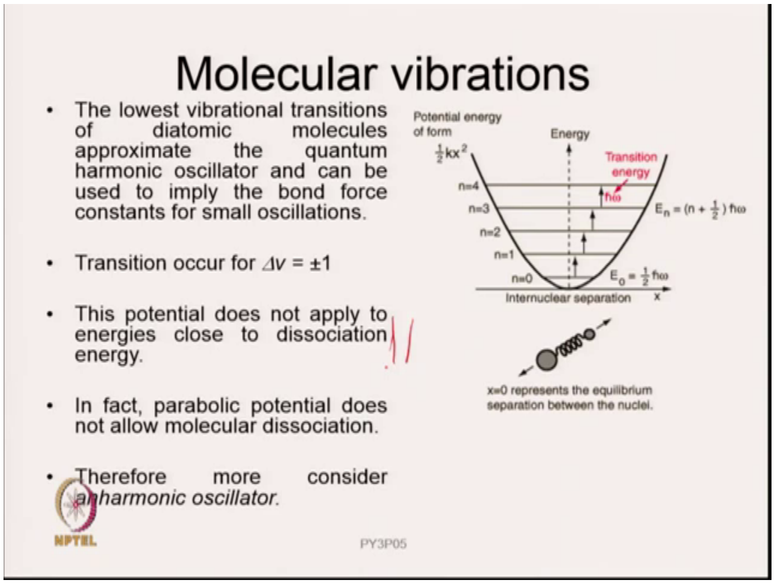

Molecular vibrations

- The lowest vibrational transitions of diatomic molecules approximate the quantum harmonic oscillator and can be used to imply the bond force constants for small oscillations.
- Transition occur for $\Delta v = \pm 1$
- This potential does not apply to energies close to dissociation energy.
- In fact, parabolic potential does not allow molecular dissociation.
- Therefore more consider anharmonic oscillator.

So, till now we talked about harmonic oscillation and the lowest vibrational transition, lowest vibrational transition atomic molecule, approximate the quantum harmonic oscillator and can be used to calculate your bond force constant for a small oscillation.

And for that if it is harmonic oscillation, then delta V is equal to plus minus 1, it means transition is allowed. But, this potential does not apply to energy close to dissociation energy. This potential does not apply to energy. This is a very important point that, if you go towards the dissociation energy, then this potential is not going to apply and for molecular dissociation do not a parabolic potential and what we have is what is known as anharmonic oscillator anharmonic oscillator. So, this is anharmonic oscillator.

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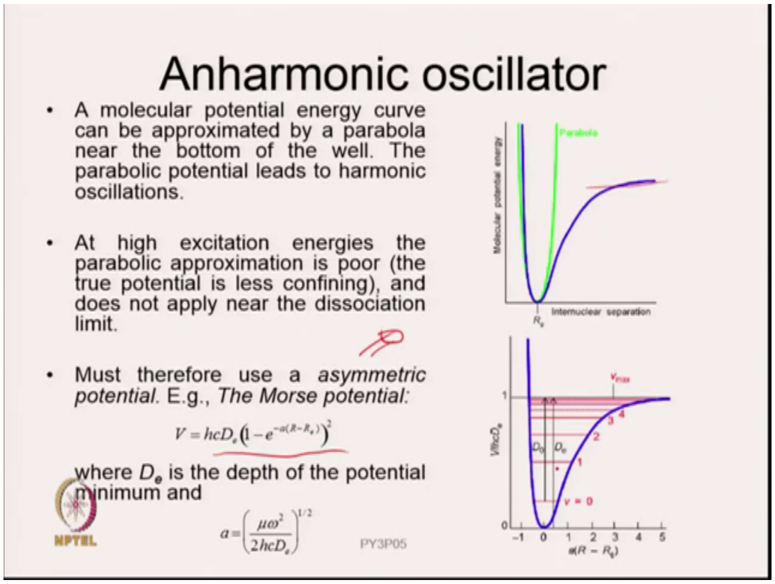

Anharmonic oscillator

- A molecular potential energy curve can be approximated by a parabola near the bottom of the well. The parabolic potential leads to harmonic oscillations.
- At high excitation energies the parabolic approximation is poor (the true potential is less confining), and does not apply near the dissociation limit.
- Must therefore use a *asymmetric potential*. E.g., *The Morse potential:*

$$V = hcD_e\left(1 - e^{-a(R-R_e)}\right)^2$$

where D_e is the depth of the potential minimum and

$$a = \left(\frac{\mu\omega^2}{2hcD_e}\right)^{1/2}$$

PY3P05

So, you see molecular potential energy verses inter-nuclear separation. This parabola is for your harmonic oscillator, but at higher R value your anharmonic oscillator potential is going to be different. So, things like this, if I; suppose this is your bond and if I stretch stretch it, at 1 point it will just break. You cannot go stretching till infinite distance. So, bonds are not like harmonic oscillator, it is at 1 point it is going to break at that point, what you see molecule are, molecule is dissociation, di atomic molecule is dissociated.

So, at high excitation energy the parabolic approximation is poor because at high energy you can see that you have a dissociation energy and your this harmonic oscillator equation is not going to be applied. So, you have to apply some something called asymmetric potential or Morse potential. So, in Morse potential your V is equal to potential energy is hc dE where d is your depth, d is depth, 1 minus exponential alpha R minus Re square and your depth can be calculated using this equation what we will discuss this in detail.

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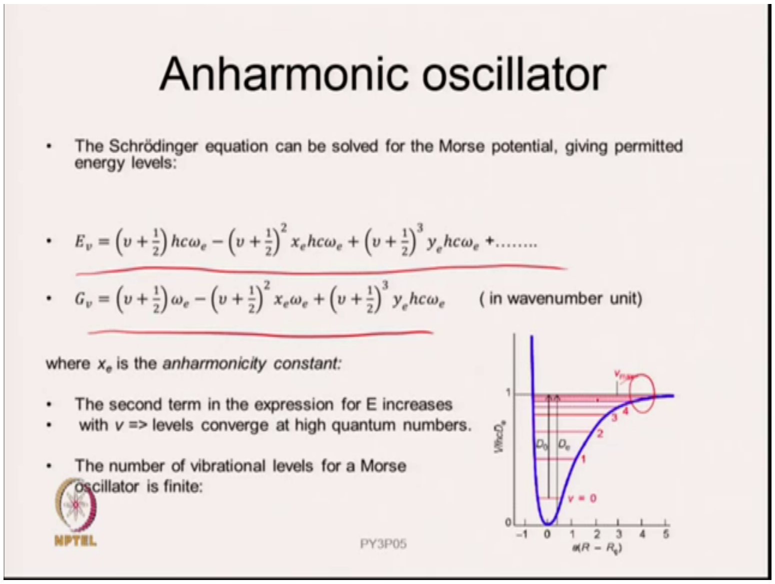

Anharmonic oscillator

- The Schrödinger equation can be solved for the Morse potential, giving permitted energy levels:
- $E_v = \left(v+\frac{1}{2}\right)hc\omega_e - \left(v+\frac{1}{2}\right)^2 x_e hc\omega_e + \left(v+\frac{1}{2}\right)^3 y_e hc\omega_e + \ldots\ldots..$
- $G_v = \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e + \left(v+\frac{1}{2}\right)^3 y_e hc\omega_e$ (in wavenumber unit)

where x_e is the *anharmonicity constant:*

- The second term in the expression for E increases
- with v => levels converge at high quantum numbers.
- The number of vibrational levels for a Morse oscillator is finite:

PY3P05

So, bonds are not a harmonic oscillator they are like Anharmonic Oscillator, if we solve Schrödinger equation using this most potential what we are going to get is, again we can get the energy levels and energy levels is given by Ev is equal to this whole term, V plus half hc omega E, again omega is wave number minus at equilibrium position, minus V half square XE hc omega E, Xe is called anharmonicity constant.

So, there is several terms here, but generally we consider only 2 terms because for a small displacement those can be neglected. This energy term can be converted to wave in the wave number unit and by dividing by hc. So, that is what we have done and now we define this as a term Gv, which is basically a wave number, wave number unit. So, V plus half omega E minus V plus half square Xe omega E plus V plus half Q pi E hc, ye is again another anharmonicity constant. At very high vibrational level, your energy is going to converge, energy is going to converge and it is not going to be infinite, ok.

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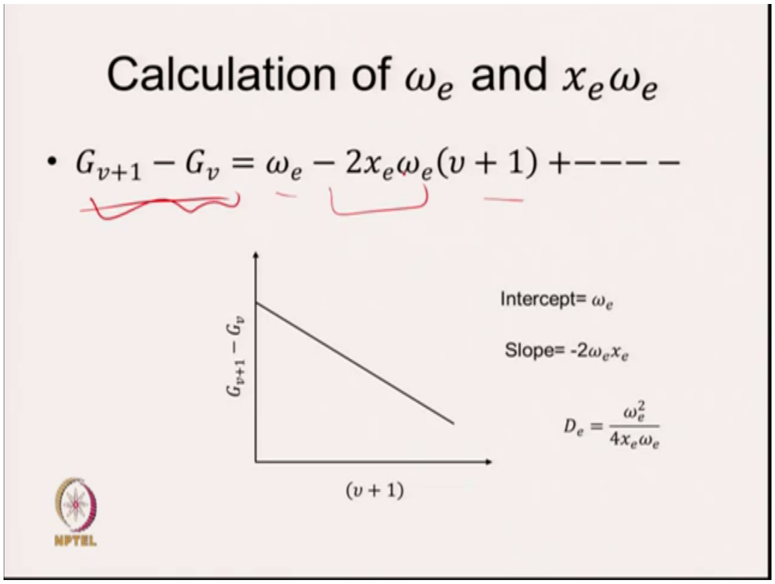

Calculation of ω_e and $x_e\omega_e$

- $G_{v+1} - G_v = \omega_e - 2x_e\omega_e(v+1) + - - - -$

Intercept= ω_e

Slope= $-2\omega_e x_e$

$$D_e = \frac{\omega_e^2}{4x_e\omega_e}$$

So, how do we calculate this omega E and Xe We? So, we know what is the selection rule for vibrational levels. So, GV plus delta V is plus minus 1. So, if we calculate GV plus 1 minus GV, what we will get is omega E minus 2 Xe omega E V plus 1 and we can neglect the higher terms we can neglect the higher terms and this gives you a very important tool to determine the value of omega E and Xe We.

So, if I plot GV plus 1 minus GV verses V plus 1, you can see GV plus 1 and this we can get from IR spectra, the wave number 4 V plus 1 and this GV. So, this we can get from Vibrational Spectroscopy, if we plot this V plus 1, your intercept will be omega E and your slope is going to be minus 2 Xe omega E. So, this gives you a tool to calculate omega E, omega E Xe and since De is related to omega E and omega E Xe, De is basically omega E square by 4 Xe omega E and so, you can calculate also dissociation, you can calculate dissociation energy.

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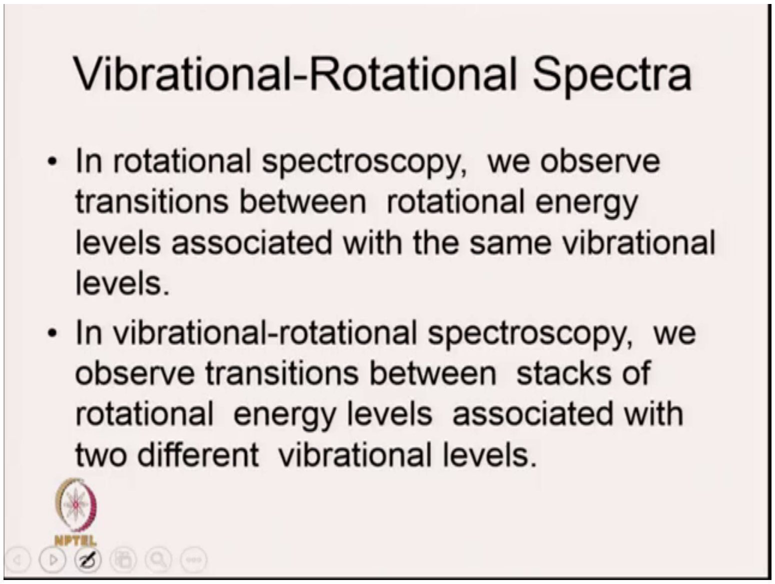

Vibrational-Rotational Spectra

- In rotational spectroscopy, we observe transitions between rotational energy levels associated with the same vibrational levels.
- In vibrational-rotational spectroscopy, we observe transitions between stacks of rotational energy levels associated with two different vibrational levels.

So, till now we are discussing Vibrational Spectroscopy. Now, we will go to Vibrational Rotational Spectroscopy. We already discussed Rotational Spectroscopy. So, what we are looking at in Rotational Spectroscopy that we are observing transition between rotational energy level associated with same vibrational level. So, for example, V is equal to 1 then within that there is rotational levels and then you are seeing for V is equal to 1 only you are trying to look at rotational level from 0 to 1 or something like that.

But, in the rotational, Vibrational Rotational Spectrum, you are looking at transition between stacks of rotational energy level associated with 2 different vibrational levels. So, here V is, you are not looking at V is equal to 1 and J is equal to something to V is equal to 1 and J is equal to something, what you are going to look at V is equal to 1 to V is equal to 2, V is equal to 1 to V is equal to 2 and then you are trying to look at different rotational level, different rotational level.

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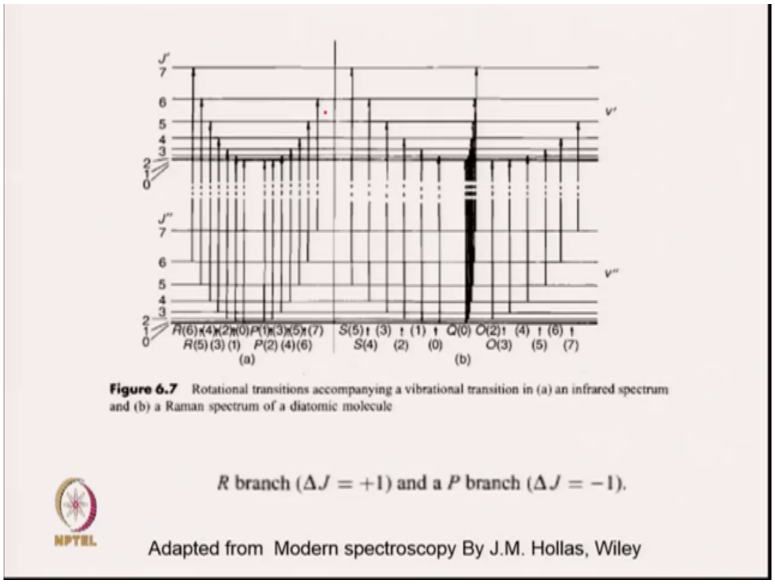

Figure 6.7 Rotational transitions accompanying a vibrational transition in (a) an infrared spectrum and (b) a Raman spectrum of a diatomic molecule

R branch ($\Delta J = +1$) and a P branch ($\Delta J = -1$).

Adapted from Modern spectroscopy By J.M. Hollas, Wiley

So, what I mean by this is given here, so, you can see that here you are going from 6 to 6 in vibrational level you see these are 2 different vibrational level. V dash and V double dash and you are going from 1 vibrational level to another vibrational level. So, transition is not between these rotational level or transition is not between these rotational level, transition is between rotational level, different rotational level of different vibrational levels.

So, you are going from 6 of V double dash to 7 of V dash, 7 of V dash. And again delta J is equal to plus 1 and delta J is equal to minus 1, this is your selection rule. So, you see this is you are going from 6 to 7, 5 to 6. So, this is delta J is equal to plus 1 and that is called R branch, R branch and here you have you can see that you are going from 7 to 6, 7 to 6. So, your delta J is minus 1, your delta J is minus 1 or the vibration is you are going from V double dash to V dash, but now you are going from seventh level in V double dash to sixth level in V dash and that is called your P branch.

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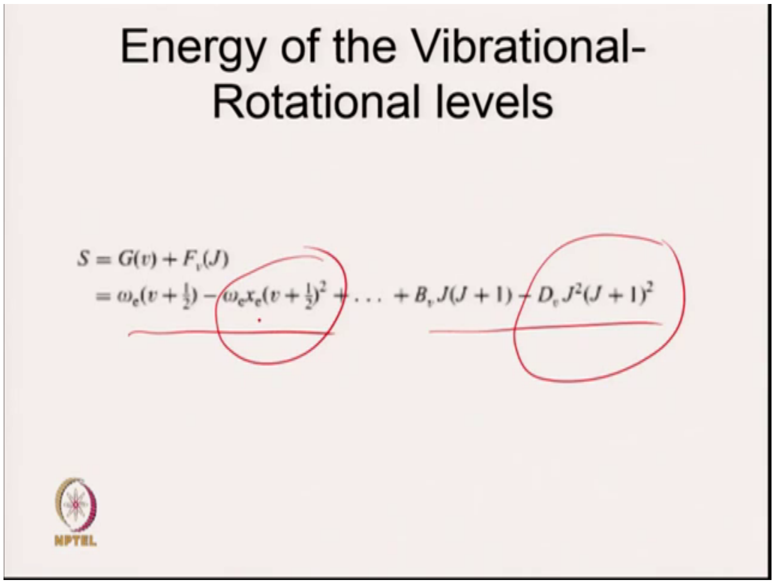

Energy of the Vibrational-Rotational levels

$$S = G(v) + F_v(J)$$
$$= \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \ldots + B_v J(J+1) - D_e J^2(J+1)^2$$

And energy of vibrational rotational level can be written the way we have derived for your vibrational rotational. So, this is for vibrational and this is for rotational, rotational spectra. So, what we are going to neglect is the second terms here, which is because of this is for anharmonic and this is because of distortion.

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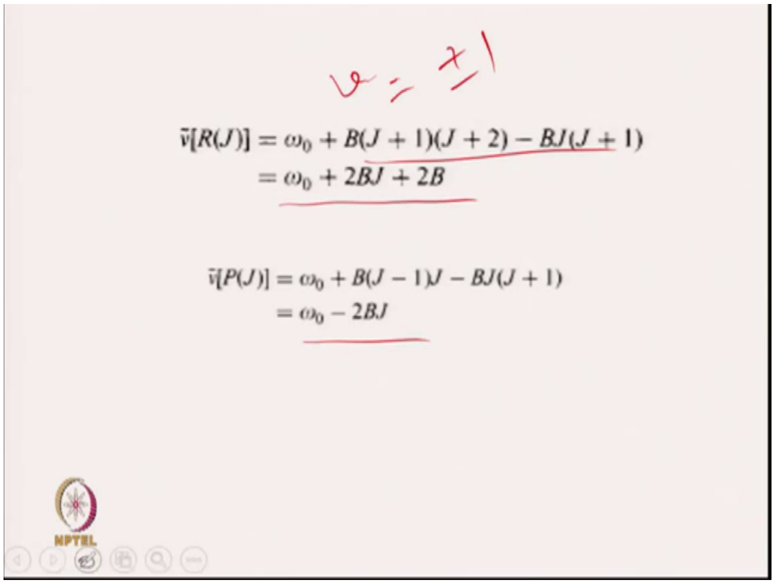

$v = \pm 1$

$$\tilde{\nu}[R(J)] = \omega_0 + B(J+1)(J+2) - BJ(J+1)$$
$$= \omega_0 + 2BJ + 2B$$

$$\tilde{\nu}[P(J)] = \omega_0 + B(J-1)J - BJ(J+1)$$
$$= \omega_0 - 2BJ$$

So, we can calculate wave number of RJ. So, what we did is for V is equal to plus minus 1, V is equal to plus minus 1, you will get simply omega naught, your wave number will be simply omega naught and this is for rotational, you are going from J to J plus 1.

So, J to J plus 1 you will get simply. So, you see this is for J plus 1, this is for J. So, what you are going to get is omega naught plus 2 BJ plus 2B. So, this is your wave number for R branch. Similarly, you can calculate wave number for P branch which is going to be this, omega naught minus 2BJ. So, I will stop at this point. In the next lecture we will discuss your Vibrational Rotational Raman Spectra.