Spectroscopic Techniques for Pharmaceutical
and
Biopharmaceutical Industries
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Lecture-7

Rotational, Rotational Raman Spectroscopy Theory and Application-I

In today's lecture, I am going to talk about Rotational Spectroscopy. First we will look at principle behind Rotational Spectroscopy and then we will go forward and see what are the applications of Rotational Spectroscopy, we will also look at Rotational Raman Spectroscopy and see what are the different aspects of Rotational Raman Spectroscopy.

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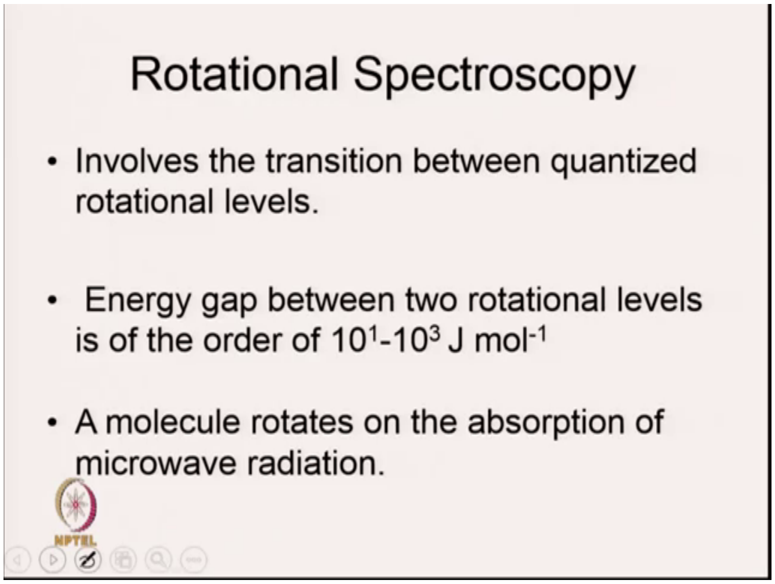

Rotational Spectroscopy

- Involves the transition between quantized rotational levels.
- Energy gap between two rotational levels is of the order of 10^1-10^3 J mol^{-1}
- A molecule rotates on the absorption of microwave radiation.

Rotational Spectroscopy as the name suggests it involves the transition between quantized rotational levels. Generally, the gap between 2 rotation levels is of the order of 10 to 1000 Joule per mole. When a molecule absorbs microwave radiation, it undergoes rotation.

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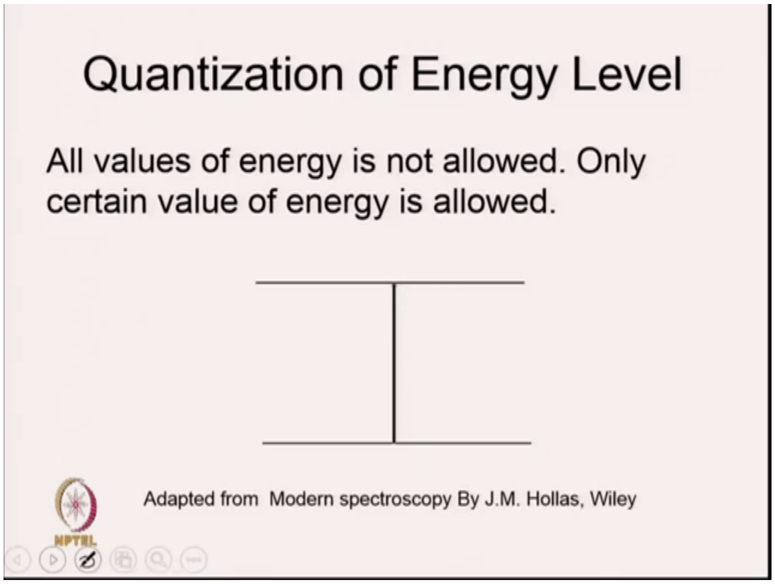

Quantization of Energy Level

All values of energy is not allowed. Only certain value of energy is allowed.

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

So, rotational energy levels are quantized, it means that not all the value of energy is allowed, only certain value of energy is allowed.

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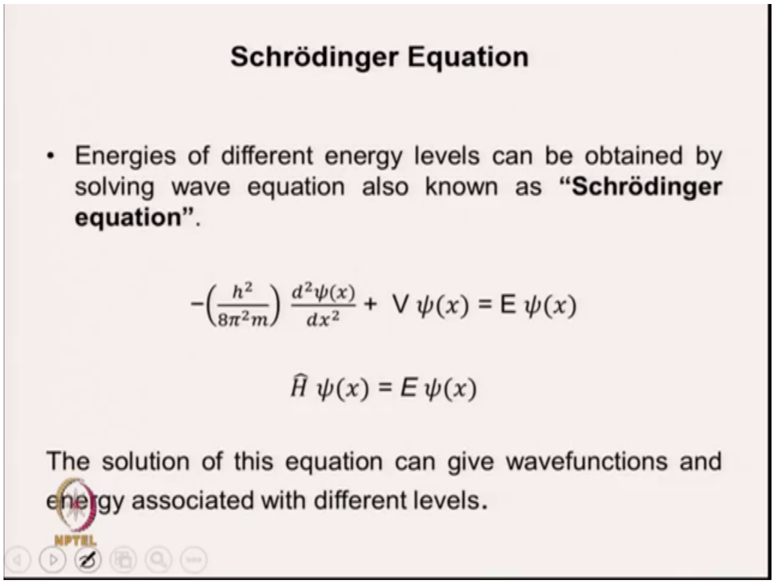

Schrödinger Equation

- Energies of different energy levels can be obtained by solving wave equation also known as **"Schrödinger equation"**.

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

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

The solution of this equation can give wavefunctions and energy associated with different levels.

The way we solve the wave function and energy of quantized energy levels is by using wave equation, known as 'Schrödinger Wave Equation'. So, here what we do is we apply the, your, Hamiltonian operator on the wave function to get, this is Hamiltonian operator on the wave function, to get energy as Eigen value of that operator. Your Hamiltonian operator consists of 2 different operators 1 is your kinetic energy operator and that is given by minus h square by 8 pi square m, d2 by dx square. And then you have a potential energy operator which is given by V.

So, your Hamiltonian operator is basically sum of kinetic energy operator and potential energy operator and when it is applied to a wave function, you can get the energy of a particular energy level. So, solution of this equation gives both the wave function associated with the energy level and the energy associated with the different levels.

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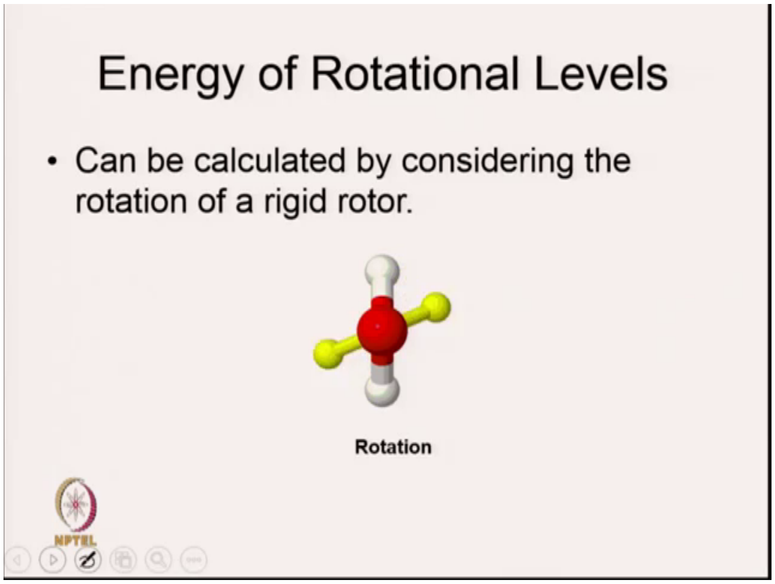

Energy of Rotational Levels

- Can be calculated by considering the rotation of a rigid rotor.

So, we can calculate energy of rotational level by considering the rotation of rigid rotor. So, this is your rotation and this we are assuming molecule as a rigid rotor and now, we are going to solve your Schrödinger equation corresponding to rotational motion to get the energy of rotational levels. So, first we will try to simplify it, we will just look at rotation in 2 dimension.

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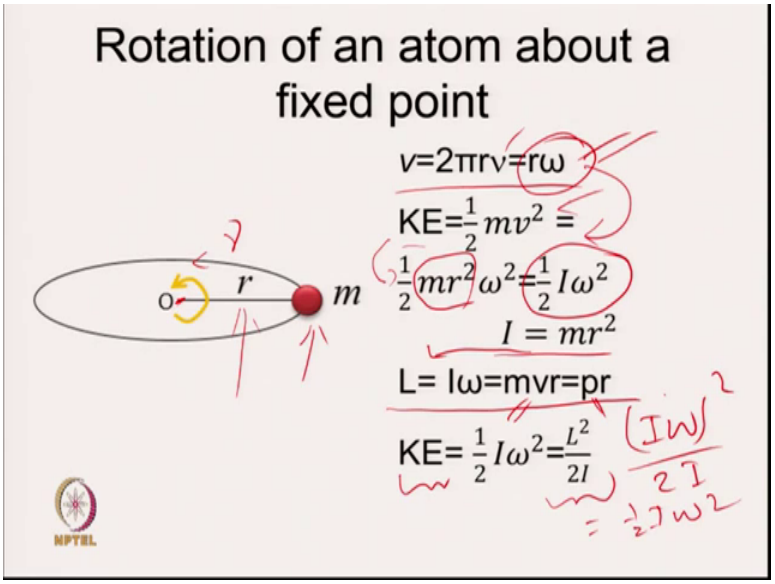

Rotation of an atom about a fixed point

$v = 2\pi r\nu = r\omega$

$KE = \frac{1}{2}mv^2 =$

$\frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2$

$I = mr^2$

L= Iω=mvr=pr

$KE = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$

$\frac{(I\omega)^2}{2I} = \frac{1}{2}I\omega^2$

So, let us consider about rotation of an atom about a fixed point. So, here is an atom with mass m, it is rotating with a frequency nu, around point O. If distance between O and this atom is r, we can calculate velocity by using this formula. Velocity will be equal to 2 pi r into frequency. This can also be given in terms of angular velocity, V will be equal to r omega. Once we know v, we can calculate kinetic energy, because kinetic energy is equal to half mv square. So, if we put value of v from here to this equation, then we will get kinetic energy which will be equal to half mr square omega square; mr square is known as moment of inertia and given by symbol I, I and so, kinetic energy can be written in terms of I and omega as half I omega square.

Similarly, we can write equations for angular momentum, angular momentum will be equal to I omega and if I put value of I from here and omega from this we can get, L is equal to mvr. And since, mv is equal to momentum, so, your L is equal to p into r. Kinetic energy can also be expressed in terms of angular momentum, we know that kinetic energy is half I omega square. So, this will be equal to L square by 2I. So, L, we know that, L is I omega; so, if you do a square of this, divided by 2I, what you are going to get is half I omega square. So, this is about kinetic energy and angular momentum of an atom rotating about a fixed point.

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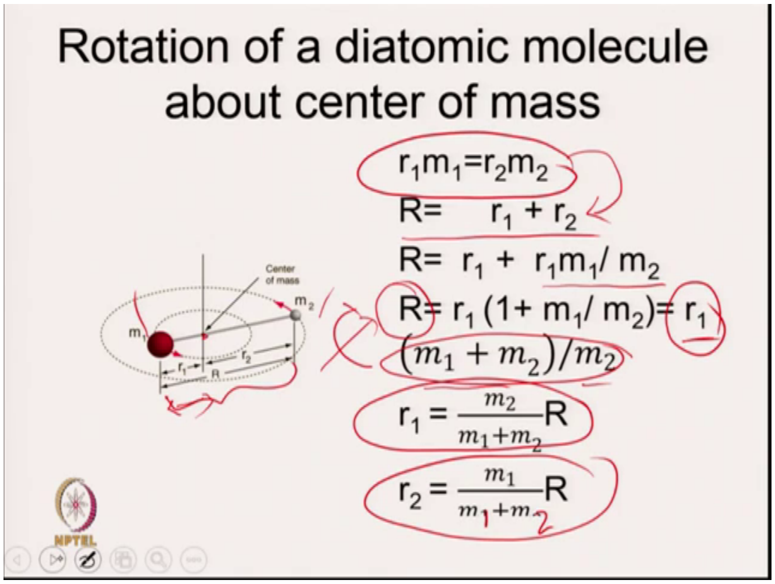

Rotation of a diatomic molecule about center of mass

$r_1m_1=r_2m_2$

$R= r_1 + r_2$

$R= r_1 + r_1m_1/ m_2$

$R= r_1 (1+ m_1/ m_2)= r_1 (m_1 + m_2)/m_2$

$r_1 = \frac{m_2}{m_1+m_2}R$

$r_2 = \frac{m_1}{m_1+m_2}R$

Now, let us consider rotation of di-atomic molecule around center of mass. So, di-atomic molecule has 2 atom with mass m1 and m2. Suppose, it is, here is center of mass and the molecule is rotating around center of mass, molecule is rotating around center of mass. If it is rotating around center of mass, it must follow this equation, r1 into m1 is equal to r2 into m2.

Where r1 is distance of atom 1 to the center of mass, where r2 is distance between center of mass and atom 2 and the distance between atom 1 and atom 2 is given by capital R. So, capital R is basically r1 plus r2 and if I put r2 value from here to this equation, what I will get is, r1 m1 by m2. And now, I can take r1 out and I will get 1 plus m1 divided by m2 and this is basically r1 multiplied by m1 plus m2 divided by m2. So, this R, capital R can be written in terms of this distance r1, which is basically your distance between center of mass and atom 1.

So, this r1 can also be expressed in terms of this capital R and it will be given by r1 is equal to m2 divided by m1 plus m2 into capital R. Capital R. You can see here that R is equal to r1 multiplied by m1 plus m2 divided by m2. So, if I want to calculate r1 I will take this to left hand side and when we do that m2 will come in the numerator and m1 plus m2 will come in denominator.

So, r1 is equal to m2 divided by 1 plus m2 multiplied by R. Similarly, we can calculate r2; r2 is m1 divided by m1 this is m1 plus m2 and multiplied by R. So, now, we have expressed r1 and r2 in terms of capital R, which is the distance between 2 atoms, distance between 2 atom.

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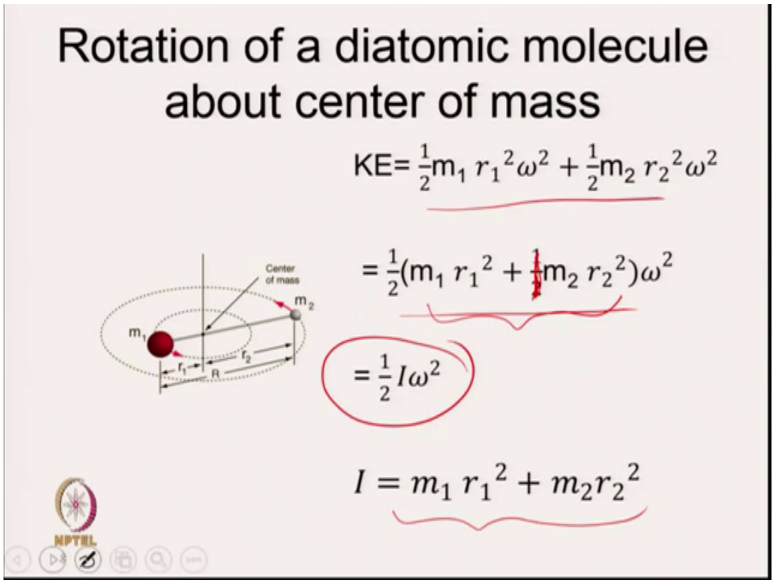

Rotation of a diatomic molecule about center of mass

$$KE = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$$

$$= \frac{1}{2}(m_1 r_1^2 + \cancel{\frac{1}{2}} m_2 r_2^2)\omega^2$$

$$\boxed{= \frac{1}{2} I \omega^2}$$

$$I = m_1 r_1^2 + m_2 r_2^2$$

Now, we can go ahead and calculate kinetic energy, kinetic energy will given by half m1 r1 square omega square plus half m2 r2 square omega square. If we take omega square outside, but we will get is half m1 r1 square plus half; so, this half you can take out, then, your left with half m1 r1 square plus m2 r2 square into omega square. And this is equal to your I; here you see I is equal to m1 r1 square plus m2 r2 square. So, we can write kinetic energy equal to half I omega square.

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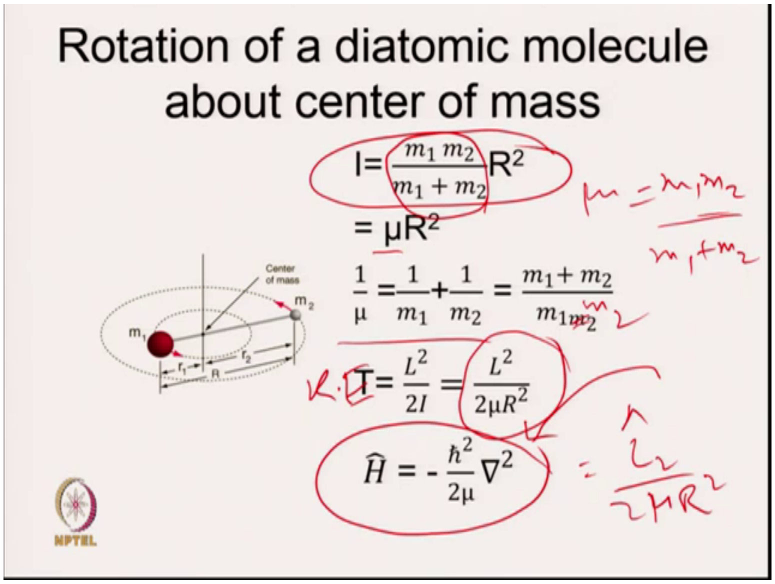

Rotation of a diatomic molecule about center of mass

$$\boxed{I = \frac{m_1 m_2}{m_1 + m_2} R^2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$= \mu R^2$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}$$

$$K.E\ T = \frac{L^2}{2I} = \boxed{\frac{L^2}{2\mu R^2}}$$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2} = \frac{\hat{L}^2}{2\mu R^2}$$

Where I is equal to m1 m2 divided by m1 plus m2 into R square. So, if you go back you see I is equal to this m1 r1 square plus m2 r2 square and if you put the value of r1 value of r1 from here and value of r2 from here, what you are going to get is, I is equal to this equation, m1 m2 divided by m1 plus m2 multiplied by R square.

This whole thing is called Reduced Mass and given by symbol mu. So, I is equal to mu into R square. I is equal to mu into R square And so, mu is equal to m1 m2 divided by m1 plus m2, m1 plus m2. If you inverse it 1 by mu will be equal to (your) 1 by m1 plus 1 by m2. And, so, that your this inverse is equal to m1 plus m2 divided by m1 into m2, m1 into m2. And we know that kinetic energy, this is your kinetic energy, kinetic energy is L square by 2I.

So, if I put, I is equal to mu R square, we can get L square by 2 mu R square. So, kinetic energy of a di-atomic molecule rotating about center of mass is given by, angular momentum square divided by 2 pi R square. And then we can simply get Hamiltonian from this angular momentum and Hamiltonian will be given by only kinetic energy operator, because in this case potential energy is 0 and so, your Hamiltonian operator will be equal to kinetic energy operator and that will be given by L square operator by 2 mu R square and that is equal to h cross (square) minus h cross square by 2 mu multiplied by del square.

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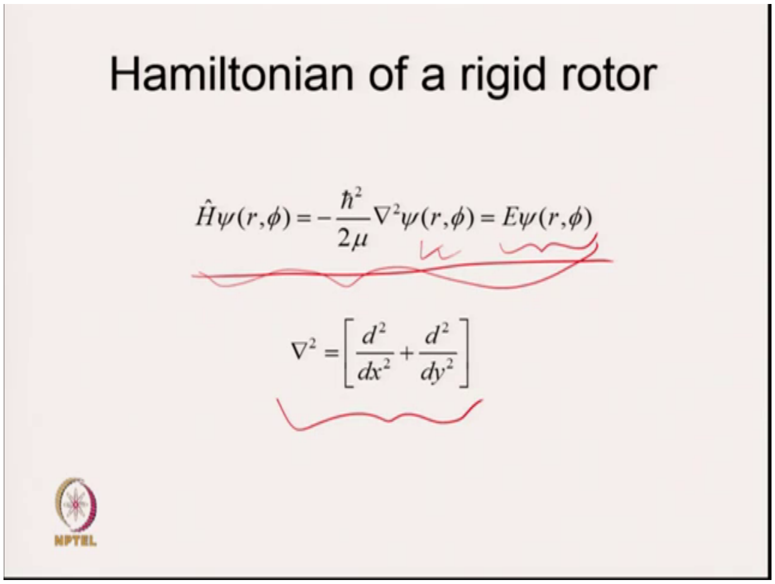

Hamiltonian of a rigid rotor

$$\hat{H}\psi(r,\phi) = -\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\phi) = E\psi(r,\phi)$$

$$\nabla^2 = \left[\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right]$$

So, Hamiltonian of a rigid rotor is given by, here this equation, H si is equal to minus h cross square by 2 mu del square si, this is your Laplacian Operator and that will give you your E si.

Here, del square is equal to d square by dx square plus d square by dy square. So, del square basically Laplacian Operator is equal to d square by dx square plus d square by dy square.

This is we are talking about rotation in a plane, rotation in a 2-diamentional plane. But, to solve this equation, this Schrödinger equation, we need to convert this equation from a Cartesian Co-ordinate System to your Cartesian Coordinate System to Polar Coordinate System. Once we do that, then we will be able to solve the Schrödinger equation and we can get energy of different rotational levels.

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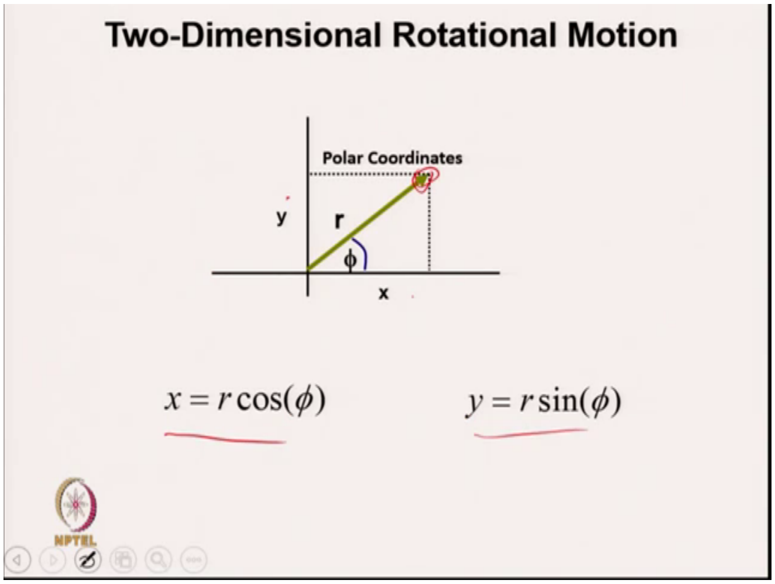
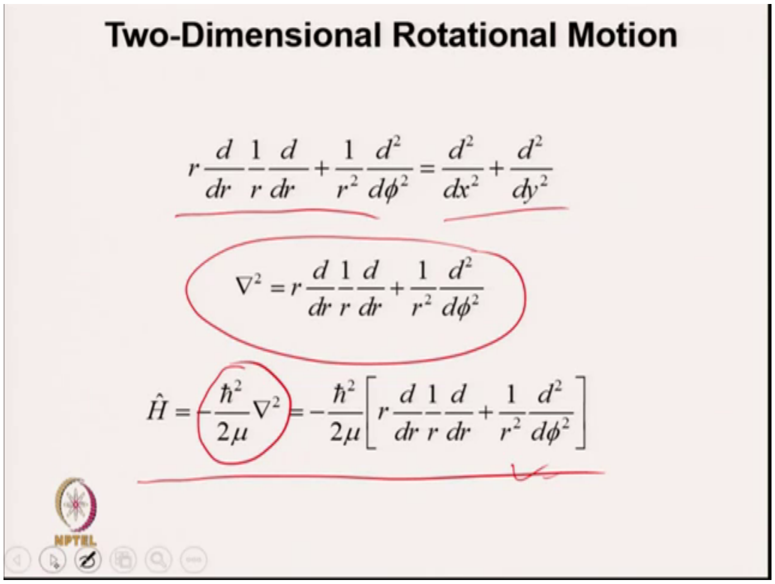


Two-Dimensional Rotational Motion

$x = r\cos(\phi)$ $y = r\sin(\phi)$



Two-Dimensional Rotational Motion

$$r\frac{d}{dr}\frac{1}{r}\frac{d}{dr}+\frac{1}{r^2}\frac{d^2}{d\phi^2}=\frac{d^2}{dx^2}+\frac{d^2}{dy^2}$$

$$\nabla^2 = r\frac{d}{dr}\frac{1}{r}\frac{d}{dr}+\frac{1}{r^2}\frac{d^2}{d\phi^2}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\left[r\frac{d}{dr}\frac{1}{r}\frac{d}{dr}+\frac{1}{r^2}\frac{d^2}{d\phi^2}\right]$$

So, using x is equal to r cos x is equal to r cos phi and y is equal to r sin phi, we can convert this Laplacian Operator in the terms of differential with respect to r and differential with respect to phi.

So, this is your Laplacian operator and now, we are going to use it to calculate kinetic energy part and overall energy. So, overall energy the operator, Hamiltonian operator will be given by just kinetic energy parts since potential energy is 0 and then you have this operator in the polar coordinates.

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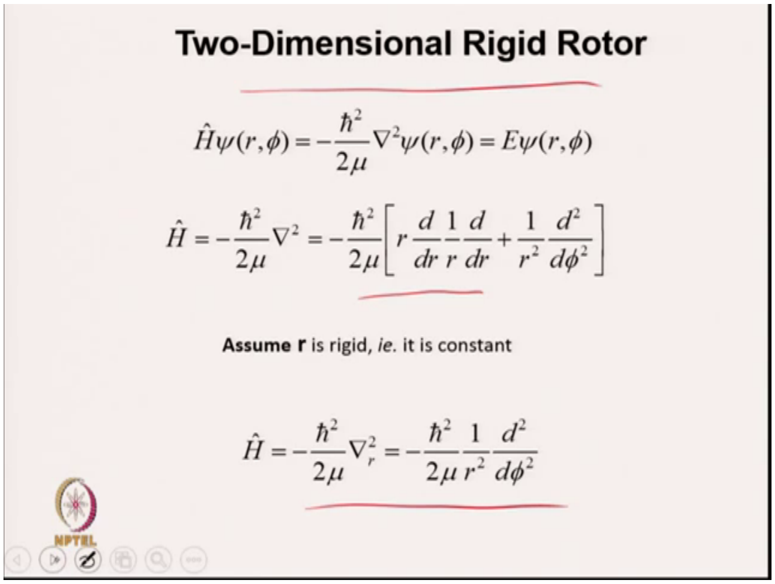

Two-Dimensional Rigid Rotor

$$\hat{H}\psi(r,\phi) = -\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\phi) = E\psi(r,\phi)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\left[r\frac{d}{dr}\frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\phi^2}\right]$$

Assume r is rigid, *ie.* it is constant

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_r^2 = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d^2}{d\phi^2}$$

Now, this operator again since we are assuming the rigid rotor, so, r part is constant what does that mean is this differential part is going to be 0. So, your Hamiltonian is a simplified term which can be expressed in terms of a differential with respect to phi. So, this is your Hamiltonian operator.

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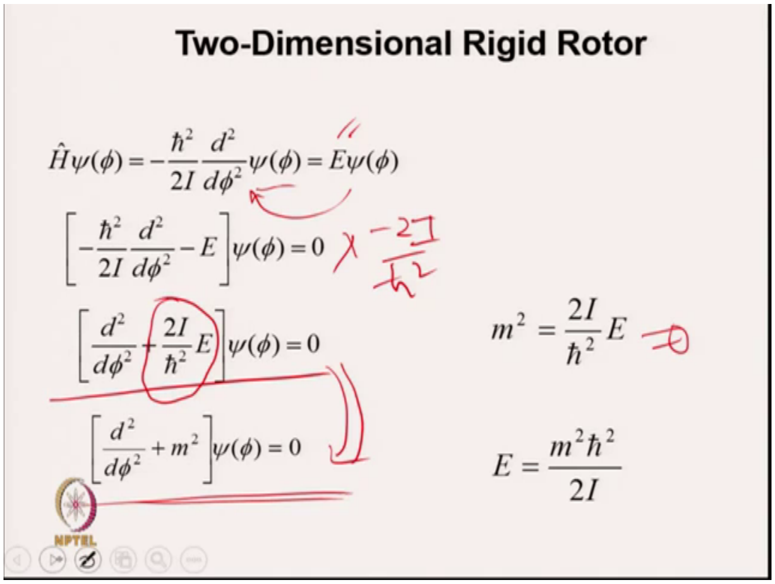

Two-Dimensional Rigid Rotor

$$\hat{H}\psi(\phi) = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\psi(\phi) = E\psi(\phi)$$

$$\left[-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} - E\right]\psi(\phi) = 0 \quad \times\ \frac{-2I}{\hbar^2}$$

$$\left[\frac{d^2}{d\phi^2} + \frac{2I}{\hbar^2}E\right]\psi(\phi) = 0$$

$$\left[\frac{d^2}{d\phi^2} + m^2\right]\psi(\phi) = 0$$

$$m^2 = \frac{2I}{\hbar^2}E \quad = 0$$

$$E = \frac{m^2\hbar^2}{2I}$$

Now, if we apply to the wave function of this rotational motion, then we can get energy, we can get energy. So, you have minus h bar square by 2I, d square by d phi square and if you bring it here, minus E si phi is equal to 0 and just to simplify it, just multiply this equation by your minus 2I by h bar square h bar square, you will get this equation.

Why we are simplifying this? Because, solution of this kind of equation is well known, we can express this equation into another simplified equation, where you can assume that 2I by h bar square E, is equal to m square that is what we do assumption and if you do that, now, solution of this equation is well known, solution of this equation is well known, and here we have assume that to 2I by h bar square into E is equal to m square and that can be used to calculate the energy of your 2-diamentional rigid rotor.

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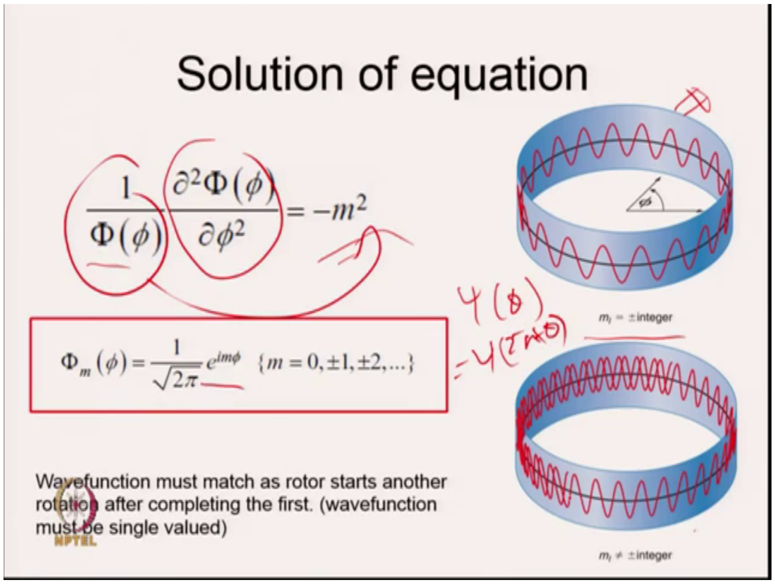

Solution of equation

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2$$

$$\boxed{\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \quad \{m = 0, \pm1, \pm2, \ldots\}}$$

$\psi(\theta)$

$= \psi(2\pi+\theta)$

Wavefunction must match as rotor starts another rotation after completing the first. (wavefunction must be single valued)

So, this is the equation, the differential equation which is a function of phi and solution of this is well known and the solution is simply exponential i m phi, exponential i m phi and exponential i m phi, if you take a differential of this what you will (get) get is i m exponential i m phi and double differential will give you i m square E i m phi, which is nothing but minus m square, the, multiplied by wave function. So, you see that this differential will be equal to minus m square into the wave function.

And, so, it is quite simple differential equation and that is why we did so many simplification. So, once you know the solution, now, we have to apply boundary conditions because wave function must match as rotor starts and other rotation (up) after completing the wave function. So, this is boundary condition. So, allowed values are when m is equal to integer, because, once you have like that, your si, si at theta will be equal to 2pi plus theta.

And that is only possible when m has integer value, if m is not an integer then you can see that si is not matching after 1 rotation, si is not matching after 1 rotation. And thus m can take only some specified value. And since energy dependent on m, your energy has some specified value and that is why you see, that energy of a rotational levels are quantize.d.

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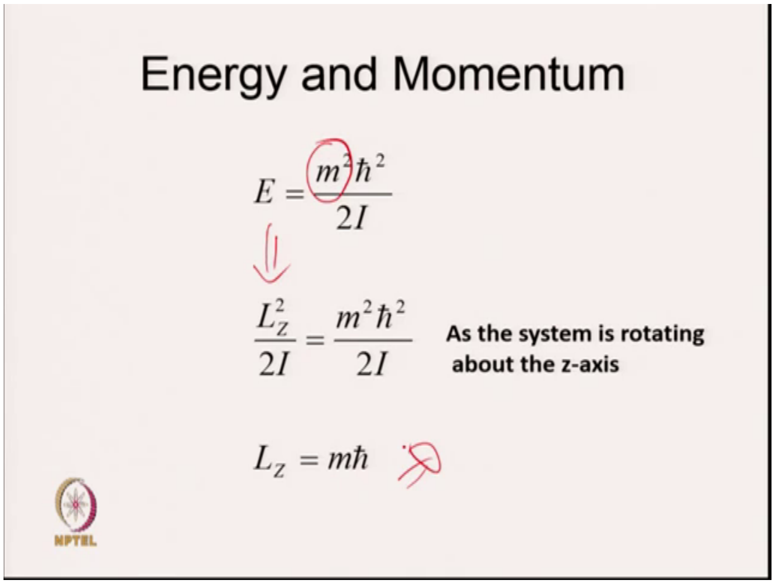

Energy and Momentum

$$E = \frac{m^2\hbar^2}{2I}$$

$$\frac{L_Z^2}{2I} = \frac{m^2\hbar^2}{2I}$$

As the system is rotating about the z-axis

$$L_Z = m\hbar$$

So E is equal to m square h bar square by 2I; that is what we assume last time and it is dependent on quantum number and m can take value from an integer value. You know that energy is your Lz square by 2I and from that we can get a Lz value, which is m h bar.

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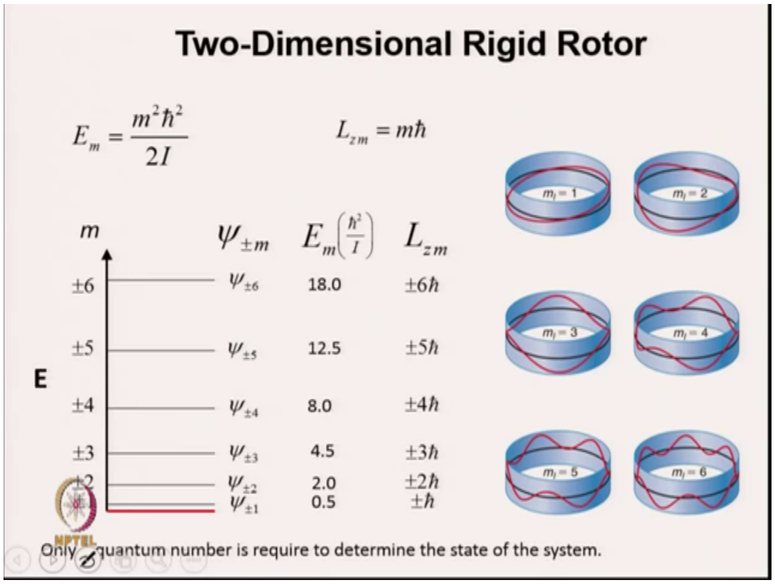

Two-Dimensional Rigid Rotor

$$E_m = \frac{m^2\hbar^2}{2I} \qquad L_{zm} = m\hbar$$

m	$\psi_{\pm m}$	$E_m\left(\frac{\hbar^2}{I}\right)$	L_{zm}
± 6	$\psi_{\pm 6}$	18.0	$\pm 6\hbar$
± 5	$\psi_{\pm 5}$	12.5	$\pm 5\hbar$
± 4	$\psi_{\pm 4}$	8.0	$\pm 4\hbar$
± 3	$\psi_{\pm 3}$	4.5	$\pm 3\hbar$
± 2	$\psi_{\pm 2}$	2.0	$\pm 2\hbar$
	$\psi_{\pm 1}$	0.5	$\pm\hbar$

Only quantum number is require to determine the state of the system.

So, for 2-diamentional Rigid Rotor we have 1 quantum number that is m, your linear momentum is given by this. And for different value of m you have, energy. So for example, if you take 6 and this is 6 square h bar square by 2I. So, 36 divided by 2 is 18 h bar square by I. So, this h; 18 h bar square by I. Similarly, for 5 it will be 12.5 h bar square by I and for 4, it will be 8 h bar square by I. And Lz value is simply m h, h bar. So, 6 h bar, 5 h bar, 4 h bar, 3 h bar, and just like that. So, here we need only 1 quantum number which is m to define the energy.

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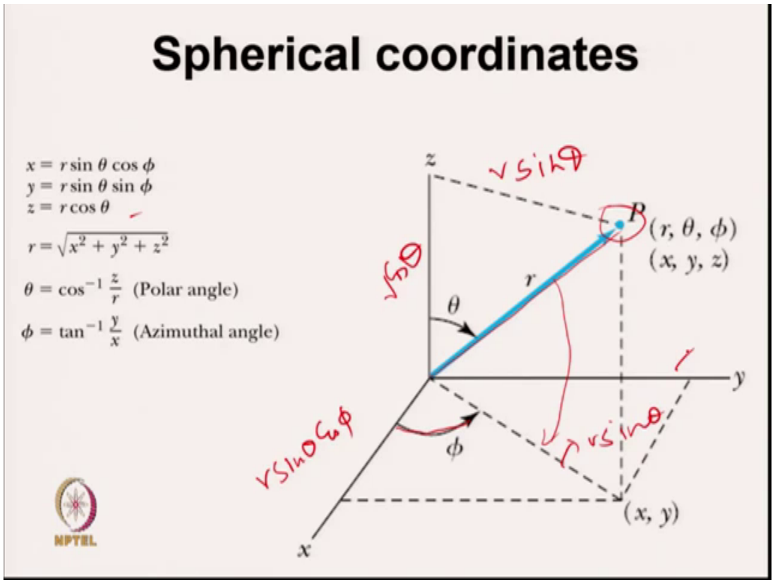

Spherical coordinates

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

$r = \sqrt{x^2 + y^2 + z^2}$

$\theta = \cos^{-1}\frac{z}{r}$ (Polar angle)

$\phi = \tan^{-1}\frac{y}{x}$ (Azimuthal angle)

And so, now let us go to 3-dimensional rigid rotor. So, for the rotation of 3-dimensional body, we will take this is your coordinate system XYZ. So, now we are not only just looking at the rotation in xy plane, but we are looking at the 3-dimensional plane. So, let us assume that this angle is theta, this is your rigid rotor and this makes angle theta.

Here is your atom and this makes r, this distance is r, and so, this is the angle, theta is the angle with the Z axis. If you take projection of this on xy plane, then phi is the angle between x and this projection, angle between projection and x axis is phi. Now, you can think of here is r and this angel is theta. So, this is your r cos theta. So, z value is your r cos theta and then if this is r cos theta, this will be r sin theta. It means this, this is also r sin theta.

This is r sin theta and since this angle is phi, so, x is equal to r sin theta cos phi. And this will be y is equal to r sin theta sin phi. So, using that now, we have seen that what is the relation between r theta phi with x y z.

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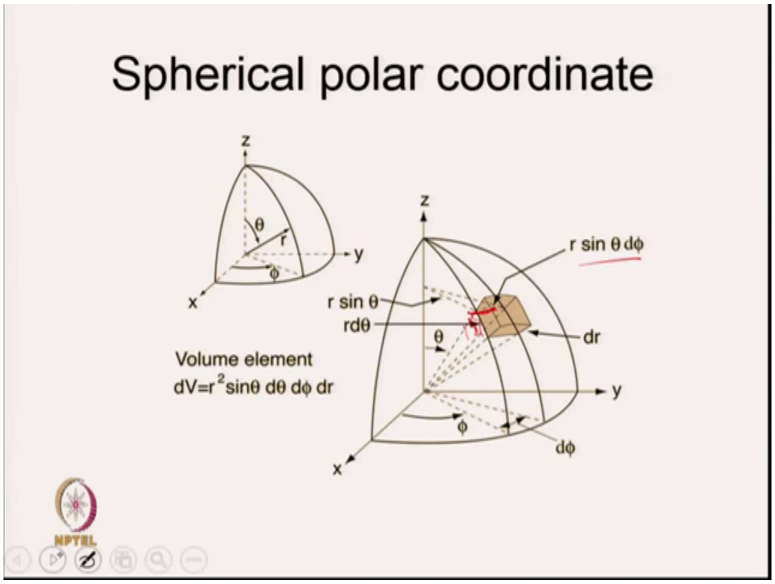

Spherical polar coordinate

Volume element
$dV = r^2 \sin\theta \, d\theta \, d\phi \, dr$

So, now, we can go and calculate or see what will be the Laplacian operator in polar coordinate system. For that, we need to calculate volume element and now, you see the way we do as. So, this is, if you remember this is theta and this, this is your r.

So, this will be r cos theta then this will be r sin theta. So, this is your r sin theta. And if this angle is phi, this angle is phi then this whole this angle is phi. So, whole length will be r sin theta d phi. This angle is your, this angle is your, d theta. So, this length will be r d theta; and since this is d r. So, now, you have a volume element is equal to r square sin theta d theta d phi into d r. So, you have your this is r sin theta d phi multiplied by your r dr and multiplied by your so, this is this, this is your r sin theta and r d theta.

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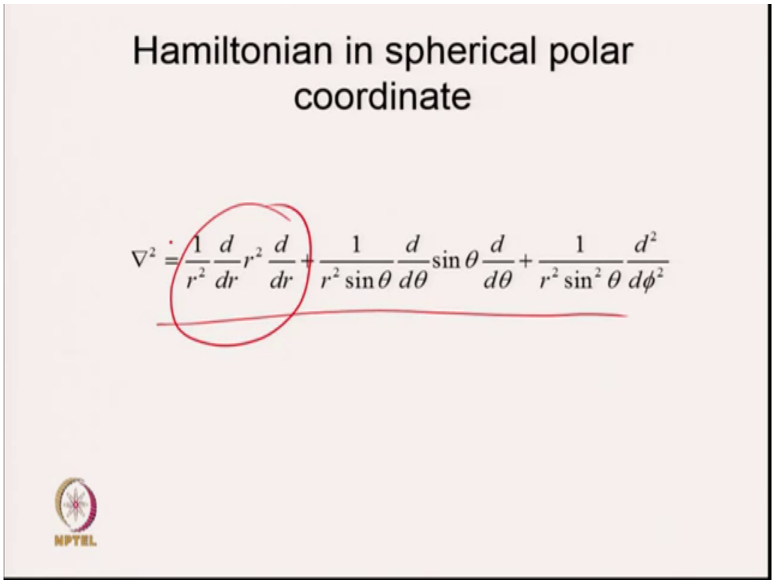

Hamiltonian in spherical polar coordinate

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{1}{r^2\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \frac{1}{r^2\sin^2\theta}\frac{d^2}{d\phi^2}$$

So, you can calculate the volume element, once you know that then you can express your Laplacian operator in a spherical polar coordinate and this is the way you can express Laplacian operator in a spherical polar coordinates. Now, since we are again taking really rotors what does that mean that this term will go to 0 because your r is constant.

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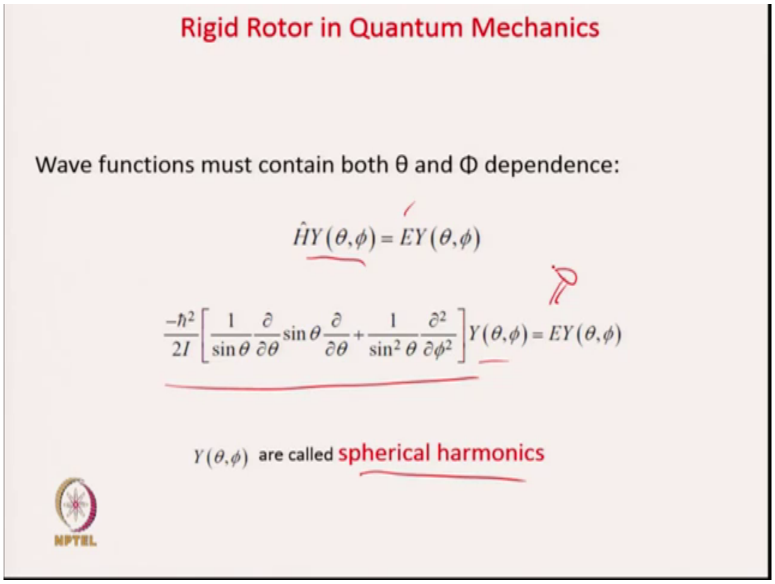

Rigid Rotor in Quantum Mechanics

Wave functions must contain both θ and Φ dependence:

$$\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$$

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = EY(\theta,\phi)$$

$Y(\theta,\phi)$ are called spherical harmonics

So, your Laplacian operator will have only dependence on your theta and phi, theta and phi and since your wave function depend on theta and phi if we are assuming that your, this rotation is like rigid rotor and that kind of wave function is known as 'Spherical Harmonics'.

So, now, we are going to apply Hamiltonian operator on this spherical harmonics to get to your energy, to get your energy and this is the, again, we applied Hamiltonian operator or we can say Laplacian operator in polar coordinates on the Spherical Harmonics and what we expect to get is energy of the rotational levels, ok.

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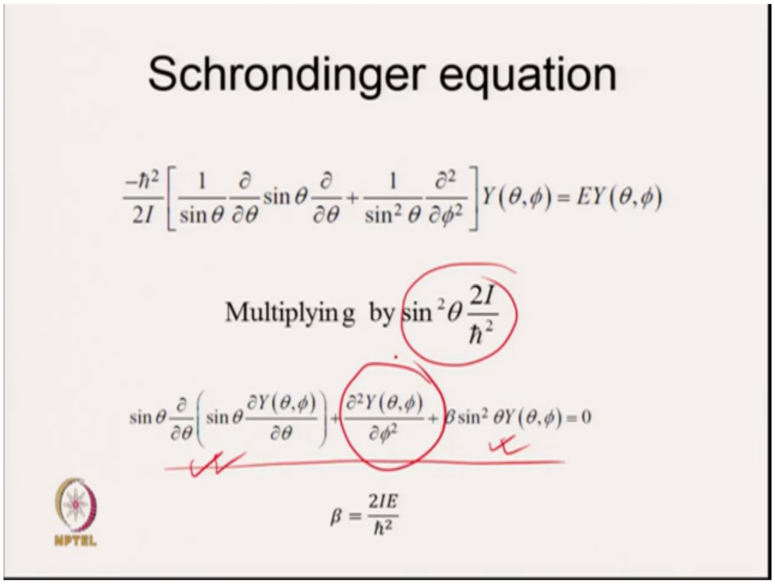

Schrondinger equation

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi)=EY(\theta,\phi)$$

Multiplying by $\sin^2\theta\frac{2I}{\hbar^2}$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\beta\sin^2\theta Y(\theta,\phi)=0$$

$$\beta=\frac{2IE}{\hbar^2}$$

So, again we will try to simplify and express this whole differential equation in form of a standard differential equation. So, that, we will be able to solve it. So, first thing what we did is just multiplied by sin square theta 2I by h bar square and what we will get is this term, all this term, ok. And here we assume beta is equal to 2IE by h bar square. So, here beta is 2IE by h bar square. So, simple thing is we are trying to express this in a well known differential equation whose solution is known, ok. So, sin theta del by del theta, sin theta so dy by d theta, del 2y by del phi square beta sin square theta y theta phi is equal to 0.

1 of advantage of this is that now you can see that you are able to separate your theta part with phi part. So, this, this is only function of theta, this is only function of theta, whereas this is a function of phi, function of phi. So, this is whole purpose of this multiplication.

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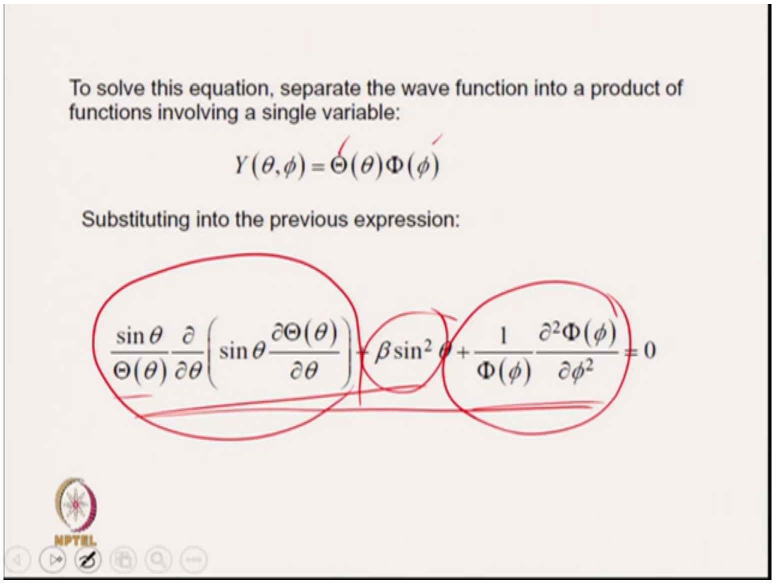

To solve this equation, separate the wave function into a product of functions involving a single variable:

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

Substituting into the previous expression:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta+\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=0$$

Now, if we have this kind of differential equation, then you can divide your wave function into 2 part, 1, which is function of theta and another which is function of phi. So, now, what we are doing is we are expressing your Spherical Harmonics into a function which depends only on theta and a function with depends only on phi, when we put that what we are going to get is see this is totally function of theta and this is totally function of theta and this is a function of phi. So when you substitute that that is what you are going to get.

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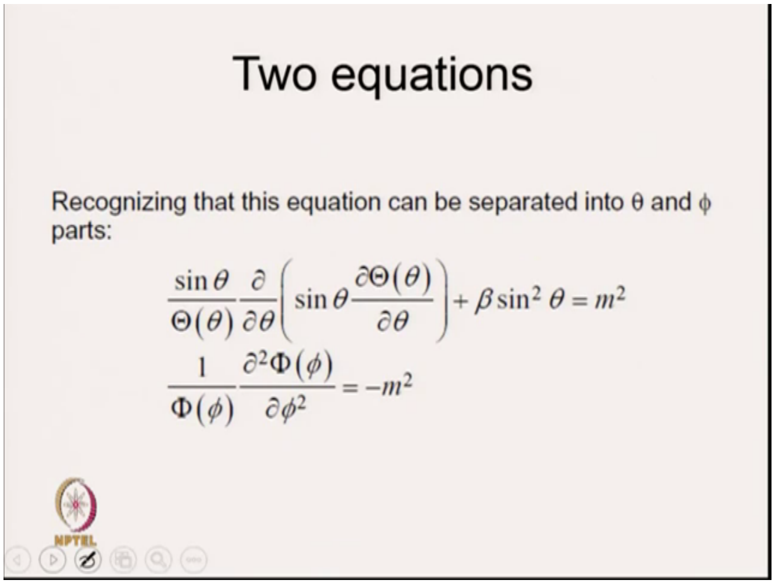

Two equations

Recognizing that this equation can be separated into θ and ϕ parts:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2$$

And since the 2 parts are either depend either dependent on theta or phi, so, the 2 terms must be equal to some constant and here we define this is equal to m square, and if this will be m square, so, this will be minus m square and so, whole term will be 0.

So, this plus m squared minus m square that will give you 0 and now, it is easier to solve these 2 equation. This we have already solved when you are dealing with 2 dimensional rigid rotor and solution this is well known.

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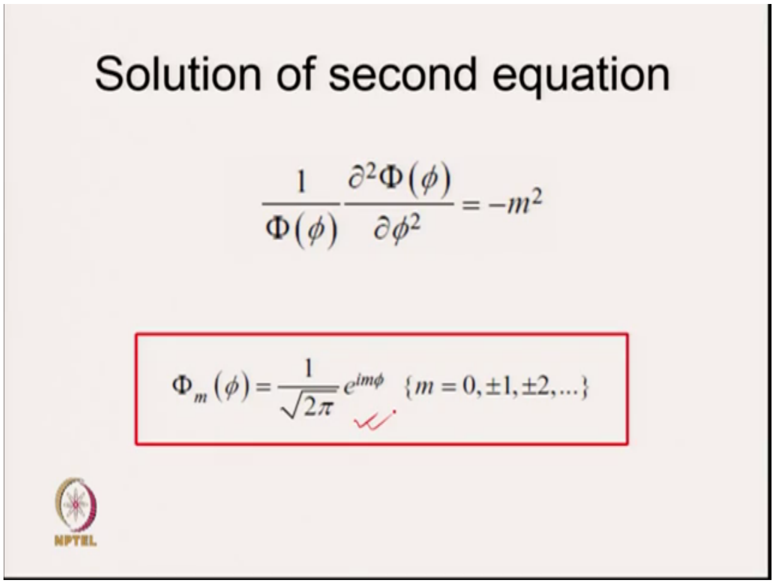

Solution of second equation

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2$$

$$\boxed{\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \quad \{m = 0, \pm 1, \pm 2, \ldots\}}$$

And that will be given by exponential i m phi multiplied by a normalization factor; again m can take value from 0 plus minus 1, plus minus 2. Now, the second differential equation, look at how to solve this.

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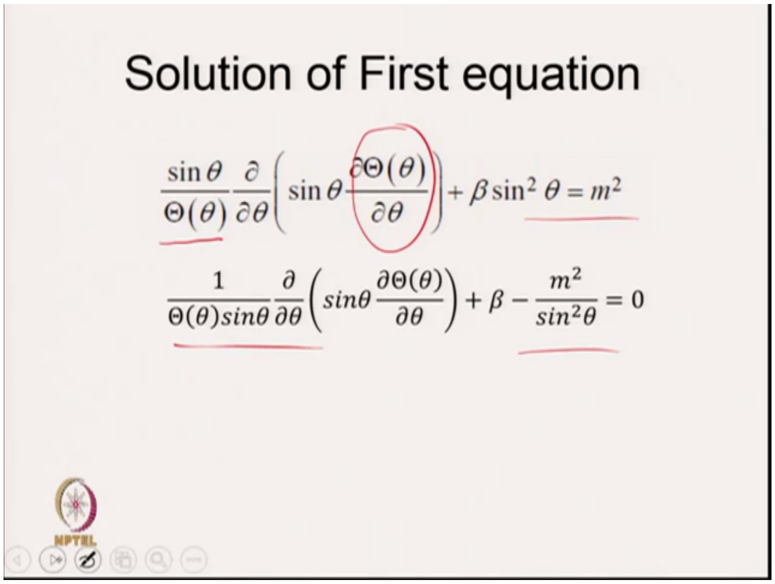

Solution of First equation

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Theta(\theta)sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta-\frac{m^2}{sin^2\theta}=0$$

So, this is your sin theta by capital theta which is your function of theta. So, capital theta is basically for wave function where theta is for the angle, small theta is for angle. So, sin theta by capital theta del by del theta sin theta, again this is the differential and this we need to solve if we want a solution. So, 1 thing we can do is just divide by sin square theta and when you do that, what you will get is here sin theta at the denominator and then this will cancel out and minus m square you take left hand side you will get minus m square by sin square theta.

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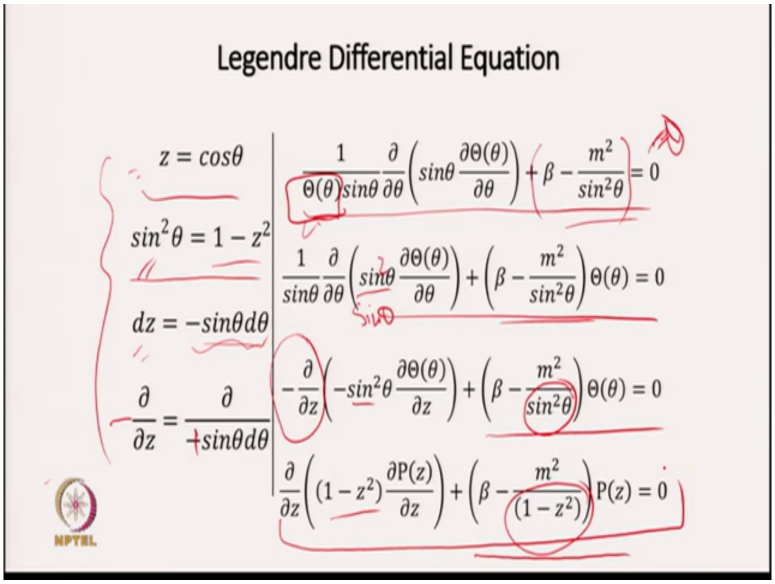

Legendre Differential Equation

$z = cos\theta$

$sin^2\theta = 1 - z^2$

$dz = -sin\theta d\theta$

$\frac{\partial}{\partial z} = \frac{\partial}{-sin\theta d\theta}$

$$\frac{1}{\Theta(\theta)sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta-\frac{m^2}{sin^2\theta}=0$$

$$\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\left(\beta-\frac{m^2}{sin^2\theta}\right)\Theta(\theta)=0$$

$$-\frac{\partial}{\partial z}\left(-sin^2\theta\frac{\partial\Theta(\theta)}{\partial z}\right)+\left(\beta-\frac{m^2}{sin^2\theta}\right)\Theta(\theta)=0$$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial P(z)}{\partial z}\right)+\left(\beta-\frac{m^2}{(1-z^2)}\right)P(z)=0$$

Again this all things are done to simplify the equation. So, in the last slide, we obtain this differential equation. Now, what we are going to do is simplify a bit to make it into some standard differential equation whose solution is known. So, first thing what we do is multiply this equation by the wave function cap theta cap theta. If we do that this cap theta will get removed and will get multiplied by this factor.

So, you see theta, theta multiplied by this factor. And now, what we will do is we assume z is equal to cos theta, z is equal to cos theta. If z is equal to cos theta, then sin square theta will be equal to 1 minus z square. So, first thing is sin square theta 1 minus z square. Now, if we differentiate this z is equal to cos theta, what we are going to get is dz is equal to minus sin theta d theta. What does that mean is, del by del z or the by dz is simply d by minus sin theta d theta. And once we assume this, now, we are going to simplify the second equation.

So, 1 by sin theta del by del theta, if you see here, 1 by sin theta del by del theta is equal to minus del by del z and that is what we substituted here. So, 1 by sin theta del by del theta is substituted by minus del by del z. Similar thing we are going to do here and the way we can do is let us take this sin square theta by sin theta. So, what I did is I multiplied sin theta in a numerator and divided by sin theta in the denominator.

Why I am doing that, because I know that 1 by sin theta del by del theta is equal to minus del by del z. So, del by sin theta d theta is equal to minus del by del z. So, you can do minus here plus, ok. So, if I do that, then 1 by sin theta del by del theta is equal to minus del by del z and sin square theta remains, sin square theta remains. And then you have plus part same thing we can take from the second line. So, beta minus m square by sin square theta and then cap theta is a function of theta, is equal to 0.

Now, you see sin square theta we just expressed in terms of z and sin square theta is 1 minus z square. Let us put it here. So, you will get your sin square theta is 1 minus z square and this minus, minus becomes plus. Similarly, we can replace this sin square theta by 1 minus z square. This is well known differential equation, this is a well known differential equation which is known as a Legendre Differential Equation, Legendre Differential Equation whose solution is known, whose solution is known.

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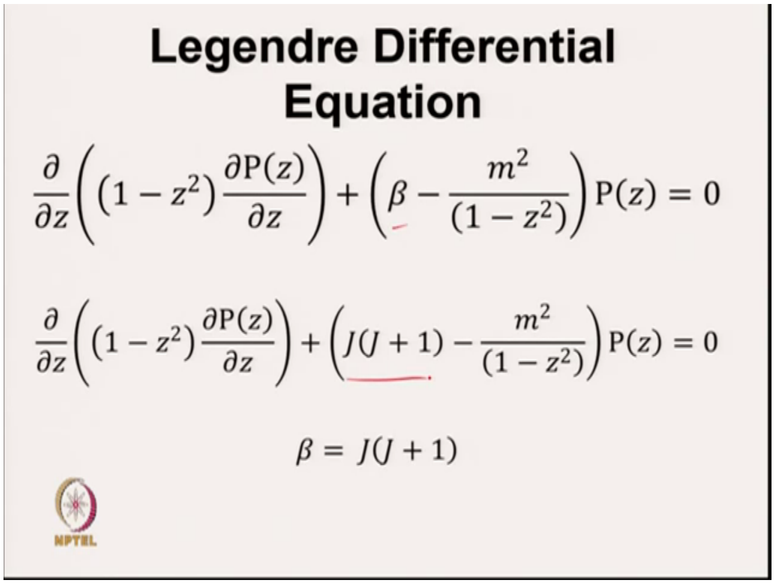

Legendre Differential Equation

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+\left(\underline{\beta}-\frac{m^2}{(1-z^2)}\right)\mathrm{P}(z)=0$$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+\left(\underline{J(J+1)}-\frac{m^2}{(1-z^2)}\right)\mathrm{P}(z)=0$$

$$\beta = J(J+1)$$

And so, this is your whole equation that is what we got, del by del z 1 minus z square d P z by D z plus beta minus m square 1 minus z square P z is equal to 0; here z is equal to cos theta. So, just by putting z is equal to cos theta, you are able to get a differential equation which is known by name of Legendre Differential Equation. And the solution of this is well known, and that is why we were doing so many simplification.

So, in this case, you will get a multiple value of your wave function and energy and the way to solve it give beta is equal to J, J plus 1. So, beta is equal to J J plus 1.For each value of J there will be a different solution and we will go and so, how (solution) is value of J and m you can get different solution and those are the allowed (wa wa) wave function for the rotational level and the corresponding energy is the energy of that level.

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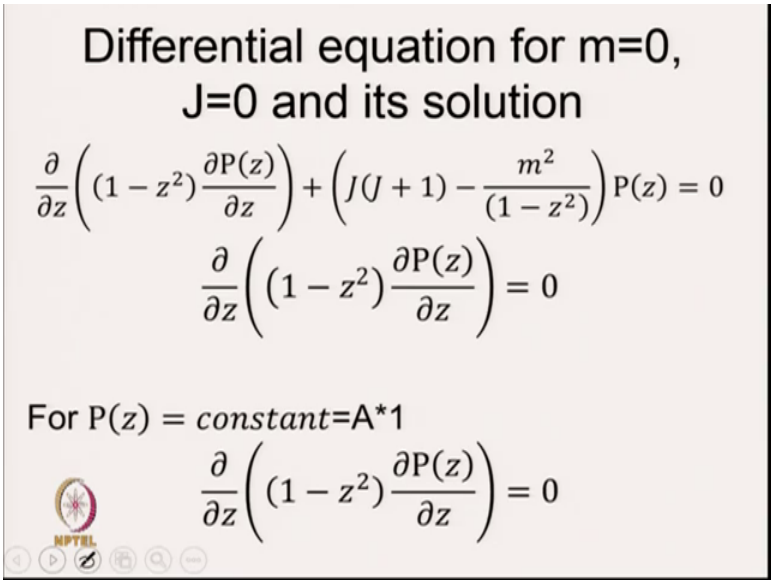

Differential equation for m=0, J=0 and its solution

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+\left(J(J+1)-\frac{m^2}{(1-z^2)}\right)\mathrm{P}(z)=0$$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)=0$$

For $\mathrm{P}(z) = constant$=A*1

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)=0$$

So, let us think about the differential equation for m is equal to 0 and J is equal to 0 and what will be its solution. So, this was the differential equation which we just seen in the last page. So, if we put m is equal to 0 and J is equal to 0 what you will get is this equation. So, this part is 0 this part is 0 and so, you are left with just the first part del by del z 1 minus z square del P z by del z is equal to zero. So, now think of solution of this differential equation must be a constant, because if you take constant then this will be 0 and the whole thing becomes 0 and then differential will be 0.

If suppose you take some function of z, then you see that z square will get multiplied by some constant and if it is first order, if it is second order, it will be multiplied by z, and the differential of that is not going to be 0. So, only solution of this differential equation is constant and so A into 1 and if you put 1 here, you can see that if you put 1 here then this will be 0, and everything will be 0. So, solution of this equation is z is equal to 1 or z is equal to a constant.

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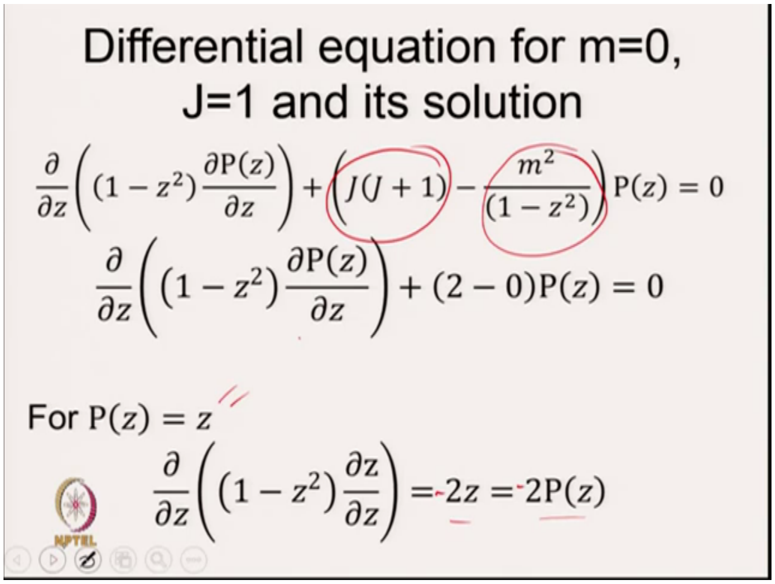

Differential equation for m=0, J=1 and its solution

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+\left(J(J+1)-\frac{m^2}{(1-z^2)}\right)\mathrm{P}(z)=0$$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+(2-0)\mathrm{P}(z)=0$$

For $\mathrm{P}(z)=z$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial z}{\partial z}\right)=-2z=-2\mathrm{P}(z)$$

Now, let us think about if we try to solve this differential equation for m is equal to 0 and J is equal to 1. So, if you put that m is equal to 0, then this part is going to be 0 and this part is going to be equal to 2. So, J is equal to 1, 1 plus 1 2, 1 into 2 is 2. Now, the solution of the this differential equation will be different than the first differential equation. So, this can be solved if you take P z is equal z or P z is equal to Z into some constant.

So, if you do that, let us see here if we replaced P z by z then we will get del z by del z, del z, del z cancels out. So, 1 minus z square and differential of that is 2z. This will be I think, minus 2z. So, this is minus 2 P z and minus 2 P z plus 2 P z it will be 0; minus 2 P z and plus 2 P z is equal to 0. Solution for the differential equation, which we got for m equal 0 and J is equal to 1 will be z multiplied by some constant.

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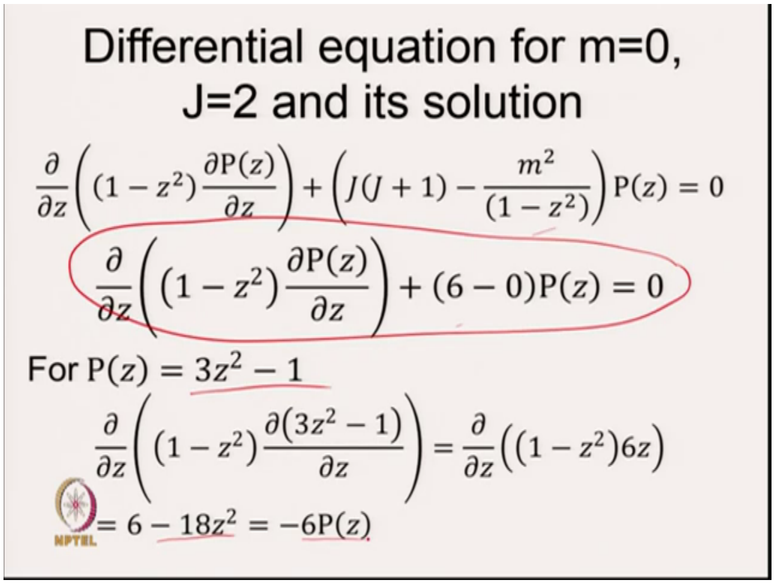

Differential equation for m=0, J=2 and its solution

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+\left(J(J+1)-\frac{m^2}{(1-z^2)}\right)\mathrm{P}(z)=0$$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial \mathrm{P}(z)}{\partial z}\right)+(6-0)\mathrm{P}(z)=0$$

For $\mathrm{P}(z) = \underline{3z^2 - 1}$

$$\frac{\partial}{\partial z}\left((1-z^2)\frac{\partial(3z^2-1)}{\partial z}\right)=\frac{\partial}{\partial z}\left((1-z^2)6z\right)$$

$$= 6 - \underline{18z^2} = -\underline{6\mathrm{P}(z)}$$

Now, similarly, you can get differential equation for m is equal to 0 and J is equal to 0 if you put here this is again 0 and 2 into 2 plus 1 is equal to 6. So, this is differential equation this is different from the earlier 2 and solution is certainly going to be different and the solution is 3z square minus 1, if you just differentiate this, you will get 6 z and if you double differentiate what you are going to get is 6 minus 18z square, which is equal to minus 6 P z, minus 6 P z and if you add here and it is going to be 0. So, we have seen the solution of 3 different differential equation for different value of m and J and what we have got is different solution for each for each m is equal to m and j value.

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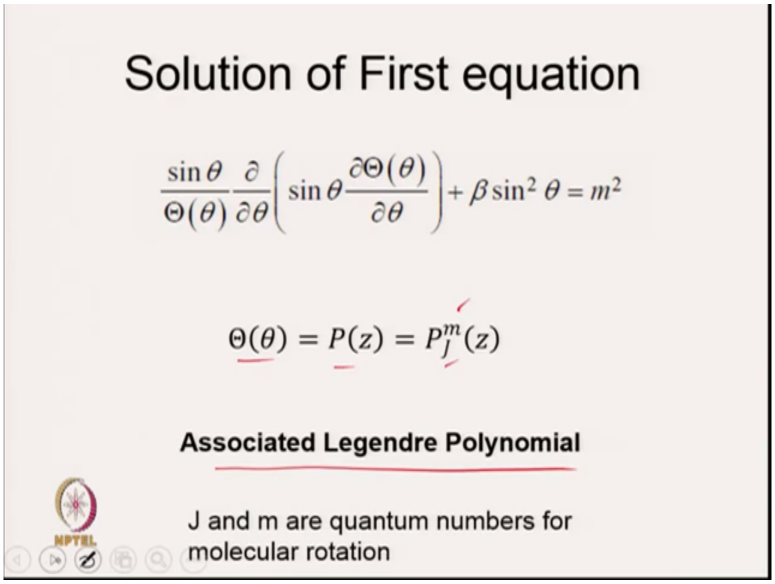

Solution of First equation

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\Theta(\theta)=P(z)=P_J^m(z)$$

Associated Legendre Polynomial

J and m are quantum numbers for molecular rotation

So, what these 3 Solutions tells us that we can get wave function. We have theta theta will be Pz and this z will depend on your J and m quantum number. And this is known as the Associated Legendre Polynomial, Associated Legendre Polynomial which will be different for different value of J and m.

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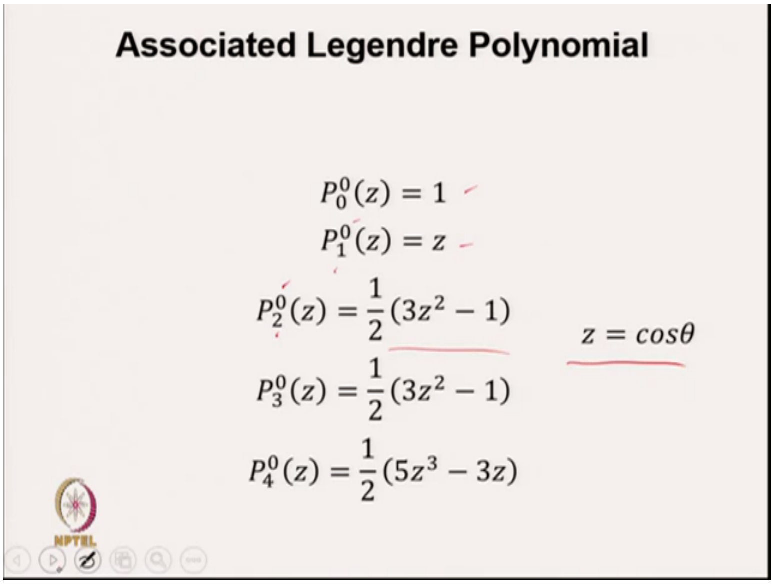

Associated Legendre Polynomial

$$P_0^0(z)=1$$
$$P_1^0(z)=z$$
$$P_2^0(z)=\frac{1}{2}(3z^2-1)$$
$$P_3^0(z)=\frac{1}{2}(3z^2-1)$$
$$P_4^0(z)=\frac{1}{2}(5z^3-3z)$$

$z=cos\theta$

The solution what we got is if J is equal to 0, m is equal to 0, we will get 1 if J is equal to 1 and m is equal to 0 then you will get z if 2, 0 then you will get half 3z square minus 1 and similarly, for different value of J and m solution will be different. Here again I will emphasize that z is equal to cos theta, z is equal to cos theta.

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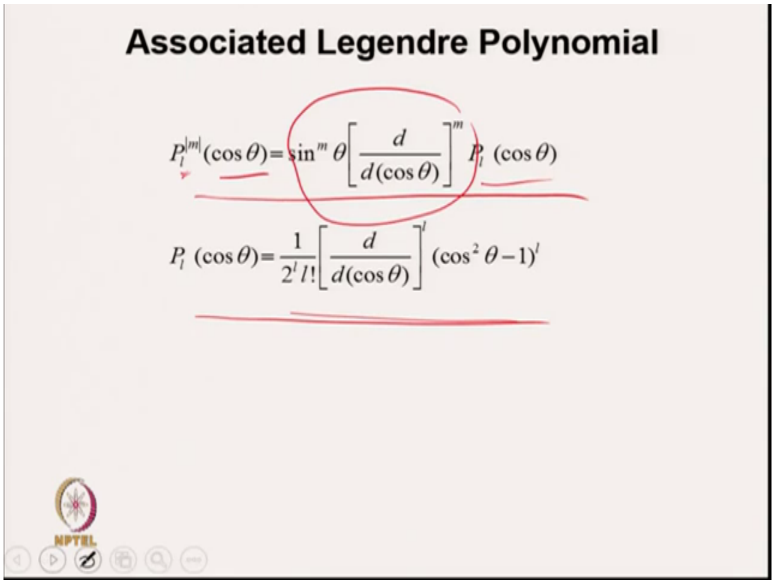

Associated Legendre Polynomial

$$P_l^{|m|}(\cos\theta)=\sin^m\theta\left[\frac{d}{d(\cos\theta)}\right]^m P_l(\cos\theta)$$

$$P_l(\cos\theta)=\frac{1}{2^l l!}\left[\frac{d}{d(\cos\theta)}\right]^l(\cos^2\theta-1)^l$$

These all solution can be written in a simple form, simple form which is given by the Associated Legendre Polynomial, Associated Legendre Polynomial, your L is basically J. So, Pjm is a function of cos theta, which we are writing z and that will be given by sin m theta differential of d d cos theta power m, Pl cos theta, where Pl cos theta is given by this.

If m is equal to 0, if m is equal to 0, this turns out to be 1 and you have simply Pl cos theta, simply Pl cos theta which is given by this equation. So, all the polynomial, solution can be expressed in terms of this differential, in terms of this differential.

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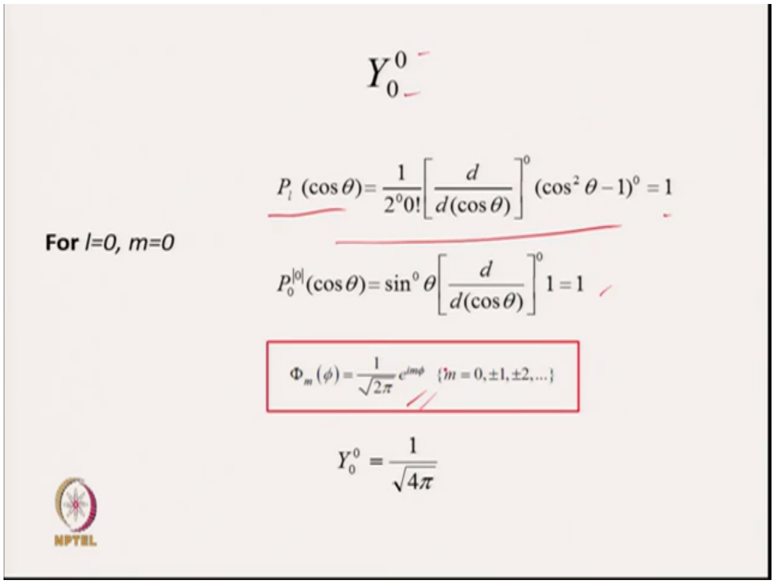

$$Y_0^0$$

For *l=0, m=0*

$$P_l\,(\cos\theta) = \frac{1}{2^0 0!}\left[\frac{d}{d(\cos\theta)}\right]^0 (\cos^2\theta - 1)^0 = 1$$

$$P_0^{|0|}(\cos\theta) = \sin^0\theta\left[\frac{d}{d(\cos\theta)}\right]^0 1 = 1$$

$$\boxed{\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \quad \{m = 0, \pm 1, \pm 2, \ldots\}}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

So, now we know the solution of theta part and solution of phi part. Now, we can go and see what will be the Spherical Harmonics. So, let us first see, if we take J is equal 0 and m is equal to 0, what will be the wave function for theta part?

So, what is the solution for the theta part? So, this is given by cos theta and 1 by 2 0 if you remember that if m is equal to 0 then we are left with only PJ cos theta or Pl cos theta and that is given by here. So, now we are going to put the value of J which is basically l; so, l is equal to 0, m is equal to 0, here l is equal to 0 and then l is equal to 0 here. So, if you put that what we are going to get is 1 and if you remember that the solution which we got for the J is equal to 0, m is equal to 0, is equal to 1.

So, here you have 1 and now, we know the solution of phi part also and that is 1 by root 2 pi e exponential minus m phi. So m is equal to 0 and so you have simply, 1 by root 2 pi. And so, your Spherical Harmonics will be your 1 by root 4 pi, Spherical Harmonics will be 1 by root 4 pi.

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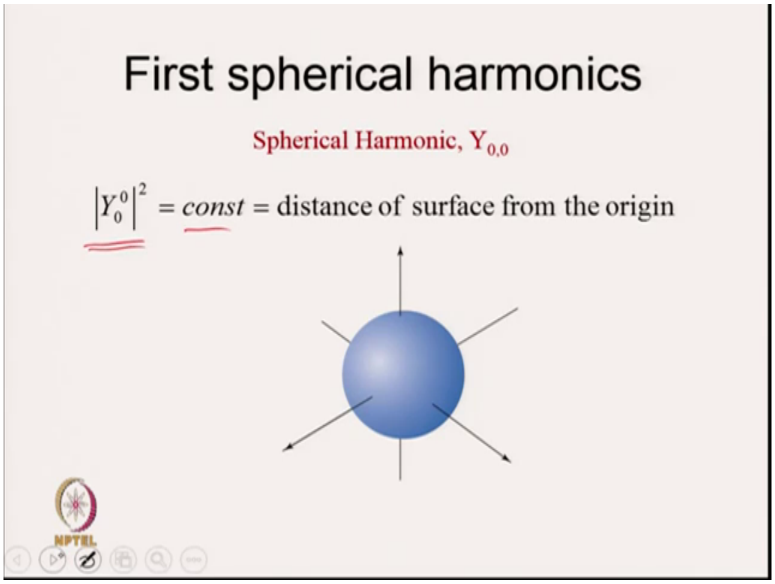

First spherical harmonics

Spherical Harmonic, $Y_{0,0}$

$$|Y_0^0|^2 = const = \text{distance of surface from the origin}$$

And since Spherical Harmonics for Y 00 is constant. So, its square is also going to be constant. And that tells you about the distance of surface from the origin. So, for any value of theta and phi, any value of theta and phi, Y is going to be constant and, so, it will have a constant value. And, so, shape will be like a sphere.

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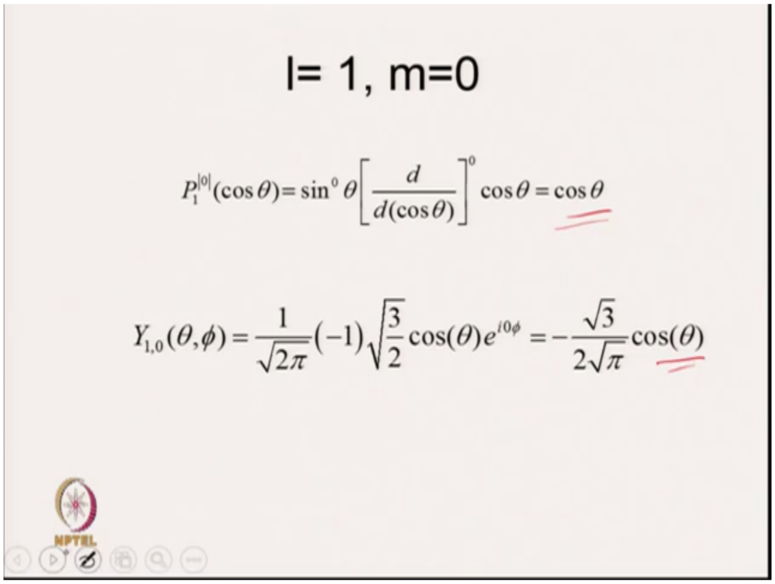

l= 1, m=0

$$P_1^{|0|}(\cos\theta)=\sin^0\theta\left[\frac{d}{d(\cos\theta)}\right]^0\cos\theta=\cos\theta$$

$$Y_{1,0}(\theta,\phi)=\frac{1}{\sqrt{2\pi}}(-1)\sqrt{\frac{3}{2}}\cos(\theta)e^{i0\phi}=-\frac{\sqrt{3}}{2\sqrt{\pi}}\cos(\theta)$$

Now, for l is equal to m and m equal 0 again, if you solve this you will get the term cos theta and so, Spherical Harmonics is root 3 by 2 root pi cos theta. Now, you see it is dependent on the theta it is not dependent on phi, but it is dependent on theta.

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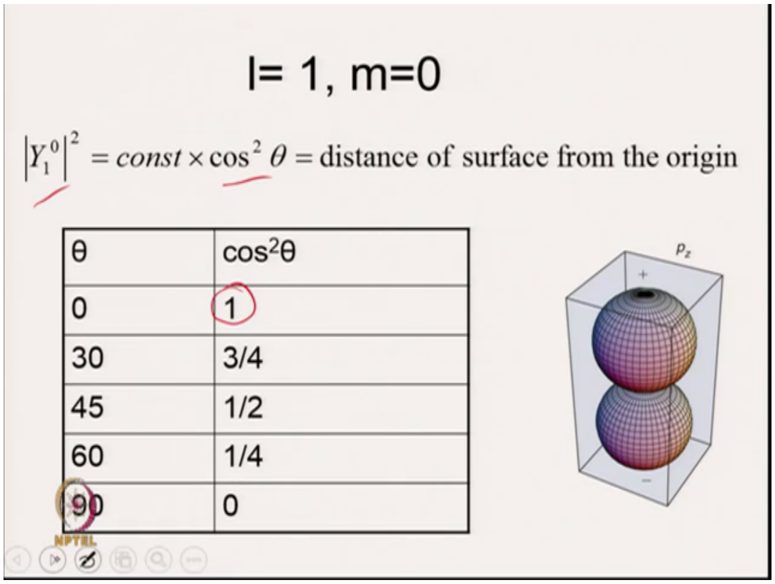

l= 1, m=0

$$|Y_1^0|^2 = const \times \cos^2\theta = \text{distance of surface from the origin}$$

θ	$\cos^2\theta$
0	1
30	3/4
45	1/2
60	1/4
90	0

So, let us see how does it will look like if we have l is equal to 1, m is equal to 0. So, square of this Spherical Harmonics will be a function of cos, cos square theta and this will give you distance of surface from origin. Now, let us take the value of theta from 0 to 90 degree. What you will see? At 0 value you can see you have got the maximum value of cos square theta, what does that means is, when theta is equal to 0, this your distance of surface from the origin will be maximum and you can see this is your theta is equal to 0, this is your theta is equal to 0 and so, you have a maximum value.

Now, you change angle. So, suppose you are going to 30 degree, this value is decreasing, decreasing, decreasing and theta is equal to 90 degree it becomes 0. So, you can see here it is 0 and since it goes to cos square theta, so, same thing will happen when you go in opposite direction. So, this gives you shape of Pz, Pz (())(40:44).

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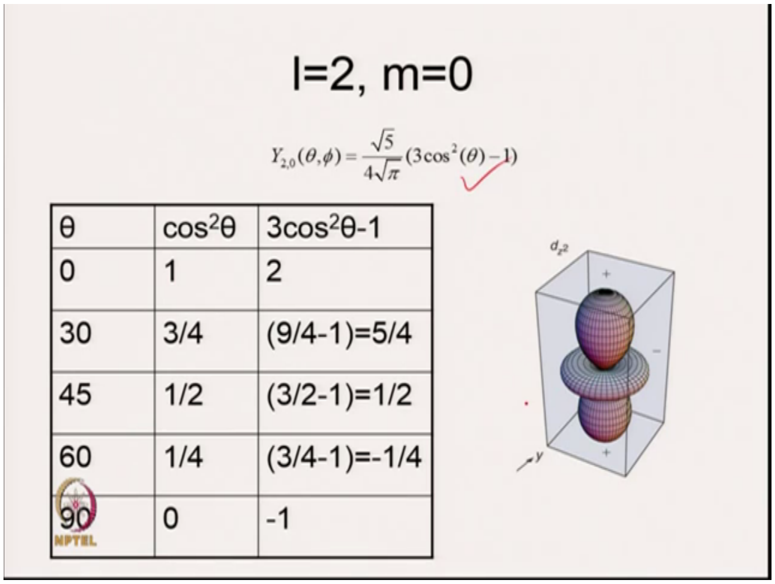

l=2, m=0

$$Y_{2,0}(\theta,\phi)=\frac{\sqrt{5}}{4\sqrt{\pi}}(3\cos^2(\theta)-1)$$

θ	$\cos^2\theta$	$3\cos^2\theta-1$
0	1	2
30	3/4	(9/4-1)=5/4
45	1/2	(3/2-1)=1/2
60	1/4	(3/4-1)=-1/4
90	0	-1

Similarly, for l is equal to 2 and m is equal to 0, your Spherical Harmonics will be dependent on 3 cos square theta minus 1. It will dependent on 3 cos square theta minus 1 and I have calculated the value of cos square theta for given value of theta and then we calculated 3 cos square theta minus 1. So, you are going from 0 to 5 by 4, 1 by 2, 1 by 4, 2 minus 1. So, now you see at 0 it is your maximum value. So, you are getting a maximum value at this point and they are starts to decrease. You see, it becomes your 3 cos square theta 1 by 4 for this kind of shape at the value of 0.

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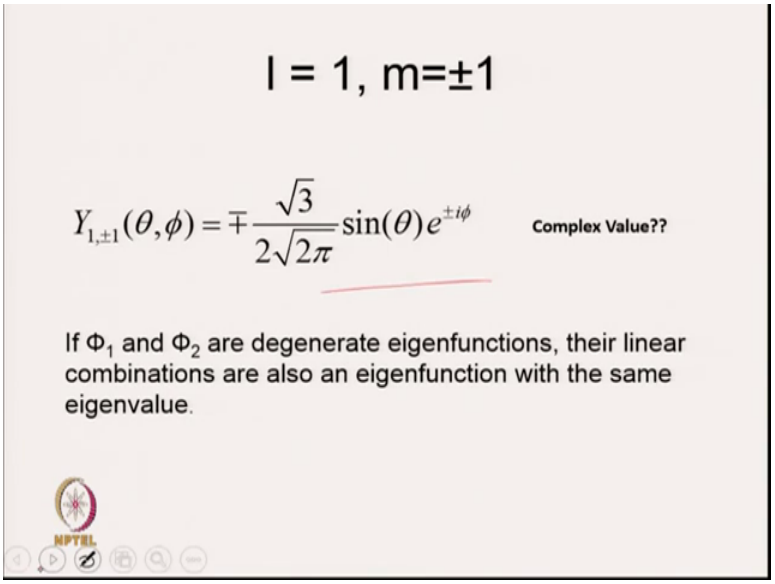

l = 1, m=±1

$$Y_{1,\pm1}(\theta,\phi)=\mp\frac{\sqrt{3}}{2\sqrt{2\pi}}\sin(\theta)e^{\pm i\phi}$$

Complex Value??

If Φ_1 and Φ_2 are degenerate eigenfunctions, their linear combinations are also an eigenfunction with the same eigenvalue.

If we change the value of m then dependence of Spherical Harmonics or Spherical Harmonics will going to depend on phi also apart from theta and in that case, you will get a complex value. This so, 2 values you will get and these values are degenerate eigenfunctions, their linear combination is also going to be eigenfunction with the same eigenvalue.

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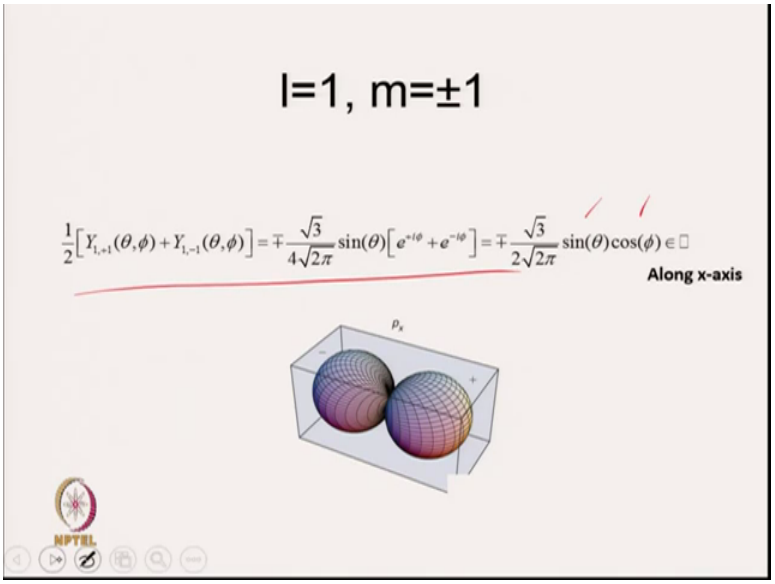
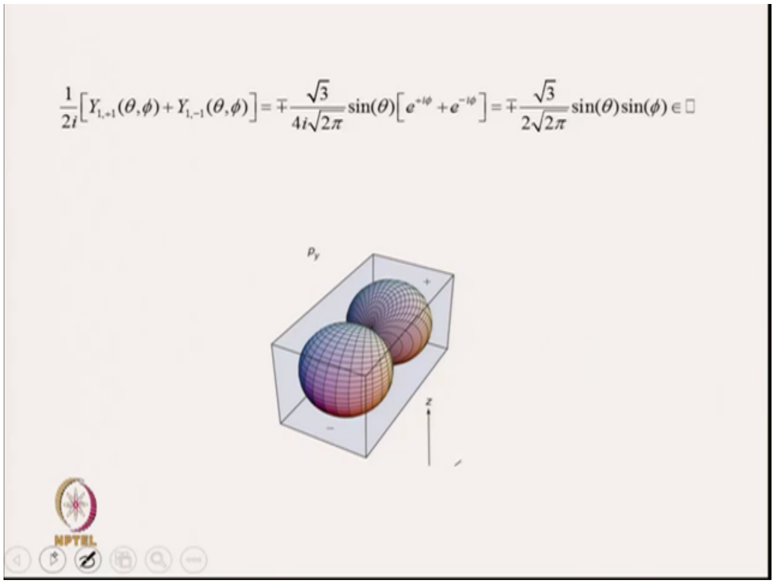


l=1, m=±1

$$\frac{1}{2}\left[Y_{1,+1}(\theta,\phi)+Y_{1,-1}(\theta,\phi)\right]=\mp\frac{\sqrt{3}}{4\sqrt{2\pi}}\sin(\theta)\left[e^{+i\phi}+e^{-i\phi}\right]=\mp\frac{\sqrt{3}}{2\sqrt{2\pi}}\sin(\theta)\cos(\phi)\in\square$$

Along x-axis



$$\frac{1}{2i}\left[Y_{1,+1}(\theta,\phi)+Y_{1,-1}(\theta,\phi)\right]=\mp\frac{\sqrt{3}}{4i\sqrt{2\pi}}\sin(\theta)\left[e^{+i\phi}+e^{-i\phi}\right]=\mp\frac{\sqrt{3}}{2\sqrt{2\pi}}\sin(\theta)\sin(\phi)\in\square$$

And, so, what is done is its linear function is taken and now you can see that it is now dependent on sin theta and cos phi, sin theta and cos phi and that gives shape of different p orbital Px and Py. And so, this is your dependence of wave function or Spherical Harmonics and theta and phi.

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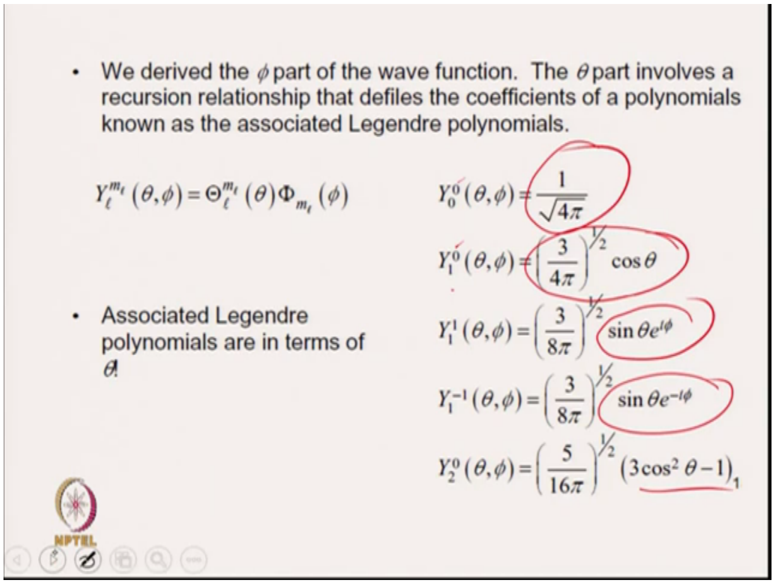

- We derived the ϕ part of the wave function. The θ part involves a recursion relationship that defiles the coefficients of a polynomials known as the associated Legendre polynomials.

$$Y_\ell^{m_\ell}(\theta,\phi)=\Theta_\ell^{m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

- Associated Legendre polynomials are in terms of θ.

$$Y_0^0(\theta,\phi)=\frac{1}{\sqrt{4\pi}}$$

$$Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_1^1(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}$$

$$Y_1^{-1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$$

$$Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$$

So, this is your overall Spherical Harmonics for value of J is equal to 0 and m is equal to 0, it is simply a constant for J is equal to 1 and a m is equal to 0 it a dependent on theta value, for 1 and 1 then it will depend on phi, 1 minus 1 it will depend on also on phi and if again it is a m is equal to 0 then it does not depend on value of phi. So, if m, if m is equal to 0 the wave function is only dependent on theta value, if m is different than 0, then you have dependence of wave function of phi also, ok.

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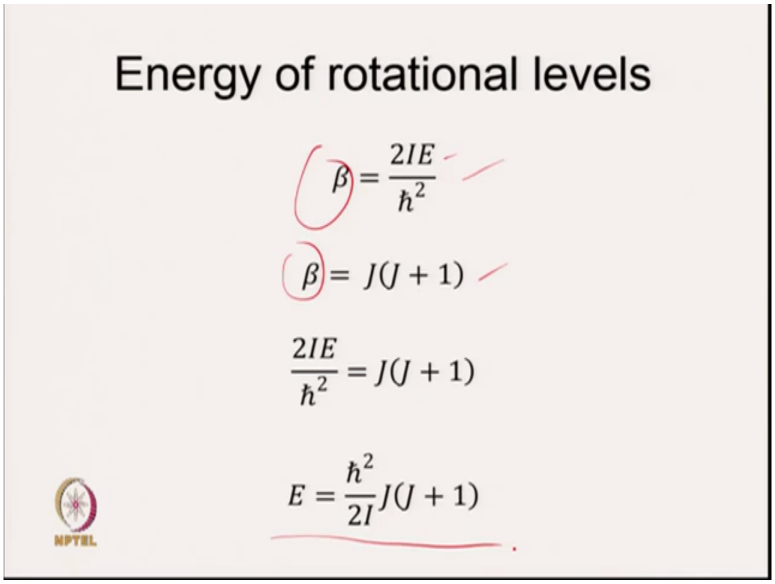

Energy of rotational levels

$$\beta=\frac{2IE}{\hbar^2}$$

$$\beta=J(J+1)$$

$$\frac{2IE}{\hbar^2}=J(J+1)$$

$$E=\frac{\hbar^2}{2I}J(J+1)$$

So, during the solving of this equation, we assume 2 different we did 2 different assumption 1 is beta is equal to 2IE h bar square and beta is equal to J, J plus 1 and this is going to give you value of E. So, since both are beta you can simply write 2IE by h bar square is equal to J, J plus 1 and that will help you in calculating value of E. So, this is the energy of your different rotational level, energy of different rotational level and since J can take some deserve value only and so, E is energy of rotational levels are quantized, energy of rotational levels are quantized.

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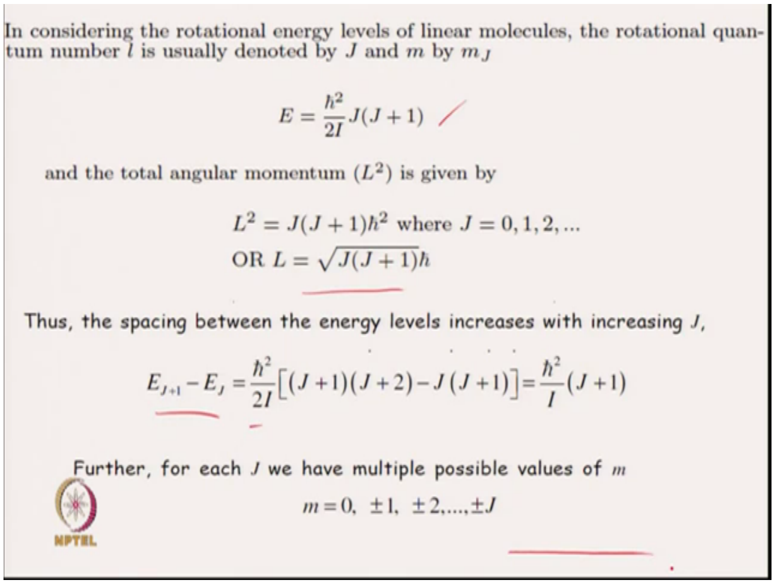

In considering the rotational energy levels of linear molecules, the rotational quantum number l is usually denoted by J and m by m_J

$$E = \frac{\hbar^2}{2I}J(J+1)$$

and the total angular momentum (L^2) is given by

$$L^2 = J(J+1)\hbar^2 \text{ where } J = 0, 1, 2, \ldots$$

$$\text{OR } L = \sqrt{J(J+1)}\hbar$$

Thus, the spacing between the energy levels increases with increasing J,

$$E_{J+1} - E_J = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] = \frac{\hbar^2}{I}(J+1)$$

Further, for each J we have multiple possible values of m

$$m = 0, \pm 1, \pm 2, \ldots, \pm J$$

So, energy is given by h bar square by 2 I, J, J plus 1. We can also calculate total angular momentum l square, l square is simply your given by E into 2I. So, E into 2I h bar square J, J plus 1or l is equal to square root of J, J plus 1 multiplied by h bar. We can also calculate the spacing between 2 different energy levels and that is shown here EJ plus 1 EJ.

So, h bar square by 2 I will be common and then J plus 1, J plus 2, minus J, J plus 1 will give you h bar square by I, J plus 1. So, here we see that energy is only dependent on J not on m. And so, for different value of m. So, here (de) degeneracy is there, (your) you will have 2 J plus 1 degenerate energy levels.

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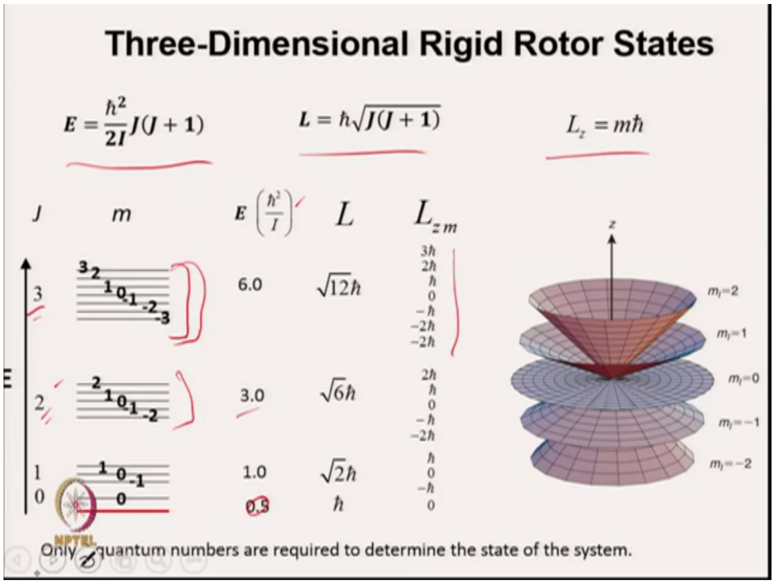

Three-Dimensional Rigid Rotor States

$E = \frac{\hbar^2}{2I}J(J+1)$ $L = \hbar\sqrt{J(J+1)}$ $L_z = m\hbar$

J	m	$E\left(\frac{\hbar^2}{I}\right)$	L	L_{zm}
3	3 2 1 0 -1 -2 -3	6.0	$\sqrt{12}\hbar$	$3\hbar$ $2\hbar$ $\hbar$ 0 $-\hbar$ $-2\hbar$ $-2\hbar$
2	2 1 0 -1 -2	3.0	$\sqrt{6}\hbar$	$2\hbar$ $\hbar$ 0 $-\hbar$ $-2\hbar$
1	1 0 -1	1.0	$\sqrt{2}\hbar$	$\hbar$ 0 $-\hbar$
0	0	0.5	$\hbar$	0

Only quantum numbers are required to determine the state of the system.

So, let us think about how does this different parameters for 3 dimensional rigid rotor looks like. So, energy is your h bar square by 2 I J J plus 1 your momentum is your h bar root J J plus 1 and momentum along z direction is m h bar.

So, for the 0, 2 J plus 1 is 1. So, its degeneracy will be 1 and your energy will be your if you put J is equal 0 and 0 into 0 plus 1, so, this will be 0. So, energy will be 0, energy will be 0, I believe, ok. Let us see here, if J is equal to 3, so, 3 into 4, 12 divided by 2 is equal to 6 into h bar square by I. This is energy for J is equal to 3. For J is equal to 2, you have 2 into 3 6, 6 by 2 is 3 h bar square by I. For J is equal to 1, you have 1 into 2. So, you have 2, 2 2 cancel so 1 h bar square by I and for J is equal to 0, J is equal to 0 and this would be 0 this would be 0, ok.

Your, you can calculate similarly, l and l will be this value. Now, you see this energy level these are the different degenerate levels. So, for J is equal to 3 the 2J plus 1. So, seven levels are there which are degenerate but their angular momentum will be along the z axis will be different, along the z axis will be different. For 2 you have 2 J plus 1. So, you have 5 degenerate energy levels, 5 degenerate energy levels. So, this is about specifics of 3 dimensional rigid rotors.

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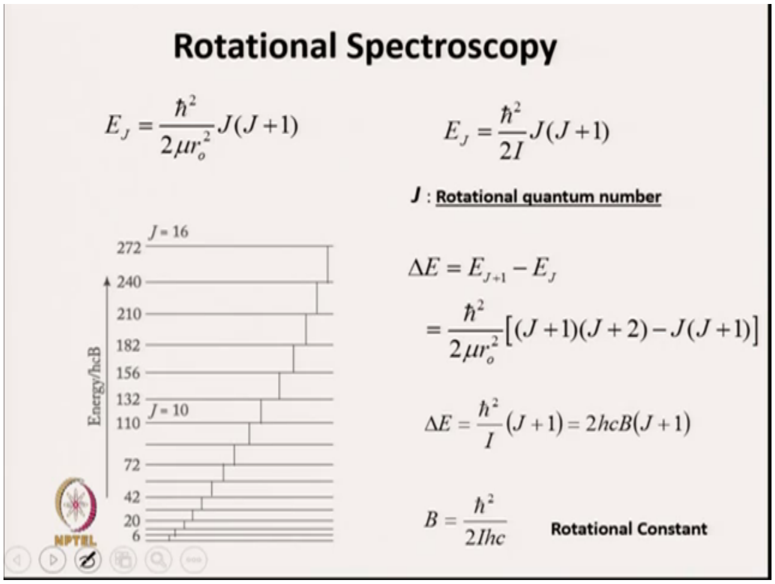

Rotational Spectroscopy

$$E_J = \frac{\hbar^2}{2\mu r_o^2} J(J+1)$$

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

J : Rotational quantum number

$$\Delta E = E_{J+1} - E_J$$

$$= \frac{\hbar^2}{2\mu r_o^2}\left[(J+1)(J+2) - J(J+1)\right]$$

$$\Delta E = \frac{\hbar^2}{I}(J+1) = 2hcB(J+1)$$

$$B = \frac{\hbar^2}{2Ihc}$$ **Rotational Constant**

Now, in Rotational Spectroscopy, what we are looking at is the transition from 1 energy level to another. Since now, we know what is the energy of particular level we can know what is the energy difference between 2 rotational level and once we know that, we can calculate what will be the wave number or frequency associated with that transition. So, E we already know is h bar square by 2I J, J plus 1. So, we can calculate the difference between 2 energy level, consecutive energy level from J to J plus 1 and that comes out to be here 2 hcB J plus 1, 2 hcB J plus 1. Where B is equal to your h bar square by 2Ihc, h bar Square by 2Ihc. So, here it is in unit is in Joule.

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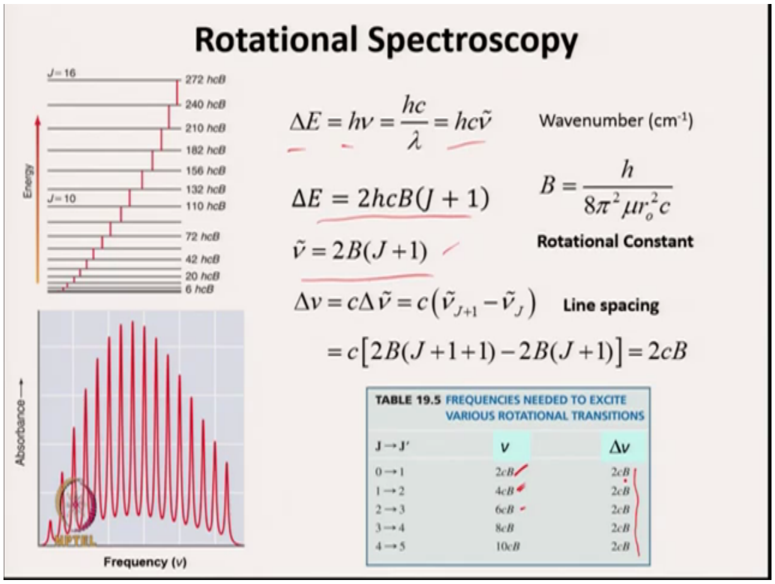

Rotational Spectroscopy

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$$ Wavenumber (cm^{-1})

$$\Delta E = 2hcB(J+1)$$

$$B = \frac{h}{8\pi^2 \mu r_o^2 c}$$ **Rotational Constant**

$$\tilde{\nu} = 2B(J+1)$$

$$\Delta\nu = c\Delta\tilde{\nu} = c\left(\tilde{\nu}_{J+1} - \tilde{\nu}_J\right)$$ **Line spacing**

$$= c\left[2B(J+1+1) - 2B(J+1)\right] = 2cB$$

TABLE 19.5 FREQUENCIES NEEDED TO EXCITE VARIOUS ROTATIONAL TRANSITIONS

J → J′	ν	Δν
0 → 1	$2cB$	$2cB$
1 → 2	$4cB$	$2cB$
2 → 3	$6cB$	$2cB$
3 → 4	$8cB$	$2cB$
4 → 5	$10cB$	$2cB$

So, we know that delta E is h nu and that can be written as hc nu bar, where nu bar is wave number and we already know what is delta E. So, now we can calculate what will be the wave number for the transition and that is simply 2 BJ plus 1. So, you must remember that you are going from the Jth rotational level to J plus 1 level, Jth rotational level to J plus 1 level and so, suppose you are going from J minus 1 level to J level then your frequency of transition would be 2 BJ so, keep that thing in mind some of the books write frequency in terms of 2 B 2 BJ just 2 BJ, where what they are assuming that your final energy level or excited energy level is J.

So, basically they are looking at transition from J minus 1 level to J. Here we are looking at the transition from J level to J plus 1 level and so, your wave number is 2 BJ plus 1, 2 BJ plus 1. Now, we can also look at the difference between 2 lines in the spectrum. So, 1 line you are going to get at 2 BJ plus 1. So, suppose if J is equal 0 then you are going to get at 2 BJ is equal to 1 then you are going to get at 4 B and 6 B like that.

So, what is the difference between 2 lines. So, these are the different lines here of Rotational Spectroscopy and what you are going to get is for 0 to 1 transition 2 B centimeter inverse or in terms of hertz it is going to be 2 cB where c is velocity of light. So 0 for 1 transition you will get to 2 B or 2 CB. 1 to 2 transition you are going to get 4 CB. This is the frequency and the frequency, spacing between the lines is going to be same, spacing between lines is going to be same.

So, this is your frequency for 0 to 1 transition This is frequency for 1 to 2 transition, this is frequency for 2 to 3 transition. 0 to 1, 1 to 2, 2 to 3, 3 to 4. So, (())(50:47) spacing between this 2 is going to be constant, it is going to be constant. So it will be 2 CB hertz or 2 B in centimeter inverse, 2 B in centimeter inverse, ok. So, now, we know what is the delta E or your frequency and wave number associated with different transition.

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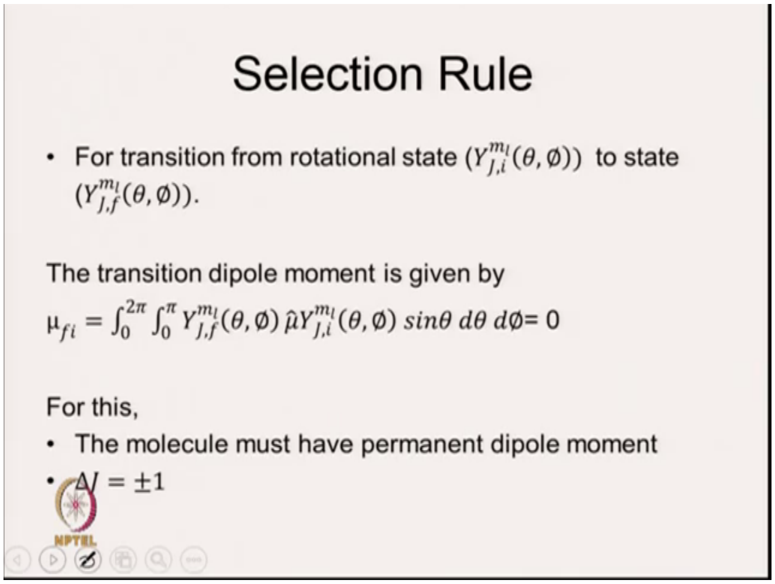

Selection Rule

- For transition from rotational state ($Y_{J,i}^{m_l}(\theta,\emptyset)$) to state ($Y_{J,f}^{m_l}(\theta,\emptyset)$).

The transition dipole moment is given by

$\mu_{fi} = \int_0^{2\pi}\int_0^{\pi} Y_{J,f}^{m_l}(\theta,\emptyset)\,\hat{\mu}Y_{J,i}^{m_l}(\theta,\emptyset)\, sin\theta\, d\theta\, d\emptyset = 0$

For this,

- The molecule must have permanent dipole moment
- $\Delta J = \pm 1$

Now, we need to know the selection of which kind of transition are allowed, which kind of transitions are allowed. And for that, we know that transition we need to calculate transition dipole moment and this will not be 0, this will not be 0, if your transition is allowed. And for this there are 2 criteria. 1 is molecule must have permanent dipole moment if it does not have dipole moment then this is going to be your transition dipole moment is going to be 0. So, molecule must have permanent dipole moment and then delta J must be plus minus 1, delta J must be plus minus 1.

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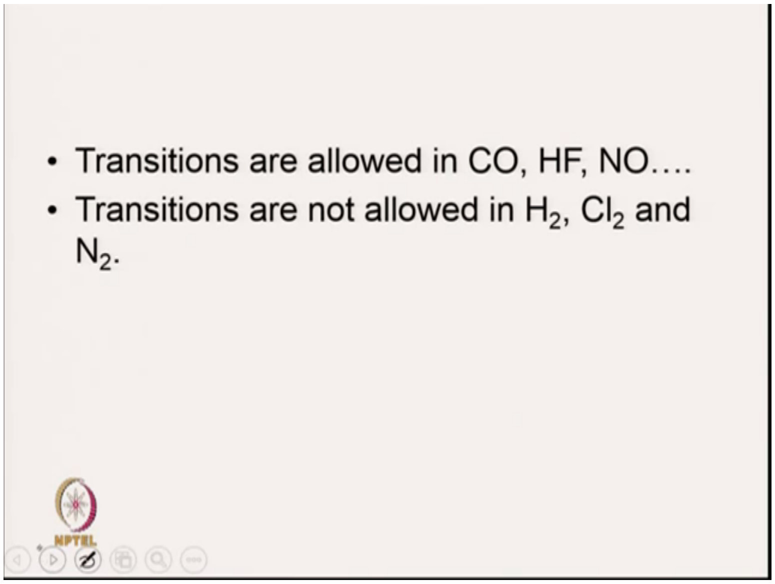

- Transitions are allowed in CO, HF, NO….
- Transitions are not allowed in H_2, Cl_2 and N_2.

So, since your molecule must have permanent dipole moment so transition are allowed in hetero diatomic, diatomic molecule like CO, HF, NO, but it is not allowed in homo, di atomic molecule. For example, H2, Cl2 and N2.

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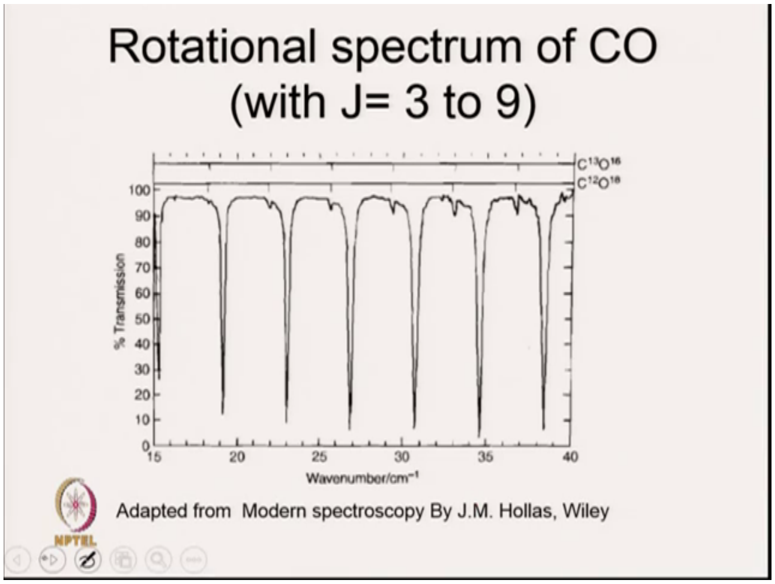

Rotational spectrum of CO
(with J= 3 to 9)

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

This is Rotational Spectrum of CO and you can see this is for J is equal to 3 to 9 and this is what has been obtain.

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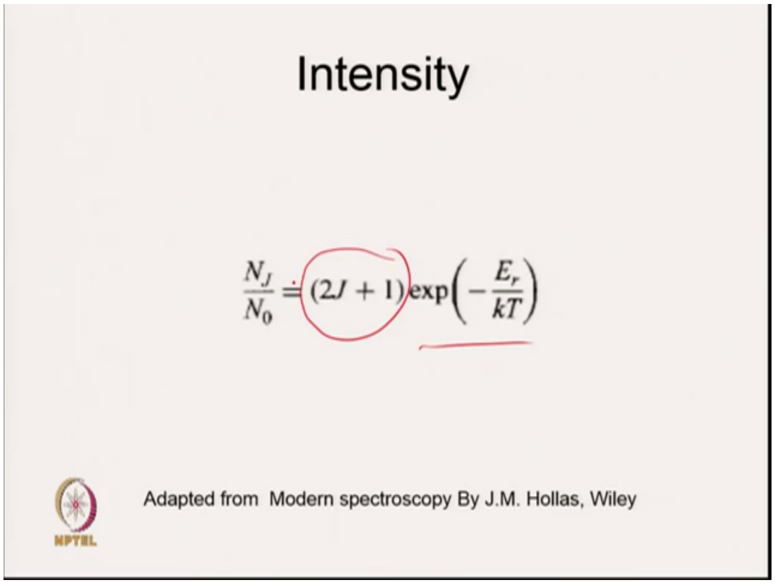

Intensity

$$\frac{N_J}{N_0} \doteq \boxed{(2J+1)}\exp\underline{\left(-\frac{E_r}{kT}\right)}$$

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

And if you notice, that, in the, if you notice in the intensity it is first going up and going down. Now, how to explain this phenomena in the Rotational Spectroscopy? So, as we discussed in previous lecture, that intensity depending on the difference between population in the ground state and excited state. So, generally, what we know is that, number of number of a species in Jth level by number of a species in 0th level can be calculated using Boltzmann distribution, Boltzmann distribution, which is basically exponential minus ER by KT. But, here since there is a your 2J plus 1 multiplicity that will also come into picture and your population also depends on multiplicity. So, basically, in the Rotational Spectroscopy, both are going to influence your intensity.

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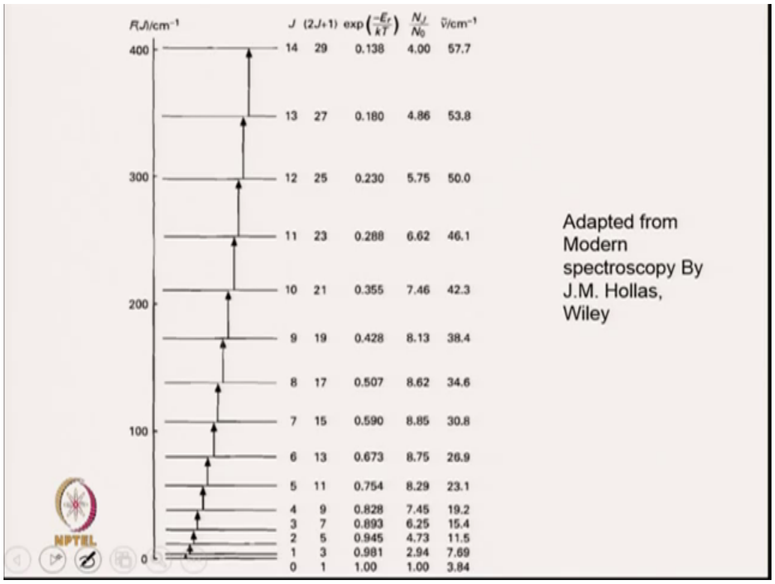

J	$(2J+1)$	$\exp\left(\frac{-E_r}{kT}\right)$	$\frac{N_J}{N_0}$	$\tilde{\nu}/\mathrm{cm}^{-1}$
14	29	0.138	4.00	57.7
13	27	0.180	4.86	53.8
12	25	0.230	5.75	50.0
11	23	0.288	6.62	46.1
10	21	0.355	7.46	42.3
9	19	0.428	8.13	38.4
8	17	0.507	8.62	34.6
7	15	0.590	8.85	30.8
6	13	0.673	8.75	26.9
5	11	0.754	8.29	23.1
4	9	0.828	7.45	19.2
3	7	0.893	6.25	15.4
2	5	0.945	4.73	11.5
1	3	0.981	2.94	7.69
0	1	1.00	1.00	3.84

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

So, let us think about the different J levels. And so, you see 0 to 14 J level and this is your 2 J plus 1. So, 2J plus 1 is calculated and the second part is calculate exponential minus ER by KT. One thing you will notice is that this is increasing, the increasing J, 2J plus 1 is increasing with increase in J whereas your exponential minus ER by KT is decreasing with the value of J is decreasing.

So, 1 factor is increasing and another is decreasing. What happens that initially your 2J plus 1 factor is more predominant and so, what happens that intensity is going to increase, intensity is going to increase, but on the later part, your exponential minus ER by KT become predominant and then your intensity is start decreasing, intensity is start decreasing. Till now we talked about rigid rotor, rigid rotor where we took R as constant, but in reality, it does not happen as.

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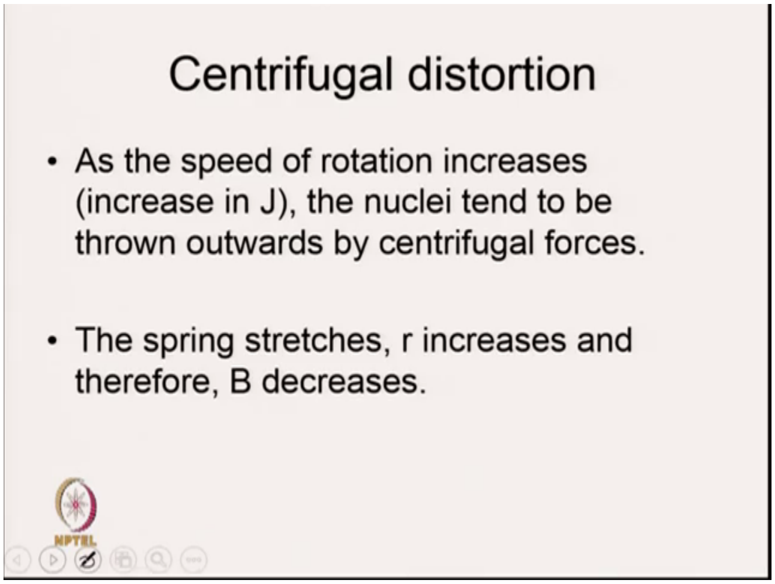

Centrifugal distortion

- As the speed of rotation increases (increase in J), the nuclei tend to be thrown outwards by centrifugal forces.
- The spring stretches, r increases and therefore, B decreases.

So, as the speed of rotation increases nuclei tend to thrown outward by centrifugal forces. So, basically your bond is stretching R increases and therefore B decreases.

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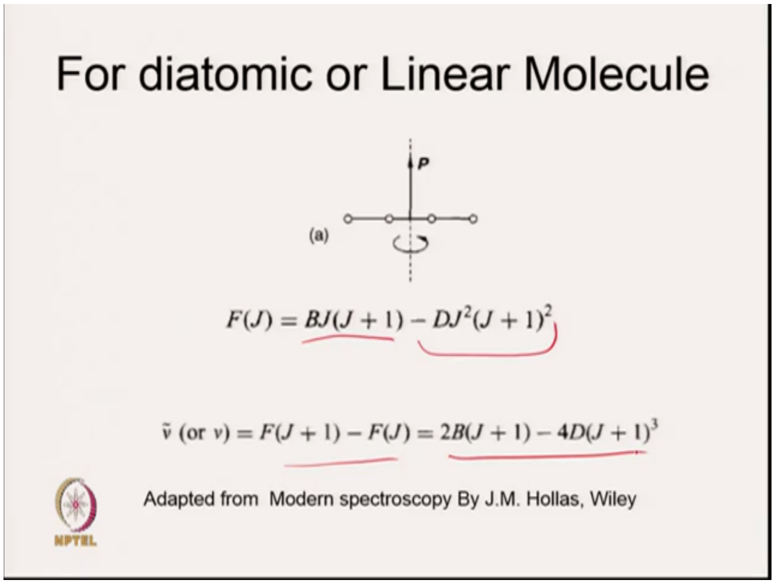

For diatomic or Linear Molecule

$$F(J) = \underline{BJ(J+1)} - \underline{DJ^2(J+1)^2}$$

$$\tilde{\nu}\ (\text{or } \nu) = \underline{F(J+1)} - F(J) = \underline{2B(J+1) - 4D(J+1)^3}$$

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

And for that, for example, if you take a diatomic linear molecule and you if you take into account that R is not constant, you are going to get another term when we calculate your wave number. So for rigid rotor we have VJ, J plus 1, that is what is the wave number what you get is another term which takes into account of distortion, account of distortion.

So, minus DJ square J plus 1 square and your we can again calculate nu bar in this case, it is simply by using your FJ plus 1 minus FJ, FJ plus 1. So, we are again looking for transition between Jth level to J plus 1 level. Since, these are the allowed transition and what you will get it 2 BJ plus 1 minus 4 DJ plus 1 cube, ok. So, we will consider another different kind of molecule till now we are mostly confined ourselves to di-atomic molecule.

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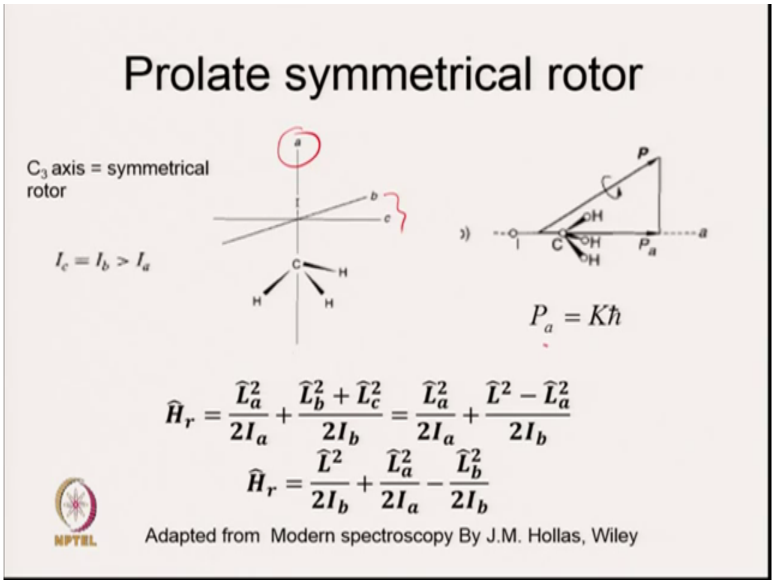

Prolate symmetrical rotor

C_3 axis = symmetrical rotor

$I_c = I_b > I_a$

$P_a = K\hbar$

$$\hat{H}_r = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2 + \hat{L}_c^2}{2I_b} = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}^2 - \hat{L}_a^2}{2I_b}$$

$$\hat{H}_r = \frac{\hat{L}^2}{2I_b} + \frac{\hat{L}_a^2}{2I_a} - \frac{\hat{L}_b^2}{2I_b}$$

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

Now, we will go to different kind of rotors for example, if we have a Prolate Symmetric rotor. 1 example of that is CH3I, CH3I. In that case, if we take CI as the axis A, this is your V axis, is this is your C axis, then you are Ic and Ib will be equal. So, Ic means your moment of inertia around axis C and axis B is going to be equal while moment of inertia around A axis is going to be smaller and your momentum will be given K h bar.

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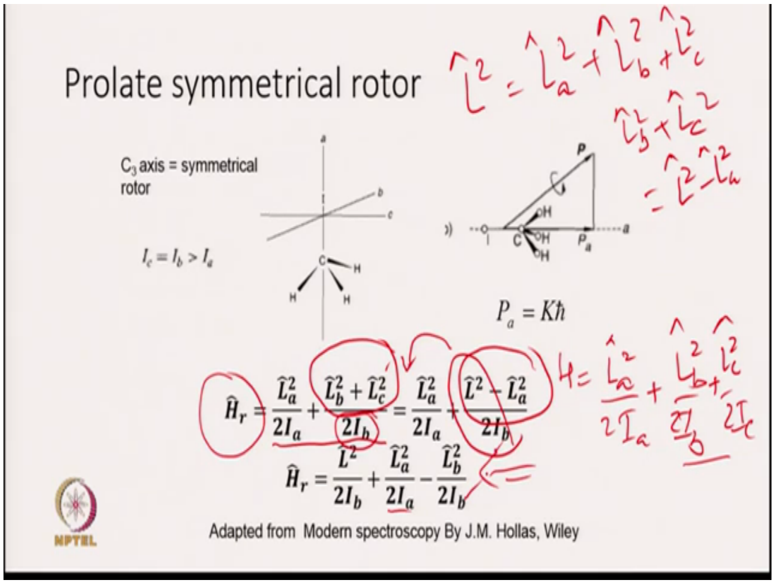

Prolate symmetrical rotor

C_3 axis = symmetrical rotor

$I_c = I_b > I_a$

$P_a = K\hbar$

$$\hat{H}_r = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2 + \hat{L}_c^2}{2I_b} = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}^2 - \hat{L}_a^2}{2I_b}$$

$$\hat{H}_r = \frac{\hat{L}^2}{2I_b} + \frac{\hat{L}_a^2}{2I_a} - \frac{\hat{L}_b^2}{2I_b}$$

$$\hat{L}^2 = \hat{L}_a^2 + \hat{L}_b^2 + \hat{L}_c^2$$

$$\hat{L}_b^2 + \hat{L}_c^2 = \hat{L}^2 - \hat{L}_a^2$$

$$H = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2}{2I_b} + \frac{\hat{L}_c^2}{2I_c}$$

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

Hamiltonian of a Prolate symmetrical rotor can be written in terms of its angular momentum operator. So, Hamiltonian is generally written as angular momentum square operator divided by 2IA plus angler moment momentum around D axis square of that, if you take operator divided by 2 IV plus LC square operator divided by 2 Ic. So, basically Hamiltonian operator is La square operator divided by 2 Ia plus LB square operator by 2 Ib plus Lc square operator by 2 Ic.

But since Ib and Ic is equal, so, you can write Hamiltonian operator as La square operator divided by 2 Ia plus lb Square operator plus Lc Square operator divided by 2 Ib, since Ib and Ic is equal and now, we also know that L square L square operator will be equal to La square operator plus Lb square operator plus Lc square operator and so, Lb square operator plus Lc square operator will be equal to L square operator minus La square operator.

And so, what we did is in place of Lb square operator plus Lc square operator, we can put L square operator minus La square operator and then, this can be written as. So, if you take this term and bring it here then what you will get is Hamiltonian for rotor is equal to L square operator divided by 2 Ib plus La square operator divided by 2 Ia minus Lb square operator divided by 2 Ib.

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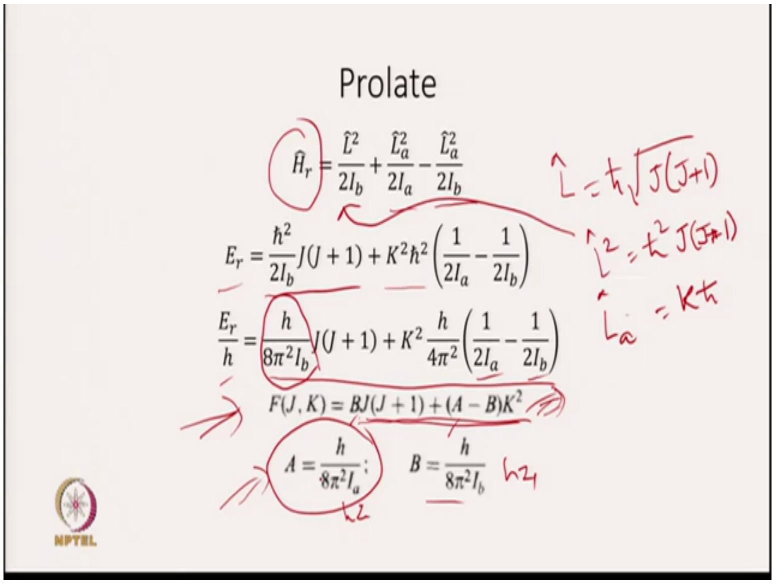

Prolate

$$\hat{H}_r = \frac{\hat{L}^2}{2I_b} + \frac{\hat{L}_a^2}{2I_a} - \frac{\hat{L}_a^2}{2I_b}$$

$$\hat{L} = \hbar\sqrt{J(J+1)}$$

$$\hat{L}^2 = \hbar^2 J(J+1)$$

$$\hat{L}_a = K\hbar$$

$$E_r = \frac{\hbar^2}{2I_b}J(J+1) + K^2\hbar^2\left(\frac{1}{2I_a} - \frac{1}{2I_b}\right)$$

$$\frac{E_r}{h} = \frac{h}{8\pi^2 I_b}J(J+1) + K^2\frac{h}{4\pi^2}\left(\frac{1}{2I_a} - \frac{1}{2I_b}\right)$$

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

$$A = \frac{h}{8\pi^2 I_a}; \quad B = \frac{h}{8\pi^2 I_b}$$

Hz

Hz

So, from the last slide, what we got is Hamiltonian operator for Prolate rotor is angular momentum square operator divided by 2 Ib plus La square operator divided by 2 Ia minus La square operator divided by 2 Ib. We know that operator is equal to h cross J J plus 1.

So, L operator is equal to H cross square root of J J plus 1. So, L square operator will be h bar square multiplied by J J plus 1, J plus 1. So, that is what we are going to plug in in this equation. So, when I put L square operator is equal to H cross square J J plus 1 what I will get is this. Then for La square, La operator that is equal to k h bar, k h bar. So, for La square operator just plug in here and what you are going to get is k square h bar square will be common and what is left is 1 by 2 Ia minus 1 by 2 Ib.

When we divide energy by h, we will get frequency and this is the equation for frequency, frequency for a Prolate rotor. So, h by 8 pi square Ib, J J plus 1, plus k square h divided by 4 pi square multiplied by 1 divided by 2 Ia minus 1 divided by 2 Ib. So, if I take h by 8 pi square Ib as B and this h by 8 pi square Ia is equal to A. And what I will get is your F, which is a function of J and K and this now frequency is equal to BJ J plus 1 plus A minus B k square, B and A are in hertz.

So, you can also get this equation when you divide Er by hc and Er by hc is also written in the same way VJ, J plus 1 plus A minus B multiplied by k square only thing is that now, in that case, B and A will be in wave number unit, will be in wave number unit and what I mean by that, is A will be equal to h by 8 pi square Iac and B will be equal to h by 8 pi square Ibc. So, this equation sometime you will find in wave number unit and sometimes you will find in frequency unit both are same, only difference is when you are talking about frequency and A and B are in frequency unit whereas, when this F is in wave number unit then A and B are also in wave number unit, wave number unit. This is here A is given in hertz, B is in hertz, but if I divide by C then I will get A in wave number unit and B wave number unit.

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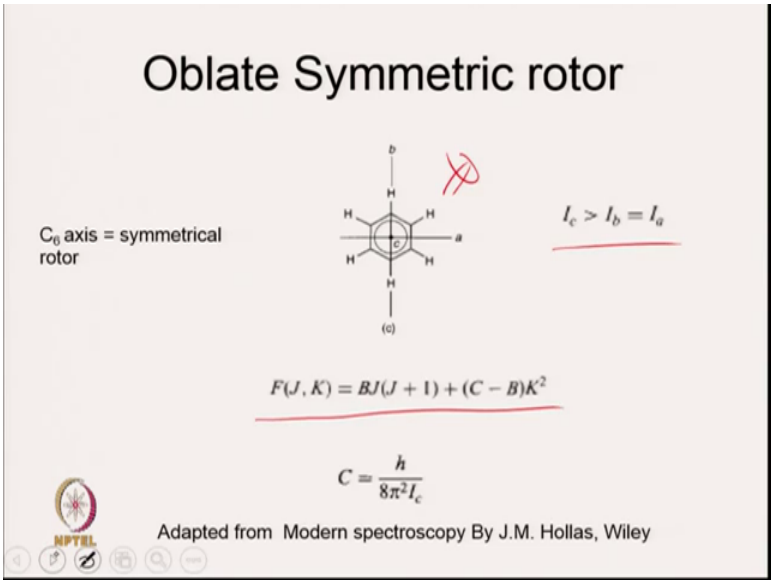

Oblate Symmetric rotor

C_6 axis = symmetrical rotor

$I_c > I_b = I_a$

$$F(J,K) = BJ(J+1) + (C-B)K^2$$

$$C = \frac{h}{8\pi^2 I_c}$$

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

Similarly, for our Oblate Symmetric Rotor which can calculate the energy term and this oblate symmetric rotor the 1 which is not equal has highest moment of inertia along the axis which is not equal is higher than a moment of inertia along the 2 axis which are equal. So, Ic is greater than Ib is equal to Ia and this is typically case of benzene molecule and for that we can again write this.

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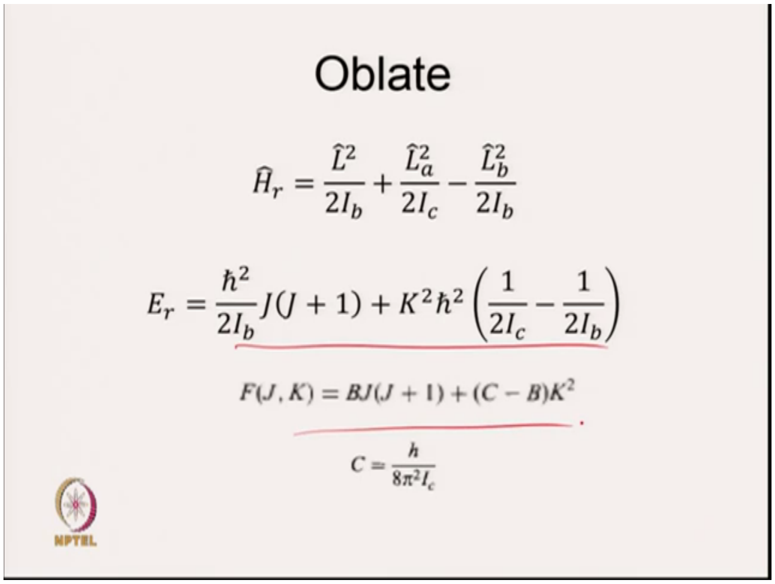

Oblate

$$\hat{H}_r = \frac{\hat{L}^2}{2I_b} + \frac{\hat{L}_a^2}{2I_c} - \frac{\hat{L}_b^2}{2I_b}$$

$$E_r = \underline{\frac{\hbar^2}{2I_b}J(J+1) + K^2\hbar^2\left(\frac{1}{2I_c} - \frac{1}{2I_b}\right)}$$

$$\underline{F(J,K) = BJ(J+1) + (C-B)K^2}$$

$$C = \frac{h}{8\pi^2 I_c}$$

And this that can be calculated the way we calculated for Prolate that HR is equal to L square by 2Ib plus La square by 2Ic minus Lb square by 2Ib and similar way we can calculate the wave number for this oblate kind of rotor.

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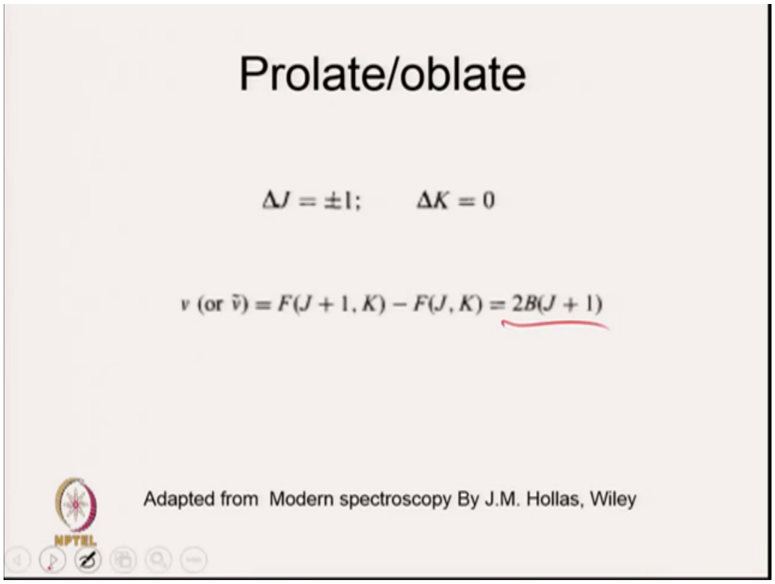

Prolate/oblate

$$\Delta J = \pm 1; \qquad \Delta K = 0$$

$$\nu \text{ (or } \tilde{\nu}) = F(J+1,K) - F(J,K) = \underline{2B(J+1)}$$

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

For Prolate Oblate kind of molecule the selection rule is delta J is equal to plus minus 1 and delta k is equal to 0. And so, you can calculate the frequency of or frequency or wave number of allowed transition and that is simply 2 BJ plus 1.

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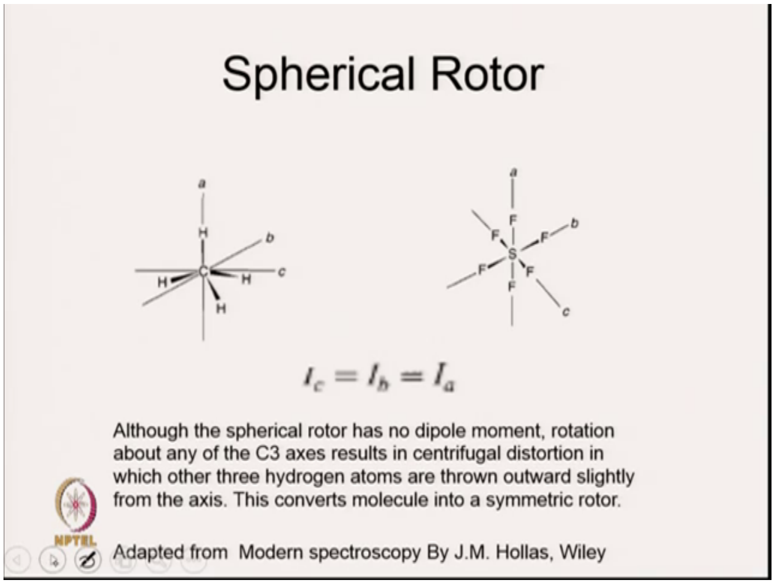

Spherical Rotor

$$I_c = I_b = I_a$$

Although the spherical rotor has no dipole moment, rotation about any of the C3 axes results in centrifugal distortion in which other three hydrogen atoms are thrown outward slightly from the axis. This converts molecule into a symmetric rotor.

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

For a Spherical Rotor it is quite simple since you have Ia is equal to Ib is equal to Ic. So, although the spherical rotor has no dipole moment rotation around any of C3 axis results in centrifugal distortion in which other 3 hydrogen bonds are thrown outwards slightly from the axis.

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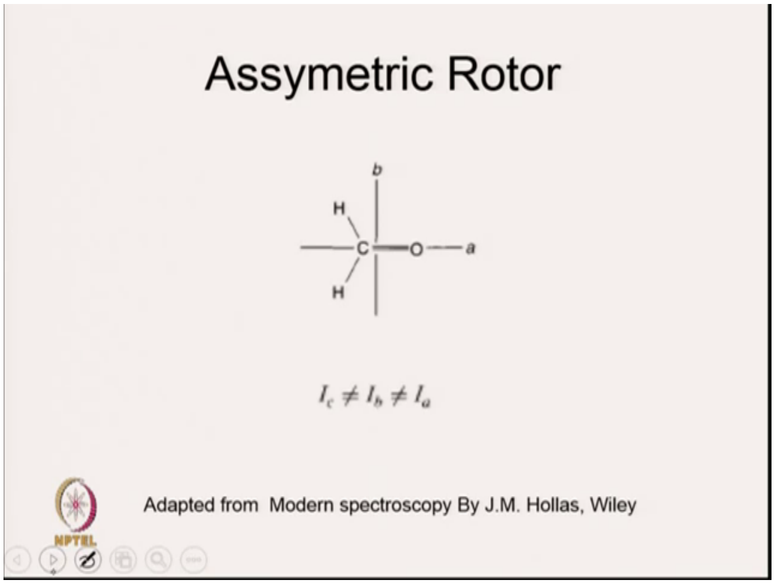

Assymetric Rotor

$$I_c \neq I_b \neq I_a$$

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

This converts molecule into Asymmetric Rotor and lastly you have molecules like formaldehyde, which are asymmetric rotor where Ia, Ib, Ic are not equal Ib, Ic. So, but it is very difficult to calculate and energy in this case.

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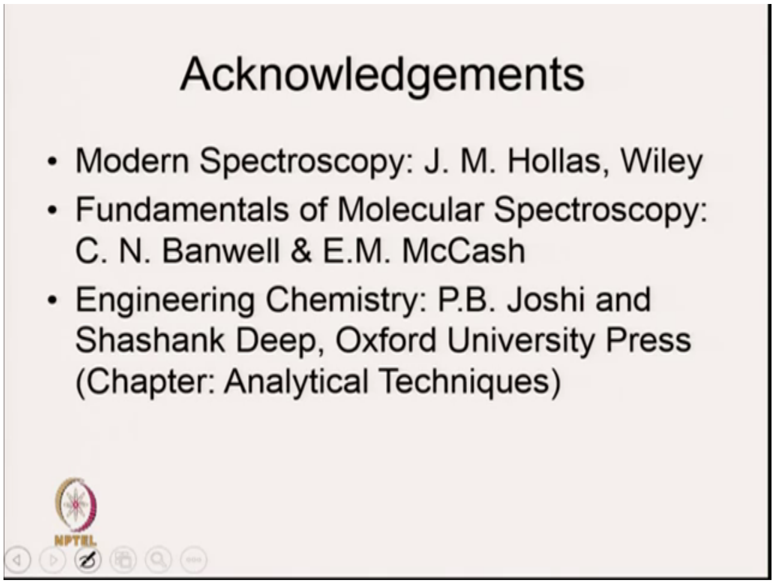

Acknowledgements

- Modern Spectroscopy: J. M. Hollas, Wiley
- Fundamentals of Molecular Spectroscopy: C. N. Banwell & E.M. McCash
- Engineering Chemistry: P.B. Joshi and Shashank Deep, Oxford University Press (Chapter: Analytical Techniques)

Today, we have seen the theory behind Rotational Spectroscopy and I will like to acknowledge these 3 books which I consulted for making all the notes and thank you for listening. Thank you for listening.