Chemistry II: Introduction to Molecular Spectroscopy

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Lecture -15
Microwave Spectra of Diatomic Molecules

Welcome back to the lectures on chemistry; in today's lecture we will examine microwave spectrum. Some of the reasons for why we have to study microwaves spectra let me give you in detail. If you want to know the geometry of the molecule or the equilibrium structure of the molecule and if the molecule possesses a dipole moment then in the gas phase microwave spectra give you spectra give you the most accurate geometry data that you can obtain.

Rotation which is the phenomenon that is associated with microwave spectra is one of the most fascinating phenomenons in quantum mechanics. Angular momentum associated with that (Refer Time: 01:16) rotations of molecules, the rotations of molecular species or molecular complexes all of them give rise to very rich spectra in the microwave region whose analysis tells you more about the electric charge distribution that is present in the molecule and therefore, also gives you a feel for how the atoms are bonded to each other and so on.

So, the precise geometry and the shape of the molecule is something that we always worry about in the gas from the gas phase spectra of many of the compounds, but what is important is of course, for the rotational spectrum or microwave spectrum to be obtained the molecule must have a permanent dipole moment or a charge asymmetry. The plus and minus charge centers must be separated from each other.

The other most important reason as a chemist or as a physicist that one is worried about microwave is that this also led to the first and most important discovery in spectroscopy called the MASERs or the Microwave Amplification by Stimulated Emission of Radiation and microwave spectra or microwaves were very important in the Second World War. The offshoot of the second world war led to a lot of this research in the spectroscopy of these molecules and eventually this led this was a precursor to the most important discovery I would think that the after the second world war namely the lasers the microwave amplification respectfully stimulated emission of radiation was a precursor to laser.

So, therefore, in both historical sense as well as in the real sense of studying the molecular geometry it is one of the most important spectroscopic tools even as a theoretician or as someone who is interested in chemical physics rotations molecular rotations and their study is a fascinating subject.

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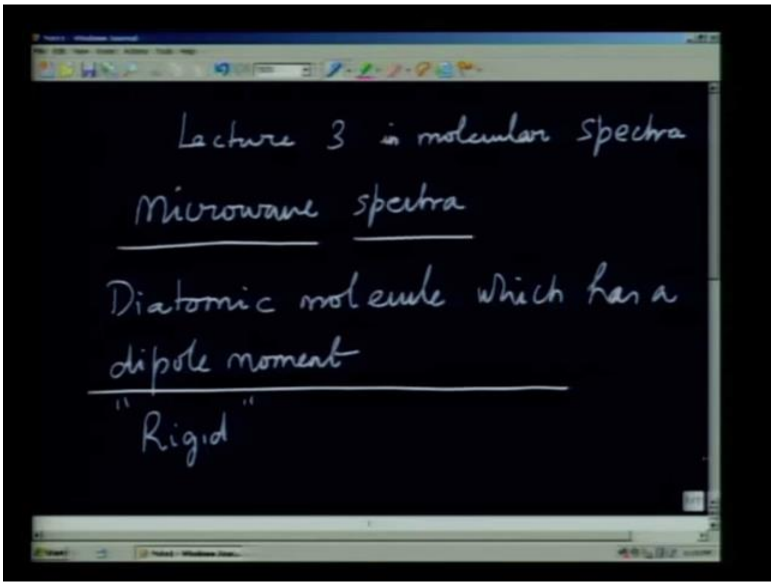

Lecture 3 in molecular spectra

Microwave spectra

Diatomic molecule which has a dipole moment

"Rigid"

Let us look at the microwave spectrum for a typical diatomic molecule which has a dipole moment. Let us assume that the diatomic molecule is a rigid molecule. This is an important assumption because no molecule is rigid even at zero kelvins. In harmonic oscillator model you have studied that molecules have zero point kinetic energy zero point energy and therefore, molecules vibrate even at zero kelvin.

Therefore, the assumption of rigid molecule is something that we will do for convenience and if necessary this can be relaxed depending on the molecule energies. The rigid diatomic molecule essentially means the following that the molecule geometries do not change. If the molecular geometries do not change then it is easy to calculate the moment of inertia it is easy to calculate using the bond angles and or a tentative model of bond angles and bonds lens. Calculate the moment of inertia, calculate the spectral parameters verify them with the experiments and then go back and re do it again.

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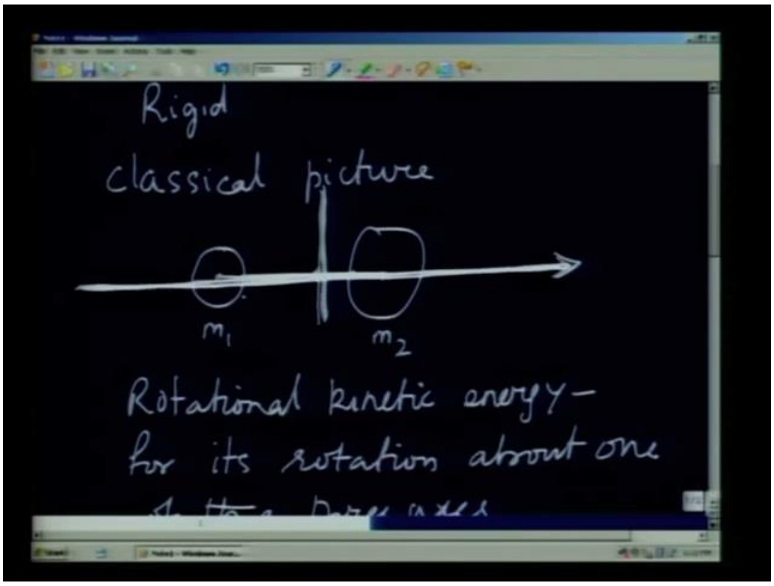

Rigid

classical picture

Rotational kinetic energy –

for its rotation about one

of the three axes

Let us do a simple example of a rigid diatomic molecule and let us assume a classical picture to begin with. Supposing we write diatomic molecule as two different masses m 1 and m 2 connected by a bond length which is connected to their centers of masses and the distance is r.

Then the rotational kinetic energy of this molecule about the axis of rotation; there are three axis of rotation there is an axis which passes through the bond, coaxial to the bond then there is a bond axis which passes through the center of mass perpendicular to that, let me remove this r for the time being and then there is an axis which is perpendicular to both this bond axis and the bond here basically perpendicular to the plane of the screen that you are watching.

So, there are three axis. Now when we calculate moments of inertia for this molecule in order to calculate the rotational kinetic energy for the system; for it is rotation about one of the axis one of the three axis what do we do; classically we calculate the distance of the atoms the perpendicular distance of the atoms from the axis multiplied by their masses; then we do what is called the m i r i square I classically about any axis A is essentially some over all the masses multiple by their perpendicular distances from the axis and summed over all the all the atoms here there are 2 atoms and therefore, what you will have is the distances from the axis as m 1 r 1 square plus m 2 r square.

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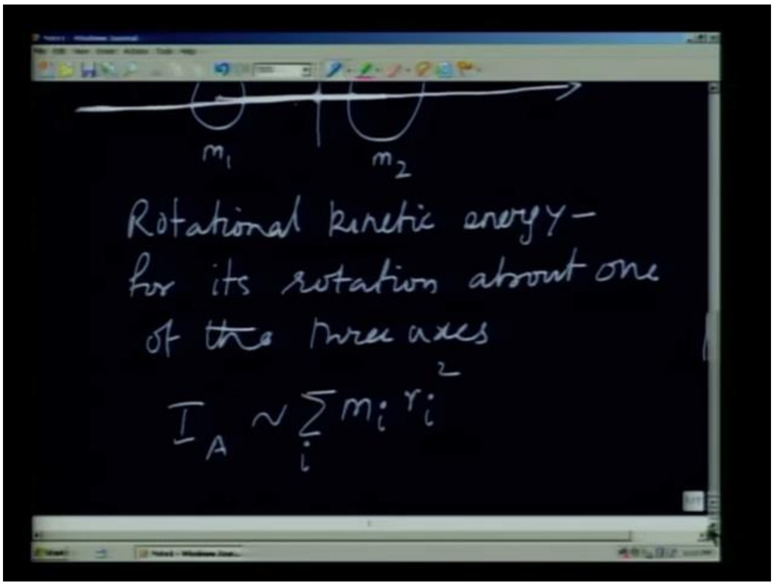

Rotational kinetic energy – for its rotation about one of the three axes

$$I_A \sim \sum_i m_i r_i^2$$

Then we do what is called the m i r i square. I classically about any axis A is essentially some over all the masses multiple by their perpendicular distances from the axis and summed over all the all the atoms here there are two atoms and therefore, what you will have is the distances from the axis as m 1 r 1 square plus m 2 r 2 square.

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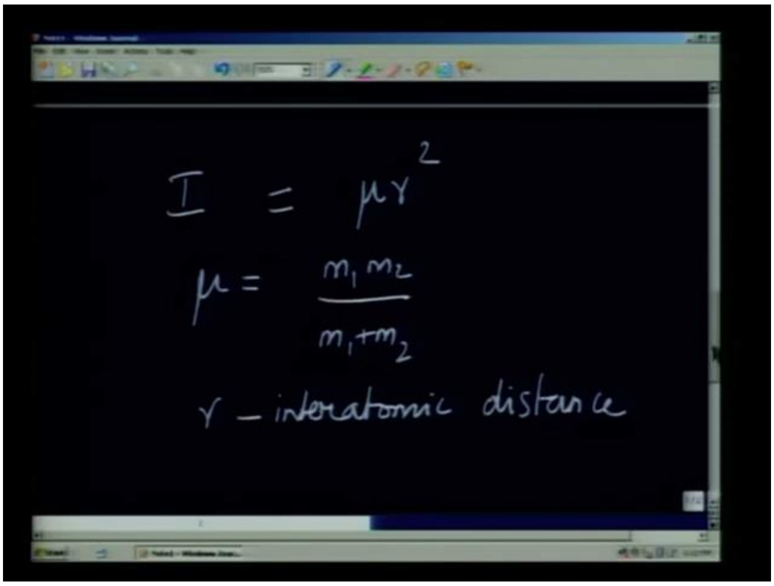

$$I = \mu r^2$$

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

r – interatomic distance

A simple two body kinetics kinematics tell you that the moment of inertia can also be expressed by this formula mu r square where mu is given as the reduced mass m 1 m 2 by m 1 plus m 2 and r is the interatomic distance. Now, the question is; about what axis?

I mentioned that there are three axis associated with the simple linear molecule a diatomic molecule.

There are three mutually perpendicular axis and if we assume the atoms to be point masses; then the perpendicular distance of the atoms m 1 and m 2 about the bond axis is zero. Therefore, there is no moment of inertia associated with rotation about this axis. There is no kinetic energy, there is no rotational kinetic energy associated with that axis.

Now what about the rotational kinetic energy associated with this axis or with the axis perpendicular to this line as well as the bond axis? The perpendicular distances are the same for both of them and the masses being m 1 m 2; this formula tells you for both of those access the moments of inertia I is given by the simple formula mu r square. It is a classical, it is a very elementary classical mechanical formula you can derive that and in fact, that should be one of the exercises for you to drive this. The mu being a reduced mass r being the interatomic distance leads you to this formula that the moment of inertia I is that given this as the moment of inertia.

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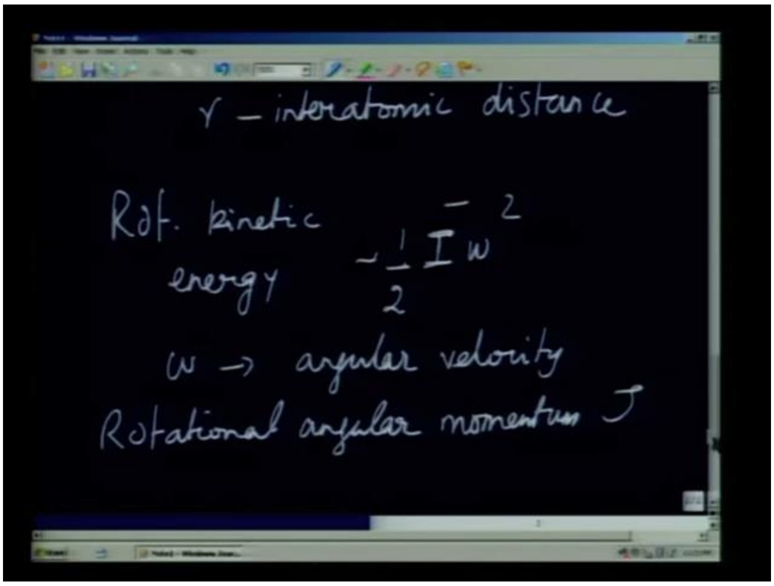

r – interatomic distance

Rot. kinetic energy $\sim \frac{1}{2} I \bar{\omega}^2$

$\omega \rightarrow$ angular velocity

Rotational angular momentum J

The rotational kinetic energy classically is given for such bodies as the rotational velocity times rotational the angular velocity times the moment of inertia multiplied by half I omega square or where omega is the angular velocity which is nothing but the speed of rotation about the given axis in terms of rotational angular momentum J which you know again from classical mechanics J is given by I omega; you know that the rotational kinetic energy is given by J square over 2 I.

This is a classical formula and the rotational kinetic energy is the same about both of the axis and under the point mass approximation remember the third moment of inertia is 0.

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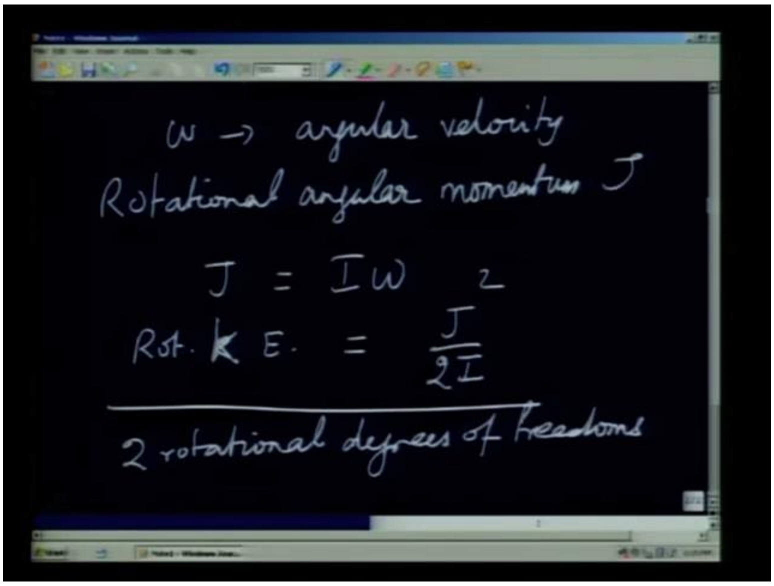

$\omega \rightarrow$ angular velocity

Rotational angular momentum J

$$J = I\omega$$

$$\text{Rot. K E.} = \frac{J^2}{2I}$$

2 rotational degrees of freedoms

Therefore there are only 2 degrees of freedom associated to rotational degrees of freedom associated with in linear molecule under the point most approximation. If the masses are not point masses but the atoms have a mass distribution, a size and a charge and all those things you might find out that the moment of inertia is so small that you still need not have to be concerned with the rotational degree of freedom about the axis; it is almost a free rotation with more energy associated with it.

Therefore there are only for a linear molecule there are only two rotational degrees of freedom and for the rigid molecule both these degrees of freedom have the same moment of inertia and therefore, there is only one moment of inertia associated with the rotational motion of a linear molecule.

Now this is classical mechanical formula; the spectroscopy is studied by looking at the molecule energy levels which are obtained by solving the molecular Schrodinger the equation and the Schrodinger equation as you know from the previous models and the lectures we write down the classical kinetic energy and the potential energy we write down the classical Hamiltonian and then we transform that into the quantum mechanical formula.

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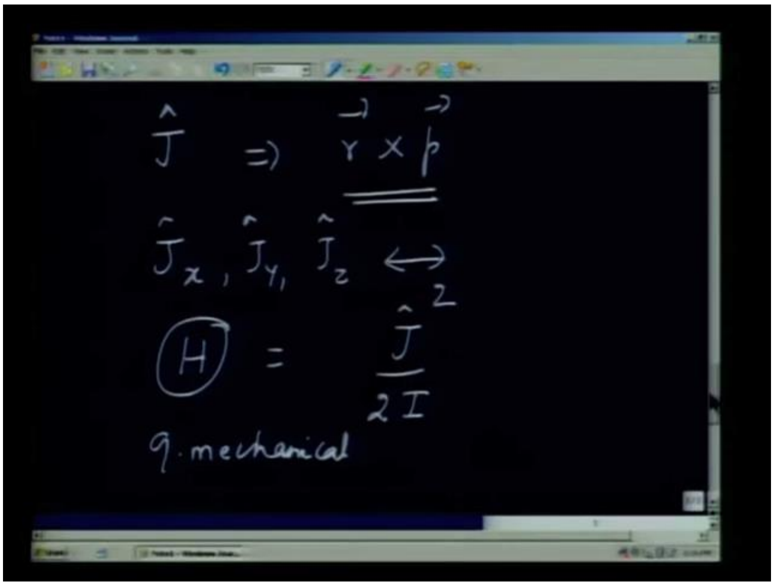

$$\hat{J} \Rightarrow \underline{\underline{\vec{r} \times \vec{p}}}$$

$$\hat{J}_x, \hat{J}_y, \hat{J}_z \leftrightarrow$$

$$\boxed{H} = \frac{\hat{J}^2}{2I}$$

q. mechanical

And when we do that the angular momentum J in classical mechanics which is given by r cross p formula becomes the corresponding the quantum mechanical operators for J become the J x, J y and the J z components just like you had the in the case of momentum and these can be written down and you can go through a whole lot of algebra to write down the Hamiltonian for the system again as the operator J square by 2 I with the difference that this is quantum mechanical and the angular momentum; J is now a quantum mechanical quantity and therefore it has very special properties which are not the same as the classical angular momentum. We will look into this more as and when we required the details just.

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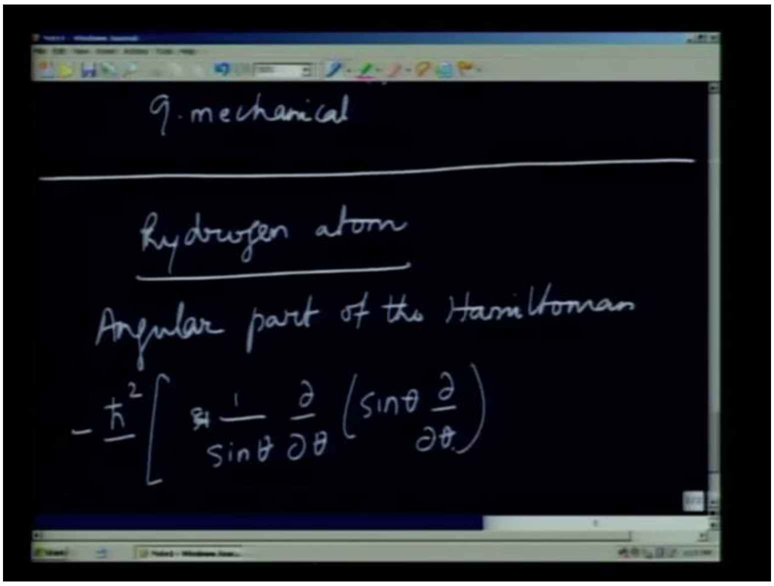

q. mechanical

Hydrogen atom

Angular part of the Hamiltonian

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right.$$

Just let me take you aside to the rotational to the problem of the hydrogen atom which was done several lectures ago. In hydrogen atom when we solved the Hamiltonian; we expressed the hydrogen atom Hamiltonian in terms of spherical polar coordinates and you might recall that the angular part of the hydrogen atom Hamiltonian; you recall remember that that was nothing but minus h bar square sine one by sine theta dou by dou theta sine theta dou by dou theta plus 1 by sine square theta dou square by dou phi square. This was the angular part that you recall from the hydrogen atoms solution.

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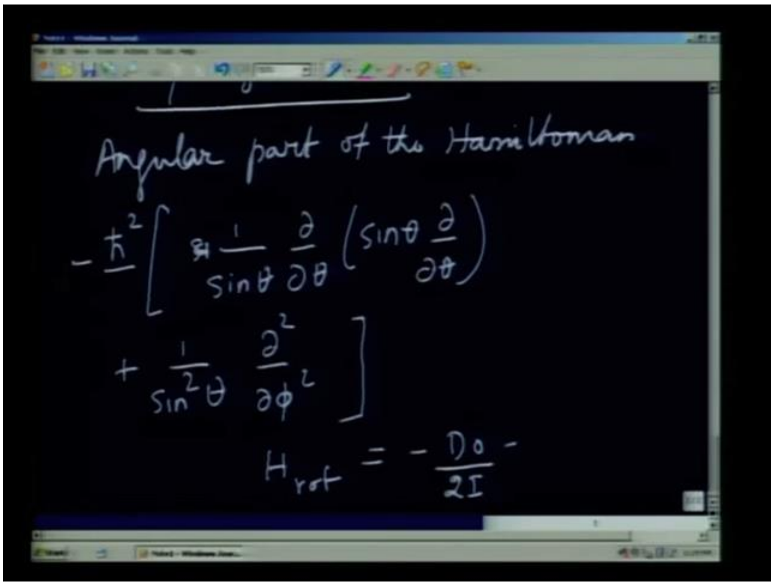

Angular part of the Hamiltonian

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

$$H_{rot} = -\frac{Do}{2I} -$$

Now the properties of the angular momentum operators J x, J y and J z the components of the angular momentum operator in an x y z coordinate system that is associated with the center mass of the molecule; if it is expressed in spherical polar coordinates you get exactly the same form as you have in the case of hydrogen atom angular parts.

Therefore the Hamiltonian for the rotational motion becomes exactly ditto of what you have here with the one difference that there is a 2 I in the denominator which corresponds to the J square by 2 I part of the J square the angular momentum part is given by this formula. Therefore what is obvious immediately is that

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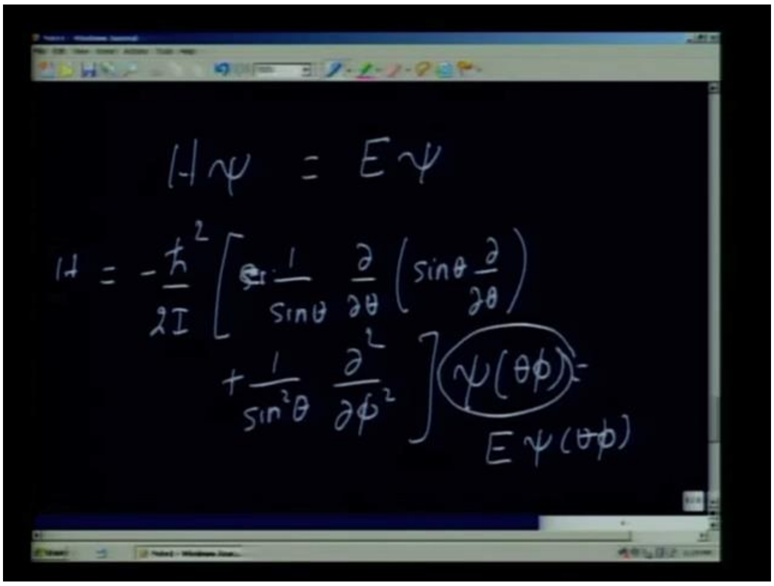

$$H\psi = E\psi$$

$$H = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta\phi) = E\psi(\theta\phi)$$

If we have the Schrodinger equation written as H psi is equal to E psi and if the H is written as minus h bar square by 2 I times the formula that you have sine theta sorry 1 by sine theta dou by dou theta sine theta dou by dou theta plus 1 by sine square theta dou square by dou phi square psi which is a function of theta and phi is equal to E times psi theta and phi then the solution sine theta phi you know exactly what it should be and this is nothing other than the spherical harmonics that you derived earlier.

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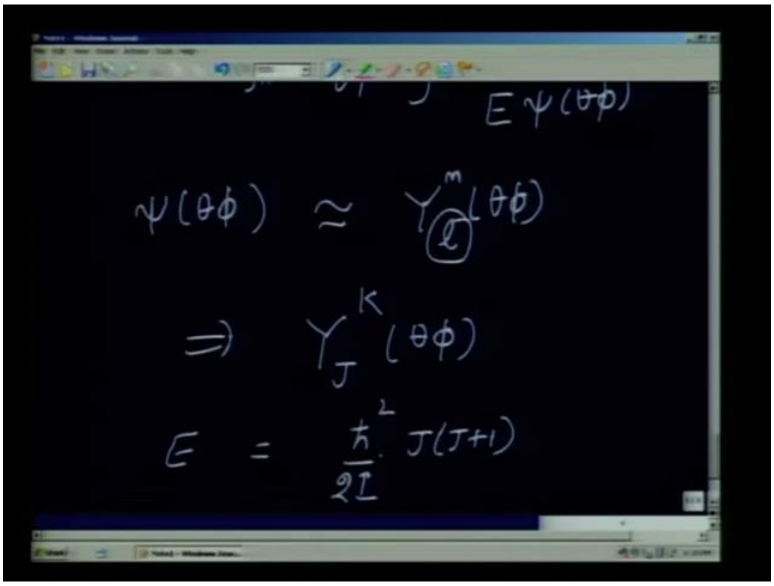

$E\psi(\theta\phi)$

$$\psi(\theta\phi) \simeq Y_{\boxed{l}}^{m}(\theta\phi)$$

$$\Rightarrow Y_{J}^{K}(\theta\phi)$$

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

psi theta phi is the spherical harmonics Y I use the symbol l m theta phi earlier for denoting the orbital angular momentum, but here now the quantum number is the rotational angular momentum quantum number and this is now replaced by Y J K theta phi where K has the same role as the m and J is the quantum number associated with the rotational motion of the molecule.

This also tells you immediately what should be the value of the energy and the energy is you remember that there is h bar square by 2 I which is there on the left hand side here H psi equal to E psi gives you earlier it gave you L into L plus 1; now you will get J into J plus 1 which is the quantum number associated with the rotational motion and therefore, what you have is h bar square by 2 I J into J plus 1 is the rotational kinetic energy associated with the diatomic molecule.

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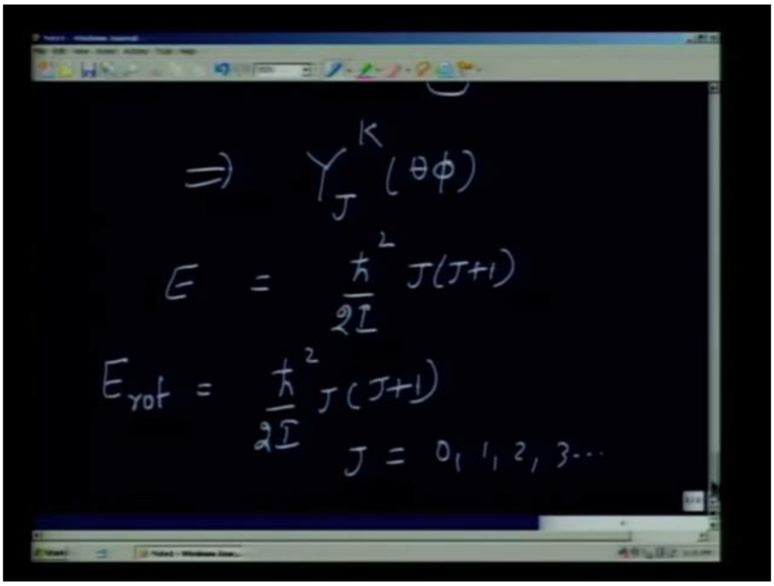

$$\Rightarrow Y_J^K(\theta\phi)$$

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

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

$$J = 0, 1, 2, 3 \cdots$$

E rotational there is no potential energy here we are only worried about the rigid atom rigid body motion the rotational kinetic energy is the total energy after rotating diatomic molecule therefore E rotation is now given by h bar square by 2 I into J into J plus one. This is a simple rigid by atomic model with the values of J being 0, 1, 2, 3 etcetera all the way up and the value of K if you remember is the same as the value of m earlier K goes from minus J, minus J plus 1 to J minus 1 up to J.

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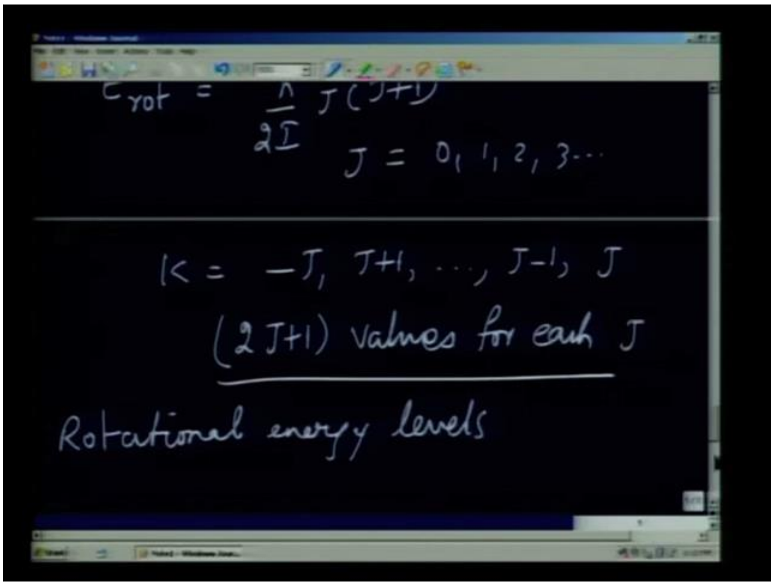

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$

$$J = 0, 1, 2, 3 \cdots$$

$$K = -J, J+1, \ldots, J-1, J$$

$\underline{(2J+1) \text{ values for each } J}$

Rotational energy levels

So, there are 2 J plus 1 value for each J which means that the rotational energy levels associated with the diatomic molecule.

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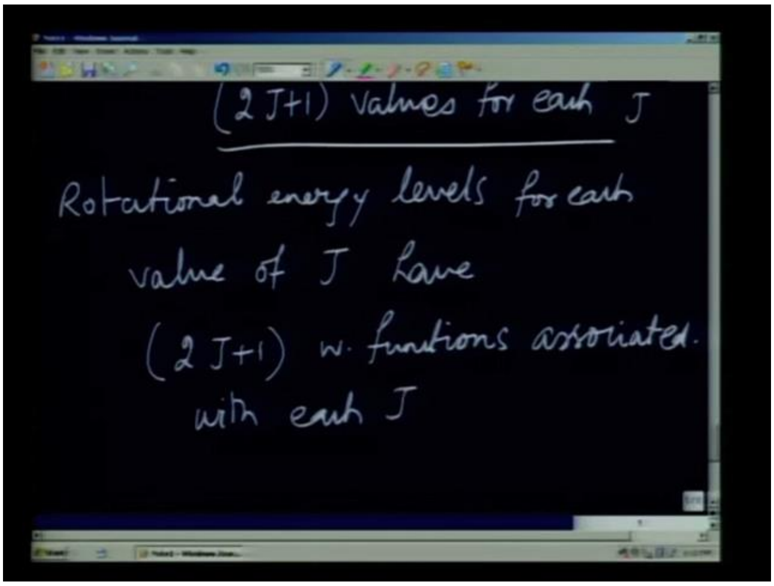

$(2J+1)$ values for each J

Rotational energy levels for each value of J have $(2J+1)$ w. functions associated. with each J

For each value of J have 2 J plus 1 wave functions associated with them associated with each J.

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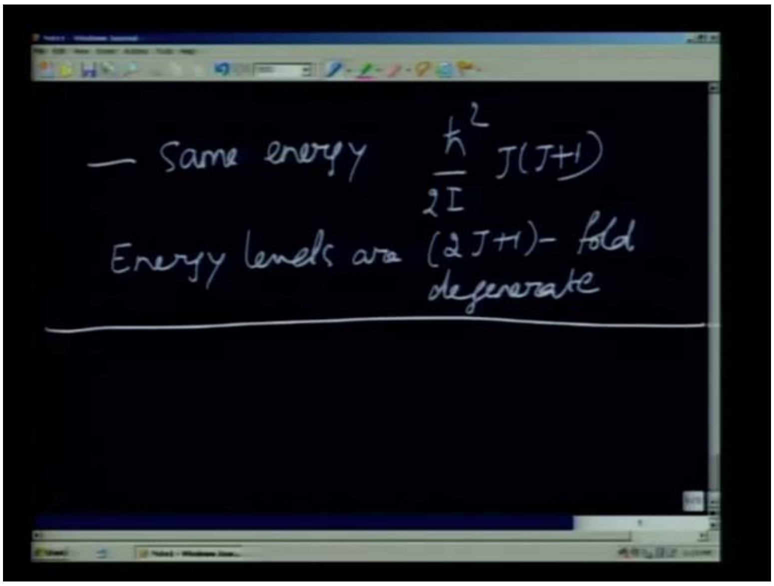

— Same energy $\frac{\hbar^2}{2I} J(J+1)$

Energy levels are $(2J+1)$- fold degenerate

The all of them have the same energy given by this formula h bar square by 2 I J into J plus 1. Therefore, the energy levels are degenerate or 2 J plus 1 fold degenerate.