Quantum Chemistry of Atoms and Molecules
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Lecture-20
Rigid Rotor: Part 3

For rigid rotor we have discussed how one can set up Schrodinger equation starting from the square of angular momentum operator. And we have worked out the Phi dependent part and we have given you the answer for the theta dependent part.

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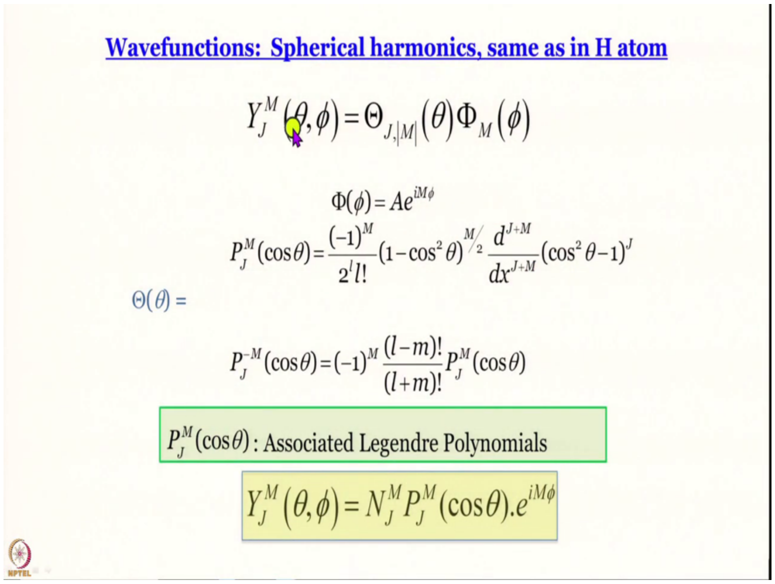

Wavefunctions: Spherical harmonics, same as in H atom

$$Y_J^M(\theta,\phi)=\Theta_{J,|M|}(\theta)\Phi_M(\phi)$$

$$\Phi(\phi)=Ae^{iM\phi}$$

$\Theta(\theta) =$

$$P_J^M(\cos\theta)=\frac{(-1)^M}{2^l l!}(1-\cos^2\theta)^{M/2}\frac{d^{J+M}}{dx^{J+M}}(\cos^2\theta-1)^J$$

$$P_J^{-M}(\cos\theta)=(-1)^M\frac{(l-m)!}{(l+m)!}P_J^M(\cos\theta)$$

$P_J^M(\cos\theta)$: Associated Legendre Polynomials

$$Y_J^M(\theta,\phi)=N_J^M P_J^M(\cos\theta).e^{iM\phi}$$

And the answer we have discussed is wave function essentially spherical harmonics theta phi is equal to the theta dependent part multiplied by phi dependent part and now we can talk about what is J and what is M? This M is something that arises out of solution of your phi dependent part of the equation remember capital phi turned out to be A multiplied by e to the power I M phi what is A? We will work out in the assignments. What does M stand for? It stands for the z component of angular momentum.

What are the allowed values 0 plus minus 1 plus minus 2 and so on and so forth. What is J? J is another quantum number that comes when we work out the theta dependent part also do not forget that J the theta dependent part and phi dependent part are related by this M square. So, it also gives us a limit to the value of M ok. So, J turns out to be 0 1 2 3 4, 0 and positive integers and the limit of M turns out to be J right.

So if J equal to 3 for example you can have M equal to zero plus minus 1 plus minus 2 plus minus 3, so we have 2 J + 1 values of M ok will come back to this once again when we talk about hydrogen atom. The theta dependent part is basically a constant multiplied by a an associated legendary polynomial in cos theta ok that is what it is. So, the theta dependent part is a polynomial and the phi dependent part is an imaginary exponential term factor ok.

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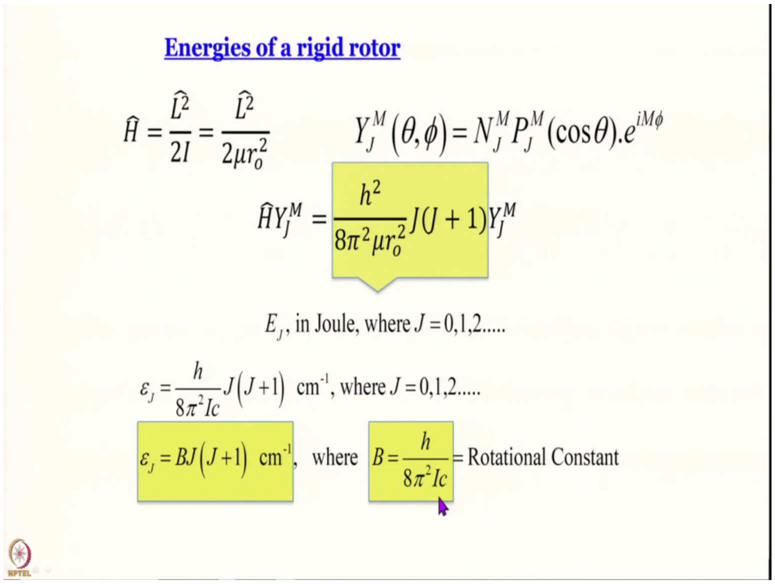

Energies of a rigid rotor

$$\hat{H} = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2\mu r_0^2} \qquad Y_J^M(\theta,\phi) = N_J^M P_J^M(\cos\theta).e^{iM\phi}$$

$$\hat{H}Y_J^M = \frac{h^2}{8\pi^2\mu r_0^2}J(J+1)Y_J^M$$

E_J, in Joule, where $J = 0,1,2.....$

$\varepsilon_J = \frac{h}{8\pi^2 Ic}J(J+1)$ cm^{-1}, where $J = 0,1,2.....$

$\varepsilon_J = BJ(J+1)$ cm^{-1}, where $B = \frac{h}{8\pi^2 Ic}$ = Rotational Constant

Now what happens when we try to find the energy for that we go back to total angular momentum we are going to discuss angular momentum and its component in a little more detail in the next module for now just believe me when I write when the square of angular momentum operator operates on this spherical polar harmonics when the it operates on spherical harmonics. I get back the same spherical harmonics wave function multiplied by its corresponding eigen value h cross square multiplied by J into J + 1.

So total angular momentum is h cross square multiplied by J into J + 1 how did we obtain the Hamiltonian? You obtain the Hamiltonian by dividing the square of angular momentum operator by 2I, so that 2I is essentially a constant for the molecule. So, I can very simply write this the Hamiltonian is l square by 2 mu r 0 square, so this is the wave function and we know that this L square operates on the wave function to device give us now i have written out h cross and i have written explicitly h by 2 pi square of that multiplied by J into J + 1 ok.

This is a Schrodinger equation. Now I simply ok divided by your 2I. let us go back on that a little bit maybe this is L square from there we go to Hamiltonian and to get go to the Hamiltonian I have simply divided by what we had in the denominator we have 2 mu r 0 square. So, that gives us h square by 8 pi square mu 0 square so constant multiplied by J into J + 1 multiplied by the wave function that is your Schrodinger equation.

This is the eigen value of energy in joule where J is equal to 0 1 2 3 so on and so forth. As I had said all right so what do we learn from here, before going there this is something that i write essentially because I am a spectroscopist generally spectroscopies do not want to work with joule they prefer centimeter inverse especially when working about rotational spectroscopy. So, generally we convert this to epsilon J is equal to h by eight pi square i c multiplied by J into J + 1 which is simply multiplying by h c and that is in centimeter inverse.

And its simply written epsilon J equal to b into J into J + 1 centimeter inverse where b is h by 8pi square IC this is called the rotational constant.

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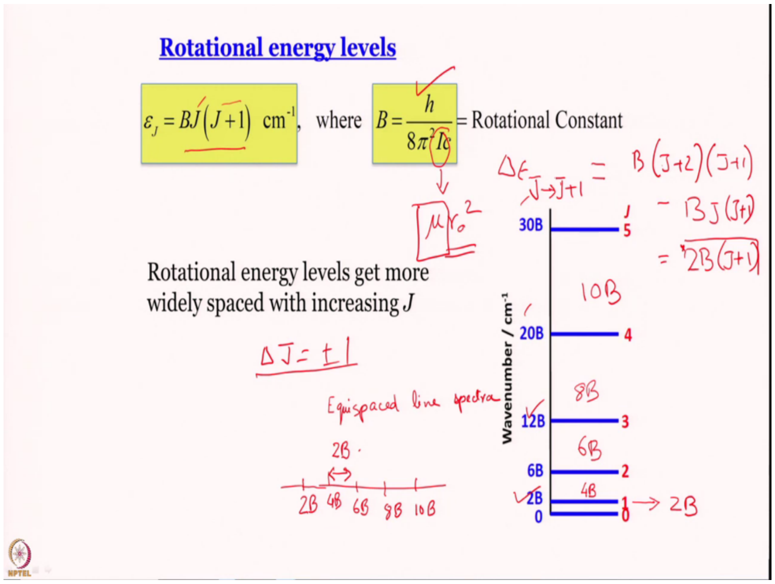

Rotational energy levels

$\underline{\varepsilon_J = BJ(J+1)}$ cm^{-1}, where $B = \frac{h}{8\pi^2 Ic}$ = Rotational Constant

$I \rightarrow \boxed{\mu} r_0^2$

$\Delta\varepsilon_{J\rightarrow J+1} = B(J+2)(J+1) - BJ(J+1) = \boxed{2B(J+1)}$

Rotational energy levels get more widely spaced with increasing J

$\underline{\Delta J = \pm 1}$

Equispaced line spectra

So, this is where we are right let us take a look at this first of all b into J into J + 1 what is the minimum value of J, 0. What is the minimum value of energy then, 0. So, remember for a quantum harmonic oscillator energy could never be 0 because the oscillator if it is at rest then the position is 0 plus minus 0 x delta x delta p p x is also 0 plus minus 0. So, delta x and delta px are both 0 and that violates uncertainty principle which is not allowed.

Here what happens is let us say this is my rigid rotor ok this has a tail. Let us say this is my rigid rotor so it can rotate in any direction any theta phi can be spanned. Let us say it has come to rest ok. It is true that the uncertainty in angular momentum is 0 what is the uncertainty in position? For that we need to know delta theta and delta phi. Well uncertainty theta del well theta can be anything right it can come to rest here or here or here anything anywhere.

So uncertainty in theta is effectively infinite of course it cannot be more than pi but in that domain that is infinity. Uncertainty in phi can be again anything between 0 and 2 pi yeah which is infinity. So, even though uncertainty in angular momentum is 0, uncertainty in the positional coordinates is infinity that is why the day is saved and A quantum rotor, rigid rotor can come to rest anywhere in space ok.

Uncertainty principle is not violated that is point number one. So, minimum rotational energy is zero now look at this epsilon J equal to B into J into J + 1 B equal to h by 8 pi square IC so what is J what is the next level after 0, J equal to 1. When you put J equal to 1 what do we get? May be I can just write that the minimum rotational energy is 0 we have written. What happens when I will write like this J values are already given here is not it.

What is the energy corresponding to J equal to 1, energy corresponding to J equal to 1 you can put J equal to 1 here so J equal to 1, J + 1 equal to two so the energy turns out to be 2 right, 2 what happens when J equal to 3? You can work that out J equal to 3, J + 1 equal to 4. So sorry why did I go to J equal to 3 when it is ok 12. So, 12 I missed J equal to 2 here for some reason ok. So, you can work out the energies and the values are all written here.

Now let us work out something interesting. What is the energy gap between J equal to 1 and J equal to 0 obviously 2B because this energy is to be this energy is 0 difference is 2B. What is the energy gap between J equal to 2 and J equal to 1, 6B – 2B so you can write it here the energy gap is 4B. What is the energy gap between J equal to 3 and J equal to 2 levels? 12B – 6B that is 6B. You see a pattern coming up J equal to 4 and J equal to 3, 20B – 12B that is 8B.

And J equal to 5 and J equal to 4, 30B – 20B is 10B ok not very difficult to work out really right because what I am trying to work out is delta epsilon for sensitive spectroscopist I always write in terms of spectroscopy J to J + 1 transition that turns out to be equal to what? You can work it out B into instead of J I will write J + 2. So, J + 1 becomes well J + 1 becomes J + 2 and J becomes J + 1 - B J into J + 1, so J + 1 is common and inside the bracket you have J +2 - J so it is 2B into J + 1.

So the energy gaps turn out to be 2B into J + 1 ok. So, energy gap keeps increasing as you go higher up the ladder in rotational energy manifold. Does it remind you of something reminds me of particle in a box that is exactly what happened there also. Now this has profound implications in rotational spectroscopy turns out and I will not derive it here once again it is there in our molecular spectroscopy lectures.

One can work out the selection rule. The selection rule turns out to be delta J equal to plus minus 1, which means that rotational lines in rotational spectra lines will occur at intervals of how much the first one will occur at 2B corresponding to the delta is equal to plus minus 1 right. So, you can go from 0 to 1 that energy gap is 2B then you cannot go from 0 to 2 but you can go from one to two remember delta is equal to plus minus 1.

So that energy gap is 4B then again you cannot go from 1 to 3 you can go from 2 to 3 that energy gap is 6B. The next one is 8B next one is 10B and so on and so forth. So, what you end up getting is spectra with lines that are equal spaced for a rigid rotor. So, what we get is equvi spaced line spectra, how is it useful? It is useful because that difference in energy is 2B into J + 1 no sorry difference in energy is not 2B into J + 1 difference energy is 2B.

Difference in lines differential energy of lines is essentially 2B. So, once you record a spectrum from the spacing you can work out B and if you work out B then you can work out this this is B so h is known pi is known C is known so knowing B you can work out I, I remember is mu r 0 square again if you know which molecule you are working with mu is known. So, you can figure out what r 0 is?

From the spacing's you can find out r 0, what is r 0? For a diatomic molecule it is a bond length. So, this rotational spectroscopy provides a means for determination of bond length that is the application of the rigid order model that we have discussed so far. Of course is a simple model life is not so simple so it is very possible that the rotor is not rigid the molecule while rotating does not keep its bond length constant.

But all that comes into the domain of a little higher level quantum mechanics and spectroscopy will not go into that right now it is discussed in our molecular spectroscopy course of course. For now we close this discussion but it is not completely over because remember we still have to discuss angular momentum in a little more detail and in doing so we will learn some elegant features of quantum mechanics in the next module.