Fundamentals of Spectroscopy

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Lecture-16
Rotational Spectroscopy: Degeneracy

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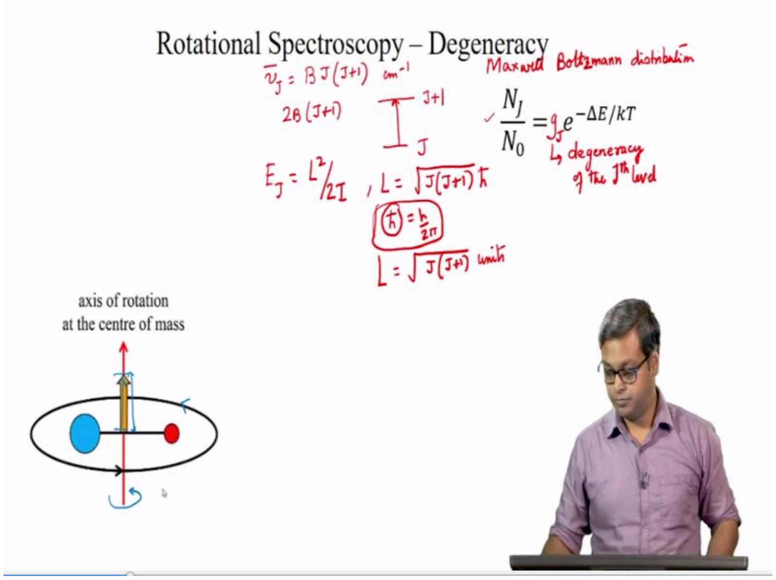

Rotational Spectroscopy – Degeneracy

$\bar{\nu}_J = BJ(J+1)$ cm^{-1}

$2B(J+1)$

$E_J = L^2/2I$, $L = \sqrt{J(J+1)}\hbar$

$\boxed{\hbar = \frac{h}{2\pi}}$

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

Maxwell Boltzmann distribution

$$\frac{N_J}{N_0} = g_J e^{-\Delta E/kT}$$

↳ degeneracy of the Jth level

Hello everyone, welcome to this lecture. So for in the earlier lectures on rotational spectroscopy, we have only considered the energies of different rotational levels. We saw that the energy is given by B times J times J + 1. So, this is the energy nu bar J in wave numbers. So, that is the energy depends on only one quantum number J that is the rotational quantum number. We also focused on the energies of the lines in the rotational spectrum and these energies of the lines are given by 2 B times J + 1 for a transition from J to J + 1.

However, we have not focused on the relative intensities of these spectral lines, the intensity depends on population and population in turn depends on Maxwell Boltzmann distribution, so the Maxwell Boltzmann distribution is given by this equation. So, we see the population of any level, if you compare with the population with some other level, this Maxwell Boltzmann distribution depends on the energy gap between the 2 levels.

But additionally, it also depends on the degeneracy of the energy levels. So, we can write another term here, which is g J, where g J is the degeneracy of the J th level. So, there may be a number of rotational states corresponding to a given rotational energy level. In other words, for a rotational level, there may be degenerate rotational states or states with the same energy so in order to understand the intensity of the rotational spectral lines we need to work out what the degeneracy is for each of the rotational energy levels.

As we have already discussed, the rotational energy states of molecules are related to its rotational angular momentum L and the relation is given by EJ = L square / 2 I, where L = root over J times J + 1 h cross as angular momentum or L is quantized in units of h cross on h / 2 pi. So, we can write L = root over J times J + 1 units, angular momentum being affected has both magnitude and direction.

The direction of the angular momentum is along the axis about which the rotation occurs and is generally drawn as an arrow of length proportional to the magnitude of the angular momentum. So, here we have a diatomic molecule so here what we can see, this red arrow is the axis of rotation around the centre of mass. Now we can see from this arrow that this diatomic molecule is rotating anti clockwise this yellow or orange arrow shows the angular momentum factor. So this is the magnitude of angular momentum.

And this direction is the direction of the angular momentum. So the direction of the angular momentum is given by the right hand rule. That means, if you take your right hand, and if you these 4 fingers point into the direction of rotation, so I am talking about an anti clockwise rotation, the direction where your thumb points that is upward direction is the direction of the angular momentum vector. So you can see, because in this case, the rotation is anti clockwise, the angular momentum vector points upwards.

On the other hand, if the rotation is clockwise, then we have to put our hand like this when these 4 fingers points clockwise direction of rotation and you can see the angular momentum factor in this case will point downwards. So, now, let us discuss the orientation of the angular momentum vector in space. So for from quantum mechanics, we know the magnitude of the vector, but now, we want to know about the direction.

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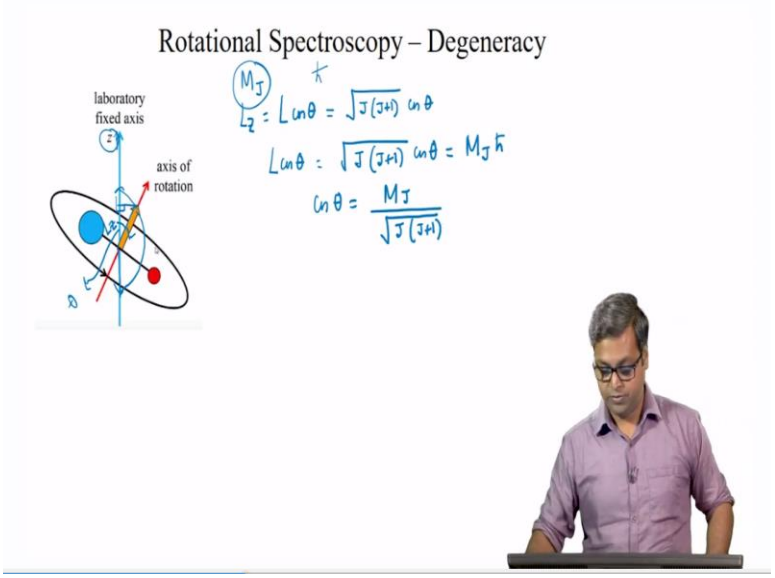

Rotational Spectroscopy – Degeneracy

$\boxed{M_J}$ $\hbar$

$L_z = L\cos\theta = \sqrt{J(J+1)}\cos\theta$

$L\cos\theta = \sqrt{J(J+1)}\cos\theta = M_J\hbar$

$\cos\theta = \dfrac{M_J}{\sqrt{J(J+1)}}$

Say, we have got an arbitrary laboratory fixed axis, this is the Z axis now, let us draw or have this dialogue molecule oriented in a particular direction. And here we have the angular momentum vector. So, we will now project this angular momentum vector on this Z axis. So, if we project what we need to do, we need to take this end of this angular momentum vector and draw a straight line such that this straight line that we have drawn and the Z axis makes an angle of 90 degrees.

So, this yellow arrow is our angular momentum vector L and the projection along the Z axis is given by L Z. So, depending on how the molecule is oriented, the value of L Z can vary anywhere from the actual magnitude of L or angular momentum in the positive direction to the actual magnitude of angular momentum L in the negative direction, if we rotate the diatomic molecule all the way around however, the molecule cannot arbitrarily orient itself with respect to the laboratory reference axis or the Z axis.

But the molecule can orient itself only in certain directions. In other words, the number of different directions, which an angular momentum vector L may take up is limited, the orientation is also quantized the component of angular momentum along a given reference direction, say along these Z direction is given by the quantum number, M J. So, we can see by the way we have projected that L Z = L cos theta, where theta is the angle formed by the Z axis and the angular momentum vector. And we can write this as root over J times J + 1 cos theta.

So for integral values of the rotational quantum number J the angular momentum vetor can only take up directions, such that this M J is 0 or an integral multiple of angular momentum units h cross. So this puts a restriction on the angular momentum vector. So, we can write L cos theta = root over J times J + 1 cos theta = M J h cross and in other words, we can write cos theta = M J divided by root over J times J + 1 in quantized angular momentum units.

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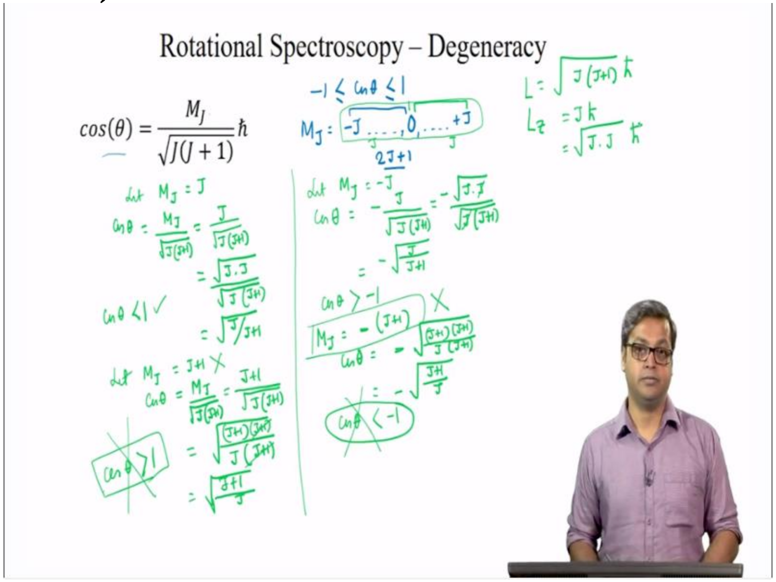

Rotational Spectroscopy – Degeneracy

$$\cos(\theta) = \frac{M_J}{\sqrt{J(J+1)}}\hbar$$

$$-1 \leq \cos\theta \leq 1$$

$$M_J : \boxed{\underbrace{-J \ldots\ldots}_{J}, 0, \underbrace{\ldots\ldots +J}_{J}}$$

$$2J+1$$

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

$$L_z = J\hbar = \sqrt{J.J}\,\hbar$$

let $M_J = J$

$$\cos\theta = \frac{M_J}{\sqrt{J(J+1)}} = \frac{J}{\sqrt{J(J+1)}} = \frac{\sqrt{J.J}}{\sqrt{J(J+1)}} = \sqrt{J/J+1}$$

$\cos\theta < 1$ ✓

let $M_J = J+1$ ✗

$$\cos\theta = \frac{M_J}{\sqrt{J(J+1)}} = \frac{J+1}{\sqrt{J(J+1)}} = \sqrt{\frac{(J+1)(J+1)}{J(J+1)}} = \sqrt{\frac{J+1}{J}}$$

$\boxed{\cancel{\cos\theta > 1}}$

let $M_J = -J$

$$\cos\theta = -\frac{J}{\sqrt{J(J+1)}} = -\frac{\sqrt{J.J}}{\sqrt{J(J+1)}} = -\sqrt{\frac{J}{J+1}}$$

$\cos\theta > -1$

$\boxed{M_J = -(J+1)}$ ✗

$$\cos\theta = -\sqrt{\frac{(J+1)(J+1)}{J(J+1)}} = -\sqrt{\frac{J+1}{J}}$$

$\cancel{\cos\theta < -1}$

So we have cos theta = M J divided by J times root over J + 1. We know that minus 1 is less than equal to cos theta less than equal to 1. So it can be shown that as the maximum and minimum value of cos theta is 1 and minus 1 respectively. M J can take values so the values that M J that can take are from minus J to plus J, which also includes the value of 0. In other words, the possible number of orientations is 2J + 1, because from minus J to minus 1 we have J values and from plus 1 to plus J we have J values we have one another value that is 0.

So, we have J in the negative side, J in the positive side plus 0 which gives 2 J + 1. So, now, we have to know how we get this extreme or the minimum value of M J as minus J and the maximum value of M J as J for a level associated with rotational quantum number J. So, let us assume M J = J. So, we can write cos theta = M J / root over J times J + 1. And because M J = J, we can write this is J / root over J times J + 1. So, we can write J as root over J times J divided by root over J times J + 1. So this becomes root over J / J + 1.

So, as J is less than J + 1 root over J / J + 1 is less than 1. So for this case we have cos theta is less than 1. So this is permissible. So, J can be 1 value of empty. Now, let us increase the value of M J by one unit. So let us say M J = J + 1. So let M J = J +1. So cos theta becomes M J / root over J times J + 1. That is J + 1 divided by root over J times J +1. So we can write this as root over J + 1 times J + 1 in the numerator and J times J + 1 in the denominator.

If you can sell out J +1, we get root over J + 1 / J. So now because J + 1 is greater than J, for this particular case, we have cos theta is greater than 1, but we know the limit of cos theta, so this value of M j is not permissible because cos theta cannot be greater than 1. So, the maximum value of M J is J. Now, let us look into the minimum value, so, let us assume M J = - J so we can write cos theta = - J times root over J times J + 1.

So, this you can write us minus root over J times J root over J times J + 1. So this becomes minus root over. So we cancel J and J in the numerator and the denominator. So we would be get is root over J / J + 1, and because we have a negative sign, and within the square root, we have a number that is less than 1. So we can say cos theta is greater than minus 1. So this is again permissible value.

So M J can take a value of minus J. However, if you put M J equals minus of J + 1 in cost data becomes minus of root over J + 1 times J + 1 divided by J times J + 1. So it becomes minus of root over J + 1 / J. So, we have a number which is greater than 1, the square root of that number is also greater than 1 and we have a negative sign. So, in this case cos theta is less than minus 1 which is not permissible.

So, this cannot happen. In other words, M J cannot be minus of J + 1. So, we saw the maximum value of M J is plus J, and the minimum value of M J is minus J. So, that is how we can say that, M J can take up these values from minus J to plus J, which actually tells us there a 2 J + 1 different orientation. In other words, each energy level is 2 J + 1 fault degenerate. So, what does this result imply? This implies that the angular momentum vector cannot be perfectly aligned to that arbitrary level 3 axis or the Z axis.

This is because L is given by root over J times J + 1 h cross but L Z, the absolute maximum value that L Z can have is J times h cross, which is root over J times J h cross. So, we can see that L is always slightly greater than L C.

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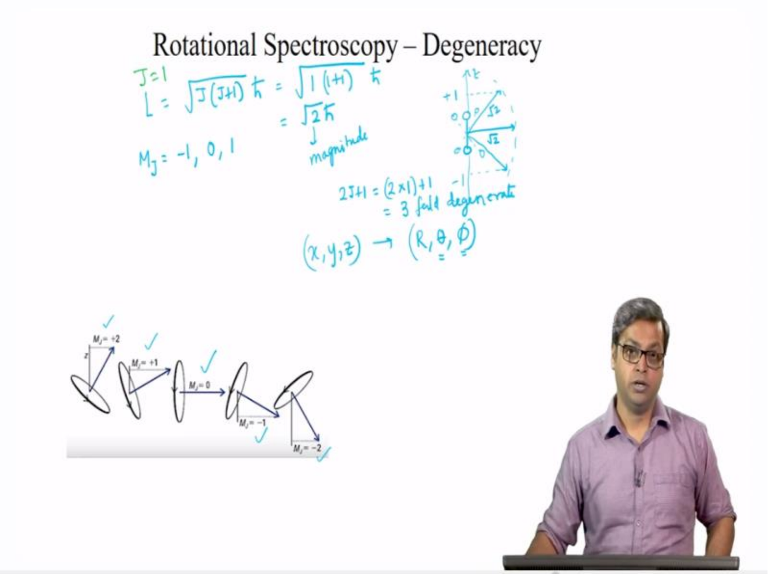

Rotational Spectroscopy – Degeneracy

$J=1$

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

$= \sqrt{2}\hbar$

magnitude

$M_J = -1, 0, 1$

$2J+1 = (2\times1)+1$

$= 3$ fold degenerate

$(x,y,z) \rightarrow (R,\theta,\phi)$

So, let us take the case of J = 1. So, because J = 1, the value of L is root over J times J + 1, h cross that is root over 1 times 1 + 1, h cross that is root over 2 h cross thus the angular momentum vector of magnitude root 2 so root 2 is the magnitude. So this vector with magnitude root 2 can have only 3 values of M J, because J = 1 M J can be minus 1, 0 and 1. So, let us take the diatomic molecule and which is initially oriented in that vertical direction, which is our Z axis.

So let the reference direction there is the Z axis is along the molecule. So, the L or the angular momentum vector is oriented perpendicular to the molecule and the value of L or the magnitude of L is root 2. Now, if this molecule reorients, so let us say the diatomic molecule reorients this way, so we have a new direction for the angular momentum factor L. The magnitude is still root 2. But if we take the projection, the projection has to be either plus 1 or for a different kind of rotation the projection has to be minus 1.

So all 3 directions have the same angular momentum that is L or root 2. And the for J = 1. It is 2 J + 1 that is 2 times 1 + 1 that is threefold degenerate. So now let us look into J = 2 for J = 2 M J can take values of plus 2 plus 1, 0 minus 1 and minus 2. So which makes that J = 2 is fivefold degenerate the reason we have 2 quantum numbers in this problem, one is J the rotational quantum number and the other is M J. Because in order to define the position of a particle on a sphere we need theta and phi.

So, in the last lecture, when we are talking about the selection rules, we made this transformation from Cartesian axis to this polar coordinates. So, all we made this transformation from x, y, z to our theta phi. So, when I am talking about this theta and phi, I am talking about this theta and phi, which we mentioned in the last lecture. So, there is a boundary condition associated with both of these coordinates theta and phi and so, there is a quantum number associated with each of these boundary conditions.

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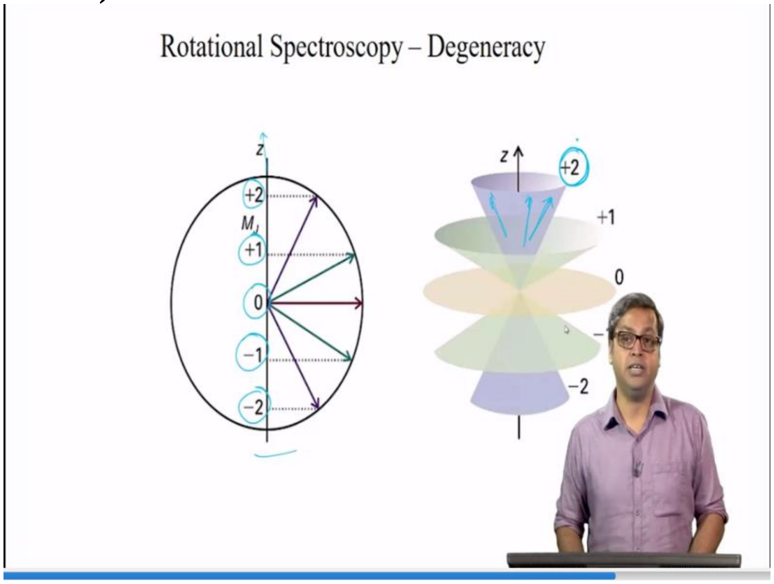

Rotational Spectroscopy – Degeneracy

So the issue of spatial degeneracy is complex. So here you see 2 different representations of spatial degeneracy see on the left the J Victor is projected on the Z axis. So when J = 2 there are 5 possible values of M J that is + 2 + 1 0 - 1 and - 2. So on the right we see the 5 cones that are being swept out to represent the angular momentum factor. The angular momentum vectors can lie anywhere on the surface of the cone for a particular value of M J, and when I draw this I have the value of MJ for this particular cone is plus 2.

So the rotational energy depends on J the rotational quantum number, but does not depend on M J. It does not matter what the orientation of the rotational axis is with respect to the laboratory. In other words, a particular direction is not more important than another, or in terms of rotation, no direction is easier to rotate than the other. The importance of this spatial orientation is the existence of the spatial degeneracy in one molecule.

Let say the molecule is in the Jth quantum state. There are 2J + 1 possible orientation which all have the same rotational energy and this is the definition of degeneracy.

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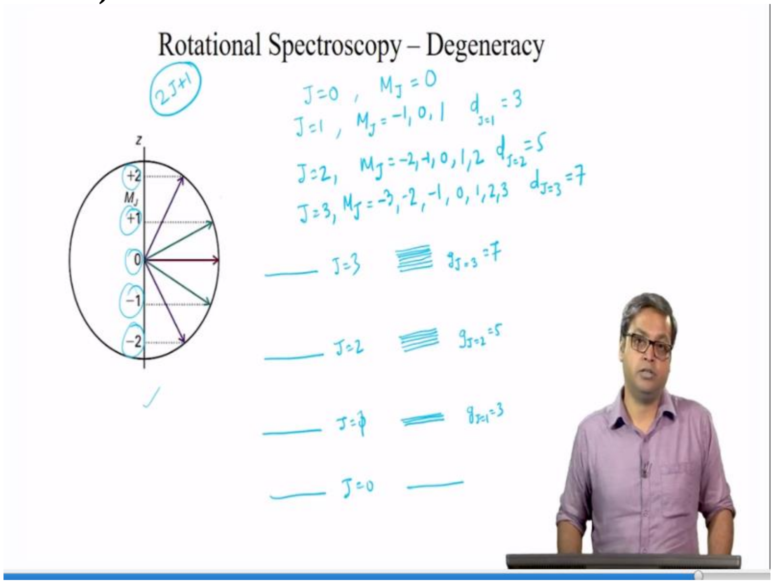

Rotational Spectroscopy – Degeneracy

$2J+1$

$J=0,\ M_J=0$

$J=1,\ M_J=-1,0,1 \quad d_{J=1}=3$

$J=2,\ M_J=-2,-1,0,1,2 \quad d_{J=2}=5$

$J=3,\ M_J=-3,-2,-1,0,1,2,3 \quad d_{J=3}=7$

$J=3 \quad g_{J=3}=7$

$J=2 \quad g_{J=2}=5$

$J=1 \quad g_{J=1}=3$

$J=0$

So, for J = 2, because the molecule can be in 5 quantum states, it means we have 5 energy states and all these 5 energy states have the same energy. That is, they are all degenerate. So, if we take J = 0, the only possible value of M J is 0. That means there for J = 0 it is not degenerate. For J = 1 M J can take values of minus 1, 0 and 1. So the degeneracy of J = 1 is given by 3 or it is threefold degenerate for J = 2 M J can take values from minus 2 minus 1 0 1 2.

So the degeneracy for J = 2 is 5 for J = 3 M J can take values of minus 3 minus 2 minus 1 0 1 2 3 or the degeneracy for J = 3 = 7. Or for any level J, the degeneracy is given by 2 J + 1. So, we see that for J = 3, 2 J + 1 = 2 times 3 + 1 that is 7. So we can see in terms of the diagrams, energy level diagrams. They said J = 0, J= 1, J = 2 J = 3. So J = 0 is non degenerate. So we can think J = 1 there are 3 levels of equal energy.

So g J = 1 = 3, J = 2, we have 5 levels of equal energy. So g of J = 2 is 5, and for J = 3 we can think there are 7 levels of equal energy. So g of J = 3 is 7. So we can say in general for J = J degeneracy, g J is 2J + 1 fault degenerate. Now, let us look into a couple of problems regarding degeneracy.

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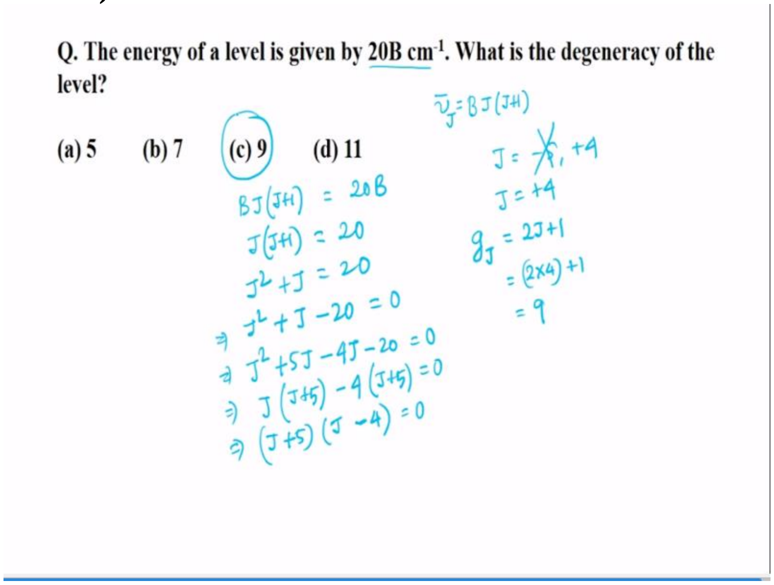

Q. The energy of a level is given by 20B cm^{-1}. What is the degeneracy of the level?

(a) 5 (b) 7 [✓ (c) 9] (d) 11

$$\bar{\nu}_J = BJ(J+1)$$

$$BJ(J+1) = 20B$$
$$J(J+1) = 20$$
$$J^2 + J = 20$$
$$\Rightarrow J^2 + J - 20 = 0$$
$$\Rightarrow J^2 + 5J - 4J - 20 = 0$$
$$\Rightarrow J(J+5) - 4(J+5) = 0$$
$$\Rightarrow (J+5)(J-4) = 0$$

$$J = \cancel{-5}, +4$$
$$J = +4$$
$$g_J = 2J+1$$
$$= (2\times 4)+1$$
$$= 9$$

The first problem we have is the energy level is given by 20B wave numbers, what is the degeneracy of the level. So, we know the energy of any level J is given by B J times J + 1, this is the nu bar J. So, here we have BJ times J + 1 = 20B. So, we have J times J + 1 = 20 or J squared + J = 20. So you can write J squared + J - 20 = 0. Or I can further write. J squared + 5J - 4J - 20 = 0.

That means J if I take common, J + 5 minus if I take 4 common, J + 5 = 0. In other words, J + 5 and J - 4 = 0. So the values that J can take is minus 5 and plus 4, but J cannot be negative. So J cannot be minus 5 so J = + 4. So if J = + 4, we know the degeneracy g of J is given by 2J + 1. So that is 2 times 4 + 1 that is 9. So in other words, because this is a multiple choice question, the correct answer is C, that means the degeneracy of the level is 9.

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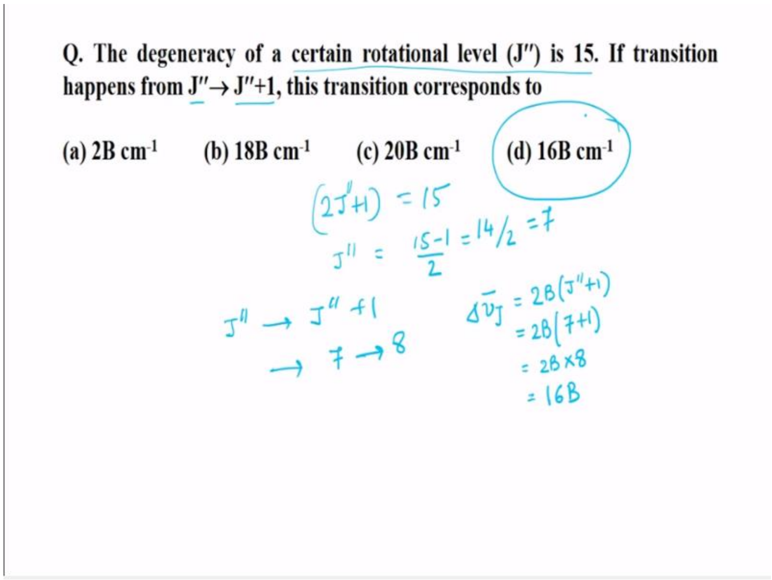

Q. The degeneracy of a certain rotational level (J″) is 15. If transition happens from J″→ J″+1, this transition corresponds to

(a) 2B cm^{-1} **(b) 18B cm^{-1}** **(c) 20B cm^{-1}** [✓ **(d) 16B cm^{-1}**]

$(2J''+1) = 15$

$J'' = \frac{15-1}{2} = 14/2 = 7$

$J'' \rightarrow J''+1$

$\rightarrow 7 \rightarrow 8$

$\Delta\bar{\nu}_J = 2B(J''+1)$

$= 2B(7+1)$

$= 2B \times 8$

$= 16B$

So now we have another question, the degeneracy of a certain rotational level double prime is 15. So, here in the last problem, we calculated the degeneracy in this problem, the degeneracy is given. So, if transition happens from J double prime to J double prime plus 1 this transition corresponds to so we have 4 options we have to choose 1. So, because degeneracy is 15, we can write 2J + 1 = 15.

And because we are talking about a particular level, which is a double prime will write 2J double prime + 1 = 15. So J double prime = 15 – 1 divided by 2 = 14 / 2 = 7. So, we are talking now about a transition that happens from J double prime to J double prime plus 1, there is a transition is from 7 to 8. So, the energy for this transition should be delta nu bar J that is given by 2B times J double prime plus 1. So that is 2B times 7 + 1. So that is 2B times 8 that is 16B. So the correct answer out of all these choices is d that is 16B.