Fundamentals of Statistical Thermodynamics

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Lecture – 31

The Rotational Contribution to Molecular Partition Function

Welcome back to further discussion on Rotational Contribution to Molecular Partition Function. We have been discussing different contributions to overall molecular partition function which is equal to product of partition functions for different contribution there. For example, $Q_{translational}$ into $Q_{rotational}$ into $Q_{vibrational}$ into $Q_{electronic}$ and if there is any other contribution. In the previous couple of lectures, we have discussed rotational contribution for a linear rotor and when we talk about linear rotor it could be diatomic, it could be triatomic, but as long as the molecule is linear. Then this linear molecule for example, if we talk about diatomic molecule, it can be homonuclear, it can be heteronuclear. The difference in the final expression for homonuclear and heteronuclear diatomic molecule has been the inclusion of the symmetric symmetry number and therefore, we need to have a prior knowledge of what the symmetry number will be. Today we will further extend the discussion on rotational contribution to molecular partition function for a linear rotor. We will solve some example and then we will proceed towards discussion on rotational contribution to non-linear rotor. Let us proceed. In the previous lecture let us have some background of that.

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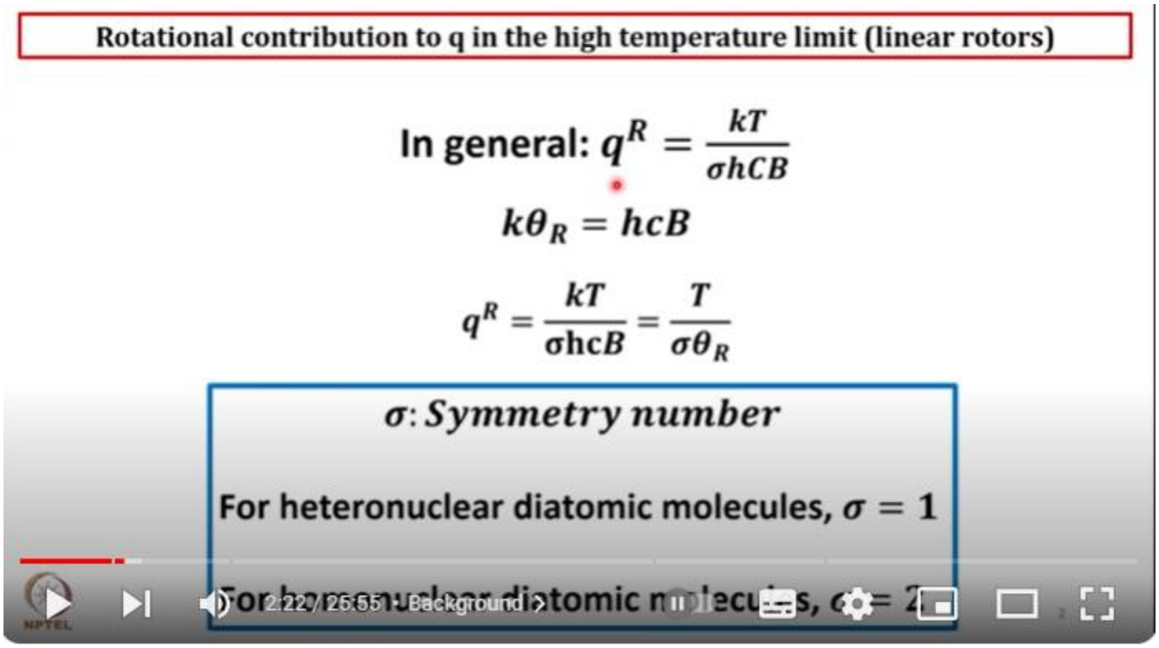

Rotational contribution to q in the high temperature limit (linear rotors)

$$\text{In general: } q^R = \frac{kT}{\sigma hCB}$$

$$k\theta_R = hcB$$

$$q^R = \frac{kT}{\sigma \mathrm{hc}B} = \frac{T}{\sigma\theta_R}$$

σ: Symmetry number

For heteronuclear diatomic molecules, $\sigma = 1$

For homonuclear diatomic molecules, $\sigma = 2$

We have discussed that in general rotational contribution to partition function is given by kT divided by σ h CB and remember that this expression is based upon the assumption that the rotational energy levels are close to each other and under normal conditions of temperature there are several rotational energy levels which are populated and the approximation was that we can consider the summation as equal to integration. Now, above what temperature that approximation is valid will be decided by this equation. In this equation q^r is the characteristic rotational temperature. So above this temperature if the temperature is much much higher than q^r then we will say that it is safe to assume high temperature approximation limit. Otherwise, we will have to go by exclusively summation method and when we were talking about heteronuclear and homonuclear diatomic molecules we talked about the inclusion of symmetry number in the denominator.

For heteronuclear diatomic molecules σ is equal to 1, for homonuclear diatomic molecules σ is equal to 2, the reason for σ equal to 1 and σ equal to 2 we have discussed in the previous lectures. So, one of the ways of representing rotational contribution to partition function for a linear rotor is k T by σhCB and if we express in terms of rotational temperature where hCB upon k, we will write equal to q^r. So, therefore, you can also write rotational contribution for a linear rotor to overall partition function equal to T by σ into θ_r. So therefore, whether you use this equation or you use this equation it essentially means the

same thing. After having this background let us try to solve some numerical problem.
Let us take a look at the problem given to us is that the bond length of oxygen molecule is 120.75 pm. Use the high temperature approximation to calculate the rotational partition function of the molecule at 300 K.

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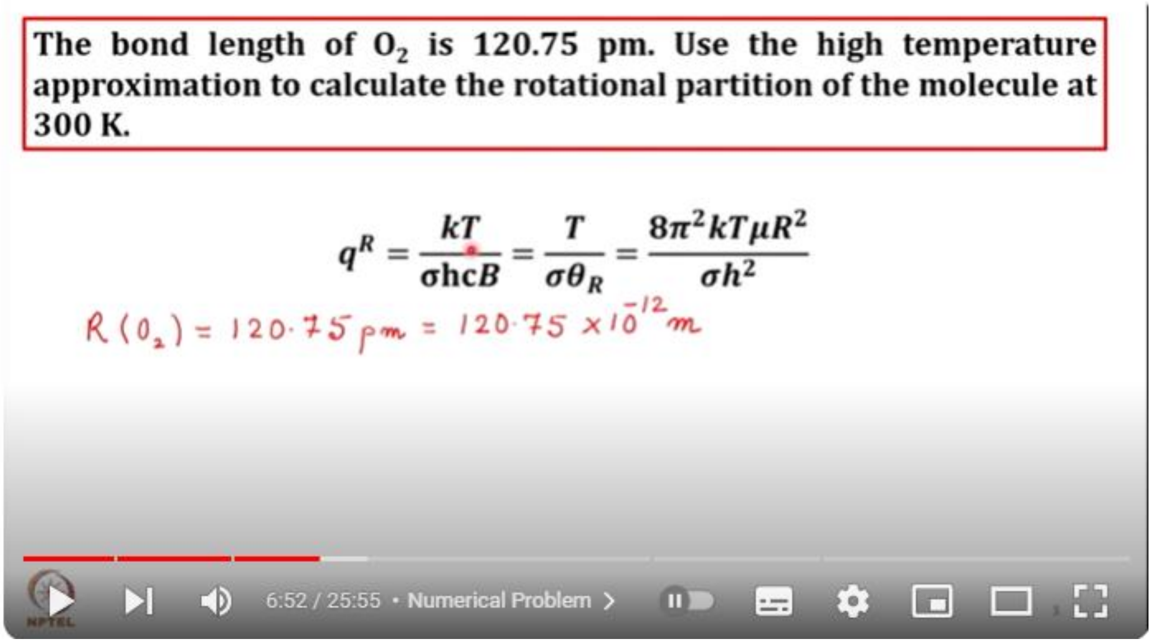

The bond length of O_2 is 120.75 pm. Use the high temperature approximation to calculate the rotational partition of the molecule at 300 K.

$$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\sigma\theta_R} = \frac{8\pi^2 kT\mu R^2}{\sigma h^2}$$

$$R(O_2) = 120.75\ pm = 120.75 \times 10^{-12}\ m$$

So, it is given to us that you use the high temperature approximation. So if such an information is already given to us then we do not need to worry about calculating θ_r unless you are using this expression.
So since it is given that use high temperature approximation we will straight away use q_r is equal to k T over σ h c b. The given information to us is the bond length of oxygen. So let me say r of oxygen is given as 120.75 π picometer which is equal to 120.75 multiplied by 10 raised to the power minus 12 meter.

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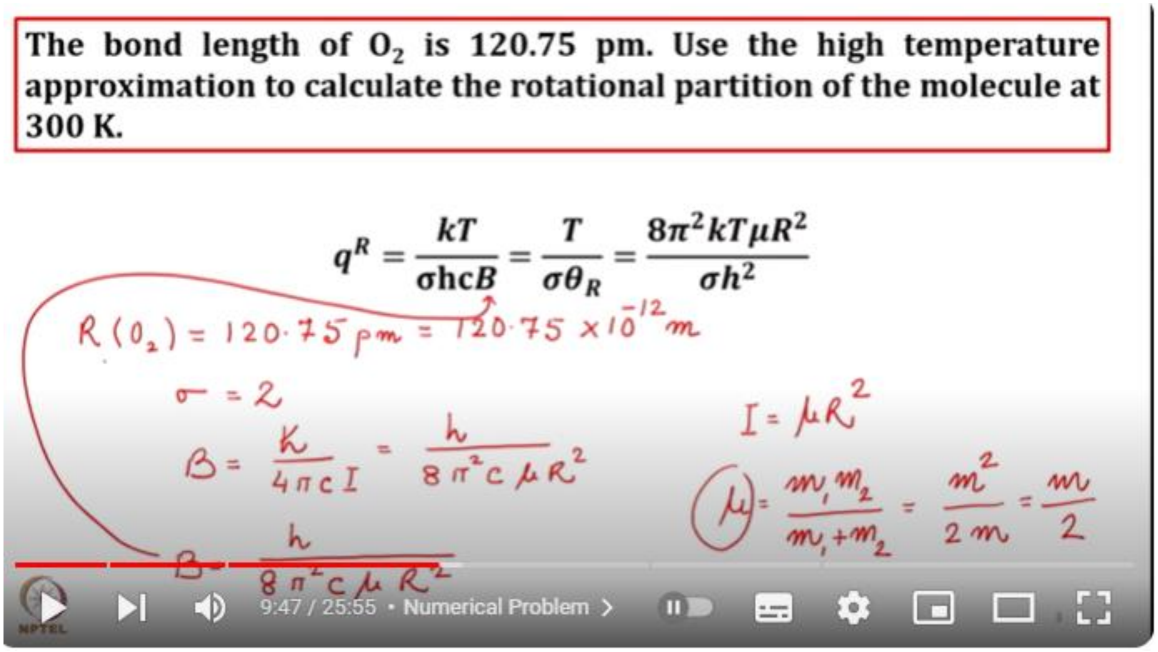

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$$R(O_2) = 120.75\,pm = 120.75 \times 10^{-12}\,m$$

$$\sigma = 2$$

$$B = \frac{\hbar}{4\pi c I} = \frac{h}{8\pi^2 c\mu R^2}$$

$$I = \mu R^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m^2}{2m} = \frac{m}{2}$$

$$B = \frac{h}{8\pi^2 c\mu R^2}$$

This information is given to us. Now if you carefully look at this expression, we have to now transform this expression to something else where you use the given information. K is Boltzmann constant it is a constant, T temperature is given to you it is 300 Kelvin, σ is symmetry number, oxygen is a linear molecule. So therefore 180° rotation leaves the molecule into an indistinguishable state. Therefore, σ we can straight away write σ is equal to 2.

Then next c is the speed of light which is fixed and b which is rotational constant is h cross over 4 π c into I which is equal to h cross is h over 2 π. So, it becomes 8 π square c and I which is moment of inertia this is equal to μ r square. So, let me write this instead of I I will write μ r square and what is μ? μ is equal to reduced mass m 1 m 2 over m 1 plus m 2. In the given case it is oxygen so therefore 1 and 2 both are oxygen oxygen atoms. So, this will be equal to m square where m is the mass of oxygen atom over 2 m which is equal to m by 2.

So now I have b is equal to h over 8 π square c and what I have μ r square. You can for the time being let me retain μ r square and this b which is h over 8 π square c μ r square can be substituted over here. Once you substitute over here you will get this expression. When you put b over here which is h over 8 π square c μ r square and then c and c will get cancelled. So essentially you will have 8 π square k t μ r square σ h square and what is μ?

μ can be expressed in terms of mass of single oxygen atom and you are given information on the bond length.

Let us use this information. So, the expression that I am going to use is q_r is equal to 8 π square k T μR square divided by σ h square. So, q^R is equal to 8 into 22 by 7 square k is 1.381 into 10 raise to the power minus 23 joules per Kelvin. Temperature is 300 Kelvin.

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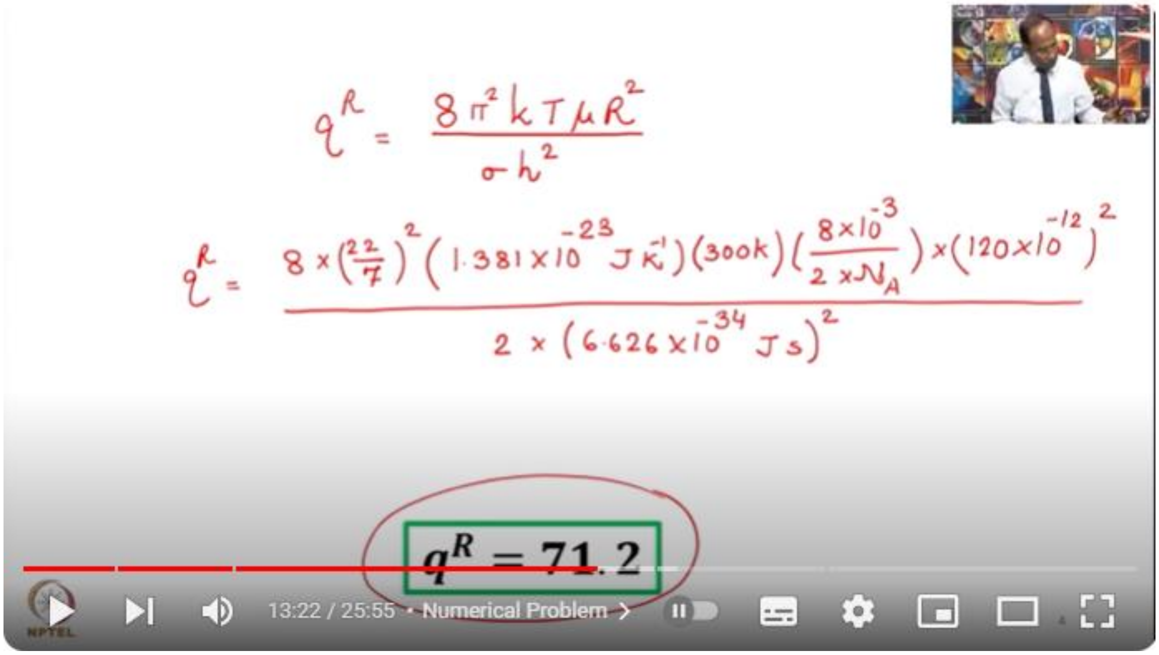

$$q^R = \frac{8\pi^2 kT\mu R^2}{\sigma h^2}$$

$$q^R = \frac{8\times\left(\frac{22}{7}\right)^2\left(1.381\times10^{-23}\,JK^{-1}\right)(300k)\left(\frac{8\times10^{-3}}{2\times N_A}\right)\times\left(120\times10^{-12}\right)^2}{2\times\left(6.626\times10^{-34}\,Js\right)^2}$$

$$\boxed{q^R = 71.2}$$

μ is half m that means 8 into 10 raise to the power minus 3 over 2 into N a. N a is Avogadro constant. Half m. Half m 8 into 10 raise to the power minus 3 to convert into kg per mole and divided by Avogadro constant where you are converting it into per molecule or per atom and what you have is now R 120 into 10 raise to the power minus 12 whole square μ R square divided by σ is equal to 2 into h square 6.626 into 10 raise to the power minus 34 joule second square.

So therefore, now your q^R when you calculate this, it turns out to be 71.2. So carefully you check q^R is 8 into π. π is 22 by 7 whole square into 1.381 into 10 raise to the power minus 23 joules per Kelvin. 300 is the temperature and half μ r square which is 120 into 10 raise to the power minus 12 whole square σ is 2 and the Planck's constant is here 6.626 into 10 raise to the power minus 34. Alright. So, this calculation gives you a q_r value of 71.

2. Now this value of 71.2 is a sizable value. That means at 300 K, 71 thermally accessible rotational states are present. If you increase the temperature, carefully if you examine, this q_r rotational partition function is directly proportional to temperature. It is directly proportional to bond length and it is inversely proportional to the symmetry number.

The variables in this if you see, k is constant, π is constant, temperature can affect the value of rotational partition function. So as long as the molecule is fixed, means a fixed value of μ, fixed value of r, fixed value of σ, q_r will increase directly as a function of temperature. It makes a sense when the temperature becomes higher, more and more thermally accessible rotational states are present. Therefore, the value of 71 for rotational partition function which itself suggests significant population of the upper states can further increase as the temperature is further raised.

Alright. After having discussed the linear rotors, let us now have some discussion on non-linear rotors. Non-linear molecule, some examples of non-linear molecules are given in this table. For example, water. Water is a non-linear molecule. Ammonia is a non-linear molecule.

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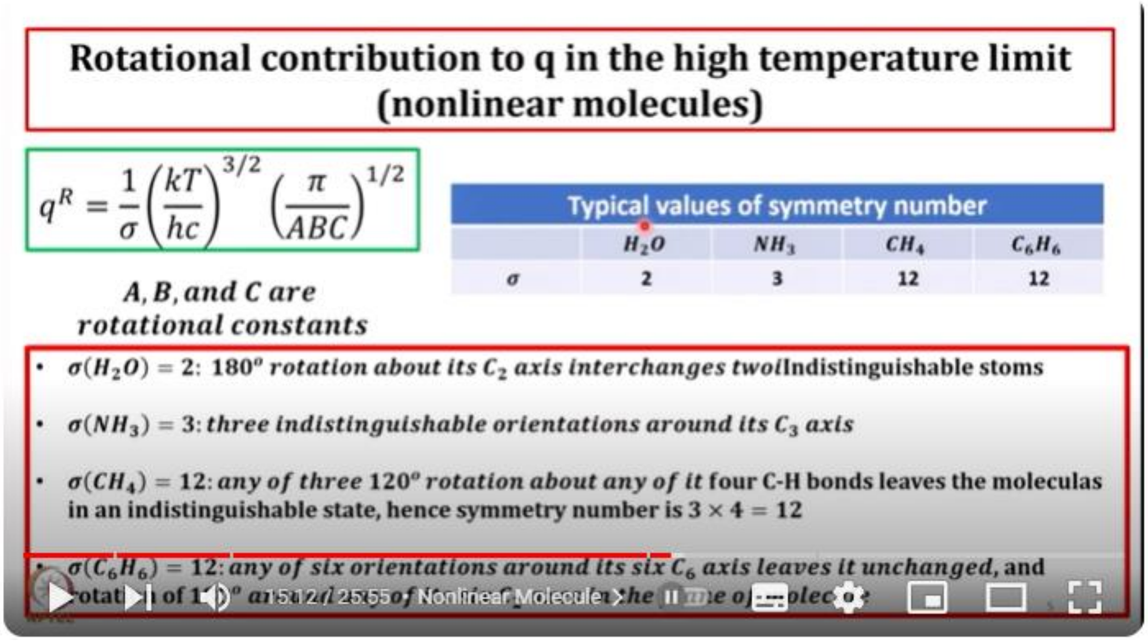

Rotational contribution to q in the high temperature limit (nonlinear molecules)

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

A, B, and C are rotational constants

Typical values of symmetry number				
	H_2O	NH_3	CH_4	C_6H_6
σ	2	3	12	12

- $\sigma(H_2O) = 2$: 180° *rotation about its* C_2 *axis interchanges two*Indistinguishable stoms
- $\sigma(NH_3) = 3$: *three indistinguishable orientations around its* C_3 *axis*
- $\sigma(CH_4) = 12$: *any of three* 120° *rotation about any of it* four C-H bonds leaves the moleculas in an indistinguishable state, hence symmetry number is $3 \times 4 = 12$
- $\sigma(C_6H_6) = 12$: *any of six orientations around its six* C_6 *axis leaves it unchanged*, and rotat[illegible] of 1[illegible]° a[illegible] the [illegible] molec[illegible]

CH_4 methane is a non-linear molecule. Benzene C_6H_6 that is also a non-linear molecule. For linear rotors, we have derived expression for rotational partition function and I am reiterating again and again that in order to use high temperature approximation, we need to have knowledge of characteristic rotational temperature. So therefore, as long as the experimental temperature is µch higher than characteristic rotational temperature, we can use the high temperature approximation result. For linear rotor, we did a detailed derivation.

For non-linear rotor, the derivation is quite involved. So therefore, we are not going into too µch mathematical complexity. Those who are interested can separately do that. We will write the result and have a discussion on the result. The rotational partition function for a non-linear rotor is given by 1 by σ k T by h c raised to the power 3 by 2 π by a b c square root, where a b and c are rotational constants for the rotation of molecule or associated with the rotation of molecule in three dimensions.

It is possible that depending upon the type of rotor, a b or c any of these two may also be equal. So therefore, experimentally to obtain the value of rotational partition function, we need to have information on these three rotational constants a b and c. All in centimeter inverse, we need to have experimental information on these. Like b is equal to h cross by 4 π c i, a and c also have the similar form. Only thing is there the moment of inertia for the rotation of the molecule in three dimensions or three dimensions respectively will be different.

Alright. Once we have that experimental information, we can plug in those numbers and at a given temperature we can calculate the value of rotational partition function for a non-linear molecule. However, the caution that we µst divide by the symmetry number. So, therefore, a knowledge of symmetry number becomes important. We have earlier discussed that what is the need to include this symmetry number. For example, if we consider even water, let us say consider water.

Water is a bent molecule. So, if you consider, let us say I will write somewhere here, H O H. Now, if I rotate water, you know, around this axis, it interchanges the two atoms. This atom will occupy this position and this atom will occupy this position. So, that means, its rotation by 180 ° will leave the molecule in two indistinguishable forms, in an indistinguishable form. So, therefore, the symmetry number for water will be equal to 2.

Now, consider ammonia. If you consider ammonia and then if you consider its C_3 axis, you will see that every 120° rotation will leave the molecule in an indistinguishable form. I repeat, take the C_3 axis, rotate ammonia molecule, it will be observed that every 120° rotation will leave the molecule in an indistinguishable state. So, that means, the symmetry number in case of ammonia is 3 and the higher the value of symmetry number, the lower becomes the rotational partition function because you do not want to over count the number of rotational states which are thermally accessible. Now, let us consider about methane. You know, methane has tetrahedral arrangement around carbon atom.

So, πck up any C-H bond and rotate the molecule by 120°. You will see that the molecule is in the indistinguishable form. 120° rotation means in total 360° rotation, there will be 3 indistinguishable forms, but methane has 4 C-H bonds. So, therefore, you can choose any of the C-H bond and carry out 120° rotation. Each rotation will leave the molecule in an indistinguishable form.

Therefore, the symmetry number in this case is going to be 3 into 4. 3 comes from each 120 ° rotation and 4 comes from 4 C-H bonds. The symmetry number becomes 12. The symmetry number of methane is also 12. Any of 6 orientations around its C_6 axis leaves its unchanged and rotation of 180 ° around any of its C_2 axis in the plane of molecule.

So, therefore, the symmetry number in this case will become 12. I have discussed for simple molecules, but for complex molecules, definitely if you have studied symmetry, that will help you in finding out the symmetry number. But for our purpose, what is important is to recognize that symmetry number is required because you do not want to over count the number of accessible rotational states. So, what we have discussed by now as far as the rotational contribution to partition function is concerned, first of all we should identify whether the molecule or the rotor is linear or non-linear because for linear rotor the forµla is different, for non-linear rotor the forµla is different. Second thing, in order to use the high temperature approximation, even this one, even this result is a high temperature approximation.

That means even to use this result, you µst first calculate A, B and C. You µst have information about A, B and C and then from these calculate the characteristic rotational constants. Then if the experimental temperature is µch higher than the characteristic rotational temperature, we are free to use this high temperature approximation result. After having decided whether to use direct summation method or to use high temperature approximation, then we need to have information about symmetry number. Once you have these informations, it is very easy to calculate the rotational contribution to partition function.

But let us keep in mind that rotational energy levels are not very far separated. Therefore, under normal conditions of temperature, several rotational states will be thermally accessible therefore, the value of rotational partition function is going to be sizable. Now after having discussed the rotational contribution to partition function, we will move to discussion on vibrational contribution and electronic contribution to partition function, molecular partition function, but that we will discuss after solving few more numerical problems. So, I hope that with the knowledge of the rotational partition function for non-linear and linear molecule, we will be able to apply to a variety of problems. Thank you.