Fundamentals of Statistical Thermodynamics

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Lecture: 29

The Rotational Contribution to Molecular Partition Function

Welcome back. We have been discussing different contributions to molecular partition function. In the previous lecture, we discussed that overall molecular partition function is a product of different contributions to the molecular partition function, which is overall Q is equal to Q translational into Q rotational into Q vibrational into Q electronic and if there is any other contribution. And we have already discussed the translational contribution to molecular partition function for a particle, for a molecule or for an atom to move in one dimension, two dimension, three dimension. For three-dimensional movement, we have discussed that Q translational is equal to V over λ cube where λ is thermal wavelength of the particle. Now, we will switch over to rotational contribution to molecular partition function.

When will the rotation come into structure? If we are only talking about monatomic perfect gases, the gas consists of only atoms and atoms cannot have rotational degree of freedom. Therefore, the minimum requirement for the rotational contribution will be that at least the molecule should be diatomic. If there are two atoms in a molecule, then the molecule can not only rotate, but also can vibrate also. So, therefore, beyond monatomic species, there will be in addition to translational contribution, rotational contribution also, vibrational contribution also and anyway electronic contribution is there.

Now, when we talk about the rotational contribution, here the rotor can be a linear rotor as well as it can be a non-linear rotor. What I mean is that the molecule can be linear, for example, diatomic. Diatomic means it will be linear. If it is triatomic, it may be linear, it may be non-linear. Examples, carbon dioxide or water, these represent linear and non-linear rotors.

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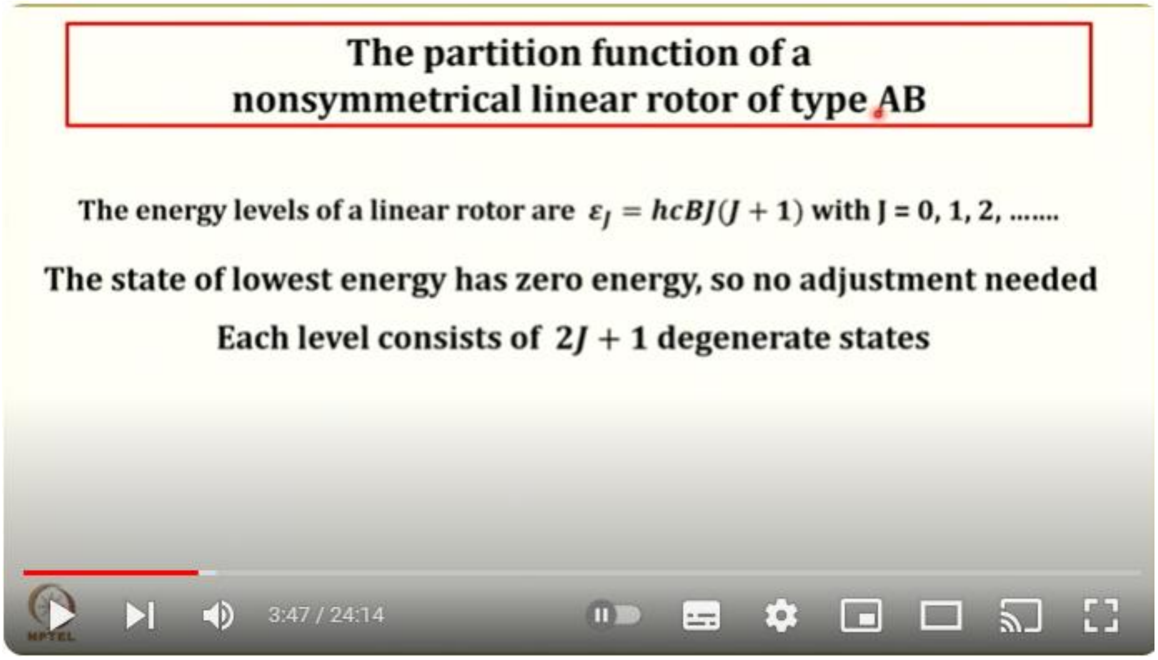

The partition function of a nonsymmetrical linear rotor of type AB

The energy levels of a linear rotor are $\varepsilon_J = hcBJ(J+1)$ with J = 0, 1, 2, ...

The state of lowest energy has zero energy, so no adjustment needed

Each level consists of $2J+1$ degenerate states

So, therefore, now in this lecture, we are going to discuss first the rotational contribution to molecular partition function specifically for a linear rotor. So, first, let us talk about a non-symmetrical linear rotor. When I say non-linear rotor of non-symmetrical in nature, that means I am talking about type AB. Type AB kind molecules can be HCl, HBr, carbon monoxide, right. So, these are non-symmetrical linear rotors.

Here we need some information from your spectroscopy knowledge. I am sure that you have studied rotational spectroscopy. If you have not studied, you will study at some point, but I am going to take some concepts, some formulae from those toπcs. The energy levels of a linear rotor are E_j is equal to h c B into J into J plus 1, where j is equal to 0, 1, 2, etcetera. So, if I write E_j is equal to h c B J into J plus 1, where J can vary from 0, 1, 2, etcetera.

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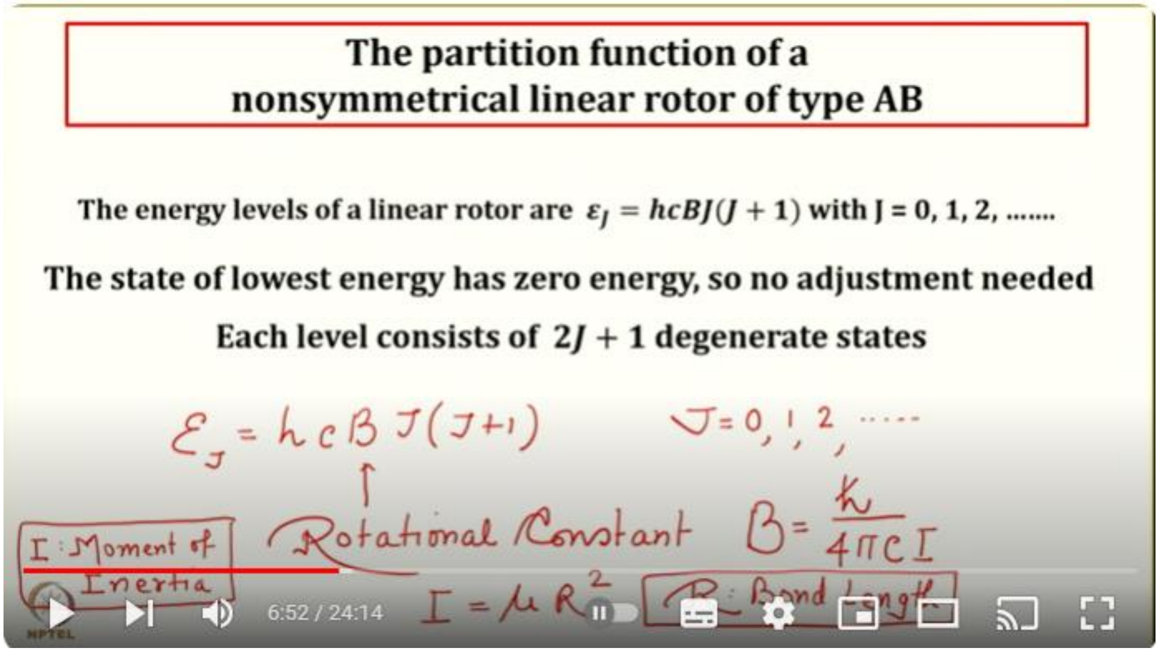

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$\mathcal{E}_J = hcB\,J(J+1) \qquad J = 0, 1, 2, \cdots$

$\uparrow$

Rotational Constant $\quad B = \dfrac{\hbar}{4\pi c I}$

$\boxed{I : \text{Moment of Inertia}}$

$I = \mu R^2 \quad \boxed{R : \text{Bond Length}}$

J is the rotational quantum number. c is the speed of light. B is a rotational constant. J is the rotational quantum number and the value of J can vary from 0, 1, 2, etcetera, etcetera. Now B, rotational constant B is equal to h cross by 4 π c i, where i is equal to μ r square. R is bond length. This information we are taking from your knowledge from spectroscopy, rotational spectroscopy. When we write an expression for the molecular partition function, what we need is the degeneracy of each level and we also need the expressions for the energy levels. The expression for the energy levels are here. E_j is equal to h c b J into J plus 1, where h is Planck's constant and c and b and g we have just described. B rotational constant is h cross. h cross is h over 2 π over 4 π c i. I is μ r square, which is moment of inertia and if you now work out the units, B will have units of wave number centimeter inverse. So this μ c h knowledge is required to proceed further. Another important point that you must note that each level consists of 2 J plus 1 degenerate states that is the degeneracy of each level and also when you look at the expression for the energy h c b J into J plus 1 that means when J is equal to 0, then energy itself becomes 0.

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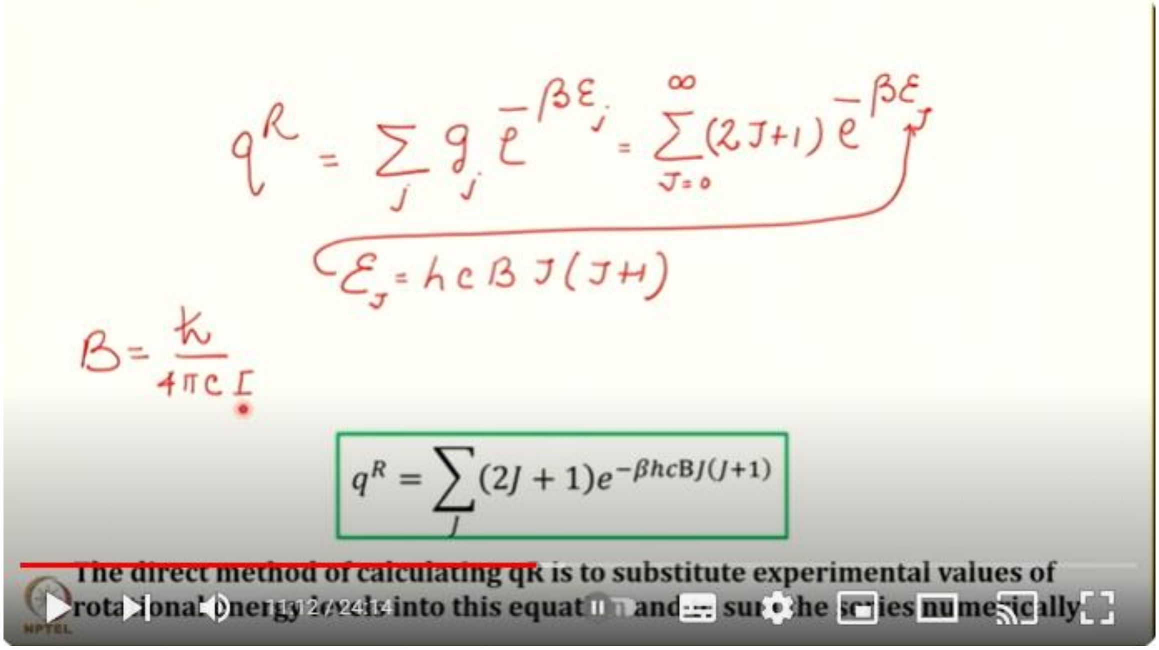

$$q^R = \sum_j g_j e^{-\beta\varepsilon_j} = \sum_{J=0}^{\infty}(2J+1)e^{-\beta\varepsilon_J}$$

$$\varepsilon_J = hcBJ(J+1)$$

$$B = \frac{\hbar}{4\pi c I}$$

$$\boxed{q^R = \sum_J (2J+1)e^{-\beta hcBJ(J+1)}}$$

The direct method of calculating qR is to substitute experimental values of rotational energy levels into this equation and sum the series numerically

That means the state of lowest energy has 0 energy. Therefore, no adjustment is needed over here. Like you know we have to do some adjustments in the case of translational contribution to partition function. q the partition function since we are talking about rotational partition function, this is equal to summation j g $_j$. This is general definition I am writing exponential minus β e j is a general definition, but here when we write for rotational one, I will write J from 0 to infinity. So, E_j from 0 to infinity is 2 J plus 1 exponential minus β e j and we have just discussed that E_j is equal to h c b J into J plus 1. Therefore, when we substitute this E_j over here, what we get is this expression that is in place of degeneracy we are writing 2 J plus 1 and exponential minus β and energy levels are h c B J into J plus 1. So, therefore, you can use this expression and put the value of j from 0 onwards 0, 1, 2, 3, etcetera and you can directly have a summative value. That is what is commented upon here is that the direct method of calculating rotational contribution to partition function is to substitute experimental values of rotational energy levels into this equation and sum the series numerically. Experimental information when you say experimental values of rotational energy levels that means we are talking about b which is equal to h cross over 4 π c I because if you look into other parameters over here you have β, β is 1 over k T, h is blanks constant, c is speed of light, J 0, 1, 2, etcetera.
What we need experimentally is b and that b requires measurement of moment of inertia and moment of inertia is equal to μ over r square that means you require microwave spectroscopy, you require a spectroscopy which can allow you to determine the value of bond length. So, but this is a method for numerical evaluation of rotational partition function. Is there any shortcut like you know when we derived expression for translational partition function? We discussed that in a container laboratory sized container the length of the container is very, very large compared to the size of the molecule and remember that

E n at that point for when we talked about particle which is free to move in one dimension E n is equal to n square h square over 8 m l square. So, l was very large therefore, the translational energy levels were very close to each other and there we converted summation into integration. Can we do such things over here also? In order to use that approximation we will have to first check whether the rotational energy levels are close to each other or they are far separated.

Let us look into that. Now rotational partition function expression where J in summation this J can vary from 0, 1, 2, 3 etcetera onwards onwards and we have this expression we have discussed this.

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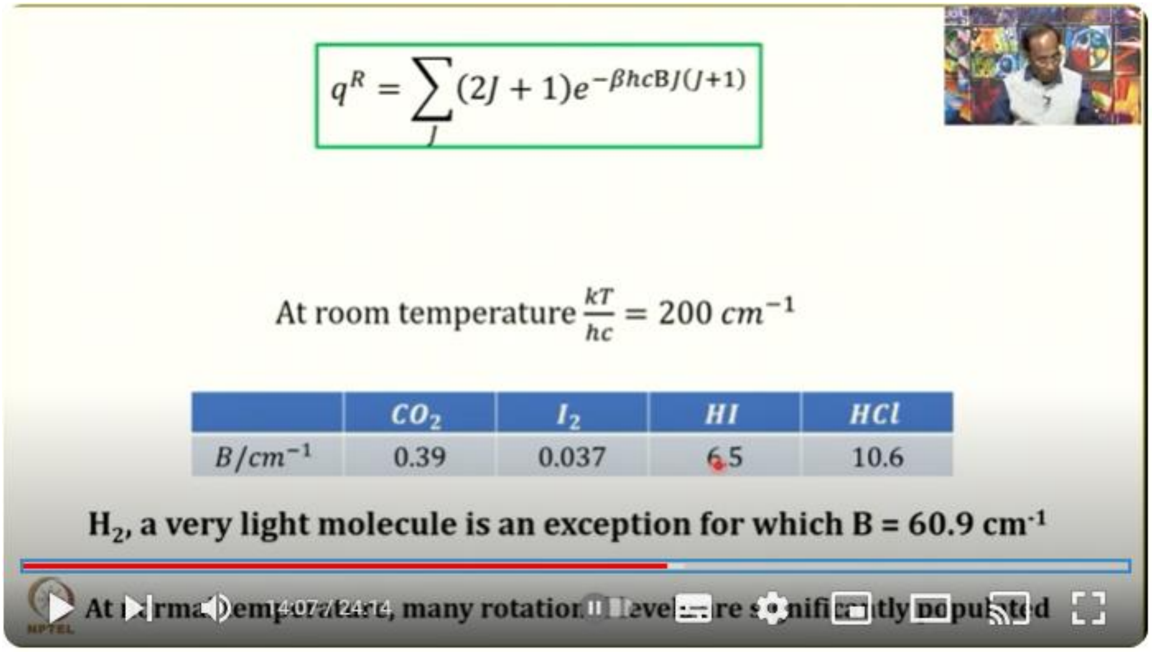

$$q^R = \sum_J (2J+1)e^{-\beta hcBJ(J+1)}$$

At room temperature $\frac{kT}{hc} = 200\ cm^{-1}$

	CO_2	I_2	HI	HCl
B/cm^{-1}	0.39	0.037	6.5	10.6

H_2, a very light molecule is an exception for which B = 60.9 cm^{-1}

At [illegible]rma[illegible] temperature, many rotation[illegible] levels are significantly populated

Now let us see the value of B rotational partition rotational constant value of B rotational constant in centimeter inverse is 0.39 for carbon dioxide, 0.037 for iodine, 6.5 for hydrogen iodide, and 10.6 for hydrogen chloride. B is h cross over 4 π c i and if you look at the value of k T by h c at room temperature it is 200 centimeter inverse. Therefore, we can easily say that at normal temperature many rotational levels are significantly populated because if you compare k T by h c with the rotational constants both in the same units of centimeter inverse you see k T by h c is 200 centimeter inverse, but your rotational constant is very small compared to k T by h c. That means you expect that even at room temperature at normal temperature many rotational levels will be significantly populated. However, when the rotational constant becomes close to k T by h c for example, in case of hydrogen, hydrogen is a very light molecule. This is an exception because B 60.9 compared to 200 it cannot be ignored immediately. So therefore, one has to be careful when you use that approximation that for a certain molecule at normal temperature significant population of rotational energy levels will be there one has to be very very careful when these numbers are no more so different than one can be ignored. But in general, as you see here rotational constants for a variety of molecules is small compared to k T by h c at normal temperature or at room temperature.

Therefore, we can consider that this summation can be converted into integration. Let us do that because the rotational energy levels are close there is a significant population of rotational energy levels. Let us convert this summation into integration. Integration j is equal to 0 to j is equal to infinity 2 J plus 1 exponential minus β h c B J into J plus 1 d j. So, our now goal is to solve this integration bring it into some condensed form.

What will be the easier way? Easier way will be let us consider the derivative of exponential minus β h c B J into J plus 1 with respect to J. Let us consider this let us see what we get this is going to be exponential minus β h c B J into J plus 1 into minus β h c B J into J plus 1 into minus β h c B J into J plus 1. B h c B will be there β h c B J square plus 1 J square plus J J into J plus 1 is J square plus J that will be 2 J plus 1. You see that this is taking us now towards solving this integration easily. So, that means, 2 j plus 1 into exponential minus β h c B J into J plus 1 is equal to minus 1 by h c B J into J plus 1 into minus β h c B d d j of exponential minus β h c B J into J plus 1.

I can substitute this over here. So, what I have now is q^R is equal to minus 1 over β h c B J into J plus 1. So, this becomes h c B integration 0 to infinity d d j exponential minus β h c B j into J plus 1 d j. This becomes now easier because you have simultaneously integration 0 to infinity integration and differentiation which cancel each other. So, therefore, we will have minus 1 over β h c B into I have exponential minus β h c B J into J plus 1 into minus the limit is from 0 to infinity.

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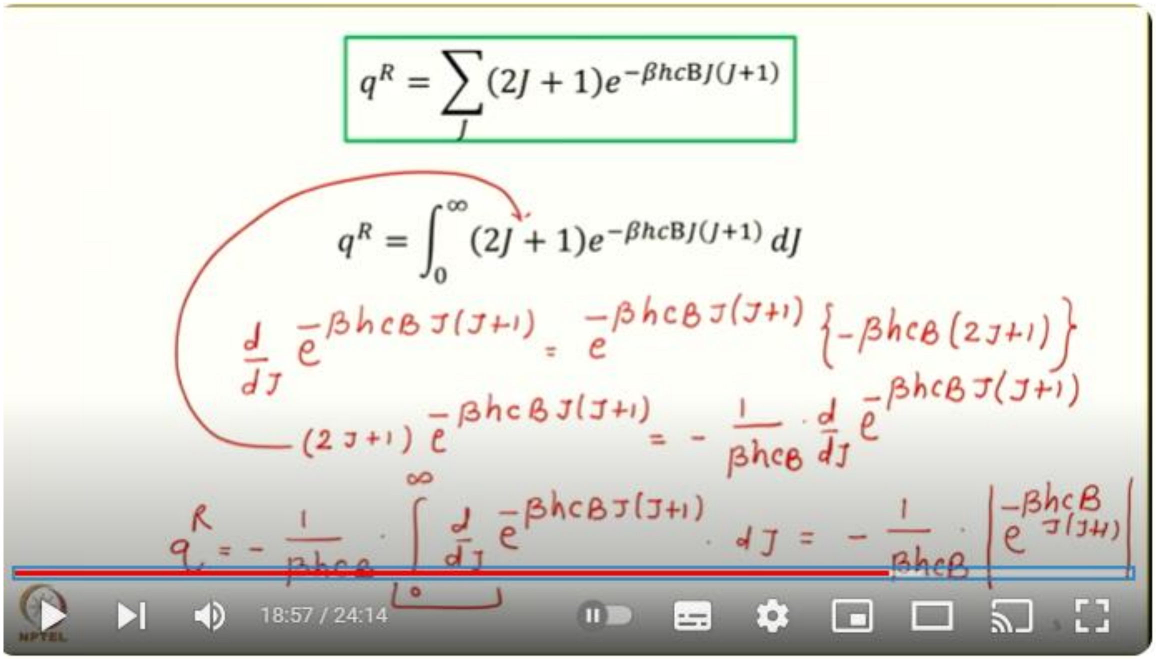

$$q^R = \sum_J (2J+1)e^{-\beta hcBJ(J+1)}$$

$$q^R = \int_0^\infty (2J+1)e^{-\beta hcBJ(J+1)}\,dJ$$

$$\frac{d}{dJ} e^{-\beta hcBJ(J+1)} = e^{-\beta hcBJ(J+1)}\left\{-\beta hcB(2J+1)\right\}$$

$$(2J+1)\,e^{-\beta hcBJ(J+1)} = -\frac{1}{\beta hcB}\cdot\frac{d}{dJ}e^{-\beta hcBJ(J+1)}$$

$$q^R = -\frac{1}{\beta hcB}\cdot\int_0^\infty \frac{d}{dJ}e^{-\beta hcBJ(J+1)}\cdot dJ = -\frac{1}{\beta hcB}\cdot\left|e^{-\beta hcBJ(J+1)}\right|$$

Let us carry it forward. So, q r we get minus 1 over β h c B and then I have exponential minus β h c B J into J plus 1 0 to infinity or in other words I have g q r is equal to 1 over β h c B and I have exponential minus β h c B J into J plus 1 0 to infinity or in other words I have g q^R is equal to 1 over β h c B and I have exponential minus β h c B J into J plus 1 and let me reverse this because I am consuming the negative sign. So, therefore, q^R is equal to 1 over β h c B and then I have when you put this equal to 0 exponential 0 is 1 minus exponential minus infinity is 1 over exponential infinity which is 0. Therefore, the answer is q^R is equal to 1 over β h c B. This is the expression for the rotational contribution to the partition function. So, this is the expression for a non-symmetric linear rotor.

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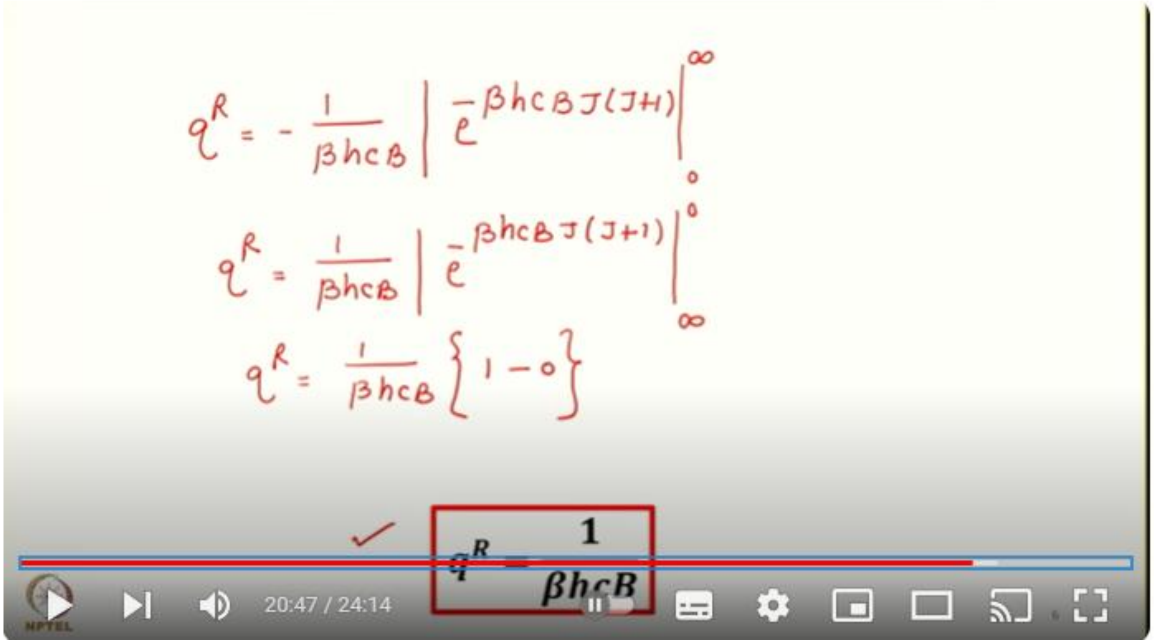

$$q^R = -\frac{1}{\beta hcB}\left| e^{-\beta hcBJ(J+1)} \right|_0^\infty$$

$$q^R = \frac{1}{\beta hcB}\left| e^{-\beta hcBJ(J+1)} \right|_\infty^0$$

$$q^R = \frac{1}{\beta hcB}\{1-0\}$$

✓ $\boxed{q^R = \frac{1}{\beta hcB}}$

Non-symmetric linear rotor where the type is of a b like h c r h b r c o. What form it takes for symmetrical linear rotor we will discuss it bit later, but first let us have some discussion further on based on this expression. So, this was a simple derivation which led us to this expression where we are now able to connect the rotational contribution to the partition function with the rotational constant. So, obviously, the question is that above what temperature this approximation can be used. You remember that the expression for rotational contribution to partition function is actually this and one can use the various values of j use the rotational constant and obtain numerically the value of rotational partition function.

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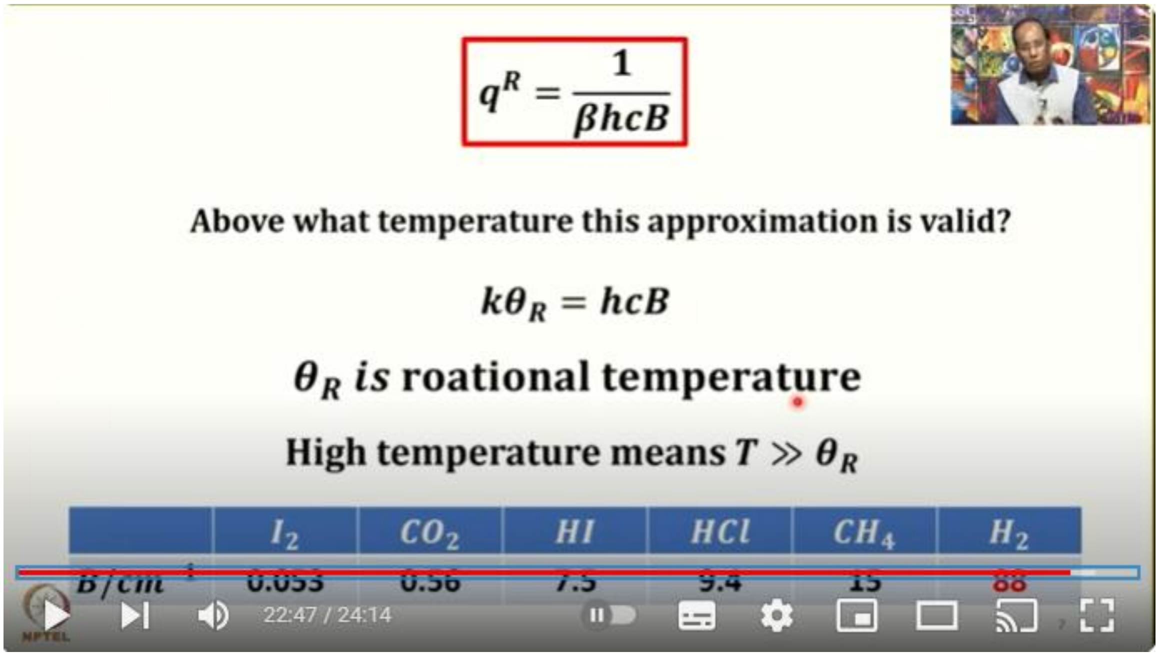

$$\boxed{q^R = \frac{1}{\beta hcB}}$$

Above what temperature this approximation is valid?

$$k\theta_R = hcB$$

θ_R *is* roational temperature

High temperature means $T \gg \theta_R$

	I_2	CO_2	HI	HCl	CH_4	H_2
B/cm^{-1}	0.053	0.56	7.5	9.4	15	88

But then we use this expression this approximation that summation can be converted into integration and that was done assuming that the rotational energy levels are close to each other. So, above what temperature because this population you know population of energy levels is temperature dependent. So, therefore, above what temperature this approximation is valid we need to discuss that and in order to obtain that temperature or in order to describe that temperature let us use this expression k theta r is equal to h c b where theta r is the rotational temperature because this will eventually you know allow you to make a comparison with h c upon k T. So, the theta r in this expression is rotational temperature or it is also sometimes called characteristic rotational temperature high temperature means when the experimental temperature is µ ch µ ch higher than the rotational temperature right high temperature means the actual temperature is µ ch µ ch higher than rotational temperature. So, therefore, when this approximation can be used depends upon what is the rotational temperature and what is the experimental temperature.

More about this we will discuss in the next lecture. Thank you very much. Thank you.