# Fundamentals of Statistical Thermodynamics

**Prof. Nand Kishore**

**Department of Chemistry**

**Indian Institute of Technology, Bombay**

## Lecture – 33

## Vibrational Partition Function - I

Welcome back to the next lecture on Contribution to Overall Partition Functions. So far, we have discussed translational contribution, and we have also discussed rotational contribution. As we have been discussing earlier, for a gas, translational contribution is always there, whether it is a monatomic or a diatomic or a polyatomic gas. At room temperature, translational contribution is always there. Now, moving on from monatomic to diatomic systems, that is from atoms to molecules, additional contributions come in such as rotational contribution, vibrational contribution, electronic contribution, and if there is any other contribution. We have already discussed rotational contribution, and in rotational contribution, we have discussed contributions for a linear rotor and contributions for a non-linear rotor.

Therefore, depending upon the system, we have to decide which expressions to use, whether for a linear rotor or for a non-linear rotor. On an energy scale, the order will be first translational contribution, then rotational, then vibrational, then electronic. And if we want to couple it with temperature, then temperature-wise also, first the translational contribution will come in, then rotational contribution will come in, and if the temperature is very high, vibrational contribution will come in, and then at very, very high temperature, electronic contributions will come in. And what are these temperatures at or above which these contributions come in? As I said, for a gas under normal conditions of temperature and pressure, translational contribution is always there.

Rotational contribution is more or less always there, and if you go back into your notes, we have derived formulae where you can get the rotational contribution by direct summation method or by an approximation method, that is, we have used an approximation and the temperature above which that approximation can be used was named as characteristic rotational temperature or simply rotational temperature. Today, we will discuss the vibrational contribution to the partition function. When you switch over from atoms to molecules, the molecules will have a rotational degree of freedom as well as vibrational degree of freedom. Let us discuss how those contributions can be accounted for. Before we switch over to the derivations, let us have a little recap of how many normal modes of vibration will be there in a given molecule.

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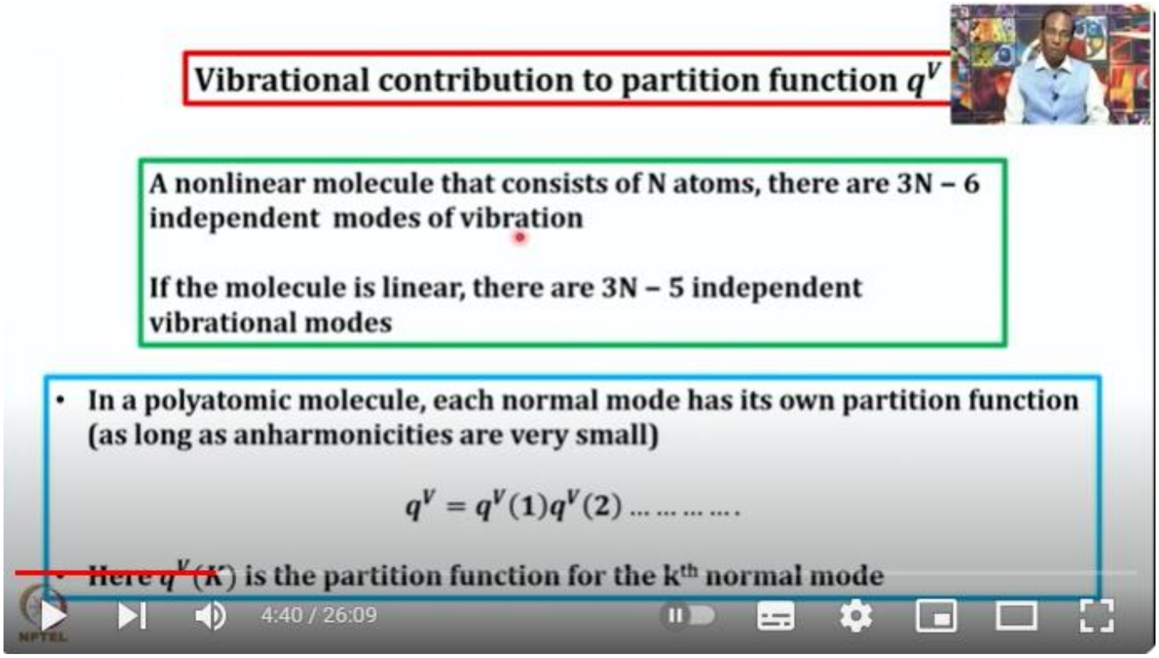

Vibrational contribution to partition function $q^V$

A nonlinear molecule that consists of N atoms, there are 3N – 6 independent modes of vibration

If the molecule is linear, there are 3N – 5 independent vibrational modes

- In a polyatomic molecule, each normal mode has its own partition function (as long as anharmonicities are very small)

$$q^V = q^V(1)q^V(2)\ldots\ldots\ldots\ldots$$

- Here $q^V(K)$ is the partition function for the $k^{th}$ normal mode

Here you will require some information from vibrational spectroscopy. We are not going to get into details of vibrational spectroscopy, but how many independent modes of vibration are there for a molecule that should be clear to us. So, look at this comment. A non-linear molecule that consists of n atoms, for that system, there are 3n minus 6 independent modes of vibration. This information you will need when you deal with the actual systems.

So, if a molecule is non-linear and has n atoms, there are 3N minus 6 independent modes of vibration, whereas if the molecule is linear, then there are 3N minus 5 independent vibrational modes. Ok. That means if the system has two atoms, a molecule which is made up of two atoms, that molecule has to be linear, that cannot be non-linear. And in that case, we will use this formula. So, 3 into 2 is 6, 6 minus 5 is 1.

There is only one independent vibrational mode. However, if there is a non-linear molecule, non-linearity will come when there are more than two atoms in a molecule. For example, water. Water is a non-linear system. And if n is equal to 3, then put 3 over here, 3 into 3 is 9, 9 minus 6 is equal to 3.

There are 3 independent modes of vibration. Why I am saying all this? If there is more than one vibrational mode, each vibrational mode is going to have its own partition function. I repeat, if there is more than one vibrational mode, each vibrational mode is going to have its own partition function. So, if there are three vibrational modes, there will be three partition functions corresponding to each frequency or each wave number of vibration. So, take a look at the comment.

In a polyatomic molecule, each normal mode has its own partition function. That's what I was talking about. As long as n harmonies are very small. As I just mentioned that we will make use of spectroscopy, vibrational spectroscopy over here. And when you study spectroscopy, you studied the harmonic oscillator, you study how n harmonicity arises.

For our discussion, we will not go into details of n harmonicity or n harmonic oscillator. We will restrict our discussion to the harmonic oscillator. So as long as n harmonies are very small, the overall vibrational contribution to the partition function is going to be the vibrational partition function due to the first normal mode multiplied by that for the second normal mode multiplied by more if at all. I refer back to our earlier discussion. Energy is additive.

When you have to write the partition function, then it is multiplicative. And that is what is being used over here. That is if there are more than one normal vibrational modes, the overall vibrational contribution to the partition function is going to be $q^v$ due to the first normal mode of vibration into $q^v$ due to the second normal mode of vibration into so on and here $q^v$ k where k can be 1, 2, 3, whatever. So $q^v$ k is the partition function for the $k^{th}$ normal mode. You have to be a little careful here.

When we were considering translational contribution to the partition function or rotational partition function, this kind of situation did not arise. Right? So in that case, we just used the contribution due to translation, the contribution due to rotation, and we just took care whether the rotor is a linear rotor or it is nonlinear. However, when you are dealing with the vibrational contributions, you have to know how many normal modes of vibration are there and calculate the partition function due to each normal mode of vibration or determine the partition function due to each normal mode of vibration and then multiply all of them. I hope it is clear. Keeping that in mind, let us take a relevant example.

Given that a typical value of the vibrational partition function of one normal mode is about 1.1. That is the information given. Estimate the overall vibrational partition function of a nonlinear molecule containing 10 atoms. Read the statement carefully.

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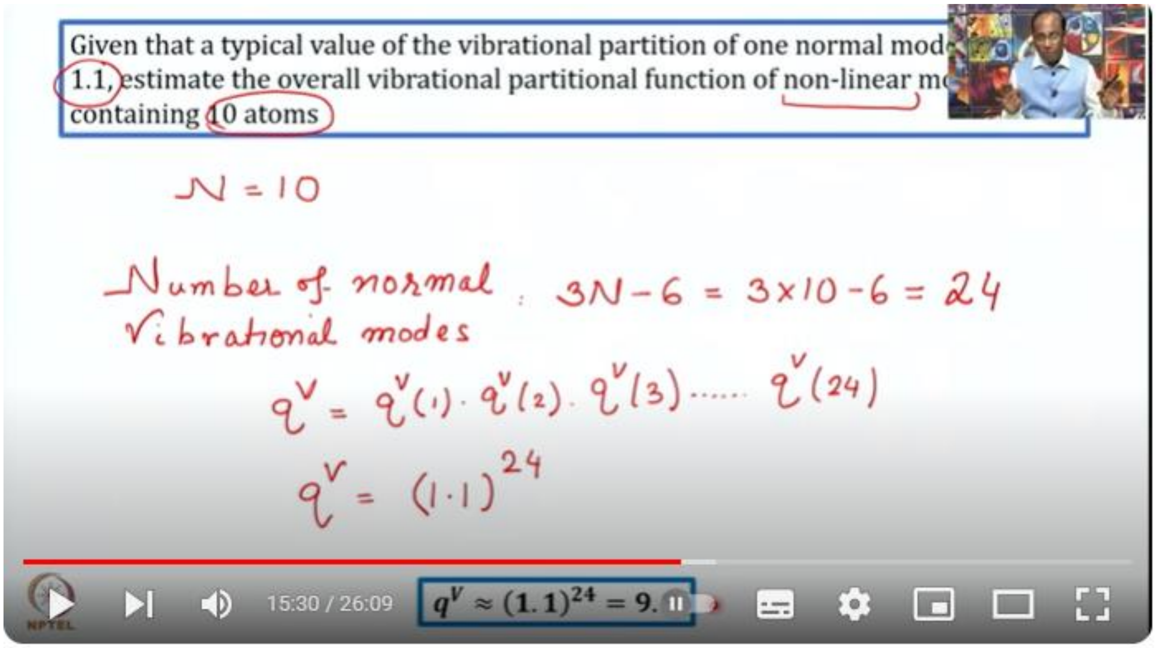

Given that a typical value of the vibrational partition of one normal mod
1.1, estimate the overall vibrational partitional function of non-linear m
containing 10 atoms

$N = 10$

Number of normal vibrational modes : $3N - 6 = 3\times 10 - 6 = 24$

$q^v = q^v(1)\cdot q^v(2)\cdot q^v(3)\ldots\ldots q^v(24)$

$q^v = (1\cdot 1)^{24}$

$q^V \approx (1.1)^{24} = 9.$

What the statement says? That a typical value of the vibrational partition function of one normal mode, that is about 1.1. That is given to us. And the other information that is given to us is that the system is nonlinear and there are 10 atoms. So that means I have n is equal to 10 and the system is nonlinear.

So, for nonlinear, the number of normal modes of vibration, the number of normal vibrational modes, this will be given by nonlinear. Nonlinear means 3n minus 6. For linear, it is 3N minus 5. So, therefore, for nonlinear, we use 3N minus 6. So that means 3 into N is equal to 10 minus 6.

34, 30 minus 6 is equal to 24. 24 normal modes of vibration. So therefore, that means here overall partition function, vibrational partition function is going to be $q^v$ of first into $q^v$ of second into $q^v$ of third into keep on going you have $q^v$ of 24. Partition function is multiplicative. And if you look at the given information, the value of $q^v$ is about 1.

It is an estimate because since they have given an approximate value, therefore they want us to estimate. So that means your $q^v$ is going to be 1.1 into 1.1 into 1.1 how many times? 24 times. And once you calculate this, the value comes out to be approximately 9.9.

And that is what I was referring to that when you compare with translational contribution, rotational contribution, then this type of situation does not arise. When we are dealing with the vibrational modes, then we have to know whether the rotor is a linear rotor or the rotor is a nonlinear rotor. If the rotor is a nonlinear rotor just like the one in this example, we are going to use 3N minus 6 formulas and that gave us 24 normal modes of vibration are there.

And the overall contribution to the vibrational partition function in that case is the multiplication of all the values. So, 1.1 raised to the power 24, the value is 9.9. At this point, we can have a general comparison with the translational contribution to partition function, rotational contribution to partition function, and vibrational contribution to partition function.

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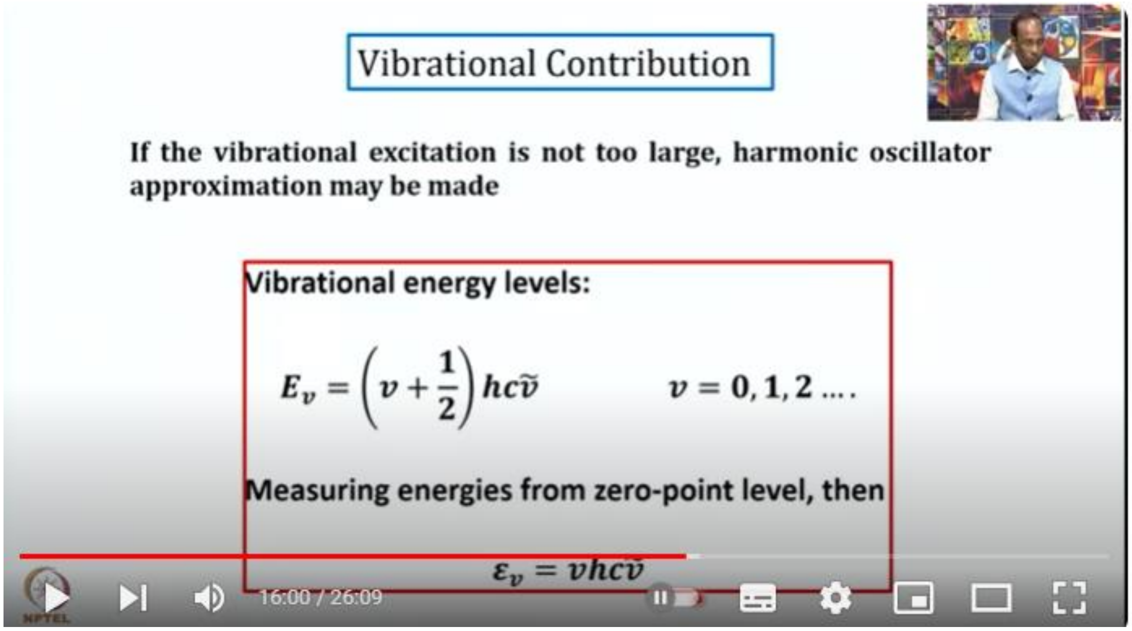

Vibrational Contribution

**If the vibrational excitation is not too large, harmonic oscillator approximation may be made**

**Vibrational energy levels:**

$$E_v = \left(v + \frac{1}{2}\right)hc\tilde{\nu} \qquad v = 0, 1, 2 \ldots.$$

**Measuring energies from zero-point level, then**

$$\varepsilon_v = vhc\tilde{\nu}$$

Recall some of the numerical problems that we solved while calculating translational partition function. Remember the value of the partition function turned out to be some number into 10 raised to the power 20, 24, 30, very large. That means at room temperature, many translational energy levels are significantly populated. And then if you open your previous notes when we discussed the nonlinear rotor, in that case, the value of QR, that is rotational partition function, was sometimes in 1000s. And now if you look at the result that we got over here, the value is 9.9.

So, therefore, the maximum contribution comes from translation followed by rotation followed by vibration and then when we discuss the electronic, we will address those at that time. So, again and again I am reiterating that in the case of vibrational contribution, just make sure that you account for each normal mode of vibration.

Now, let us move towards obtaining an expression for $q^v$. In the previous example, we just took a number and then explained how the overall Qv can be obtained. Now let us try to get an expression for $q^v$. Remember that q is equal to summation j $g_j$ exponential minus β $e_j$. In any case, we started with this expression. That means we need to worry about the degeneracy, and we need to worry about the energy levels. And in the case of non-degenerate energy levels, you do not need to worry about the $g_j$. Vibrational energy levels are given by this expression.

$E_v$, which represents vibrational energy, is v plus half hcυ bar. Where v is the vibrational quantum number and its value can range from 0, 1, 2 onwards. Whole number. And υ bar is the vibrational frequency.

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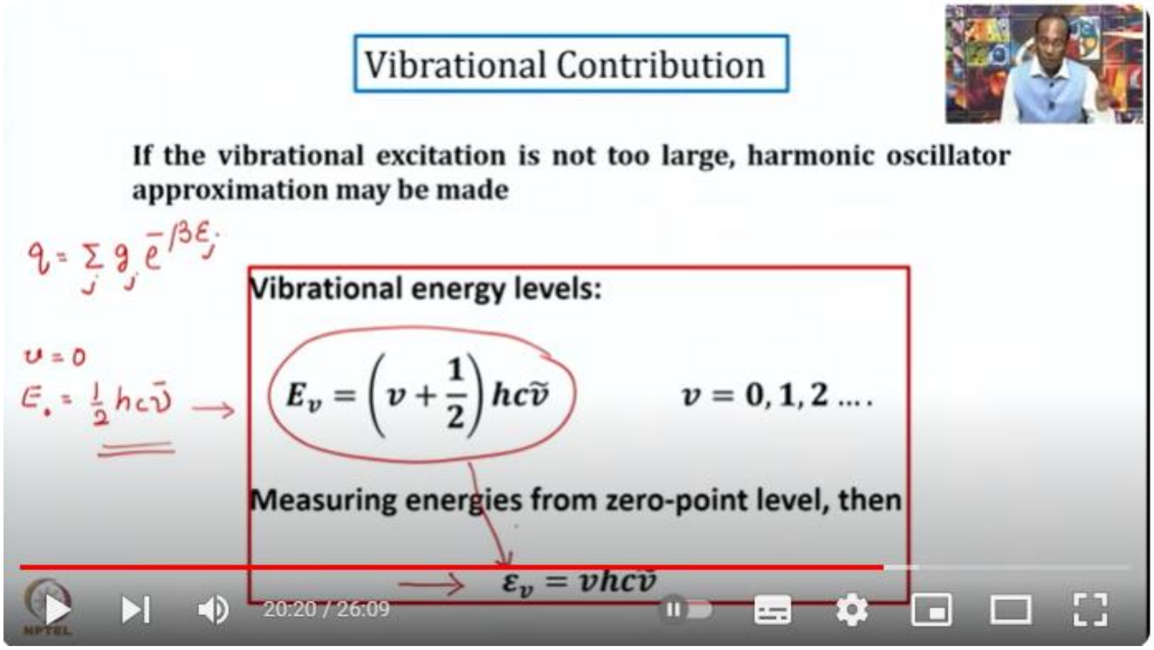

## Vibrational Contribution

**If the vibrational excitation is not too large, harmonic oscillator approximation may be made**

$q = \sum_j g_j e^{-\beta \varepsilon_j}$

$\upsilon = 0$

$E_0 = \frac{1}{2} hc\tilde{\upsilon} \rightarrow$

**Vibrational energy levels:**

$$E_v = \left(v + \frac{1}{2}\right) hc\tilde{v} \qquad v = 0, 1, 2 \ldots.$$

**Measuring energies from zero-point level, then**

$$\rightarrow \varepsilon_v = vhc\tilde{v}$$

So, hcυ bar represents the energy. Where does this come from? This comes from solving the Schrodinger equation. Let us see what happens when we put v is equal to 0. When you put v is equal to 0, let us see what do we get. If I put the vibrational quantum number to be equal to 0, then I will get E(0) is equal to half hcυ bar. This is 0-point vibrational energy, and this is not 0.

This should make you clear that when we were talking about internal energy. And in that case, we were adding U (0), right? We were writing U is equal to U (0) plus something something. Because at that point, we said that there will be a 0-point vibrational energy for an oscillator, and that is half hcυ bar. And when we were saying U minus U (0) that means essentially, we were setting U(0) is equal to half hcυ bar. For our purpose, we have always been setting the ground state energy value to be 0.

And we would like to do that over here also. Now, how we can modify this equation? This equation that when we set v is equal to 0, it should give us the value of 0. And that is possible only if I can subtract this number from this. If I subtract this number, this expression or half hcυ bar from v plus half hcυ bar, I will get this expression.

$E_v$ is equal to v hcυ bar. And now, if I put v is equal to 0, it will be E(0). E(0) is equal to 0, right? So, what we have done is modified this expression into another expression by setting E(0) is equal to 1/2 hcυ. That means now, I go back to again that discussion that if I want to know the internal energy of a system, then I will have to add the zero-point energy. Because, what is internal energy? It is the energy of the system added up in all forms.

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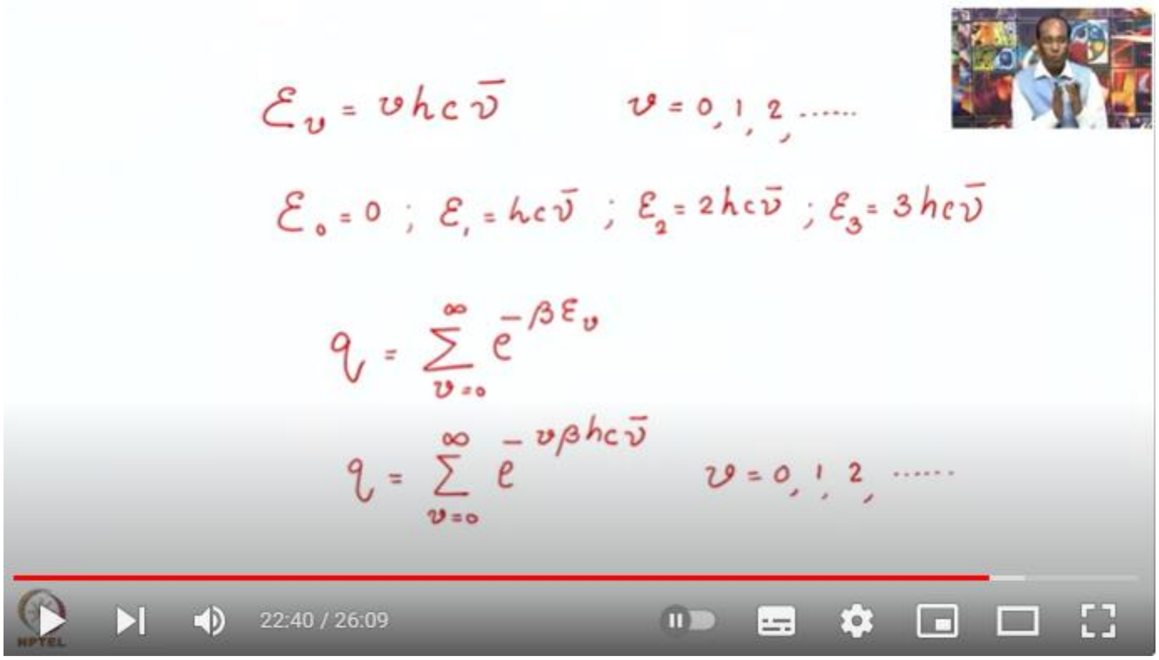

$\mathcal{E}_v = v h c \bar{\nu} \qquad v = 0, 1, 2, \ldots\ldots$

$\mathcal{E}_0 = 0 \; ; \; \mathcal{E}_1 = hc\bar{\nu} \; ; \; \mathcal{E}_2 = 2hc\bar{\nu} \; ; \; \mathcal{E}_3 = 3hc\bar{\nu}$

$$q = \sum_{v=0}^{\infty} e^{-\beta \mathcal{E}_v}$$

$$q = \sum_{v=0}^{\infty} e^{-v\beta hc\bar{\nu}} \qquad v = 0, 1, 2, \ldots\ldots$$

So, therefore, this important step, as we have been doing earlier also, is important to understand that if I subtract half hcυ bar and then if I want to know the total energy, internal energy, I will have to add back the same.

But with this modification, now E(0) will be equal to 0. So, what I have now is $E_v$ is equal to v hcυ bar, where this vibrational quantum number will be 0, 1, 2, etcetera. So obviously, here E(0) will be equal to 0 according to this, okay. So, e1 is equal to hcυ bar, e2 is equal to 2 hcυ bar, it is a whole multiple. e3 is equal to 3 hcυ bar, and then I am interested in this q is equal to summation, here is v, I will put v is equal to 0 to infinity, g is equal to 1 exponential minus $\beta E_v$.

This is what I am interested in now. So, that means the expression now becomes v is equal to 0 to infinity exponential minus v β hcυ bar. This is what now we have to work upon. Here the vibrational quantum number is 0, 1, 2, etcetera, etcetera. So, this discussion, this highlights the advantage of subtracting 1/2 hcυ bar that makes the calculations or the derivations easy, but at the same time it gives an answer to when we were discussing the expressions for u, the expressions for g, when the expressions for h, there was always U(0), $g_0$, $h_0$. If the vibrational contribution, if the vibrational excitation is not too large, then the harmonic oscillator approximation may be made.

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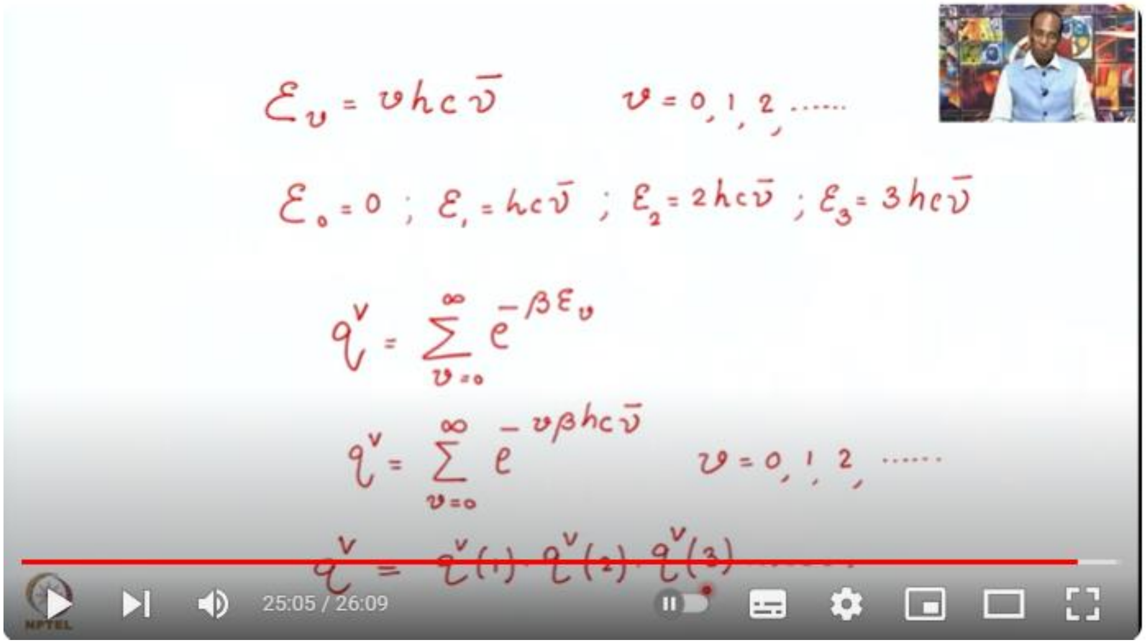

$$\mathcal{E}_v = v hc\bar{\nu} \qquad v = 0, 1, 2, \ldots$$

$$\mathcal{E}_0 = 0 \;;\; \mathcal{E}_1 = hc\bar{\nu} \;;\; \mathcal{E}_2 = 2hc\bar{\nu} \;;\; \mathcal{E}_3 = 3hc\bar{\nu}$$

$$q^V = \sum_{v=0}^{\infty} e^{-\beta \mathcal{E}_v}$$

$$q^V = \sum_{v=0}^{\infty} e^{-v\beta hc\bar{\nu}} \qquad v = 0, 1, 2, \ldots$$

$$q^V = q^V(1)\cdot q^V(2)\cdot q^V(3) \ldots$$

I urge you, request you to go through what is a harmonic oscillator and what is an n harmonic oscillator, what leads to n harmonicity, but remember this approximation over here. If the vibrational excitation is not too large, you are not making the molecule dissociate, I mean it is not too large, then harmonic oscillator approximation may be used. That means the result that we are going to get is only approximate. So, we used $E_v$ is equal to V plus half hcυ bar, where V is equal to 0, 1, 2; we have just discussed that. That is because we want to measure energies from the 0-point level; in that case, $E_v$ is equal to V hcυ bar.

So, we made use of this to discuss how to arrive at an expression, which can be further worked upon to obtain an expression for the vibrational contribution to the partition function. So, I can put a superscript here V, which represents vibrational contribution to the partition function. And then remember the overall vibrational partition function will be a product of the first normal mode, a product of the second normal mode, a product into the third normal mode of vibration, etcetera. That is, the overall vibrational contribution to the partition function is due to the overall vibration, is equal to the multiplication of the vibrational contribution to the partition function due to the first normal mode, into that due to the second normal mode, into that due to the third normal mode.

Having discussed this, now in the next lecture, we will expand this summation and see what form it takes when we change over from summation to integration. We will also discuss the temperature at or above which that approximation is valid, but all those things we will discuss in the next lecture. Thank you very much. Thank you.