Introduction to Molecular Thermodynamics
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Lecture – 26
Statistical Thermodynamics of Ideal Gases (Contd.)

Welcome back. Let us quickly recapitulate what we have been discussing in the statistical thermodynamics of a diatomic ideal gas.

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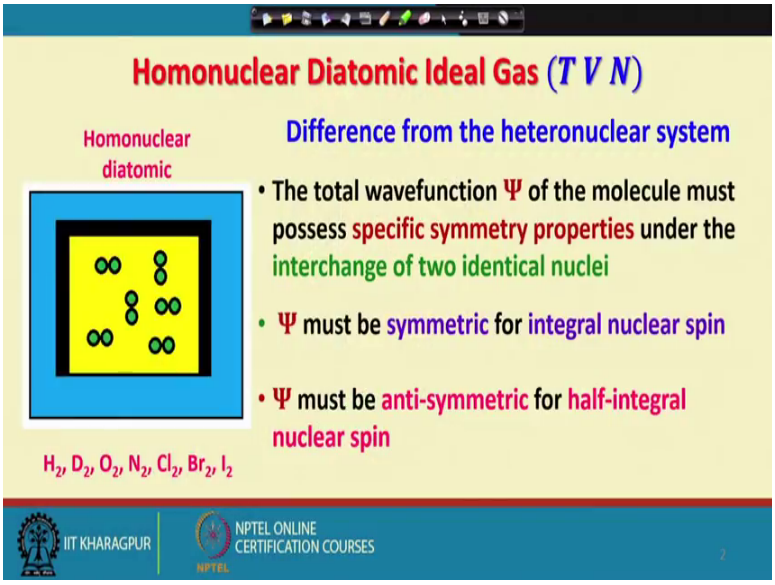

Homonuclear Diatomic Ideal Gas (T V N)

Homonuclear diatomic

H_2, D_2, O_2, N_2, Cl_2, Br_2, I_2

Difference from the heteronuclear system

- The total wavefunction Ψ of the molecule must possess specific symmetry properties under the interchange of two identical nuclei
- Ψ must be symmetric for integral nuclear spin
- Ψ must be anti-symmetric for half-integral nuclear spin

And here what we are doing is, we are trying to see that for a homonuclear diatomic ideal gas what happens in the different from the heteronuclear system. And we have already specified that in the case of a homonuclear diatomic there are certain symmetry properties of the total wave function that is required depending on whether there is an integral or half integral spin on the nucleus.

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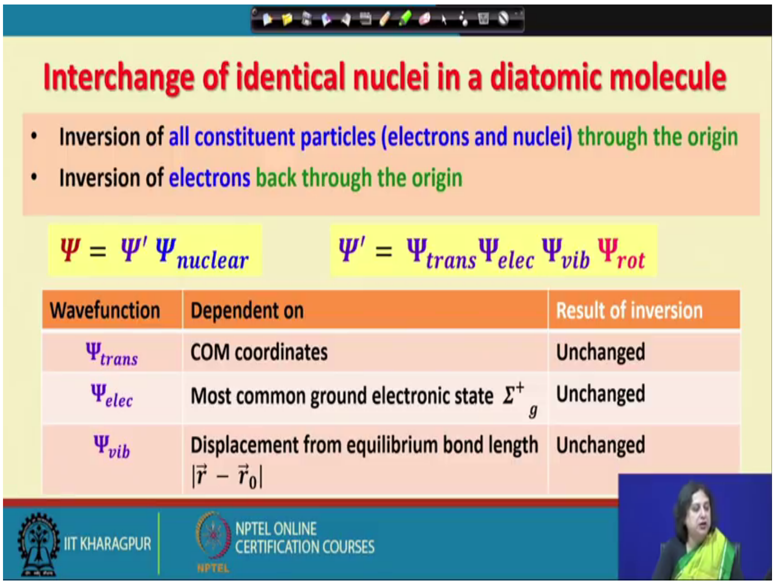

Interchange of identical nuclei in a diatomic molecule

- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

$\Psi = \Psi' \, \Psi_{nuclear}$

$\Psi' = \Psi_{trans} \Psi_{elec} \, \Psi_{vib} \, \Psi_{rot}$

Wavefunction	Dependent on	Result of inversion
Ψ_{trans}	COM coordinates	Unchanged
Ψ_{elec}	Most common ground electronic state $\Sigma^{+}{}_{g}$	Unchanged
Ψ_{vib}	Displacement from equilibrium bond length $\lvert\vec{r} - \vec{r}_0\rvert$	Unchanged

Now, in this connection we examined the overall behavior of psi in terms of psi and psi prime and psi nuclear, where psi prime is comprised of the contributions coming from psi trans psi electronic, psi vibration and psi rotation, and it was shown that all these first 3 terms are generally symmetric with respect to exchange of the identical nuclei in the diatomic molecule.

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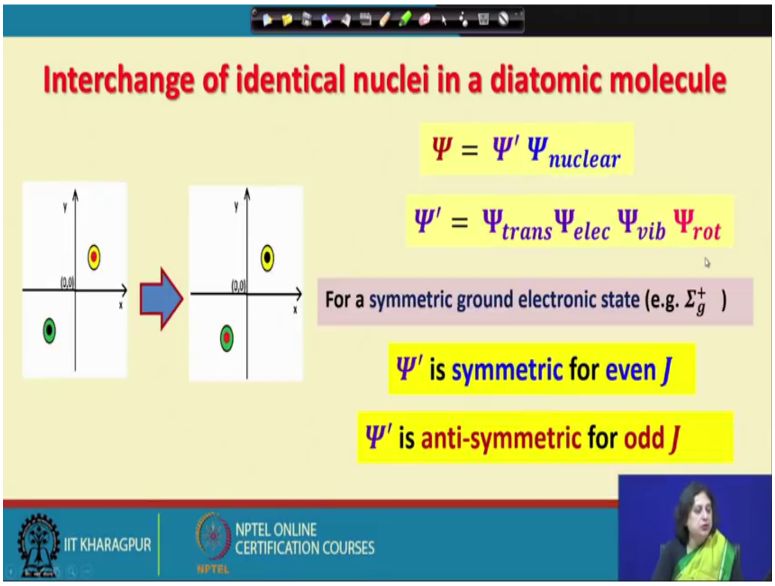

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \, \Psi_{nuclear}$

$\Psi' = \Psi_{trans} \Psi_{elec} \, \Psi_{vib} \, \Psi_{rot}$

For a symmetric ground electronic state (e.g. Σ_g^+)

Ψ' is symmetric for even J

Ψ' is anti-symmetric for odd J

And we also looked at what happens to the psi rot and it was found that for a symmetric ground electronic state then psi rot actually is antisymmetric for even for odd values of J the associated quantum number and it is symmetric with respect to for even values of J. And therefore, on the whole we can say that the wave functions psi prime will be symmetric with respect to interchange of identical nuclei in the diatomic molecule if we have the rotational energy states corresponding to even values of the rotational quantum number J and psi prime is going to be anti symmetric under identical conditions if we have the psi rot corresponding to odd values of the rotational quantum number J.

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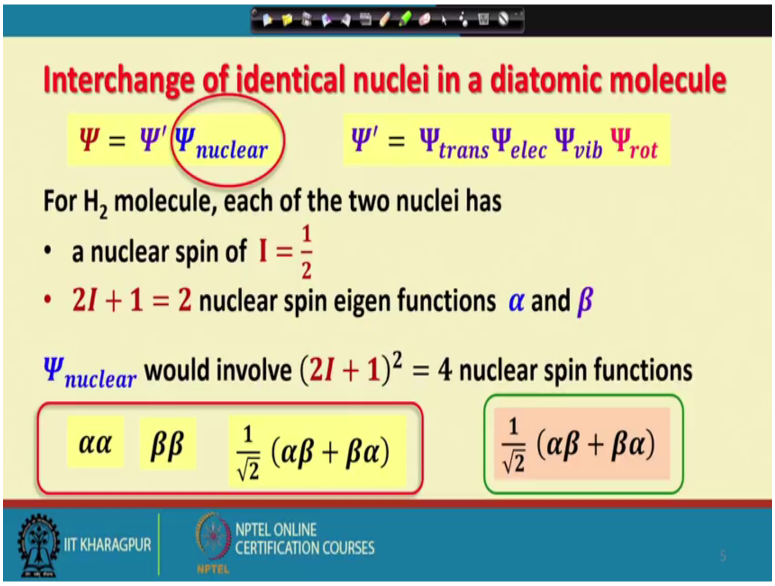

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

For H_2 molecule, each of the two nuclei has

- a nuclear spin of $I = \frac{1}{2}$
- $2I + 1 = 2$ nuclear spin eigen functions α and β

$\Psi_{nuclear}$ would involve $(2I + 1)^2 = 4$ nuclear spin functions

$\alpha\alpha$ $\beta\beta$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$

So, that was the first part for psi prime. We still have to understand the symmetry requirement of the nuclear wave function. So, that is what we started discussing and we took this example of a hydrogen molecule where each nucleus has a nuclear spin of half and associated with them they have 2 nuclear spin eigen functions which are denoted as alpha and beta. And then we understood that the total nuclear spin function will now have 4 possible combinations one is alpha alpha, and another is beta beta, and this is the third option, and this is a fourth option.

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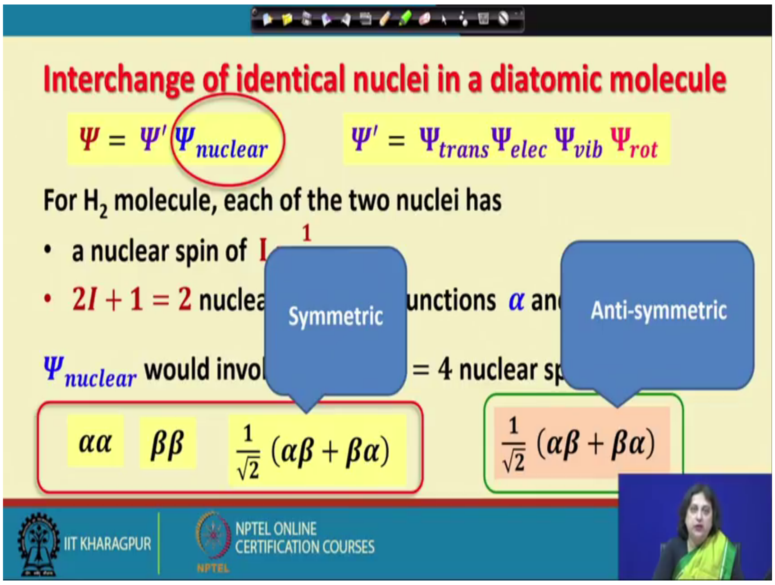

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

For H_2 molecule, each of the two nuclei has

- a nuclear spin of I $\frac{1}{}$
- $2I+1=2$ nuclea unctions α an

$\Psi_{nuclear}$ would invol = 4 nuclear sp

$\alpha\alpha$ $\beta\beta$ $\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)$

$\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)$

And then we understood that out of these 4 nuclear spin functions, 3 are going to be symmetric and only 1 is going to be anti symmetric with respect to interchange of the identical nuclei in this diatomic molecule. Now, this is valid only for the hydrogen molecule.

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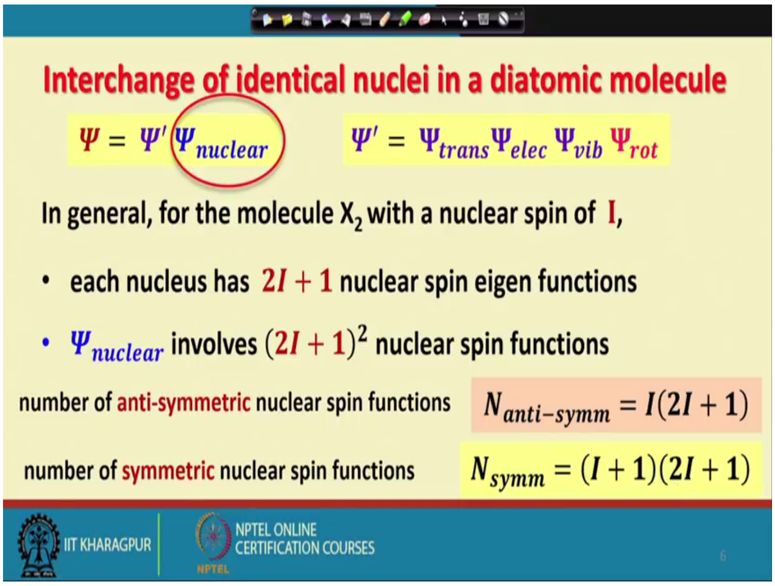

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

In general, for the molecule X_2 with a nuclear spin of I,

- each nucleus has $2I+1$ nuclear spin eigen functions
- $\Psi_{nuclear}$ involves $(2I+1)^2$ nuclear spin functions

number of anti-symmetric nuclear spin functions $N_{anti-symm} = I(2I+1)$

number of symmetric nuclear spin functions $N_{symm} = (I+1)(2I+1)$

So, let us try and move over and see what happens for a general diatomic molecule which is homonuclear and let me call it x 2. So, for the molecule x 2 if the nuclear spin on each nucleus is I in that case each nucleus will have 2 I plus 1 nuclear spin eigen functions and then the psi nuclear will involve 2 I plus 1 nuclear spin functions. Now, this is exactly what we have been showing for the hydrogen molecule, the only difference that we had was we had a specific value of I. And then it can very be very easily shown that out of this 2 I plus 1 whole square nuclear spin functions some will be anti symmetric with respect to the exchange of the 2 nuclei and their number is given by I into 2 I plus 1. And there will be symmetric nucleus spin wave functions as well and their number will be given by I plus 1 into 2 I plus 1.

Now, let us check if we have done things correctly here. So, in the case of hydrogen I said I is equal to half. So, what is 2 I plus 1? 2 I plus 1 is equal to 2.

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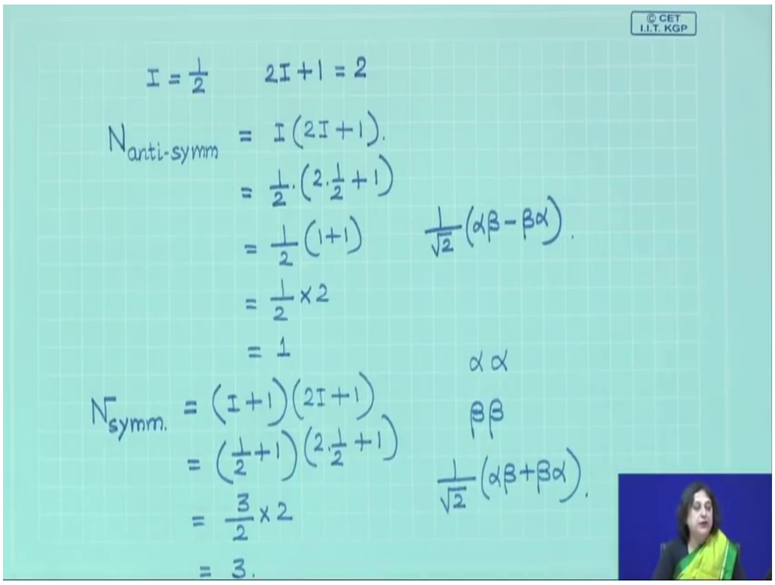

$I = \frac{1}{2} \qquad 2I+1 = 2$

$N_{\text{anti-symm}} = I(2I+1).$

$= \frac{1}{2}.(2.\frac{1}{2}+1)$

$= \frac{1}{2}(1+1) \qquad \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha).$

$= \frac{1}{2} \times 2$

$= 1$

$\alpha\alpha$

$N_{\text{symm.}} = (I+1)(2I+1) \qquad \beta\beta$

$= (\frac{1}{2}+1)(2.\frac{1}{2}+1) \qquad \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha).$

$= \frac{3}{2} \times 2$

$= 3.$

Now, I am interested in finding out the number of anti symmetric nucleus spin functions in the case of hydrogen and what I have written down here without proving it that this number is equal to I into 2 I plus 1. Now, if I put the value of I here then what I find is this is given by this value. So, half into 1 plus 1 and that is equal to half into 2 and that is equal to 1. Now, what was the nuclear spin wave function that we found which is anti symmetric? There was only one such wave function and that was 1 by root 2 alpha beta minus beta alpha.

Now, if I try to write down the number of symmetric nucleus spin wave functions in hydrogen, in general this number is given by I plus 1 into 2 I plus 1.Now what is I plus 1? That is half plus 1 and 2 I plus 1 is 2 into half plus 1. So, I have here this is 3 by 2 multiplied by 2, so the answer is 3. And if you would remember that we had actually 3 possible combinations for the spin nuclear wave function here that was alpha alpha, beta beta and then 1 by root 2, alpha beta plus beta alpha. So, this general relationship that I have written down is actually correct for the general case.

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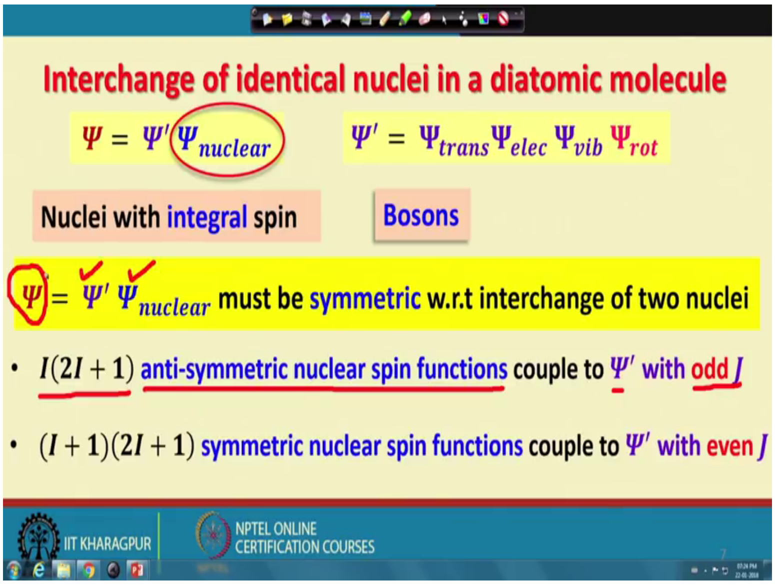

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Nuclei with integral spin Bosons

$\Psi = \Psi' \Psi_{nuclear}$ must be symmetric w.r.t interchange of two nuclei

- $I(2I+1)$ anti-symmetric nuclear spin functions couple to Ψ' with odd J
- $(I+1)(2I+1)$ symmetric nuclear spin functions couple to Ψ' with even J

Now, let me look into the different cases where I have the different spin properties of the nucleus whether it has an integral spin or it has a half integral spin. If I consider first the nuclear with integral spin by definition these are Bosonic particles and for Bosonic particles as we have discussed in our earlier lectures, that Bosonic particles must have a wave function that is symmetric with respect to exchange of the identical nuclei or the two particles if I have to go Bosonic particles they are identical with each other and the overall wave function is symmetric with respect to exchange of the two particles.

In this case I have two identical nuclei and they if they have integral spin they are Bosonic in nature and therefore, overall size should be symmetric with respect to exchange of these identical nuclei. Now, it has now two consequences. The first one as we see here is as follows. If I want to make this symmetric with respect to the interchange I either must be having this anti symmetric as well as this anti symmetric or I can have the following in order to make this symmetric I must be having this symmetric as well as this symmetric no other combination will preserve the Bosonic properties of the overall wave function.

Now, let us try and have a look under what condition the symmetry properties of psi prime and psi nuclear allow for such combination. If I look back, if I have anti symmetric nuclear spin functions for the nucleus with an integral spin I, how many such nuclear spin functions are there? I into 2 I plus 1, and they must couple with those side prime values which are associated with odd values of J. In that case only psi prime is anti symmetric and psi nuclear is also anti symmetric and in combination they would make the overall wave function psi symmetric with respect to exchange of the interchange of the 2 nuclei.

There is another case of course, as I have already mentioned that if it so, happens that my nuclear spin function psi nuclear is symmetric in nature then it must couple to psi prime under conditions that psi prime is also symmetric. When can this happen? This happens when I have psi prime or the this psi prime wave functions corresponding to even values of the rotational quantum number J and therefore, I would say that well for a given nucleus with an integral nuclear spin I, there are I plus 1 into 2 I plus 1 symmetric nuclear spin functions and they are going to couple with those psi prime wave functions that are associated with even values of the rotational quantum number J.

So, what is the consequence here? The consequence of this observation is as follows. Now, as you understand that the moment there are allowed combinations of the wave function they would also put some allowed combinations in the way I can have solutions for the overall Schrodinger equation and this will; obviously, have implications on the single particle partition function because my single particle partition functions depend on the solution of this Schrodinger equation.

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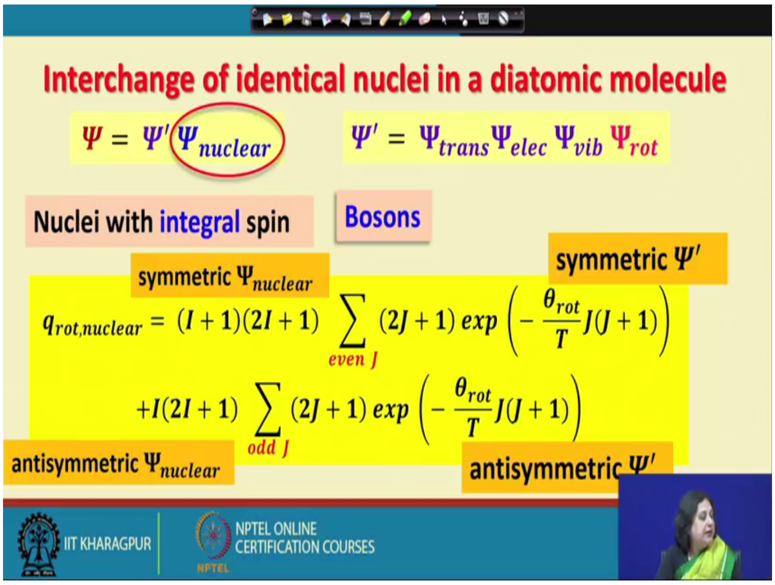

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$

$\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Nuclei with integral spin

Bosons

symmetric $\Psi_{nuclear}$

symmetric Ψ'

$$q_{rot,nuclear} = (I+1)(2I+1) \sum_{even\ J} (2J+1)\, exp\left(-\frac{\theta_{rot}}{T} J(J+1)\right)$$

$$+ I(2I+1) \sum_{odd\ J} (2J+1)\, exp\left(-\frac{\theta_{rot}}{T} J(J+1)\right)$$

antisymmetric $\Psi_{nuclear}$

antisymmetric Ψ'

So, let us have a look at what is the effect of the having a nuclear, two identical nuclei with integral spin in the case of the Bosonic systems. So, if I have a Bosonic system then I have here overall psi its symmetry property is dependent on the rotational part of psi prime and psi nuclear, and those two will control the symmetry dependent part of the of the single particle partition function which I have denoted here as q rot, nuclear.

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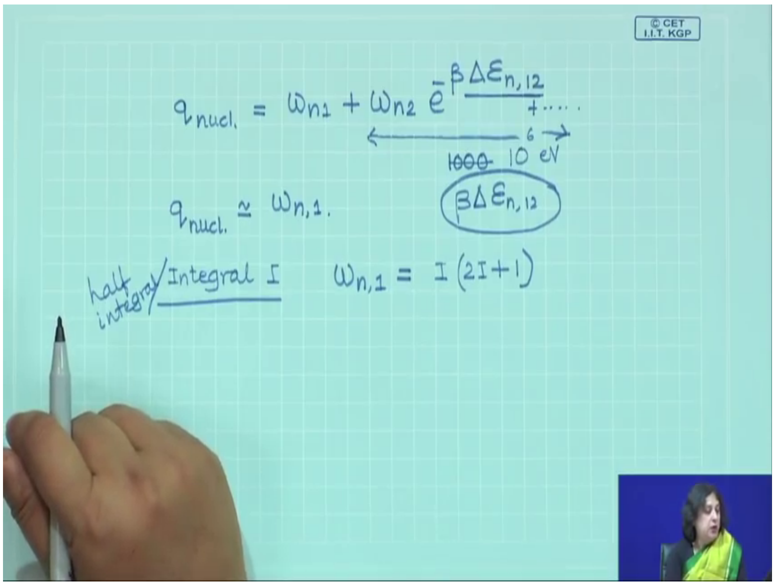

$q_{nucl.} = \omega_{n1} + \omega_{n2}\, e^{-\beta \Delta \varepsilon_{n,12}} + \dots$

~~1000~~ 10^6 eV

$\beta \Delta \varepsilon_{n,12}$

$q_{nucl.} \simeq \omega_{n,1}.$

half integral/Integral I

$\omega_{n,1} = I(2I+1)$

In general for any given system I know that what is q nuclear? q nuclear that is equal to omega n 1 plus omega into e to the power of minus beta delta e n 12 and other terms I know that these nuclear energy states are so far apart from each other it is roughly about 1000, not even 1000, 10 to the power of 6 electron volt therefore, at normal temperatures beta into epsilon n 12 this is, it is such a number that the contribution from this term is essentially 0. Then to good approximation if you are working at high enough temperature q nuclear has been written down as W n 1.

Now, if I have an integer integral nuclear spin I then what is W n 1? W n one is given by the number that this is equal to I into 2 I plus 1, integral or half integral. So, these are the possibilities for I. Now, I have already talked to you about this that, I am sorry just, let me start from that again

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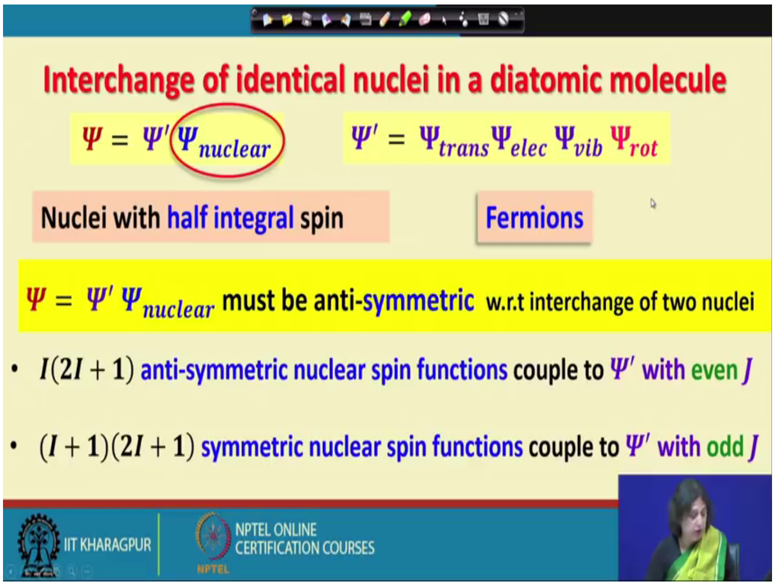

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Nuclei with half integral spin Fermions

$\Psi = \Psi' \Psi_{nuclear}$ must be anti-symmetric w.r.t interchange of two nuclei

- $I(2I+1)$ anti-symmetric nuclear spin functions couple to Ψ' with even J
- $(I+1)(2I+1)$ symmetric nuclear spin functions couple to Ψ' with odd J

That is [FL]. So, let us now have a look at the kind of single partition function that we will write for the system where I have nuclei with an integral spin or where the nuclei are Bosonic particles. And then I can write that the contribution from rotational and the nuclear parts which are going to contribute to the overall symmetry dependence of psi that is given by a sum of these two terms. This is the first term that appears and this is the second term that appears.

Now, by now you must be familiar with this kind of a term when summed over all possible values of J that gives you q rot.

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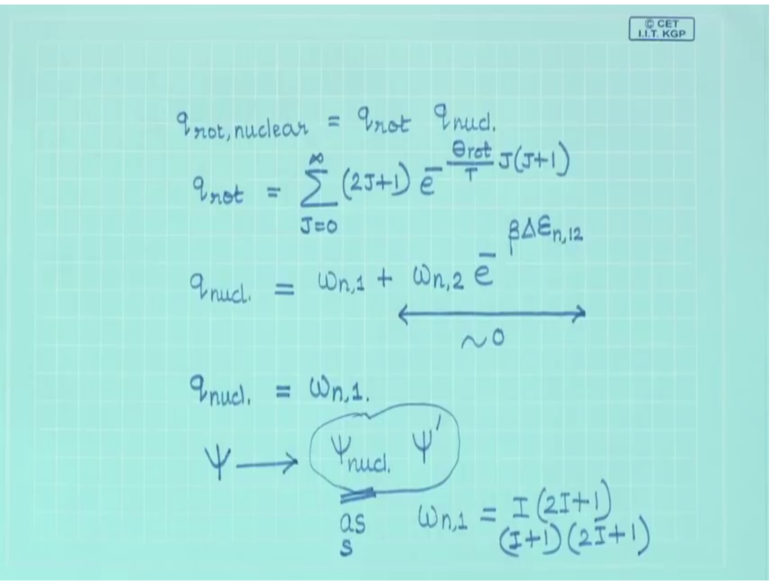

$$q_{rot,nuclear} = q_{rot}\, q_{nucl.}$$

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\frac{\theta_{rot}}{T} J(J+1)}$$

$$q_{nucl.} = \omega_{n,1} + \underset{\sim 0}{\underleftrightarrow{\omega_{n,2}\, e^{-\beta\Delta\varepsilon_{n,12}}}}$$

$$q_{nucl.} = \omega_{n,1}.$$

$$\Psi \longrightarrow \boxed{\underset{\substack{as\\ s}}{\underline{\Psi_{nucl.}}}\ \Psi'} \qquad \omega_{n,1} = \begin{array}{c} I(2I+1) \\ (I+1)(2I+1) \end{array}$$

Now, if I write down for any such system that q rot nuclear is something like q rot into q nuclear. Now, what is q rot? By definition q rot is equal to summation over J going from 0 to infinity to J plus 1 e to the power of minus theta rot by T into J into J plus 1. Now, what is q nuclear? We know that q nuclear is equal to degeneracy of the first nuclear round nuclear energy state plus degeneracy of the first excited nuclear energy state to beta epsilon, nuclear energy for the nuclear energy states the first the difference between the ground and the first excited nuclear energy states.

Now, we have already seen that contribution of this term at finite temperatures or the at the high temperatures that we are interested in this is approximately equal to 0 and there four q nuclear is going to be given simply by the degeneracy of the ground nuclear energy state.

Now, in our notation we understand that only those combinations of psi are acceptable where I have psi nuclear and psi prime coming from through psi prime coming the contribution of the rotational psi these two must have certain properties. So, when psi nuclear is let us say anti symmetric in the case of a Bosonic system. So, anti symmetric Bosonic system it will have omega n 1 as equal to I into 2 I plus 1, and if it is symmetric in that case this term will be I plus 1 into 2 I plus 1.

So, this number therefore, as you see that if you know what the nuclear spin is from experiments then you can very easily find out what is going to be q nuclear. And if you know that whether for the given system you require an anti symmetric nuclear spin function or symmetric nuclear spin function you can very easily find out the corresponding degeneracy of that nuclear state nuclear grounds energy state and accordingly you can say that well q nuclear is going to be a part either this term or this term.

So, let us have a closer look at the kind of terms that we have included in this q rot nuclear. The first term that appears it is a product of two things these two terms multiplied by a sum and the summation is over all even use of J. So, basically what I am looking at is as follows. I am looking at the contribution to q rot nuclear coming from the symmetric psi nuclear that is being coupled to symmetric psi prime. And here in this part I have the contribution of anti symmetric psi nuclear coupling to anti symmetric psi prime and therefore, you see that we have preserved the property of Bosonic particles that they their overall wave function is going to be symmetric with respect to exchange of the two identical nuclei.

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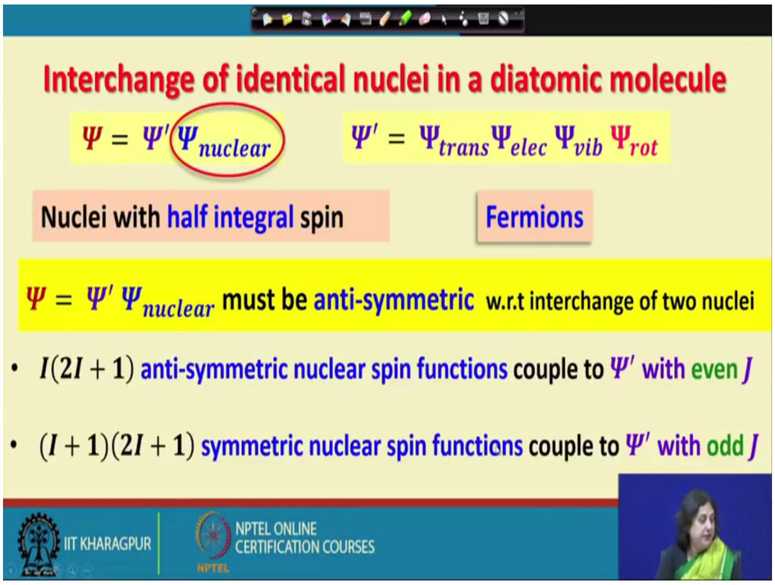

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Nuclei with half integral spin Fermions

$\Psi = \Psi' \Psi_{nuclear}$ must be anti-symmetric w.r.t interchange of two nuclei

- $I(2I+1)$ anti-symmetric nuclear spin functions couple to Ψ' with even J
- $(I+1)(2I+1)$ symmetric nuclear spin functions couple to Ψ' with odd J

Similarly, when you think about nuclei with half integral spins, in that case I should be thinking about the nuclei as the two identical nuclei as fermions and I would demand that the overall wave functions psi is going to be anti symmetric with respect to interchange of 2 nuclei. And now I must be having such combination of psi prime and psi nuclear such that this symmetry property is preserved.

Now, under which condition this can happen? The two conditions under which this can happen is if you have anti symmetric nuclear spin functions, they must couple with anti symmetric psi prime. And when does psi prime happen to be anti symmetric with respect to interchange of 2 nuclei? That happens when J can take up even values it may. So, happen that you can have the symmetric nuclear spin functions. But then that must couple to psi prime such that you have an overall anti symmetric combination and therefore, you must couple to only those psi prime values associated with odd J thereby giving you an anti symmetric psi prime and in that case the symmetric psi nuclear will couple to anti symmetric psi prime to give the total wave function as anti symmetric with respect to interchange of the 2 nuclei

So, in this case also we can see that the overall expression for q rot nuclear can be given in terms of two distinct terms.

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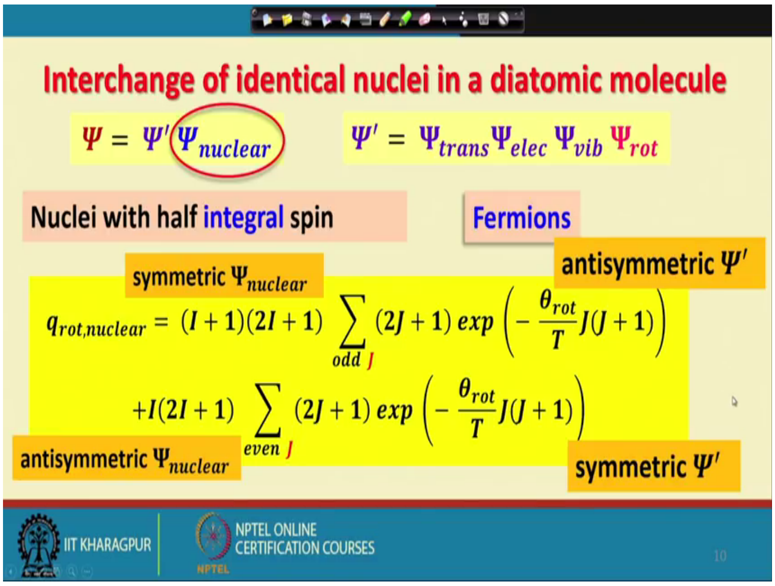

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi'\Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

Nuclei with half integral spin

Fermions

symmetric $\Psi_{nuclear}$

antisymmetric Ψ'

$$q_{rot,nuclear} = (I+1)(2I+1)\sum_{odd\ J}(2J+1)\exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right) + I(2I+1)\sum_{even\ J}(2J+1)\exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right)$$

antisymmetric $\Psi_{nuclear}$

symmetric Ψ'

The first one, as you see here is this first term where you have one number multiplied by a summation over odd values of J and then you have some other number couple to a summation that runs over even values of J. If we just look back at the rules of the game that we have introduced so far I quickly understand that the first term is obtained from a coupling of the symmetric new psi nuclear to anti symmetric psi prime and the second term is resulting from anti symmetric psi nuclear with symmetric psi prime. Now, all these are very important as far as understanding of what all possible expressions that the q rot nuclear can take and preserve the overall symmetry requirement by the underlying wave function for the diatomic molecule.

Now, if I go back then and say that, well since most of the cases I am thinking about high enough temperature which is typically room temperature.

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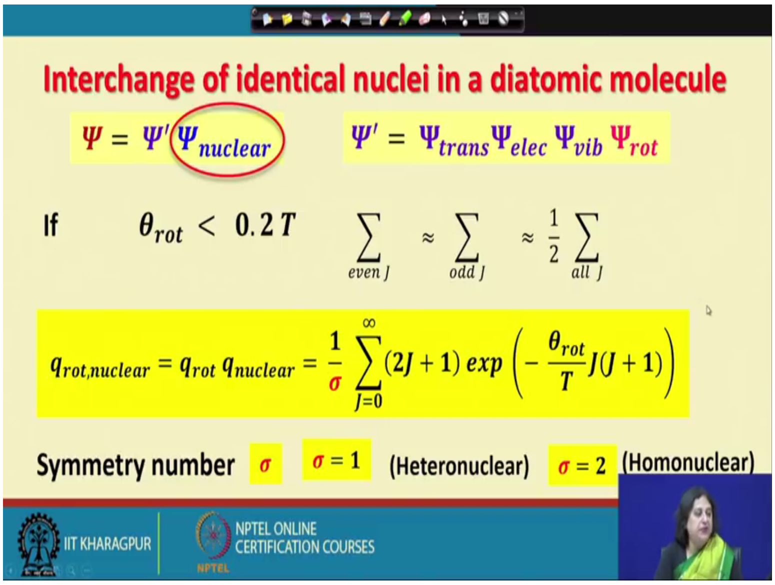

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\quad \Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

If $\theta_{rot} < 0.2\,T$ $\quad \sum_{even\,J} \approx \sum_{odd\,J} \approx \frac{1}{2} \sum_{all\,J}$

$$q_{rot,nuclear} = q_{rot}\, q_{nuclear} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1)\, exp\left(-\frac{\theta_{rot}}{T} J(J+1)\right)$$

Symmetry number σ $\quad \sigma = 1$ (Heteronuclear) $\quad \sigma = 2$ (Homonuclear)

In those cases apart from the hydrogen what happens is in those cases we generally have this relationship valid that the rotational temperature theta rot is generally much much less than the experimental temperature. And under such condition what we can do is we can very easily see that this summation over even J is approximately equal to the summation over all the odd values of J and numerically they are approximately equal to half of whatever summation that you will get if you summed over all possible values of J. Now, this actually gives a lot of simplification as far as evaluation of q rot is concerned because as you see that whenever I am trying to evaluate q rot I have to evaluate some term like this.

So, depending on whatever the contributions are in general one can have this very simple expression for q rot nuclear which takes into account all the factors that we have discussed in this class so far. And in this case as you see that we have introduced a new factor sigma. So, what is this factor sigma? This factor sigma is called the symmetry number and; obviously, this is equal to 1 when I have a heteronuclear system and this is equal to 2 when I have a homonuclear diatomic molecule.

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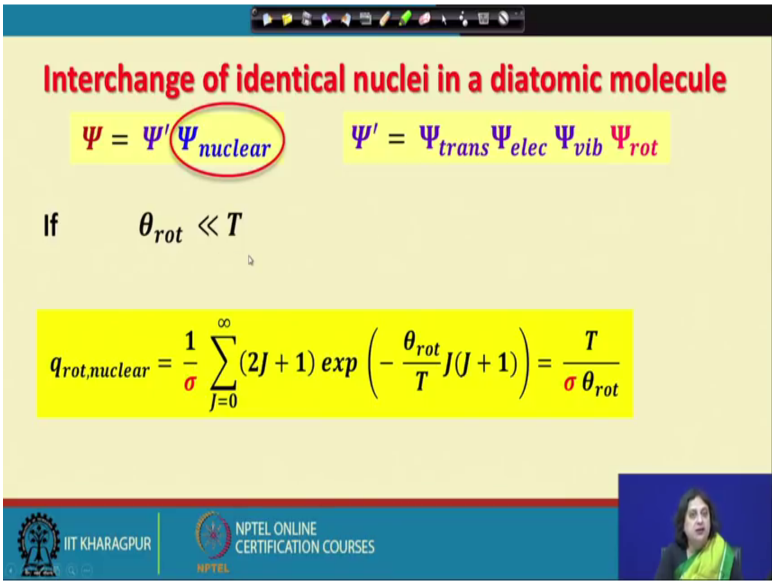

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\qquad$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

If $\qquad \theta_{rot} \ll T$

$$q_{rot,nuclear} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1)\, exp\left(-\frac{\theta_{rot}}{T} J(J+1)\right) = \frac{T}{\sigma\, \theta_{rot}}$$

Now, with this simplification then I can say that if we are interested in experimental temperatures that are much much greater than the rotational temperature of my gas molecules, in that case I can very easily write down the q rot nuclear under such circumstances by this very simple algebraic expression like this. And this is the limit of this summation under the condition that theta rot is much much less than T.

Now, I am going to put back all these results together to write down the basic information that we derived for the ideal gas comprised of capital N diatomic molecules and is maintained at a given temperature T, in a volume V.

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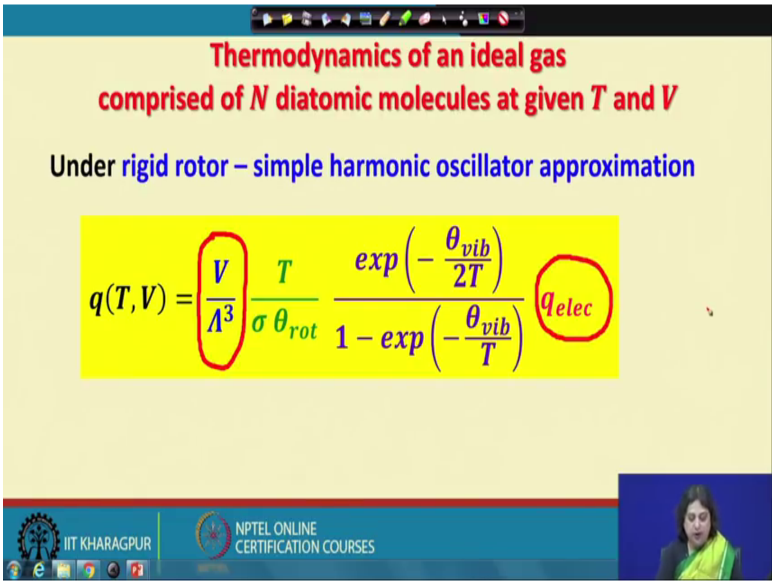

Thermodynamics of an ideal gas comprised of N diatomic molecules at given T and V

Under rigid rotor – simple harmonic oscillator approximation

$$q(T,V) = \boxed{\frac{V}{\Lambda^3}} \frac{T}{\sigma\,\theta_{rot}} \frac{\exp\left(-\frac{\theta_{vib}}{2T}\right)}{1-\exp\left(-\frac{\theta_{vib}}{T}\right)} \boxed{q_{elec}}$$

Now, what we have got is under the rigid rotor simple harmonic oscillator approximation then the single particle partition function is given by an expression like this. So, let us try and understand the source of each of these expressions. So, I know that this first term is nothing, but q trance. This term appears simply because this molecule as a whole is moving about in the confining volume V at a given temperature T.

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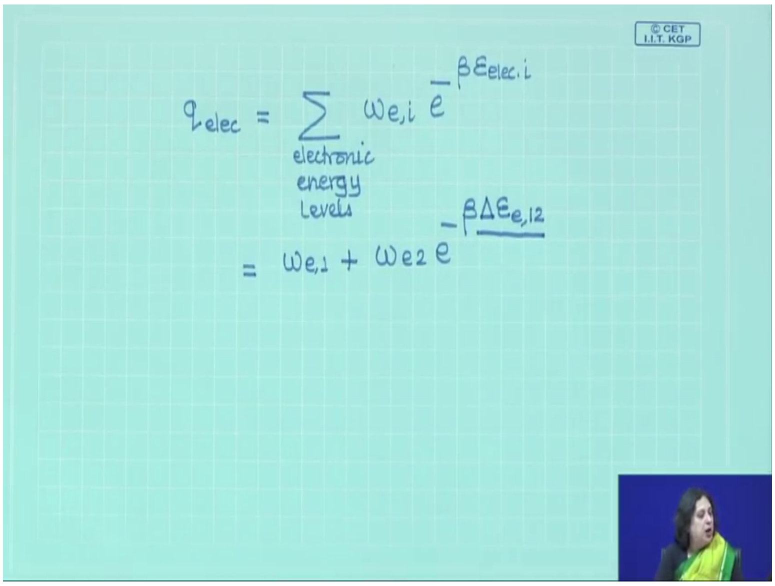

$$q_{elec} = \sum_{\substack{\text{electronic}\\ \text{energy}\\ \text{levels}}} \omega_{e,i}\, e^{-\beta\varepsilon_{elec,i}}$$

$$= \omega_{e,1} + \omega_{e2}\, e^{-\underline{\beta\Delta\varepsilon_{e,12}}}$$

Now, this term comes from the underlying electronic structure of the molecule and it requires me to talk about q electronic is equal to summation over all possible electronic energy levels, then omega e, i e to the power of minus beta epsilon electronic I. And we have seen that by setting the 0 of energy at the ground electronic state I can very easily write this as omega e 1 plus omega e 2 into e to the power of minus beta delta epsilon e 1 to, where this is the energy difference between the ground and the first excited electronic state and that can be obtained very easily from experiments.

Now, there are two terms other otherwise which appear over here. So, this term that you see, this accounts for the simple harmonic oscillator nature of the bond that is holding the 2 nuclei together and theta vibe is a temperature which corresponds to the vibrational temperature of the chemical bond that we are talking about. And this is the high temperature limit of the contribution to this small q coming from the rotational degrees of freedom. And once you know this then you can very easily go ahead and find out the partition function for all the capital N particles that are identical to each other and that are not interacting with each other. So, that is given by small q to the power of N divided by N factorial and once you have obtained this relationship then you are all set to get the thermodynamics of this ideal gas because l in capital Q is related to the Helmholtz free energy of the system.

So, in summary what we have learned so far in this course for an ideal gas is as follows. The ideal gas may be comprised of an atom, capital N atoms, it may be comprised of diatomic molecules or even it may be comprised of polyatomic molecules, of these each molecule is running about within the confining volume independent of where the other molecules are.

So, this is the part which contributes this translational part of the molecule in the confining volume contributes to the volume explicitly volume dependent part in the partition function that is V by lambda cube, where lambda is a term which is known as the thermal the Brawley wavelength. And after this you have terms which appear from the internal structure of the molecule. Now, this in this internal structure in the simplest case of atoms you have electronic energy states and the nuclear energy states contributing to small q. Now, if you have a little more complicated situation like the diatomic molecule in addition to these electronic and nuclear energy states, you are going to have to take into account the vibrational fine structure that is a vibrational energy states as well as rotational energy states associated with each electronic state.

So, for in general the strong for a given molecule at high enough temperatures you are going to have the system residing in the ground nuclear energy state. And when it resides in the ground it nuclear energy state then it may reside in the ground electronic state or even may be to some extent in the first excited electronic state at the normal working temperatures. And depending on the temperature some of the vibrational and the rotational energy states of each electronic energy state will be populated. And all of these are going to contribute to the observed average property that we measure in thermodynamics.

So, in the next lecture I will take up the problem of calculation of specific heat in an ideal gas and I will show you how the thermodynamic property is affected by the contribution of the translational degree of freedom, and the underlying structure which complements the contribution coming from the translational motion.

Thank you.