Statistical Thermodynamics for Engineers

Professor Saptarshi Basu

Indian Institute of Science, Bengaluru
Lecture 48
From Particles to assembly I

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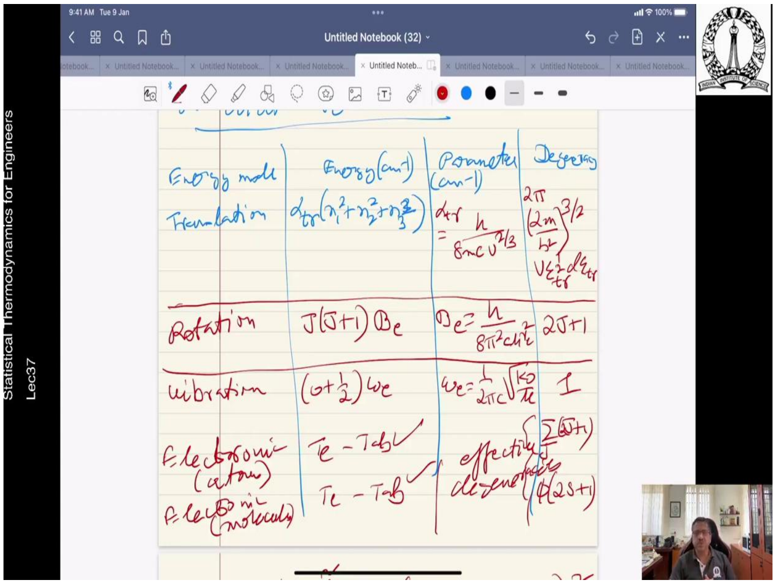

Energy mode	Energy (cm-1)	Parameter (cm-1)	Degeneracy
Translation	$\alpha_{tr}(n_1^2+n_2^2+n_3^2)$	$\alpha_{tr} = \frac{h}{8mcV^{2/3}}$	$2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\epsilon_{tr}^{1/2} d\epsilon_{tr}$
Rotation	$J(J+1)B_e$	$B_e = \frac{h}{8\pi^2 c\mu r_e^2}$	$2J+1$
vibration	$(v+\frac{1}{2})\omega_e$	$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}}$	1
Electronic (atom)	T_e - Tab ✓	effective degeneracies	$\sum_J (2J+1)$
Electronic (molecule)	T_e - Tab ✓		$\phi(2S+1)$

Welcome to lecture number 37 of the statistical thermodynamics for engineers. So, we already started looking at, how we go from articles to an assembly. So, the idea is that, we have seen quantum mechanics, we have seen spectroscopy and this has led to relationships, which gives you the energy at the degeneracy for all the four energy modes, which are basically translation, rotation vibration and electronic.

So, we have also shown that, if there is more independence then diatomic molecules mandates something called a simplex model which assumes a combined rigid rotor and harmonic oscillator. And we have done spend plenty of time actually showing that showing that thing and the table a table 8.1 from the book which we just showed here.

And here, we ensured that the translational energy can be converted to the wave number units and thus defining a term called alpha tr and we also realize that, translational energy translational energy is unique because it depends on the assembly volume. No other energy mode is affected by the assembly volume that means the macroscopic properties defined in the particle assembly.

Moreover, the degeneracy of a translational mode requires representation for a probability distribution function, which we already, did previously.

Now, we have also seen for the internal modes we require a rotational constant Be for the rigid rotor and vibrational frequency, omega e for the harmonic oscillator both of which can be determined from the spectroscopic measurements that we covered in the previous lectures. So, that what it does is that it provides tabulations for the electronic energies of atoms and molecules and what atoms the required degeneracy is evaluated by summing over the multiplate caused by the different J values.

Whereas, for the molecules we have caused what is caused by spin-splitting(())(02:33), in this particular case. So, this we already, already have done and this is we have already a fairly good idea. Now, that we know how the energy levels of the degeneracy's correspond to the translational rotational and vibrational energy modes of an independent particle assembly.

Now, we are going to use this particular knowledge to proceed towards a macroscopic description of assemblies of atoms molecules and that is exactly what we started to do over here, but as we said earlier, let us convert all of these in terms of the unit of, of temperature.

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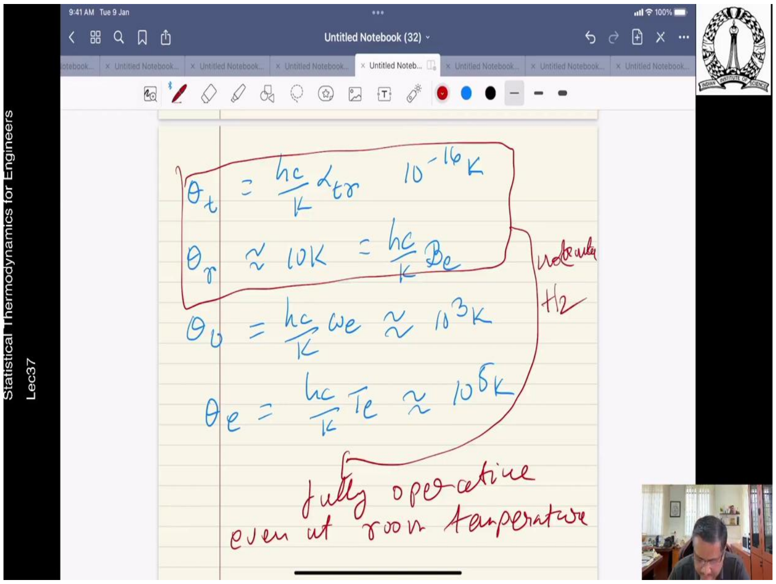


$$\boxed{\begin{aligned}\theta_t &= \frac{hc}{K}\alpha_{tr} \quad 10^{-16}K \\ \theta_r &\approx 10K = \frac{hc}{K}B_e\end{aligned}}$$

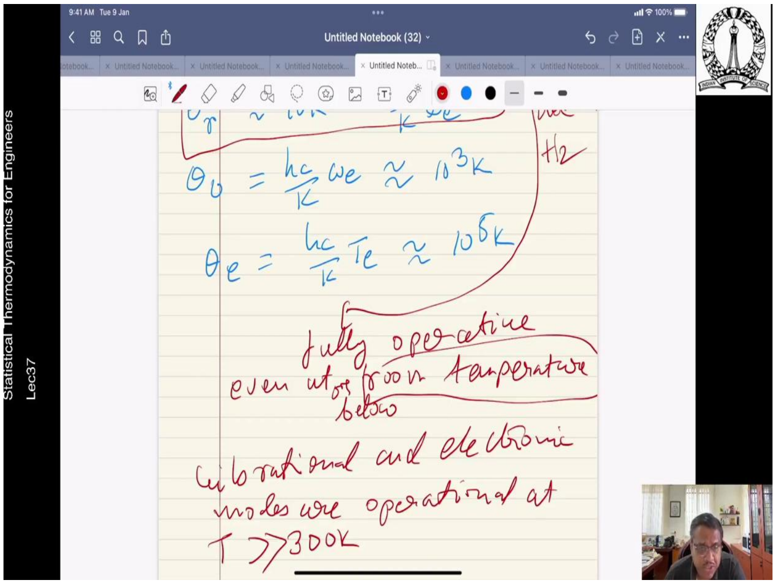
molecules

H_2

$$\theta_v = \frac{hc}{K}\omega_e \approx 10^3 K$$

$$\theta_e = \frac{hc}{K}T_e \approx 10^5 K$$

fully operative even at room temperature



$\theta_v = \frac{hc}{k}\omega_e \approx 10^3 K$

$\theta_e = \frac{hc}{k} T_e \approx 10^5 K$

fully operative even at or below room temperature

vibrational and electronic modes are operational at $T \gg 300K$

So, let us write the temperatures once again. So, for example, theta e which is translational temperature is hc by k to alpha tr, and this is roughly of the order of 10 to the power of minus 16k then of course, theta rotation which is written as theta r is approximately 10k and that is equal to hc by k into Be.

And then you have the theta vibration which is equal to hc by k into omega e which is also more or less 10 to the power of 3k and then of course, we have the electronic mode which is hc by k into Te which is 10 to the power of 5k. So, what we see over here is that these two temperatures the translational and the rotational modes are fully operative they are fully operative.

Even at room temperatures actually below room temperatures to be precise and even at room temperature. They are completely, completely accessible. And this is of course, these all these values are for same molecule hydrogen. So they are activated at room temperature or below room temperature and or below room temperature while on the other hand on the other hand the other energy modes are 10k and 10 to the power of 3k and 10 to the power 5k, 10 to the power 3 and 10 to the power 5.

So, we find that the vibrational and electronic modes, there is the vibrational and electronic modes are operational only at temperatures considerably operational at a temperature greater than 300k or much greater than 300k. So, this observation is very important because we can now use this for the prediction of the thermodynamic properties. So, you now know which temperature which mode is activated when or at what temperature so, to say.

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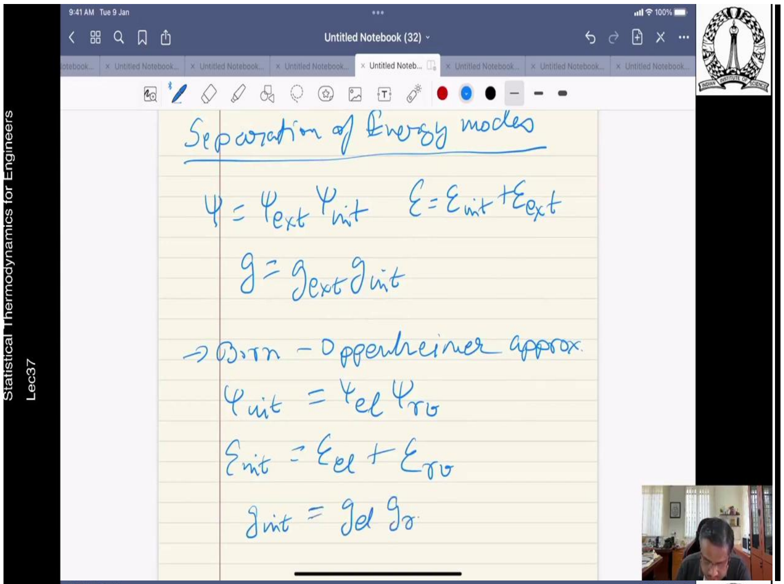


Separation of Energy modes

$\Psi = \Psi_{ext}\Psi_{int}$ $\quad \mathcal{E} = \mathcal{E}_{int} + \mathcal{E}_{ext}$

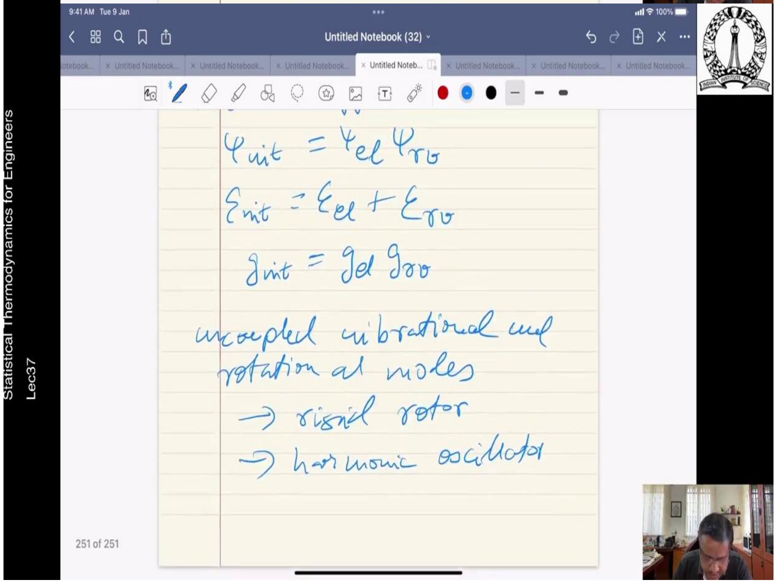
$g = g_{ext}\, g_{int}$

→ Born – Oppenheimer approx.

$\Psi_{int} = \Psi_{el}\Psi_{rv}$

$\mathcal{E}_{int} = \mathcal{E}_{el} + \mathcal{E}_{rv}$

$g_{int} = g_{el}\, g_{rv}$



$\Psi_{int} = \Psi_{el}\Psi_{rv}$

$\mathcal{E}_{int} = \mathcal{E}_{el} + \mathcal{E}_{rv}$

$g_{int} = g_{el}\, g_{rv}$

uncoupled vibrational and rotational modes

→ rigid rotor

→ harmonic oscillator

Now, what did we assume we assumed to just do a recap, we assumed that there was a separation of energy modes, right, separation of energy modes or full separation of energy modes, we first separated the external mode from the internal three, internal modes by converting to a coordinate system remember, where all translational motion with respect to the molecule center of mass in this way an inter particle motion would be expressed relative to the center of mass.

So, therefore, the wave Schrodinger's wave equation would be separated into two equations one controlling the external and one controlling the internal motion of the particles. So, therefore, therefore, we would write that external into internal energy was of course, internal plus external and g which is the degeneracy is external into internal and these are all independent of each other. So, he converted this by considering a coordinate system, using the molecules center of mass in this particular case, and we considered a full separation of the energy then we did what we did the Born Oppenheimer.

Next we did the Born Oppenheimer approximation and we found the most potential describing an any electronic state could be fashioned by solving the Schrodinger wave equation. So, the predicted electronic energy is defining the most potential assumed that there is a continuum of stationary inter nuclear distances.

So, this inter nuclear potential there was the primary input that was needed when you were solving the Schrodinger's wave equation of the combined rotational and vibrational motion. So, we have also what we did was that the internal part was further divided in the electronic and ro vibrational and the internal energy was divided into electronic plus ro vibrational and g internal which is basically the degeneracy has given as electronic into grv.

So, we uncoupled finally, what we did was that we uncoupled the vibrational and the rotational mode, uncoupled vibrational and rotational modes using two approximations one is the rigid rotor and the other one is a harmonic oscillator, these were the two modes that we used to separate.

So, these were the two approximations that we used to separate. So, what we did was that now they could be written Schrodinger's wave equation could now be written in terms of independent potential functions for both the rigid rotor and the harmonic oscillator. So, they produced independent energies and degeneracy's.

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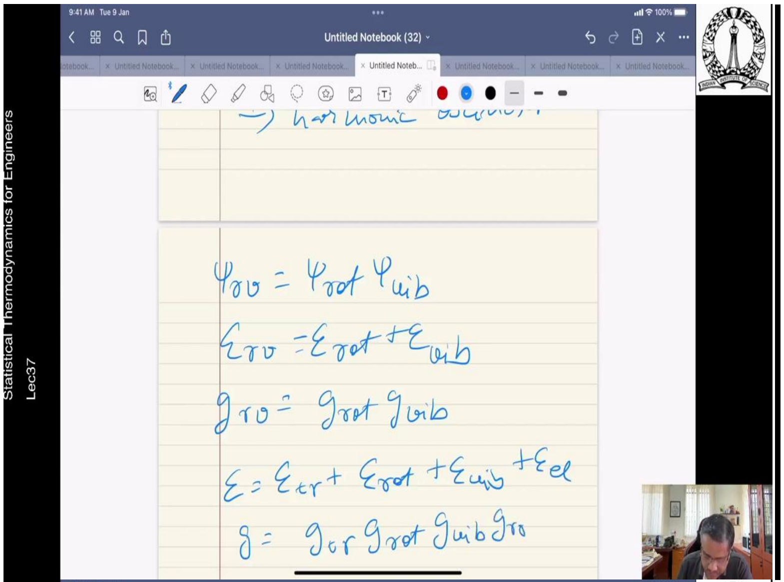


→ harmonic

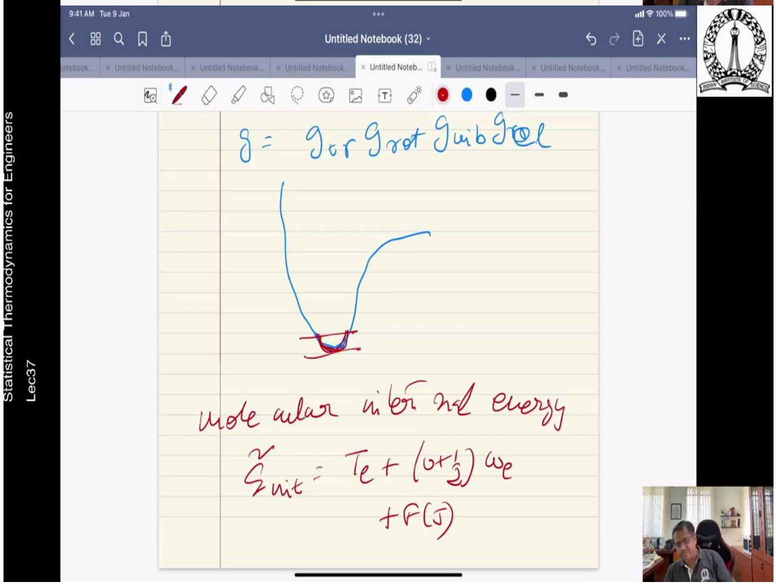
$\psi_{rv} = \psi_{rot}\psi_{vib}$

$\varepsilon_{rv} = \varepsilon_{rot} + \varepsilon_{vib}$

$g_{rv} = g_{rot}\, g_{vib}$

$\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el}$

$g = g_{tr}\, g_{rot}\, g_{vib}\, g_{ro}$



$g = g_{tr}\, g_{rot}\, g_{vib}\, g_{el}$

molecular internal energy

$\tilde{\varepsilon}_{int} = T_e + (v+\tfrac{1}{2})\,\omega_e + F(J)$

So, the ro vibrational was further divided into rotation and vibration and Erv was further divided into rotation plus vibration and the degeneracy rv was given as g rotation and g vibration. So, accumulating all these approximations and assumptions, we find that the total energy is therefore translational plus rotational plus vibrational plus electronic and g is equal to g translation g rotation g vibration g electronic.

So, in other words there is a full separation of the independent energy modes. So, the total energy is simply the sum total of the individual component energies, the overall degeneracy is the product of the component degeneracy's as anticipated, because it was a probabilistic interpretation of independent events because these were independent events to begin with. So, there were now three fundamental prescriptions one was the Born Oppenheimer approximation which gives rise to the most potential. The second was a harmonic oscillator model which works only for lower vibrational levels.

That means, it works if you recall this was the most potential and it worked right around here this was the zoom. So, it was essentially valid for the lower vibrational levels and of course, then you had the rigid rotor assumption. So, all these three assumptions or three prescriptions was what was needed to solve this particular problem.

And so, armed with this armed with this now that we know that this is what it was then we wrote the total energy or the molecular internal energy in terms of the wave number internal Te plus v plus half we plus FJ. So, the ground vibration of energy prescribes nonzero energy. So, as we know already, so, this energy level obviously replaces the lowest possible molecule of internal energy outside electronic or rotational contributions.

So, on this basis this is useful, we find it convenient, because when calculating thermodynamic properties to place a 0 of the energy at the lowest vibrational level within the ground electronic state. So, that was what was important and this is what we actually did. To evaluate directly the internal energy in an upper electronic state, we may define a revised electronic energy gap.

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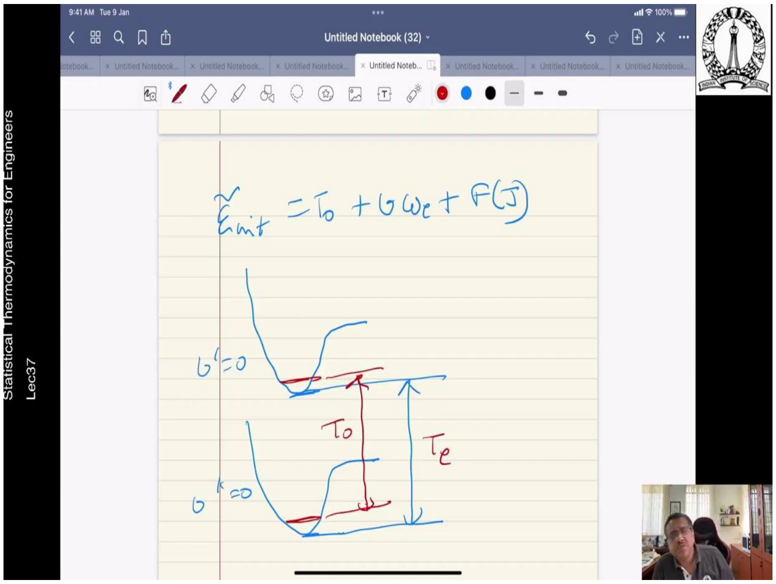
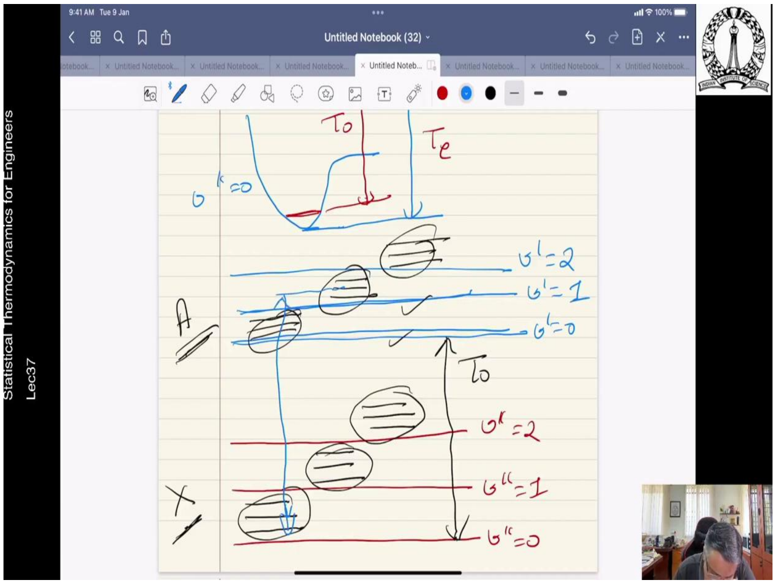
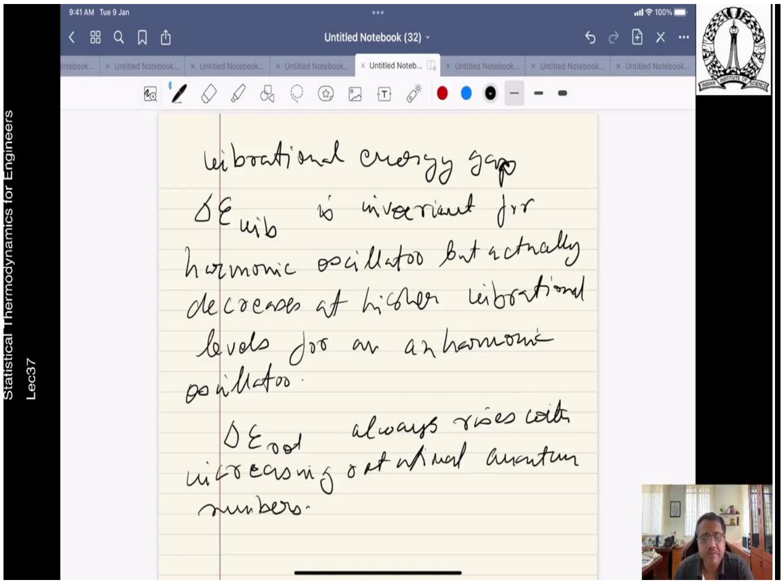


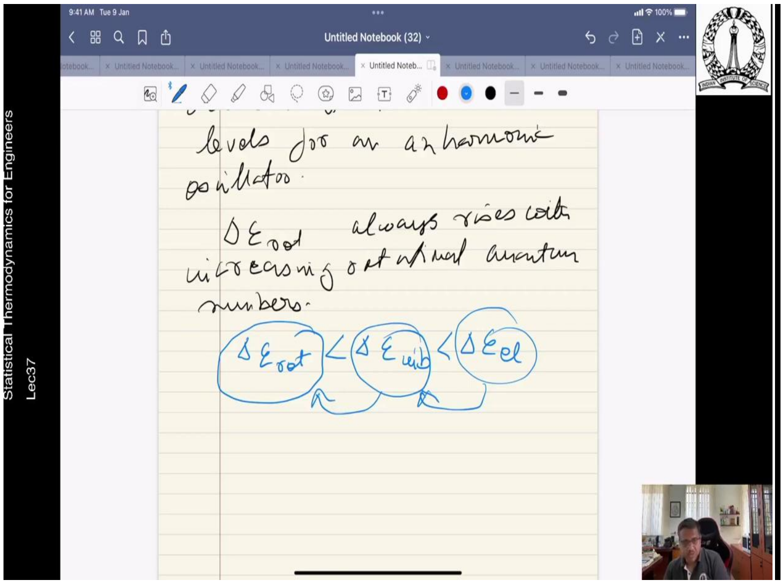
$$\tilde{E}_{int} = T_0 + v\omega_e + F(J)$$





vibrational energy gap ΔE_{vib} is invariant for harmonic oscillator but actually decreases at higher vibrational levels for an anharmonic oscillator.

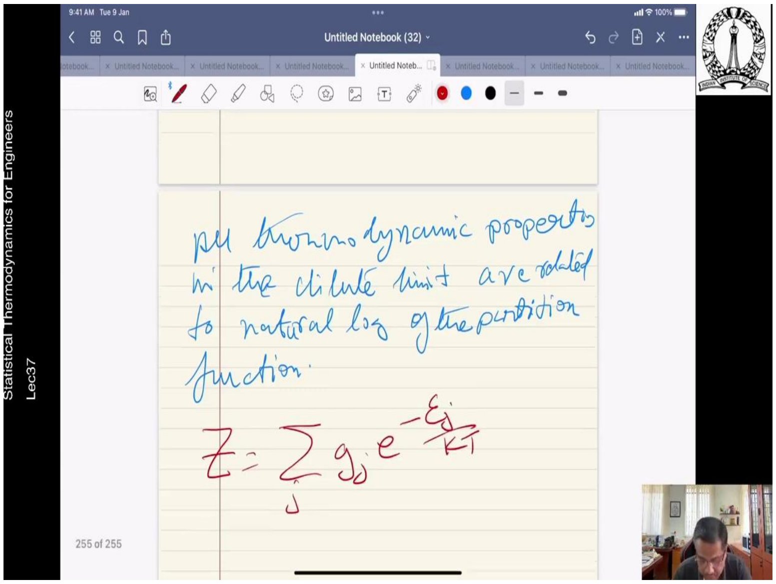
ΔE_{rot} always rises with increasing rotational quantum numbers.



levels for an anharmonic oscillator.

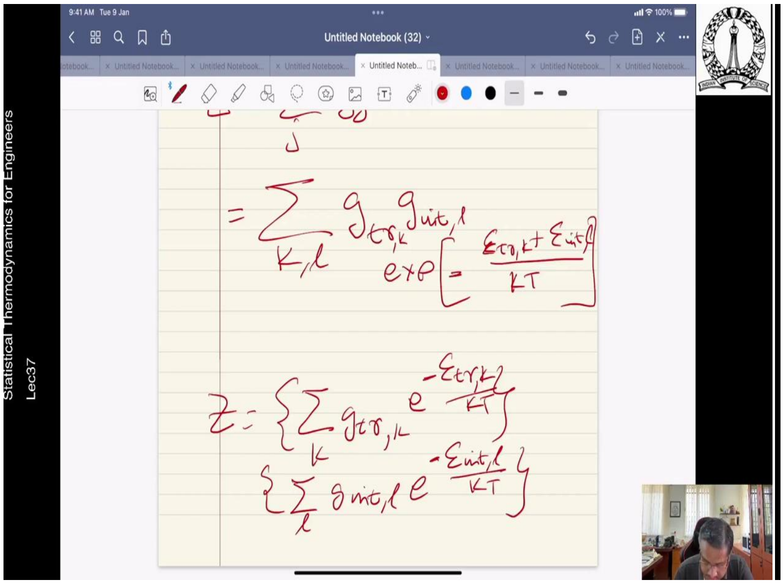
ΔE_{rot} always rises with increasing rotational quantum numbers.

$$\boxed{\Delta E_{rot}} < \boxed{\Delta E_{vib}} < \boxed{\Delta E_{el}}$$



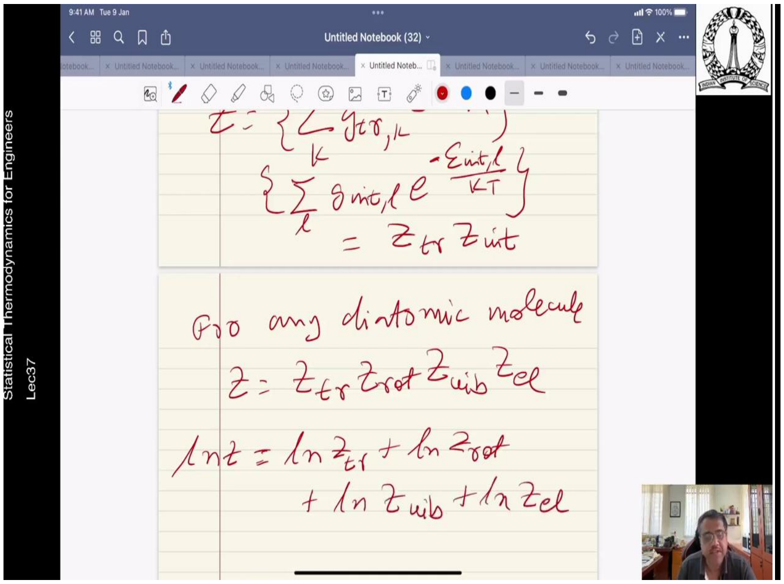
All thermodynamic properties in the dilute limit are related to natural log of the partition function.

$$Z = \sum_j g_j e^{-\frac{\varepsilon_j}{kT}}$$



$$= \sum_{k,l} g_{tr,k}\, g_{int,l} \exp\left[-\frac{\varepsilon_{tr,k}+\varepsilon_{int,l}}{kT}\right]$$

$$Z = \left\{\sum_k g_{tr,k}\, e^{-\frac{\varepsilon_{tr,k}}{kT}}\right\} \left\{\sum_l g_{int,l}\, e^{-\frac{\varepsilon_{int,l}}{kT}}\right\}$$

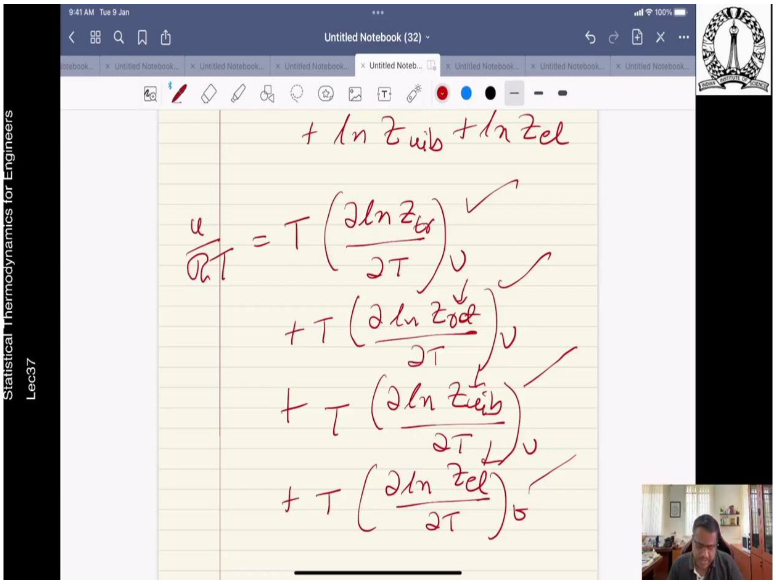


$$\left\{\sum_l g_{int,l}\, e^{-\frac{\varepsilon_{int,l}}{kT}}\right\} = Z_{tr} Z_{int}$$

For any diatomic molecule

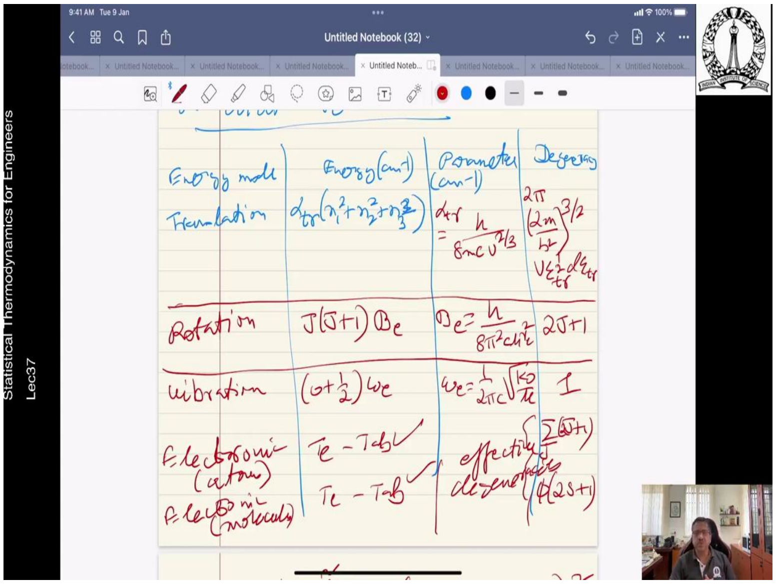
$$Z = Z_{tr} Z_{rot} Z_{vib} Z_{el}$$

$$\ln Z = \ln Z_{tr} + \ln Z_{rot} + \ln Z_{vib} + \ln Z_{el}$$



$$+ \ln z_{vib} + \ln z_{el}$$

$$\frac{u}{RT} = T\left(\frac{\partial \ln z_{tr}}{\partial T}\right)_V \checkmark + T\left(\frac{\partial \ln z_{rot}}{\partial T}\right)_V \checkmark + T\left(\frac{\partial \ln z_{vib}}{\partial T}\right)_V \checkmark + T\left(\frac{\partial \ln z_{el}}{\partial T}\right)_V \checkmark$$



Energy mode	Energy (cm-1)	Parameter (cm-1)	Degeneracy
Translation	$\alpha_{tr}(n_1^2+n_2^2+n_3^2)$	$\alpha_{tr} = \frac{h}{8mcV^{2/3}}$	$2\pi\left(\frac{2m}{h^2}\right)^{3/2} V \varepsilon_{tr}^{1/2} d\varepsilon_{tr}$
Rotation	$J(J+1)B_e$	$B_e = \frac{h}{8\pi^2 c \mu r_e^2}$	$2J+1$
vibration	$(v+\frac{1}{2})\omega_e$	$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}}$	1
Electronic (atom)	T_e - Tab ✓	effective degeneracy	$\sum_J (2J+1)$
Electronic (molecule)	T_e - Tab ✓		$\phi(2S+1)$

So, like this so you write is like this T naught plus vwe plus FJ. So, where we have in this expression you have dispensed the ground vibrational energy in the upper electronic state as this 0 point energy is in material even the definition of T naught. So, what is the definition of T naught the definition of T naught is this and let us draw a simple figure which will let you understand this.

So, this is v prime equal to 0, since the v double prime equal to 0 and the difference between these two this is Te and this is the first (())(13:59). So, this is actually your T naught. So, you understand that we brought in T naught by the definition of T naught we have eliminated the ground vibrational energy.

So, that is the half is there anymore. So, (imply) implying this revised 0, of energy now, by simply looking at this particular figure that we just now drew this particular figure the various energy levels without their most essential and shown in this particular way. Let us draw this type of also. This requires a little bit of effort.

Let us see, this can be drawn properly, is v double prime equal to 0 this is v double prime equal to 1, this is v double prime equal to 2 and then you have upper level v prime is equal to 0, v prime equal to 1, v prime equal to 2 that of course so, this is the X this is the A and so, this is basically your T naught and then you look at the different transitions then you look at the different transitions.

So, this is the diagram this is like an energy level diagram that we have drawn for and we have drawn the energy levels for both vibration and rotation within both the ground state and the first excited electronic state. So, these are the corresponding rotational lamps and these are the vibrational ones and this is A this is the ground electronic state this is the first excited electronic state.

So, the revised electronic energy gap bridges this v double prime equal to 0 to v prime equal to 0, the vibrational vibronic levels are also shown in figure in this particular figure, where the T naught is will marked here the vibrational energy gap is invariant for that harmonic oscillator, but actually decreases in higher energy levels for the anharmonicity which we know we brought into the complex problem.

In contrast, the rotational energy gap always rises with increasing rotational quantum numbers. So, we also know that the vibration energy gap, energy gap which is delta Evib vibration is invariant it is invariant, invariant or harmonic oscillator but actually decreases higher vibrational levels or an anharmonic oscillator.

In contrast the delta Erot which is basically the rotational energy gap this always rises those rises with increasing rotational quantum numbers, rotational quantum numbers. And so we can provide different transitions for example, we can provide a transition just say r equal to 1, which is basically line between blue.

So, that you could see this particular this is for example, R1 this one sample transition and we also note here we also note that delta E rotation is greater than delta E vibration and this is definitely less than delta E electron. In other words the energy gap or a vibrational mode is less than that of electronic mode.

But greater than the rotational this result of course is consistent with the characteristics temperatures for the vibrational modes the energy gap this energy gap is much more then this and this is much more than that. So, the separation now, now that we know that these can be separated and separation of energy modes now also will play an important, important role in the evaluation of the macroscopic properties. So, all thermodynamics if we take the dilute limit that all thermodynamic properties in a dilute limit are related to the natural logarithm of the partition function so, we already did.

This is significant because it ultimately says that such properties can be evaluated by adding the separate contributions arising from each energy mode, for example, so, just to write it very clearly that all thermodynamic properties just to reiterate thermodynamic properties in the dilute limit are related to the natural log of the partition function the(())(21:34) observation is very significant.

Because now we know that it can be some totaled if you recall that our Z which was the partition function was written as j g j e to the power of minus Ej by kT. If you recall this now can be written as because of the separation gtr. So, this is translation this is the internal modes this is translation k, internal mode l exponential all these are within the summation obviously, minus Etr k plus E internal l divided by kT summed over k and l.

So, this one was of course. So, that now Z can be written as summation kgtr k e to the power of translation k by kT multiplied by summation l, g internal l e to the power of minus E internal l by kT. So, this is equal to Z translation into Z internal. So, you can see the partition function is itself like that and we separated it to 2.

So, for all the four independent energy modes for any diatomic molecule or any diatomic molecule we get write therefore Z as Z or Z, Z rotation Z vibration Z electronic logarithm of Z converts all these into summation so this is ln Z translation plus ln Z rotation plus ln Z vibration plus ln Z electronic, the partition function is multiplicative whereas, the logarithm is of course iterative(())(24:10).

So, all thermodynamic properties in the dilute limit can be expressed in terms of ln Z that we have seen already. So, this implies that such properties are also edited therefore the available energy modes. So, if you recall now if we write it, this is the internal energy part. This is T ln so, you can write it like this therefore v plus T **(())(24:45)** this is rotation divided by T of course and T ln Z vibration v plus T ln that electronic divided by delta T.

So, as you can see, it is the sum total of the four such expressions. So, if we know the individual quantities, which we can know the individual quantities are dependent on the energy level and the degeneracy and we already said what the energy levels of the degeneracies are going to be, if you look at this particular table now, we already gave this numbers we already said that what will be the energy, correct, spectroscopic means and through this nice separation we are able to therefore, show that you know the eternal energy for example here is a sum total of all these individual components coming out of the four independent energy modes. So, similar should be the case with entropy and a lot of other things. So, as you can understand, we use quantum mechanics.

Now, we can evaluate the energy levels as well as the degeneracy we use those degeneracy and energy level in the part, in computing the partition function assuming a full separation of all the four energy modes and that enables us to calculate quantities macro quantities like internal energy, which is shown right here this is brilliant.

So, this is how we link the microscopic world to the macroscopic world using this. So, the next class we will see that how entropy and all the other quantities can be computed using this, and how these contributions therefore, can now go, go a long way in computing all the other quantities that we can think of enthalpy and all the other parameters.

So, we close the class here in the next class, we will go and first see that how entropy can be written for example, in terms of these individual components. So, thank you and see you in the next class.