Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 39
Combined Energy Modes for Atoms and Diatomic Molecules

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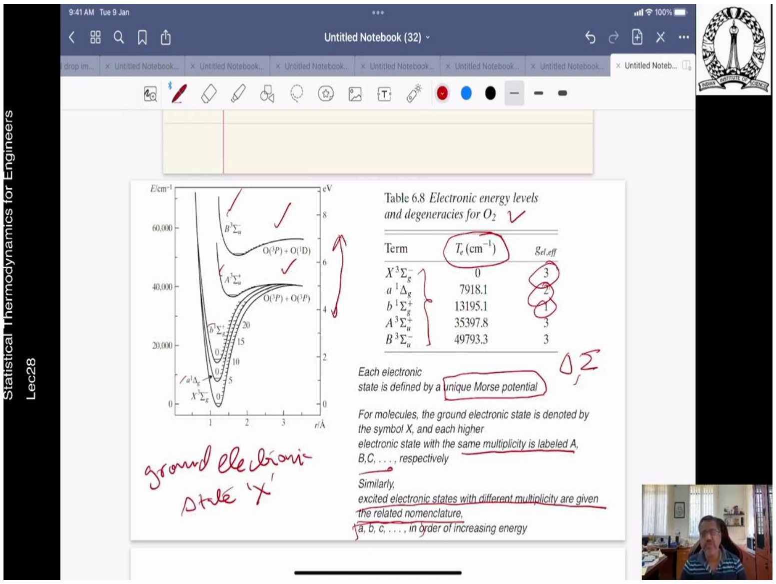


Table 6.8 *Electronic energy levels and degeneracies for O_2*

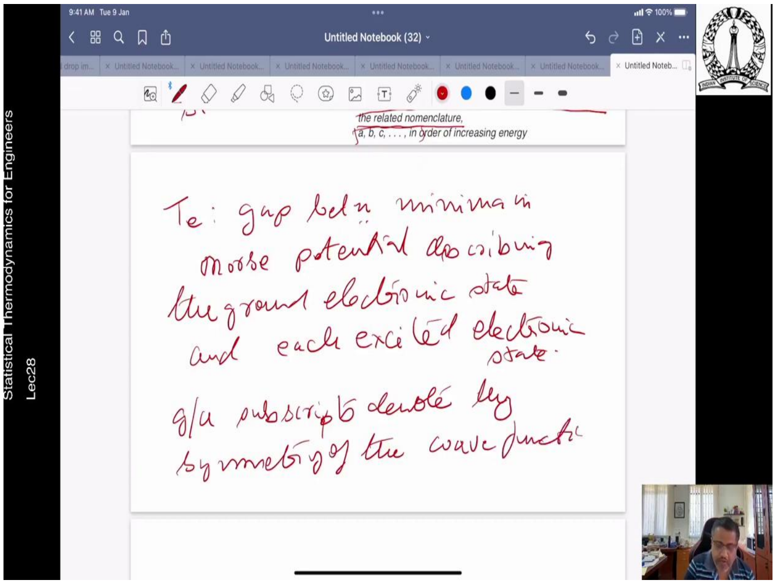
Term	T_e (cm⁻¹)	$g_{el,eff}$
$X\,^3\Sigma_g^-$	0	3
$a\,^1\Delta_g$	7918.1	2
$b\,^1\Sigma_g^+$	13195.1	1
$A\,^3\Sigma_u^+$	35397.8	3
$B\,^3\Sigma_u^-$	49793.3	3

Each electronic state is defined by a unique Morse potential

For molecules, the ground electronic state is denoted by the symbol X, and each higher electronic state with the same multiplicity is labeled A, B,C, . . . , respectively

Similarly, excited electronic states with different multiplicity are given the related nomenclature, a, b, c, . . . , in order of increasing energy

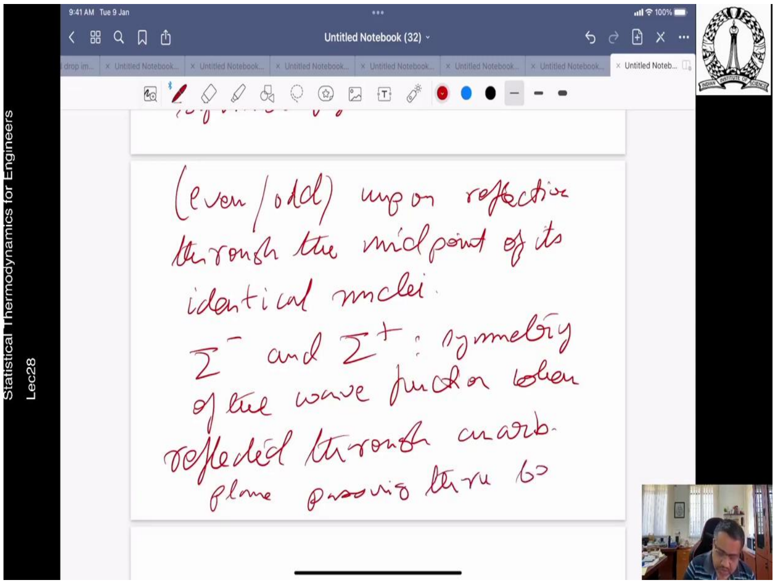
ground electronic state 'X'



the related nomenclature, a, b, c, . . . , in order of increasing energy

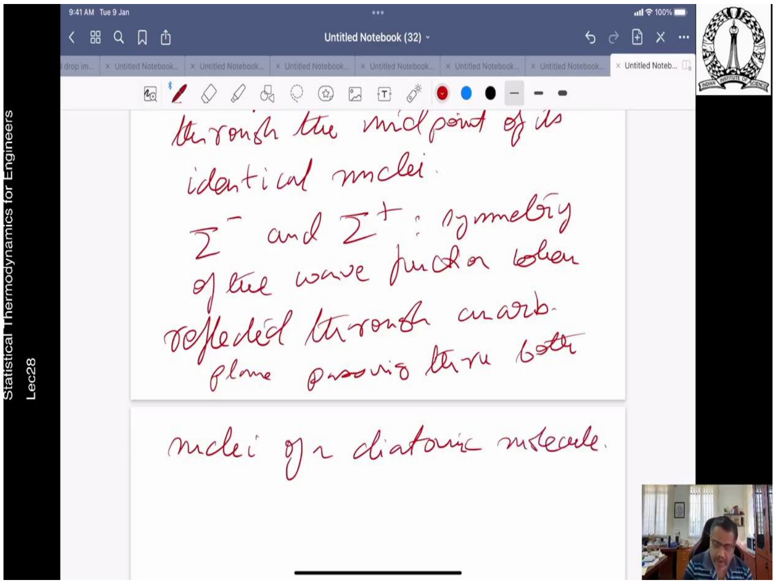
Te: gap betn minima in morse potential describing the ground electronic state and each excited electronic state.

g/u subscripts denote the symmetry of the wave functic



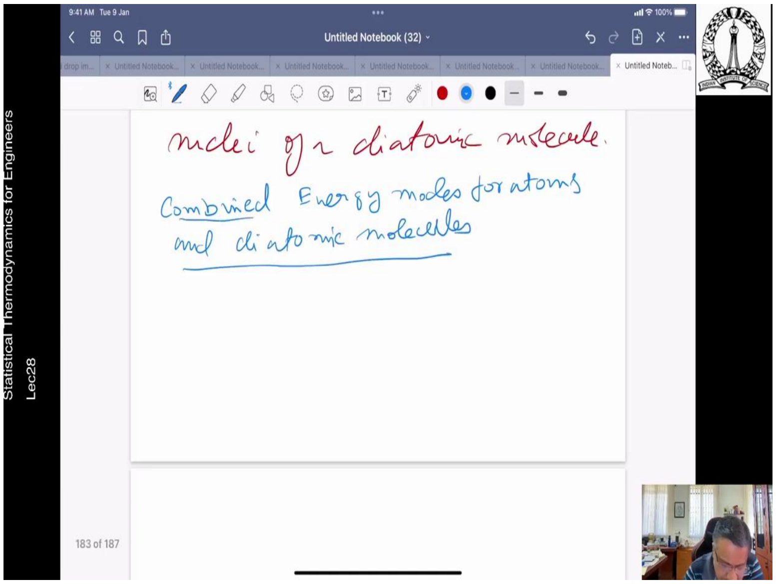
(even/odd) upon reflection through the midpoint of its identical nuclei.

Σ^- and Σ^+ : symmetry of the wave function when reflected through an arb. plane passing thru bo



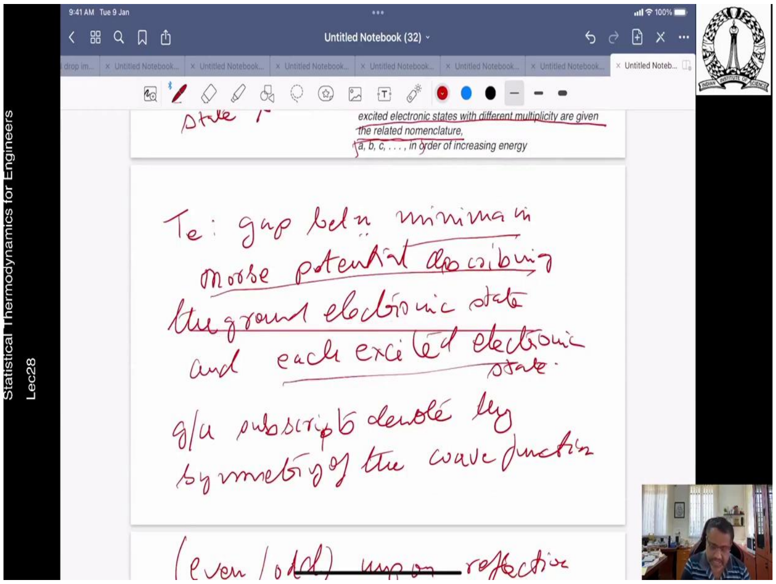
through the midpoint of its identical nuclei.

Σ^- and Σ^+ : symmetry of the wave function when reflected through an arb. plane passing thru both nuclei of a diatomic molecule.



nuclei of a diatomic molecule.

Combined Energy modes for atoms and diatomic molecules



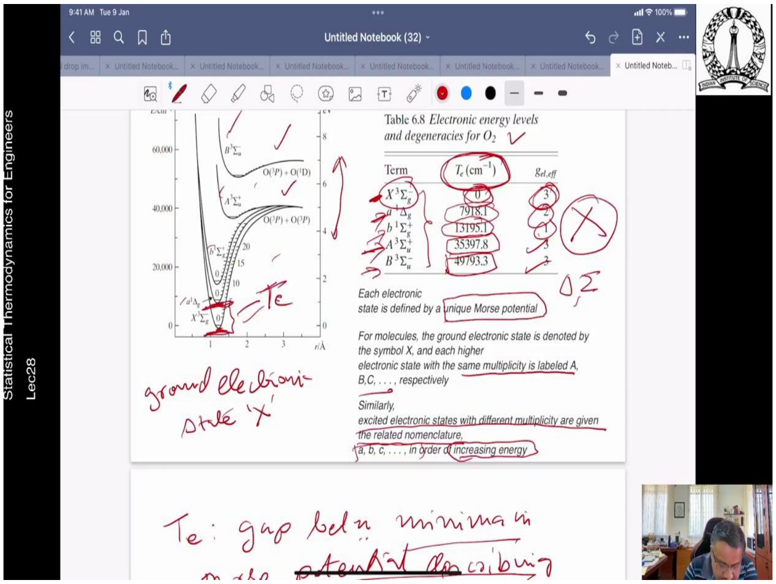
state

excited electronic states with different multiplicity are given the related nomenclature, a, b, c, . . . , in order of increasing energy

Te: gap betn minima in morse potential describing the ground electronic state and each excited electronic state.

g/u subscripts denote by symmetry of the wave function

(even / odd) upon reflection



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Δ, Σ

Each electronic state is defined by a unique Morse potential

For molecules, the ground electronic state is denoted by the symbol X, and each higher electronic state with the same multiplicity is labeled A, B,C, . . . , respectively

Similarly, excited electronic states with different multiplicity are given the related nomenclature, a, b, c, . . . , in order of increasing energy

Te: gap betn minima in the ~~potential~~ describing

So, welcome to lecture number 28 of the Stat-Thermo course. So, in this particular lecture, so previously we told you that what will be the effective degeneracy or diatomic, for diatomic molecules. So, and we have also said what is spin splitting and, and doubling and stuff like that. Usually, we say that the energy difference that is produced by gamma coupling is usually much smaller than that produced by spin splitting.

So, in accordance to it, we now can generate these kind of tables which is basically the electronic energy levels and degeneracies for oxygen here. Now, here, if you look at it carefully, if you look at this particular diagram, you will see that each electronic state is defined by a unique Morse potential. We already covered what is a Morse potential. So, for each of this electronic energy state is represented by this unique Morse potential.

So, and also the rule is that for molecules, for molecules with a ground electronic state is designated by X, the ground electronic state is represented by X, and each higher electronic state with the same multiplicity, with the same multiplicity is labeled as A, B, C et cetera A, B, C et cetera. Similarly, excited, excited electronic states with different multiplicity are given by this nomenclature, small a, small a, small b et cetera.

So, you understand that ground state electronic states are, and each higher electronic state with the same multiplicity is labeled as capital A, capital B, capital C whereas the excited electronic states, excited electronic states are represent, with different multiplicity are related as a, b, c. So, that is what you get. Now, if you look at this particular table now, if you look at this particular table now, you will find that, you will find that, if you look at this particular table, this is for oxygen.

So, you can see for example, let us take any one of the figure, so this T e that you see over here, T e, T e is nothing but represents the gap, a gap between, between minima, minima in Morse potential, in Morse potential describing, describing the ground electronic state, a ground electronic state, ground electronic state and each excited, excited electronic state.

So, it also, so if you look at this particular table now, you look at this particular table now you will find that the effective degeneracies is also given here, with effective, and this is T e. So, and this is the nomenclature that we have already established, that delta, sigma and a, b, c, we already noted what those things are going to be. But there are a couple of plus minus signs that we see which will come to it in a little bit.

So, now similarly for excited electronic states of different multiplicity, we, we know what it is given by. Now, we can see certain subscripts g and u, so g slash u subscripts, subscripts, subscripts are denote symmetry of the wave function, wave function even slash odd upon reflection, upon reflection to the midpoint of the nuclei, midpoint of its identical nuclei.

Finally, the superscript like minus and plus, they designate what we call the symmetry, the symmetry of the wave function, of the wave function, wave function when reflected, when reflected through an arbitrary plane to an arbitrary passing through both nuclei of a diatomic molecule. So, you can now have a, have a very good idea of what it is. So, now what to recap, each electronic state is represented by a separate Morse potential, which we see over here.

Now if the electronic state has not the same multiplicity, it is designated as capital A, capital B, capital C, these are every higher electronic states compared to the ground state. Ground state is always represented as X. Similarly, each excited electronic states with different multiplicity, different multiplicity is given the symbol small a, small b, small c. And the total, and T e is basically the gap between the minimum in Morse potential describing the ground electronic state and each excited electronic state.

So, that is given as T e. So, as we see that when it is a ground electronic state which is given as X, T e is obviously equal to 0, and the effective degeneracy is 3. So, we can, we know why is it, why it is going to be 3. Now, this is an excited state or which there is a T e, and the effective degeneracy is given as 2. Similarly, this is an even higher excited state because a, b, c are in order of increasing energy. That means b has got more energy than a, and c has got more energy than b.

So, naturally you see that b has got a higher energy compared to a and that is given as the degeneracy. Moving to now, you go to the another a different electronic state altogether, higher electronic state with same multiplicity now. So, that is given as this. This is T e, and so b is higher than a. So, it is given as 49793. These are the corresponding degeneracies that you have.

So, X is always given as T e equal to 0. Because this is the minima of the Morse potential to the minima of the corresponding gap between the two minimas, essentially. So, this is what is your T e. So, this is the, this is the, this is written as T e. So, that is what the intermolecular symbols looks like. Now, we can write down now the combined energy the combined energy modes, energy modes for atoms and diatomic molecules, atoms and diatomic molecules.

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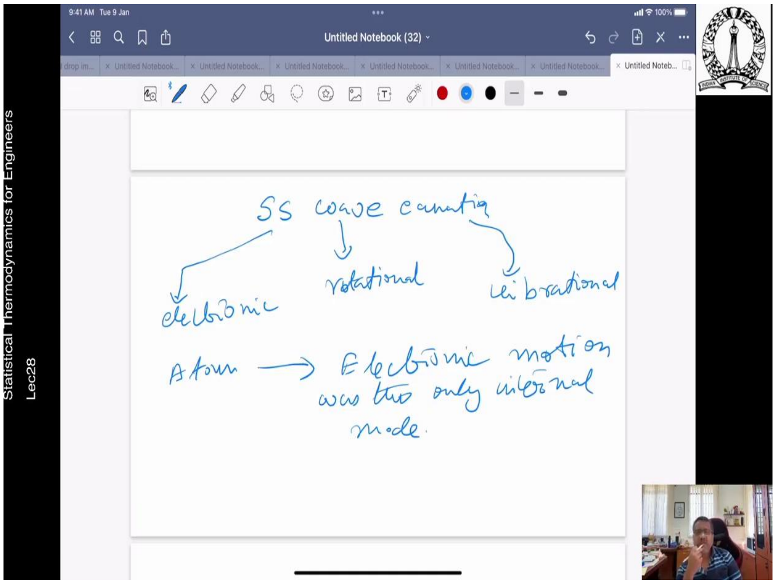


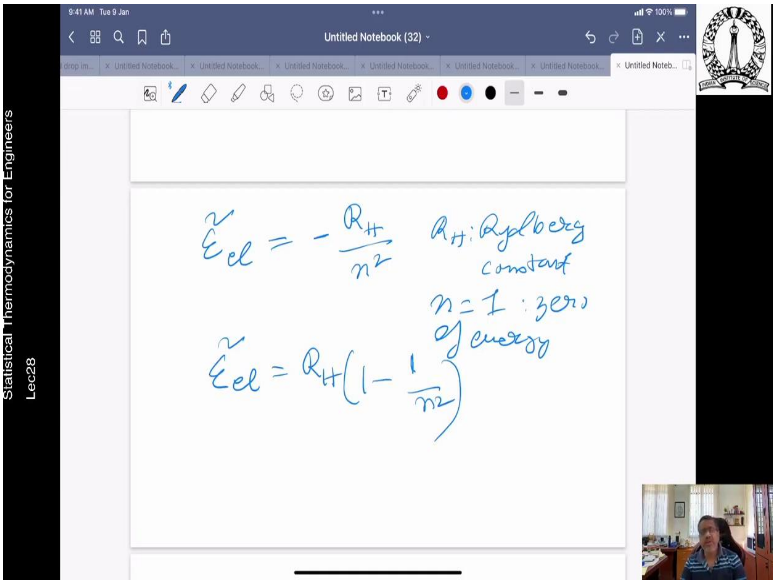
SS wave counting

electronic

rotational

vibrational

Atom → Electronic motion was the only internal mode.



$$\tilde{\varepsilon}_{el} = -\frac{R_H}{n^2}$$

R_H: Rydberg constant

$n = 1$: zero of energy

$$\tilde{\varepsilon}_{el} = R_H\left(1 - \frac{1}{n^2}\right)$$

So, typically, Schrodinger's wave equation gave us what electronic vibrational and rotational. So, what did it give us? SS wave equation gave us, gave us a few things. One is one is electronic, which we just described in details, one is a rotational, one is vibrational. These are the different modes that we got, and these are the, these are the different energy levels that we saw.

For atoms, our task was easy as electronic motion underlies the only internal energy mode. So, for atoms, we could only say that the electronic motion, electronic motion, electronic motion, electronic motion was only internal mode, internal energy mode. So, typically energy level diagrams are constructed by setting energy of the ground electronic state to 0.

So, if we consider, we, if we consider that the electronic energies for the hydrogen atom, it was like this, minus R H by n squared, sorry, n squared, where R H is the Rydberg constant and the zero of the energy is when n is equal to 1. This is the zero of energy. And therefore the electronic energy was written as R H 1 minus 1 by n squared. So, this was for atomic hydrogen. We all got this.

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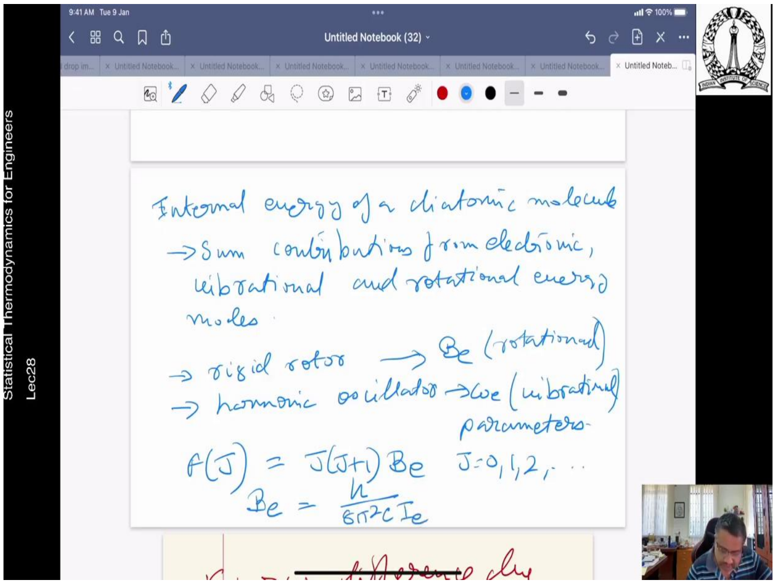

Internal energy of a diatomic molecule
→ Sum contributions from electronic, vibrational and rotational energy modes.
→ rigid rotor → B_e (rotational)
→ harmonic oscillator → ω_e (vibrational parameters.

$F(J) = J(J+1) B_e \quad J = 0, 1, 2, \ldots$

$B_e = \frac{h}{8\pi^2 c I_e}$

Now, in contrast to monoatomic species, the internal energy of a diatomic molecule. So, if we move on to internal energy of a diatomic can be obtained by summing, so what we can do is that contributions, contributions from electronic, vibrational and rotational energy modes, energy modes, so this time our assumptions were rigid rotor and we also had the harmonic oscillator.

So, for the rigid rotor was, it was B e. This is the rotational and the vibrational, and this was omega e. So, rotational and vibrational, rotational, this was vibrational parameters. So, in addition to this, if you now recall, recall the patients that we already did, and let me just write it down here for the sake of convenience. So, if you recall that, if you recall that F J was given as J into J plus 1 into B e, where J is equal to 0, 1, 2, da, da, da, and B e, if you recall, was written as h by 8 pi squared c I e.

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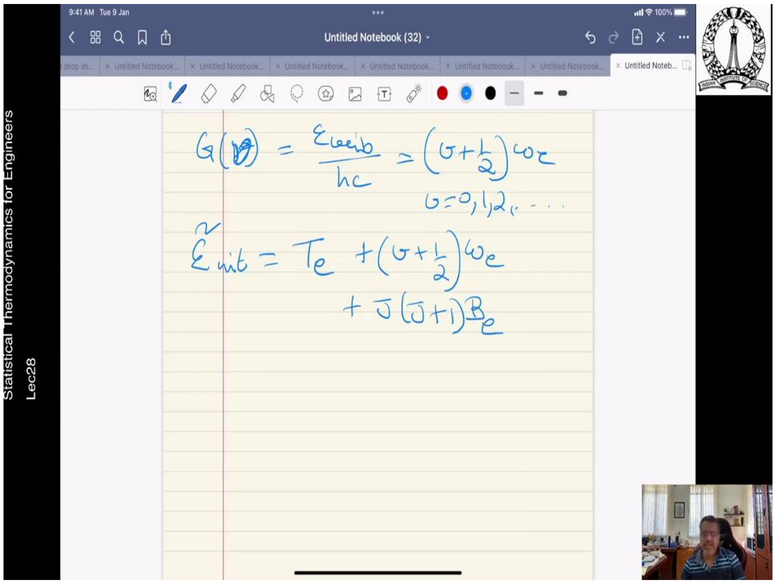
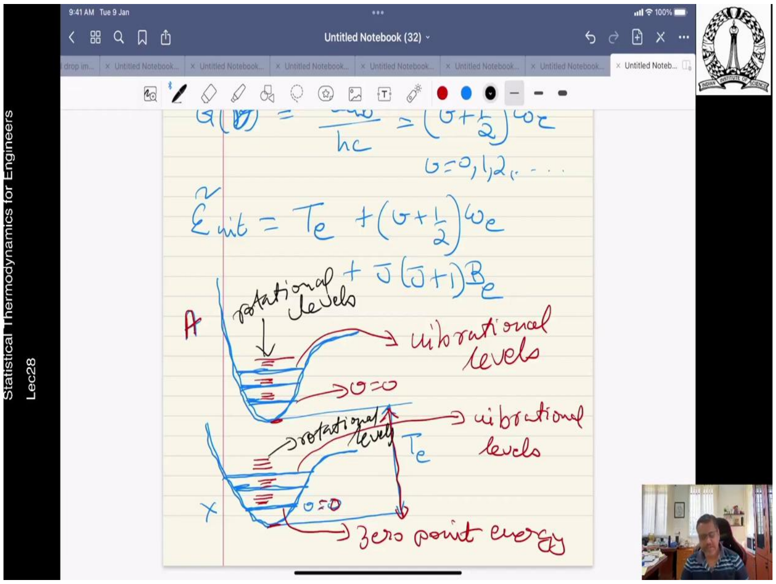


$$G(v) = \frac{\varepsilon_{vib}}{hc} = \left(v+\frac{1}{2}\right)\omega_e$$

$v = 0, 1, 2, \ldots$

$$\tilde{\varepsilon}_{int} = T_e + \left(v+\frac{1}{2}\right)\omega_e + J(J+1)B_e$$



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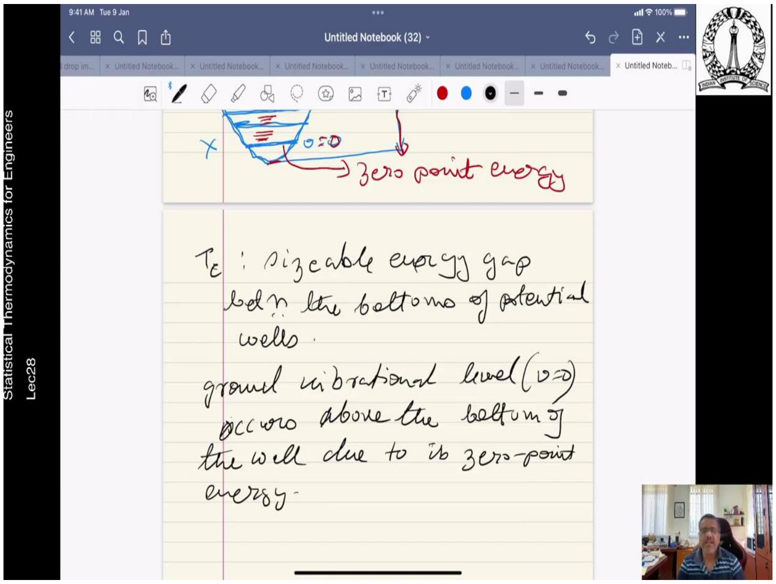
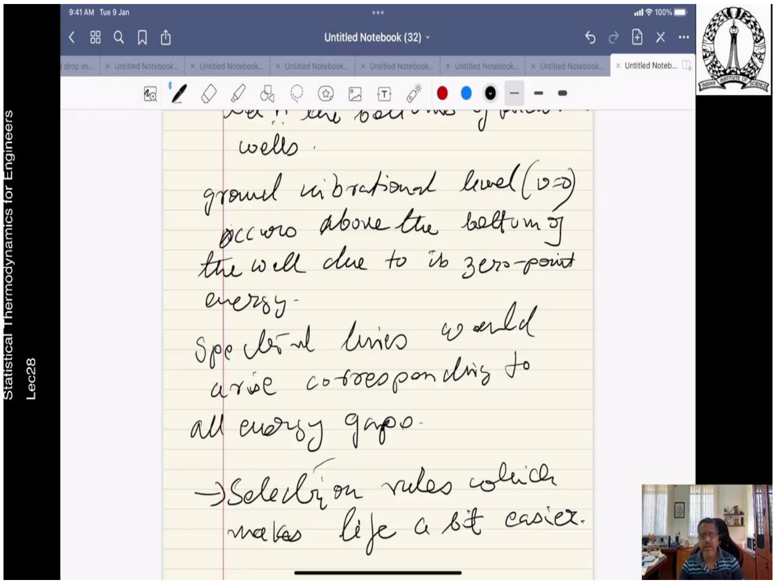


→ zero point energy

T_E : sizeable energy gap betn the bottoms of potential wells.

ground vibrational level (v=0) occurs above the bottom of the well due to its zero-point energy.

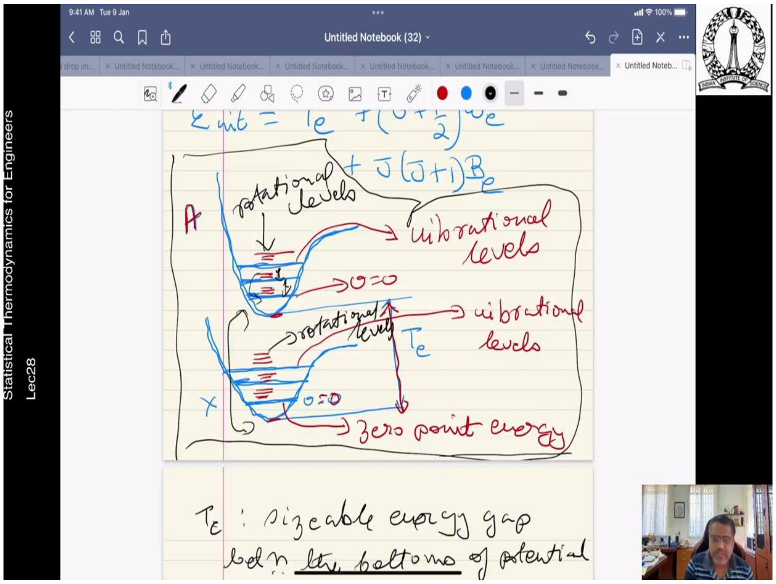


wells.

ground vibrational level (v=0) occurs above the bottom of the well due to its zero-point energy.

Spectral lines would arise corresponding to all energy gaps.

→ Selection rules which makes life a bit easier.



$E_{int} = T_e + (v + \frac{1}{2})\omega_e + J(J+1)B_e$

T_e : sizeable energy gap betn the bottoms of potential

So, that was what we wrote. And then of course, other equation that we are going to use over here is v, vibration divided by h c given as G plus half into w e, v equal to 0, 1, 2, da, d, da,. So, therefore once we know these two expressions of F J and G v, therefore we can write the internal energy as T e plus v plus half w e plus J into J plus 1 into B e. So, all these are in centimeter inverts.

So, if we look at that associated energy level diagram, this is how it should look like. So, you have, let me try to draw it the best I could. So, the difference between this and this is given as T e. So, this is your X, this is you're a. So, this is equal to 0. Now, let us use a different marker. So, what you see that v is are basically the vibrational, vibrational levels. T e is the difference between the two minimas that we are talking about.

This is A, one level higher, and this is V equal to zero, this is not at the end because of the zero point energy. So, this is, this is, this is zero point. Now, you go to the other level here, another thing here is something like that. So, now we do that. So, this is once again v equal to 0. So, these are again the vibrational levels, the vibrational levels. And these that you see, these are the rotational levels, these are the rotational levels.

So, you know that what are the what are the different levels. So, the vibrational level actually occurs above the bottom of each well. So, what we see over here that T e identifies, it is a very sizable energy gap, energy gap, sizable energy gap between the bottoms, bottoms of potential wells. So, the electronic energy is portrayed by the Morse potential. The ground vibrational, vibrational level v equal to 0, is actually a little elevated, occurs above the bottom of the well, occurs above due to zero point energy.

So, each electronic state we already said is represented by a Morse potential. So, and, so the spectral lines can all be asserted by using these energy gaps that are shown in this particular diagram. So, this is the diagram, sample diagram, sample energy level diagram that we have. And each electronic state as we said, is represented by each, electronic state is portrayed by a, by the corresponding Morse potential that we already said earlier.

So, such, we can see that there are all possible energy gaps from here to here, here to here, within the rotational band, one rotational band to one vibrational, all these. So, there are many, you can see that the spectral lines, if we look at it, spectral lines, lines can occur, can occur on all the rise corresponding to all energy gaps. But fortunately, that is not the rule. There are certain selection rules to actually rules which makes life a bit easier. There are selection rules now which makes the life a little bit easier so to say.

So, just to have, have a clear Insight now. So, now that we know all these things, we know what is spin splitting what is doubling and all those things, we now know what are the different energy, electronic energy levels, the corresponding degeneracies, everything we know, especially for diatomic and now we also have a combined energy, how we can write those combined energies. So, all these things are there.

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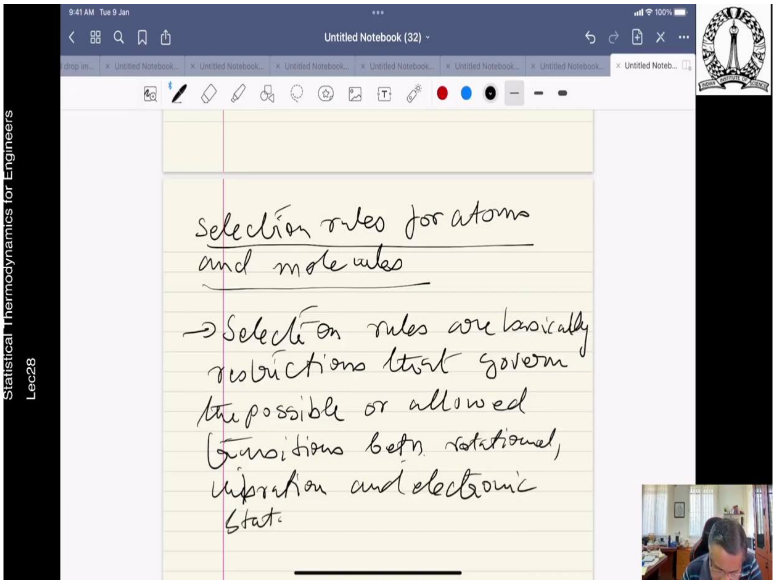
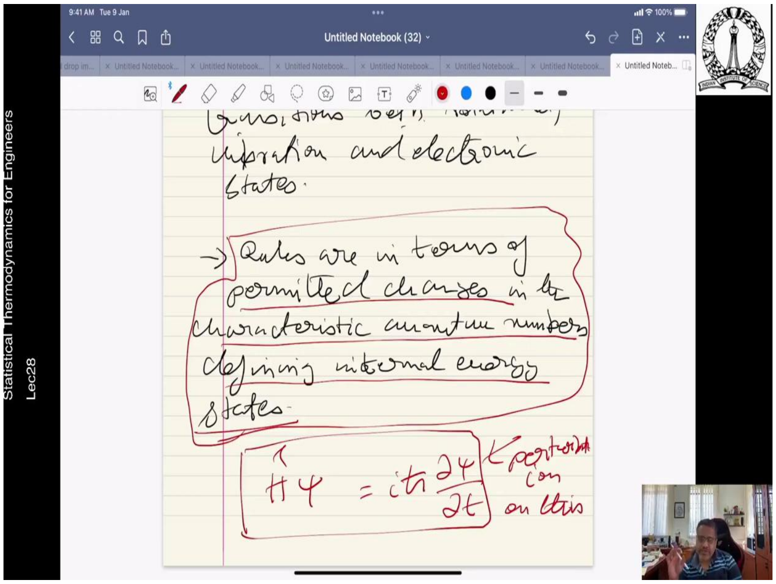


Selection rules for atoms and molecules

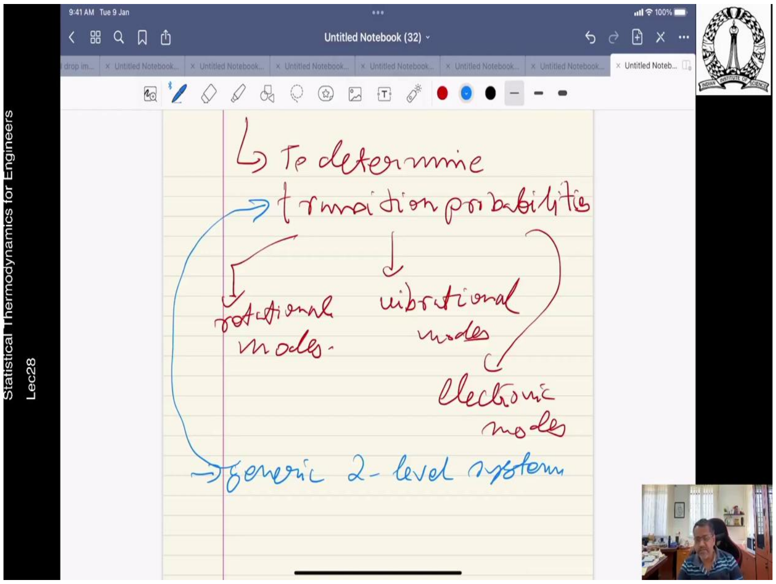
→ Selection rules are basically restrictions that govern the possible or allowed transitions betn. rotational, vibration and electronic stat.



vibration and electronic states.

→ Rules are in terms of permitted changes in the characteristic quantum numbers defining internal energy states.

$$\boxed{\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}}$$ ← perturbation on this



↳ To determine
→ transition probabilities

rotational modes.

vibrational modes

electronic modes

→ generic 2-level system

Now armed with this, we should now start looking at the selection rules, the selection rules for atoms and molecules, the selection rules for atoms and molecules. That is something that we need to know. So, selection rules, what are selection rules? Selection rules, rules are basically, basically restrictions, restrictions that govern, that govern the possible, the possible or allowed transitions, transitions between, between rotational vibrational and electronic, electronic states.

So, for each energy mode, such rules are typically in terms of the permitted change, changes in the characteristic quantum numbers. So, what these rules are, rules are in terms of permitted changes, permitted changes in the in the characteristic, characteristic quantum numbers, quantum numbers defining, defining internal energy states. So, these rules are in terms of the permitted changes in the characteristic quantum numbers defining internal energy states.

So, in general, we observe the spectral intensity of an allowable, allowed transition is much greater than that for a disallowed or forbidden transition. So, we are going to use terms like what is forbidden transition what is allowed transition. So, for electronic mode, the term symbols distinguishing atoms and molecules generally provide the basic nomenclature that is required for the construction of the selection rules.

In this case, allowed transitions normally involve jump of a single electron from one orbital to the other. While selection rules, these are experimental, there are, there has been also significant confirmation, theoretical confirmation by what we call the application of the Perturbation Theory. So, Perturbation Theory is something that you apply to the Schrodinger wave equation.

And then we can see that once there is a perturbation, what are, for a generic, if we apply it for a generic two level system, and therefore we define based on that what are the transition probabilities associated with such transitions. But the idea of selection rules is that what characteristics quantum number changes are permitted. And this can be done, and what is called forbidden transition, what is called allowed transition.

And spectroscopically, you can do a lot of these things, but non- spectroscopically, if you want to do it a theoretical analysis of this thing, therefore you apply what we call a Perturbation Theory on the time dependent Schrodinger’s wave equation. So, just recall, so this was the time-dependent Schrodinger's wave equation.

So, this was the time-dependent. So, you apply a perturbation on this, perturbation on this, apply a perturbation on the time-dependent Schrodinger’s wave equation and determine the transition probabilities. So, what it is going to be used for? To determine, to determine the transition probabilities, transition probabilities.

So, that is what we are going to do over in the next lecture that we are going to define the transition probabilities associated with, so these are transition probabilities associated with rotational, vibrational and electronic, electronic modes. And this comes, all comes from the Schrodinger's wave equation, time-dependent Schrodinger’s wave equation that we have.

And this is done for a generic, we are going to do it for a generic 2-level system level system. We have a generic 2-level system and we are going to, using that, we are going to use and find out what will be the corresponding transitional probabilities. So, in the next class we are going to go through this particular motion and see that what are the, how we can perturb the Schrodinger’s wave equation and what solutions we are going to get out of it. So, till next class. Thank you