Statistical Thermodynamics for Engineers
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Lecture 44
Rotation vibration coupling (Complex model)

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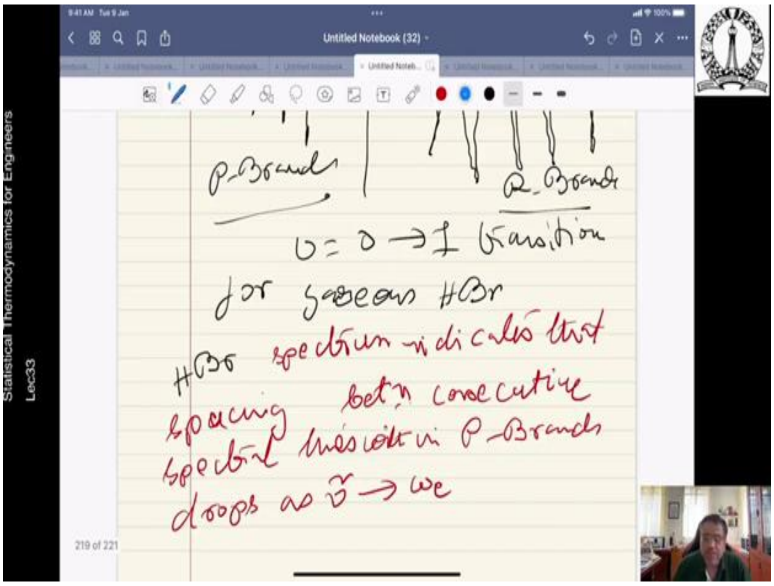
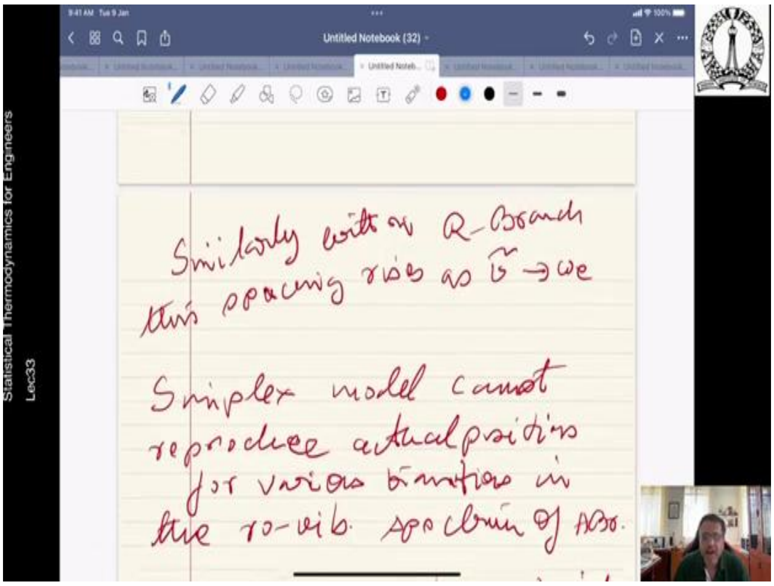


P-Branch R-Branch

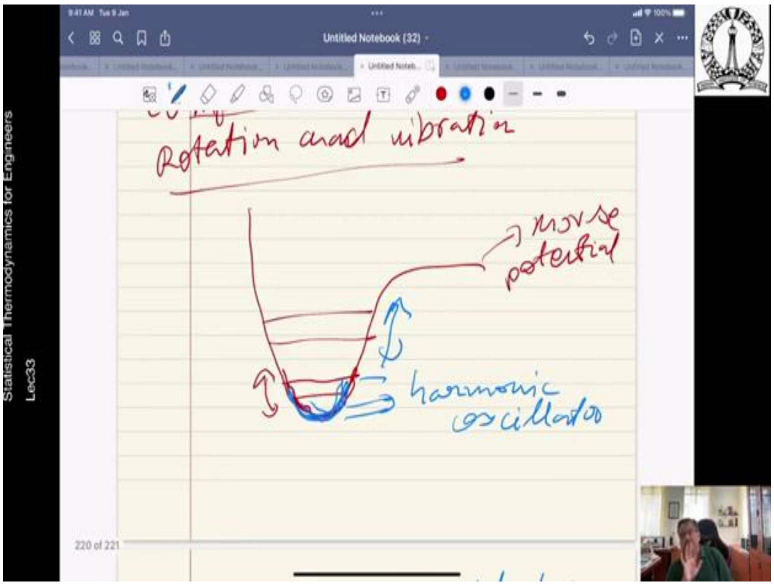
$\upsilon = 0 \rightarrow 1$ transition for gaseous HBr

HBr spectrum indicates that spacing betn consecutive spectral lines in P-Branch drops as $\tilde{\nu} \rightarrow \omega_e$

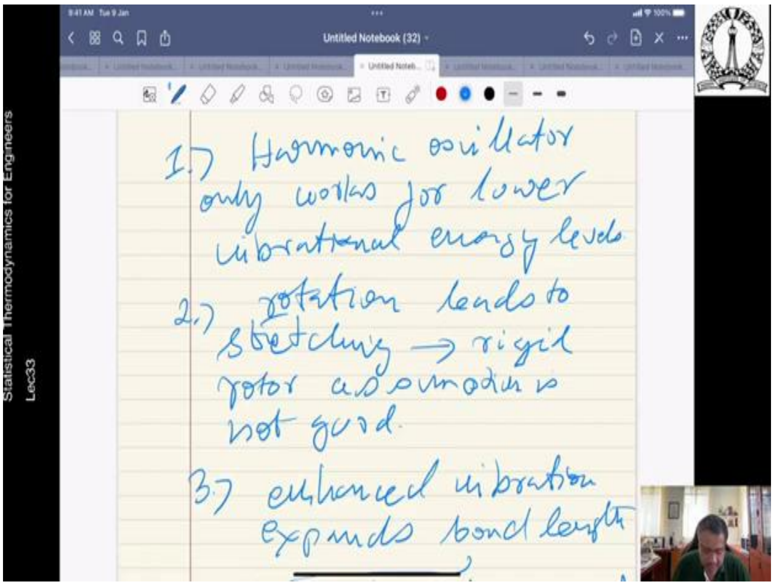


Similarly with R-Branch this spacing rises as $\tilde{\nu} \rightarrow \omega_e$

Simpler model cannot reproduce actual positions for various transitions in the ro-vib. spectrum of HBr.



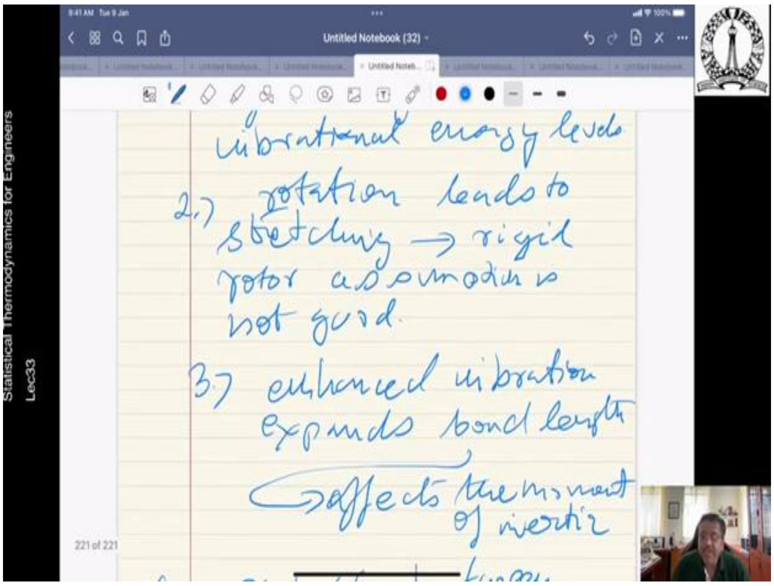
Rotation and vibration



1.) Harmonic oscillator only works for lower vibrational energy levels

2.) rotation leads to stretching → rigid rotor assumption is not good.

3.) enhanced vibration expands bond length

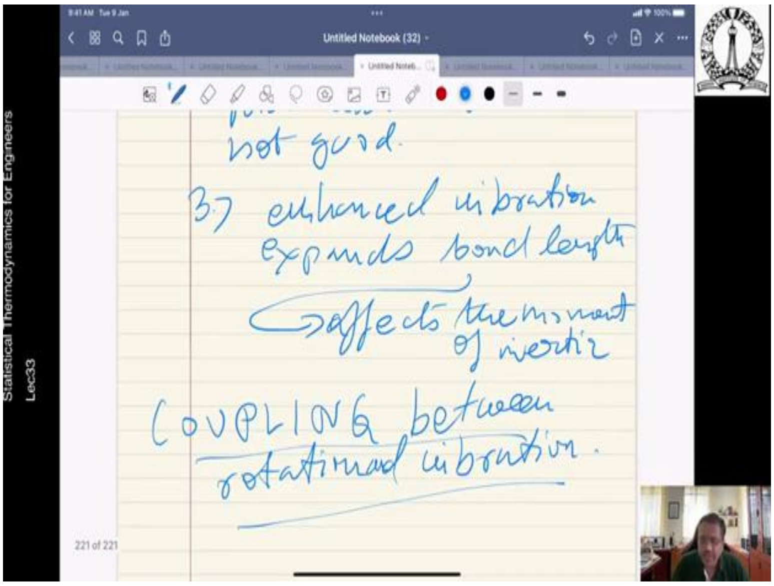


vibrational energy levels

2.) rotation leads to stretching → rigid rotor assumption is not good.

3.) enhanced vibration expands bond length

↳ affects the moment of inertia

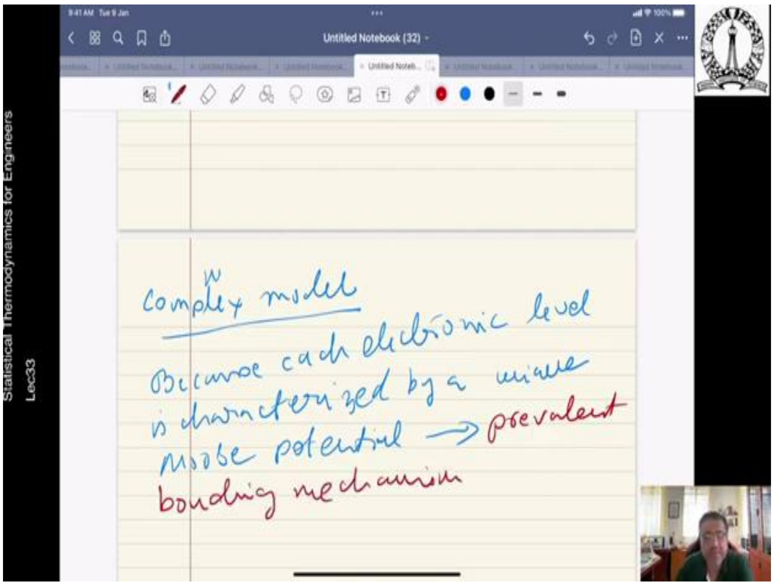


not good.

3.) enhanced vibration expands bond length

→ affects the moment of inertia

COUPLING between rotational vibration.



Complex model

Because each electronic level is characterized by a unique Morse potential → prevalent bonding mechanism

Welcome to lecture number 33, so this time as we say that the Simplex model is useful but it cannot really predict the difference in the line spacing in the spectrum as we saw in this particular diagram you see in this particular diagram we see that the spacing between the consecutive spectral lines in the P Branch for example field match actually drops as V approaches the w e.

So, in this particular exercise we also said that similarly with the R approach is spacing rises. So, the Simplex model cannot actually reproduce the actual positions other various transitions, so we need a complex model for the same and remember that the actual potential was given by the Morse potential.

Now, the Morse potential is actually something that is very complicated to begin with, so we need it we use the harmonic oscillator but the harmonic oscillator only does a very good job in the lower part where you see the blue part of the of the line. So, the harmonic oscillator only works for lower vibrational energy levels.

The rotation actually leads to stretching, so the rigid rotor assumption is not good and enhanced vibration also expands the bond length and it affects the moment of inertia. So, therefore there happens a coupling between the rotational and the vibrational energy modes. So, as a result of that we need a more complex model to describe the Ro-vibrational and the vibrational transitions which we are going to do in this particular lecture.

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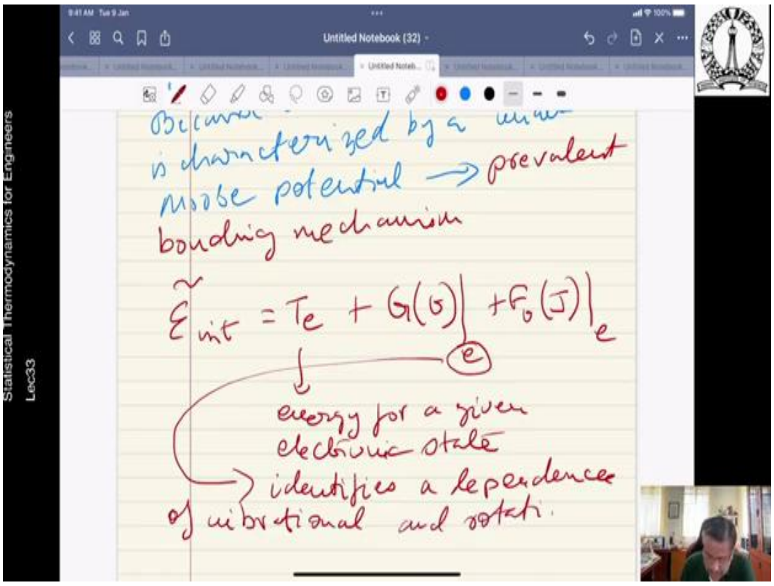
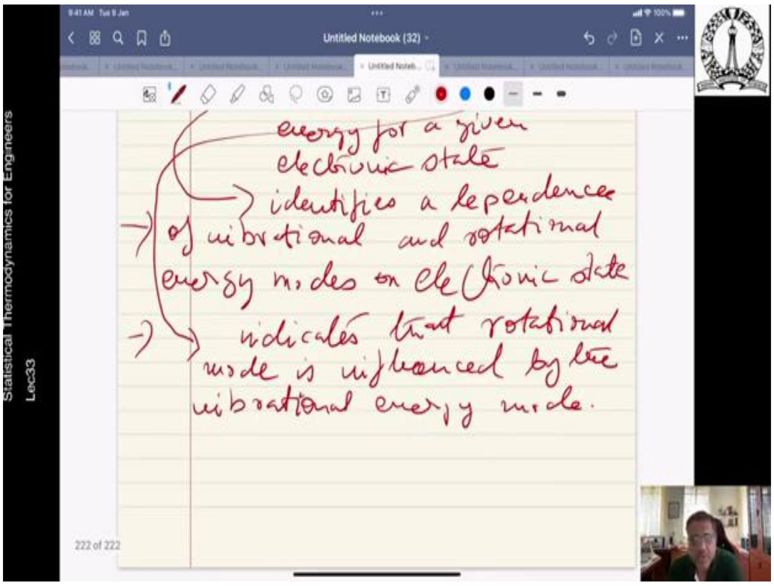


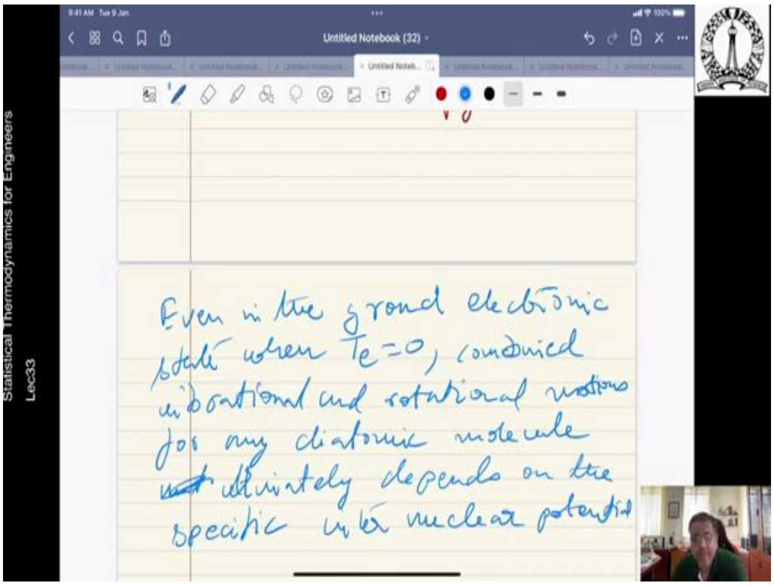
Because
is characterized by a
Morse potential → prevalent bonding mechanism

$$\tilde{\mathcal{E}}_{int} = T_e + G(v)\Big|_{e} + F_v(J)\Big|_{e}$$

energy for a given electronic state
→ identifies a dependence of vibrational and rotati.



energy for a given electronic state
→ identifies a dependence of vibrational and rotational energy modes on electronic state
→ indicates that rotational mode is influenced by the vibrational energy mode.



Even in the ground electronic state when $T_e = 0$, combined vibrational and rotational motions for any diatomic molecule intimately depends on the specific inter nuclear potential

So, let us look at now the that what are the differences in the complex model, to the complex model is what we are going to do next. So, the complex model that the we already said why it is not why the complex model is not really is required because the Simplex model does a very bad job in certain cases. So, because each electronic level is characterized by unique course potential which basically represents prevalent bonding mechanism.

So, we can actually therefore write in internal tilde(())(3:08) that is T e plus G b we will say what each of these notation section mean J e. So, T e is basically the energy for a given electronic state. The subscript e that you see over here this actually represents a dependence or identifies the dependence of vibrational energy, vibrational and rotational energy modes, energy nodes on electronic state.

And the subscript v so the subscript v that you see here it is a substitute v this subscript v indicates basically indicates that rotational energy mode is influenced by the vibrational energy mode.

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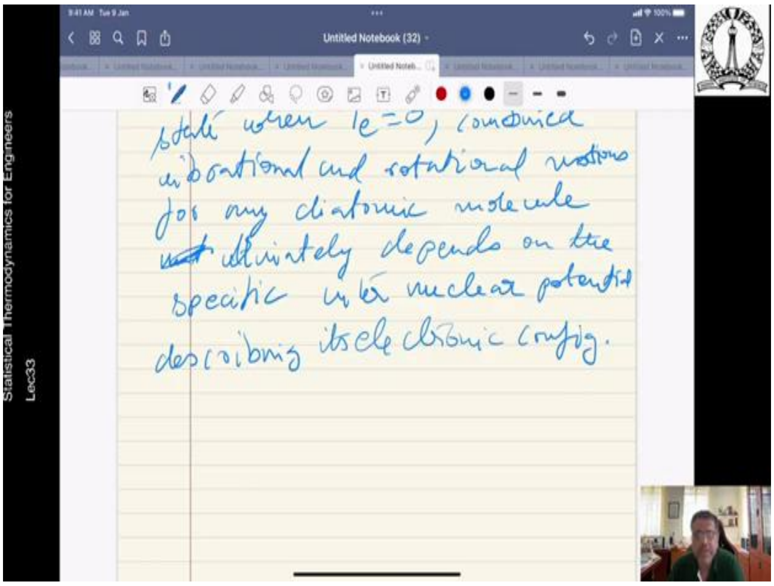
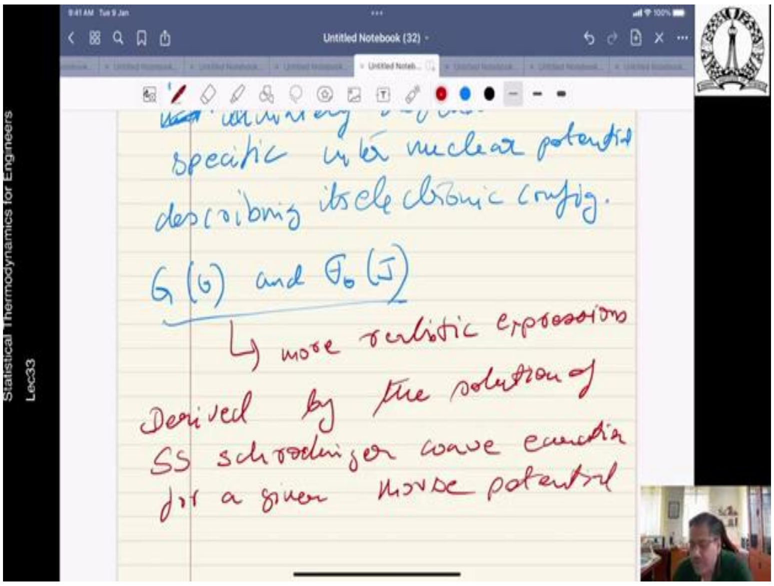


state when $T_e = 0$, combined vibrational and rotational motions for any diatomic molecule ~~ult~~ ultimately depends on the specific inter nuclear potential describing its electronic config.



specific inter nuclear potential describing its electronic config.

$G(v)$ and $F_0(J)$

↳ more realistic expressions

Derived by the solution of SS schrodinger wave equation for a given Morse potential

So, also this equation actually reminds us that even in the ground electronic state, so let us look at this even in the ground electronic state when T e is equal to 0 combined vibrational and rotational motions for any diatomic molecules ultimately depends on the specific inter-nuclear potential describing its electronic configuration. So, this is important, so it depends on the specifically on the inter-nuclear potential that actually determines it is, so even though the ground electronic energy is equal to 0.

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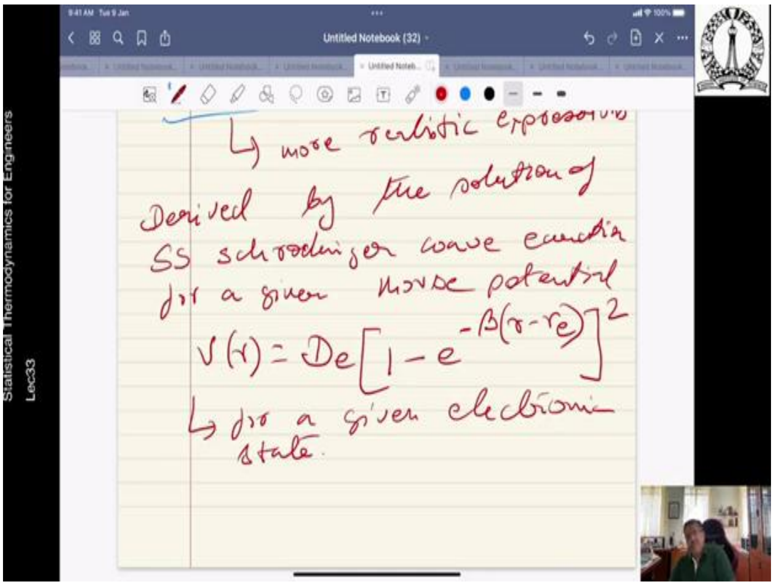
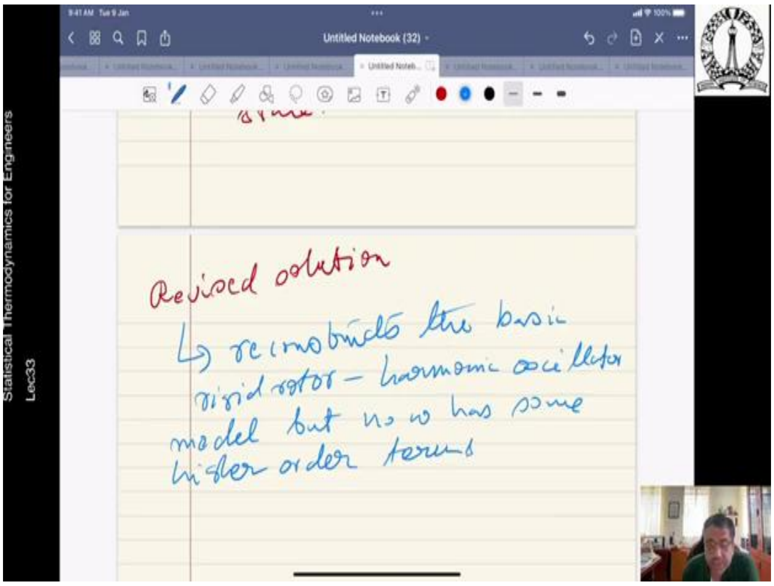


↳ more realistic expressions

Derived by the solution of SS schrodinger wave equation for a given morse potential

$V(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2$

↳ for a given electronic state.



Revised solution

↳ reintroducts the basic rigid rotor – harmonic oscillator model but now has some higher order terms

So, we have to deal with the device more realistic expressions for G e and F v J, we need more realistic expressions, so that is a good thing, so we need more realistic expressions. So, this could be essentially derived now, this would be the derived by the specific by solving by the solution of the steady state Schrodinger wave equation for a given Morse potential. So, that is what we need to do.

So, the Morse potential V r if you recall D e 1 minus e minus beta r minus re rb in the equilibrium nuclear internuclear separation distance, this is given for given electronic state, surprisingly enough an analytical solution can be obtained by using a power series representation of the Morse potential, but it is very tedious mathematically.

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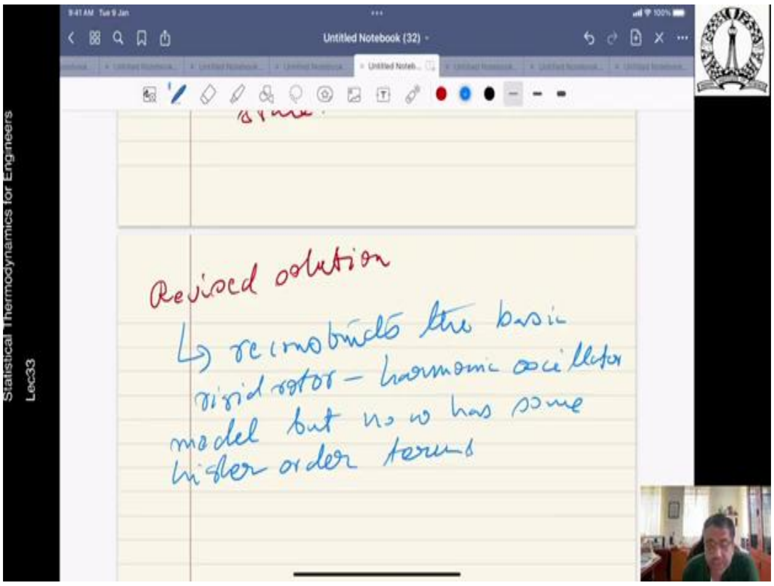
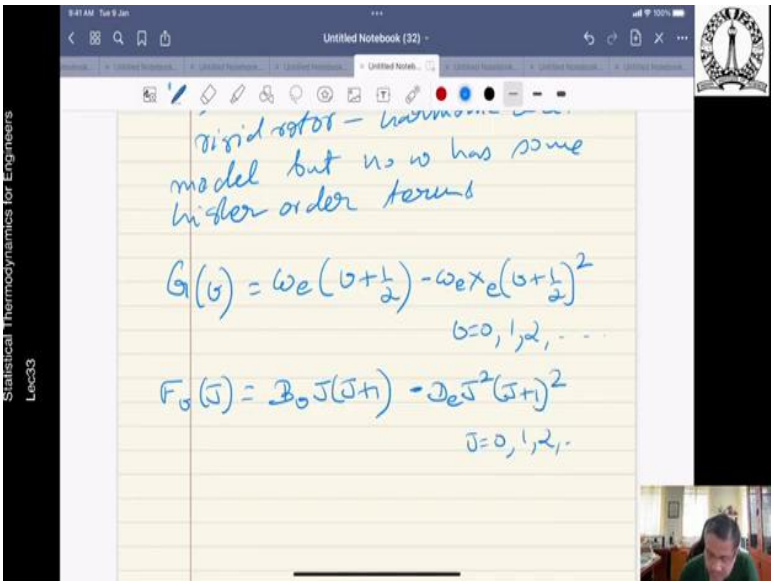


Revised solution

↳ reintroduces the basic rigid rotor – harmonic oscillator model but now has some higher order terms



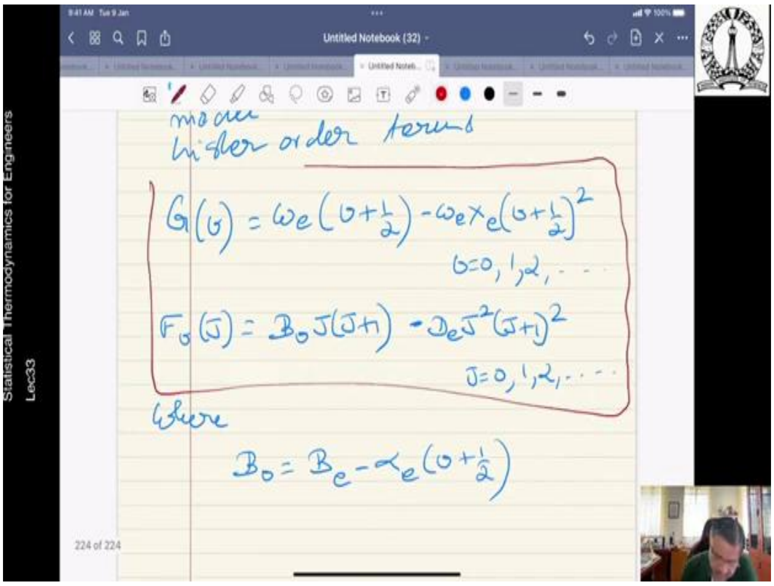
rigid rotor – harmonic ... model but now has some higher order terms

$$G(v) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2$$

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

$$F_v(J) = B_v J(J+1) - D_e J^2(J+1)^2$$

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

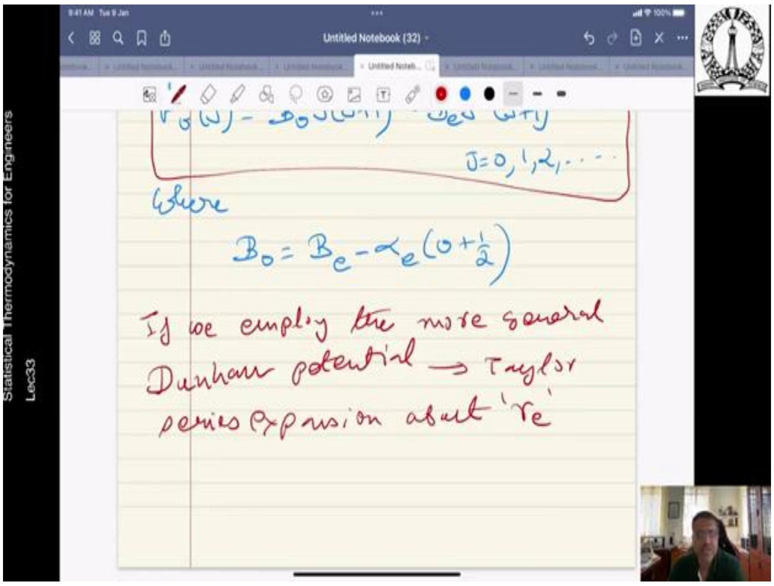


model
higher order terms

$$\boxed{\begin{aligned} G(v) &= \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 \quad v=0,1,2,\ldots \\ F_v(J) &= B_v J(J+1) - D_e J^2(J+1)^2 \quad J=0,1,2,\ldots \end{aligned}}$$

where

$$B_v = B_e - \alpha_e\left(v+\tfrac{1}{2}\right)$$



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

where

$$B_v = B_e - \alpha_e\left(v+\tfrac{1}{2}\right)$$

If we employ the more general Dunham potential → Taylor series expansion about 'r_e'

So, the revised solution but let us just see that what the revised solution actually gives us. So, the revised solution actually yields quite a few things first and foremost it reconstructs the basic a rigid rotor and harmonic oscillator model but now as some higher order terms which are not negligible.

So, if we forget all the mathematical intricacies, let us write down the solution the Gv is equal to omega e equals half minus xe equals half whole Square e go to 0, 1, 2, dot, dot, dot (())(10:08) Similarly, Fv J is given as Bv J into J plus 1, D e J square J plus 1 whole square J equals to 0, 1, 2. So, where B v is equal to B e minus sum alpha e into v plus half.

So this is the two expressions that we get. If we apply the more general Dunham potential which is basically a Taylor series expansion about r e, we merely introduced higher order terms into this equations. So, but these three equations are sufficiently accurate for most purposes, however they include all the important physical phenomena, furthermore each controlling parameter can be related to its Morse potential to a combination of varieties of things and supplementary equations.

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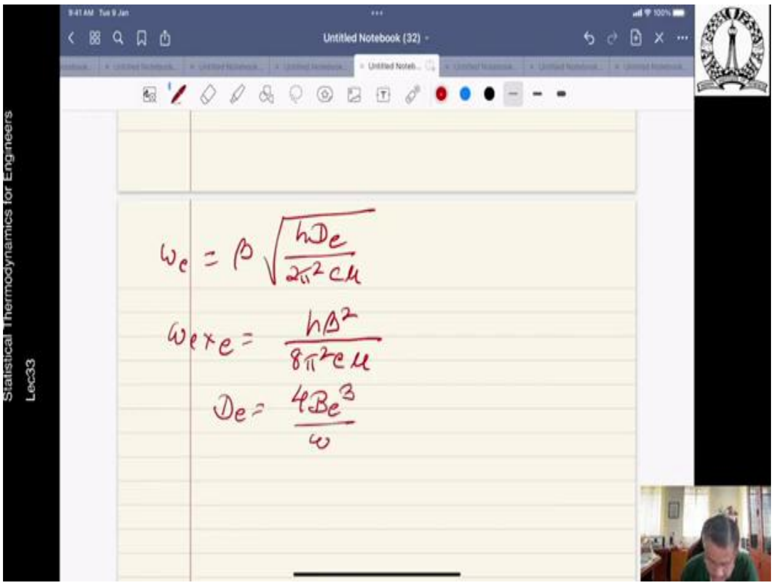
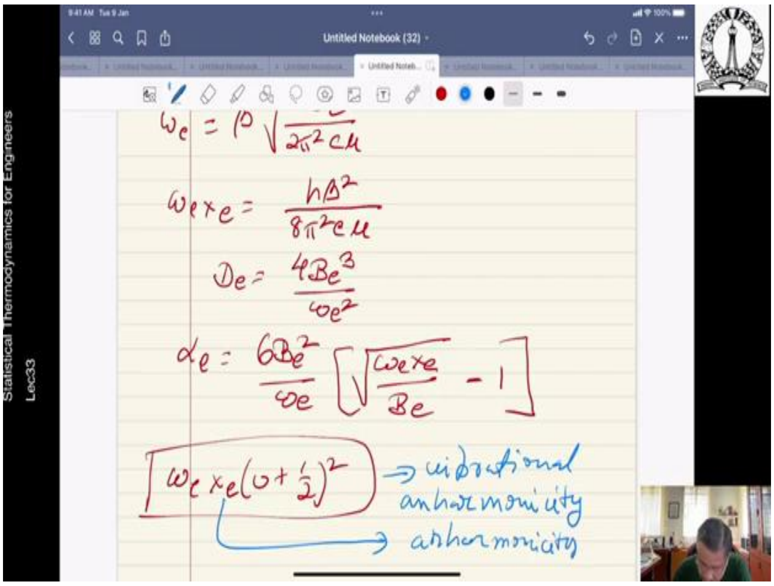


$$\omega_e = \beta \sqrt{\frac{hD_e}{2\pi^2 c\mu}}$$

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu}$$

$$D_e = \frac{4B_e^3}{\omega}$$



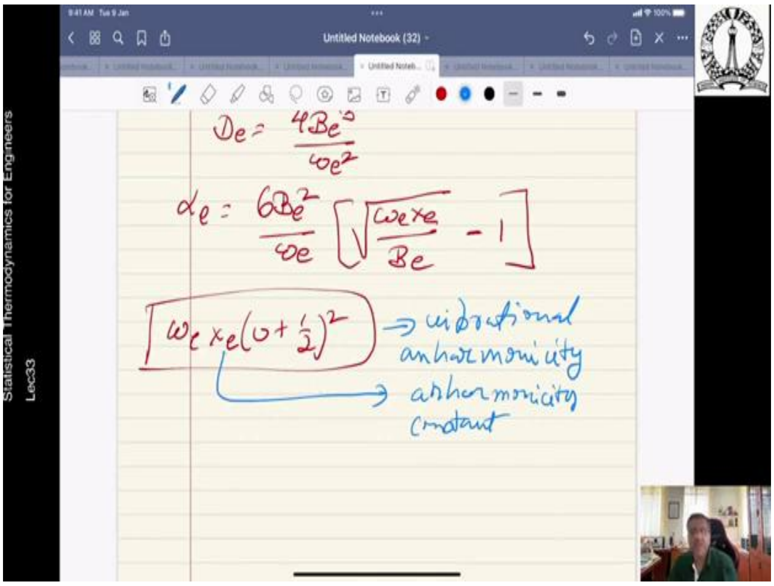
$$\omega_e = \beta \sqrt{\frac{\quad}{2\pi^2 c\mu}}$$

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu}$$

$$D_e = \frac{4B_e^3}{\omega_e^2}$$

$$\alpha_e = \frac{6B_e^2}{\omega_e}\left[\sqrt{\frac{\omega_e x_e}{B_e}} - 1\right]$$

$$\boxed{\omega_e x_e (v + \tfrac{1}{2})^2} \Rightarrow \text{vibrational anharmonicity} \rightarrow \text{anharmonicity}$$



$D_e = \frac{4B_e^3}{\omega_e^2}$

$\alpha_e = \frac{6B_e^2}{\omega_e}\left[\sqrt{\frac{\omega_e x_e}{B_e}} - 1\right]$

$\boxed{\omega_e x_e(v+\frac{1}{2})^2} \rightarrow$ vibrational anharmonicity

$\rightarrow$ anharmonicity constant

So, let us see what those supplementary equations are, so omega e for example is beta h D e divided by 2 pi square c mu, then omega xe is equal to h beta square 8 pi square c mu D e is equal to 4 B e cube omega e squared and alpha e is equal to 6 e square divided by omega e, omega e xe by B e minus 1.

So, the second, so if you look at the correction term the second correction term which is basically this one, this is the second correction term, the second correction term is represents this represents vibrational anharmonicity. So, xe is therefore all the anharmonicity constant.

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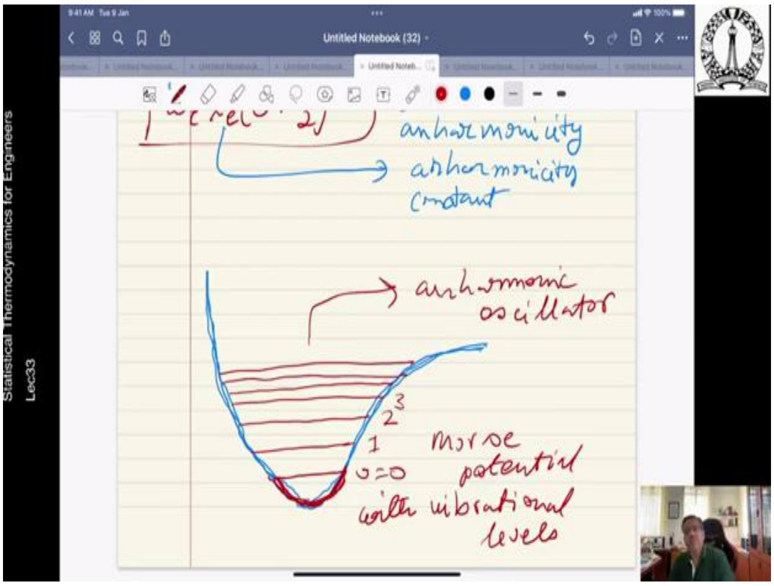

So, the typical energy levels for an harmonic oscillator it can be shown by this particular thing, just let me draw this for you this is like draw this red one single line basically, 2, it is 2, it is 3, (())(14:39) like this. So, this is Morse potential with vibrational levels and all this is for anharmonic oscillator. So, this is a sample example, so the harmonic oscillator is of course a useful thing in this lower part, it is part of the Morse potential. So, this is a useful approximation for lower vibrational numbers.

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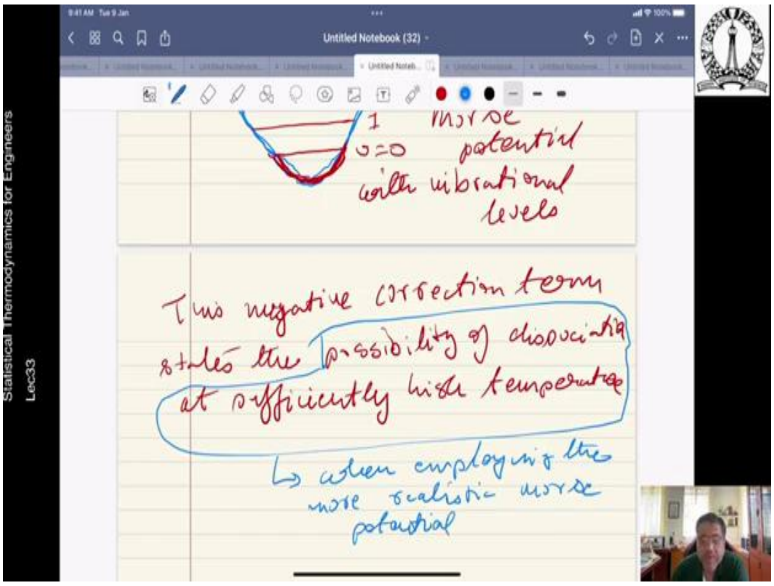
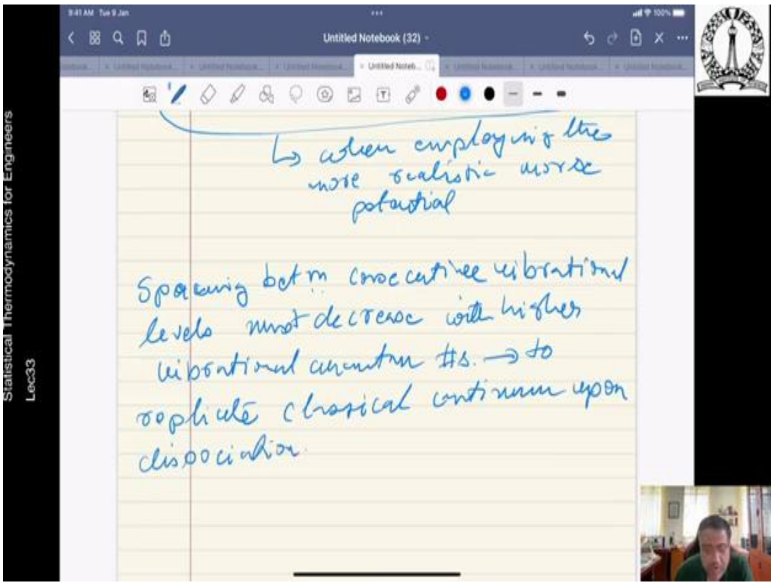


Morse potential with vibrational levels

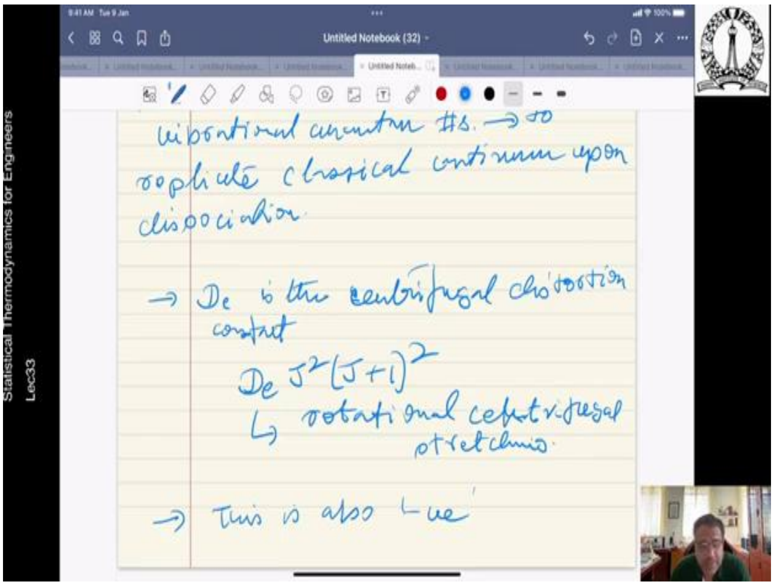
This negative correction term states the possibility of dissociation at sufficiently high temperature

→ when employing the more realistic morse potential



→ when employing the more realistic morse potential

Spacing betn consecutive vibrational levels must decrease with higher vibrational quantum #s. → to replicate classical continuum upon dissociation.



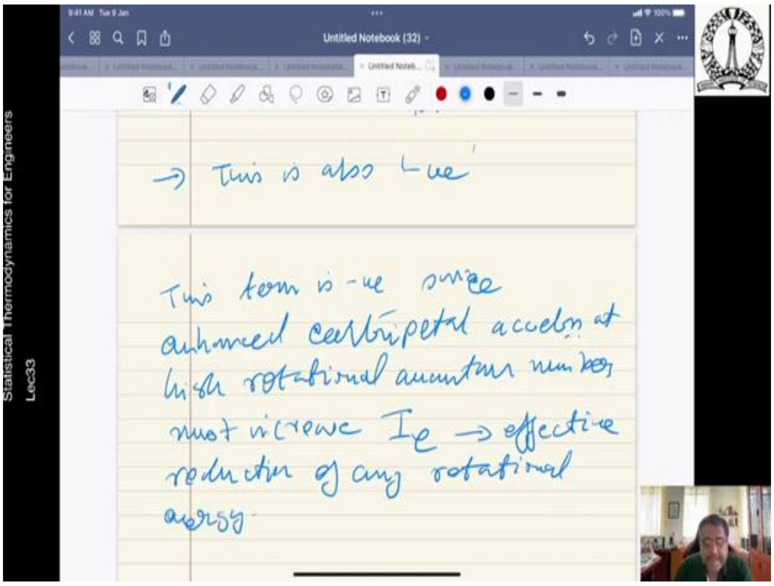
vibrational quantum #s. → to replicate classical continuum upon dissociation.

→ D_e is the centrifugal distortion constant

$$D_e J^2(J+1)^2$$

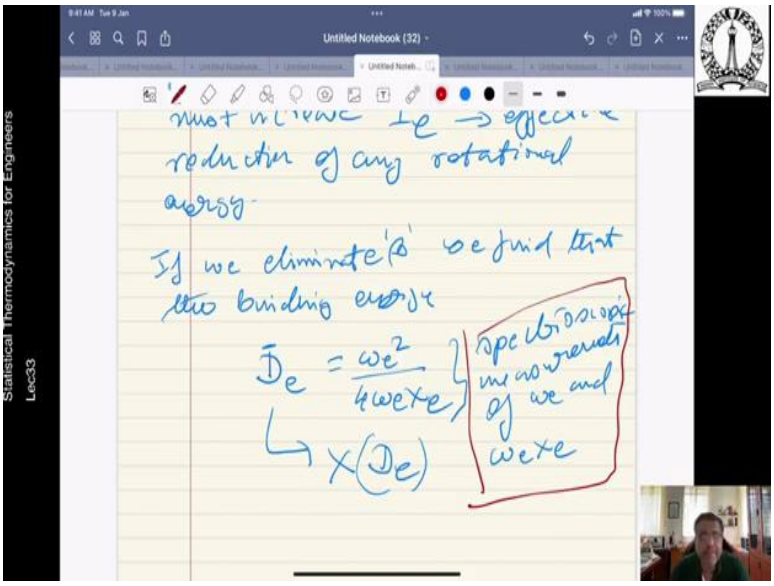
↳ rotational centrifugal stretching.

→ This is also '−ve'



→ This is also '−ve'

This term is −ve since enhanced centripetal acceln at high rotational quantum number must increase I_e → effective reduction of any rotational energy.



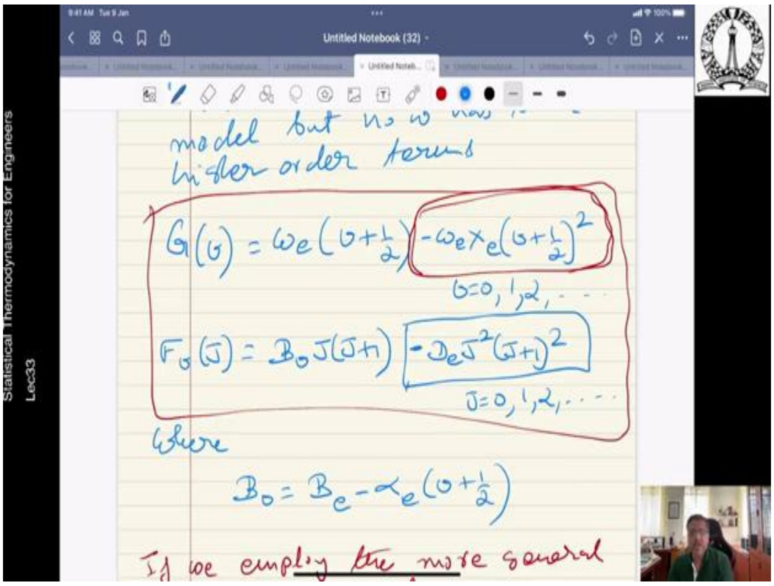
must increase I_e → effective reduction of any rotational energy.

If we eliminate 'β' we find that the binding energy

$$\bar{D}_e = \frac{\omega_e^2}{4\omega_e x_e} \Bigg\}$$

spectroscopic measurements of ω_e and $\omega_e x_e$

↳ $\times(D_e)$



model but now we have
higher order terms

$$G(\upsilon) = \omega_e\left(\upsilon+\tfrac{1}{2}\right) \boxed{-\omega_e x_e\left(\upsilon+\tfrac{1}{2}\right)^2}$$

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

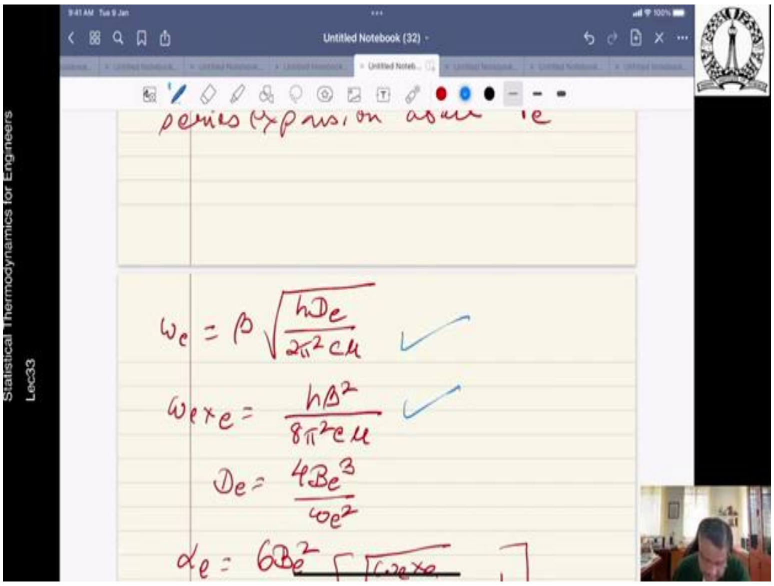
$$F_\upsilon(J) = B_\upsilon J(J+1) \boxed{-D_e J^2(J+1)^2}$$

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

Where

$$B_\upsilon = B_e - \alpha_e\left(\upsilon+\tfrac{1}{2}\right)$$

If we employ the more general



series expansion ie

$$\omega_e = \beta\sqrt{\frac{hD_e}{2\pi^2 c\mu}} \checkmark$$

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu} \checkmark$$

$$D_e = \frac{4B_e^3}{\omega_e^2}$$

$$\alpha_e = 6B_e^2\left[\sqrt{\omega_e x_e}\right.$$

Now, if you see the negative correction term if you look at this expression now it is in revisit expression, this is a negative correction term. So, this negative correction term actually states the possibility of if you think about it carefully of dissociation at efficiently high temperature. So, this actually states that there is a possibility of dissociation at high temperature, when we employ when employing, now more realistic, the more realistic Morse potential.

So, the spacing between the consecutive vibrational levels actually decrease with higher vibrational quantum numbers, this behaviour is quietly a straightforward robust manifestation of the correspondence principle. Now, you can see that the spacing between consecutive vibrational levels must actually decrease with higher vibrational quantum numbers. So, this is to replicate classical continuum upon dissociation.

Now, if you look at this term now which is basically the second the this particular equation and this particular term, the second order correction term De is basically the centrifugal distortion constant. So, here D e is the centrifugal distortion constant, so remember that due to centrifuging there will be a little bit of a change of the bond stretching and all those things.

So, this is the expression once again it is good to have it in front of you so this was the term that we were talking about. So, it basically represents, so therefore D basically represents rotational centrifugal stretching, this is also a negative correction, because why it is negative that is because enhanced centripetal acceleration at high rotational quantum numbers must increase the moment of inertia thus therefore effectively reducing any rotational energy.

So, the correction term is negative, this term is negative, since enhanced centripetal acceleration and high rotational quantum numbers must increase Ie must increase the moment of inertia, therefore this leads to effective reduction of any rotational energy. If so D e is not the same as the binding energy, so if we eliminate beta from here this expression for beta which is equations for this you have a beta and here you have a beta.

So if you eliminate beta we eliminate beta, we find that the binding energy they represent it by D e is given as omega square 4 omega e xe, this is not the same as De which is basically a rotational constant. So, we find the binding energy can be replaced by this, this utilizes specific measurements of this utilizes spectroscopic measurements of Omega e xe, if specific spectroscopic measurements that is what it does.

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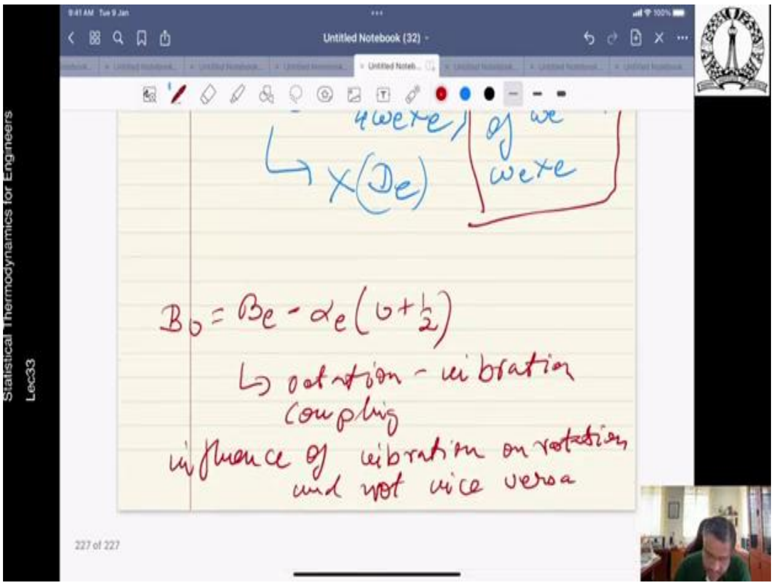


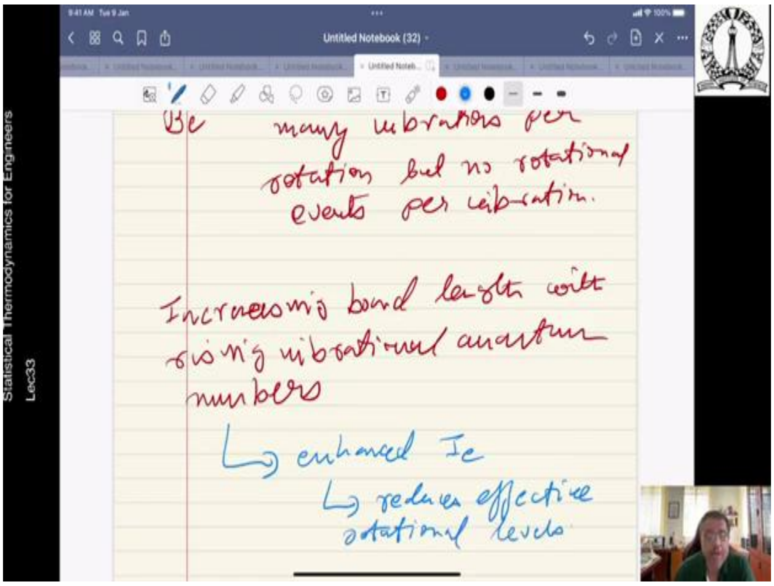
$4\omega_e x_e)$ of ω_e

↳ $\times (D_e)$ $\omega_e x_e$

$B_v = B_e - \alpha_e(v + \frac{1}{2})$

↳ rotation - vibration coupling

influence of vibration on rotation and not vice versa

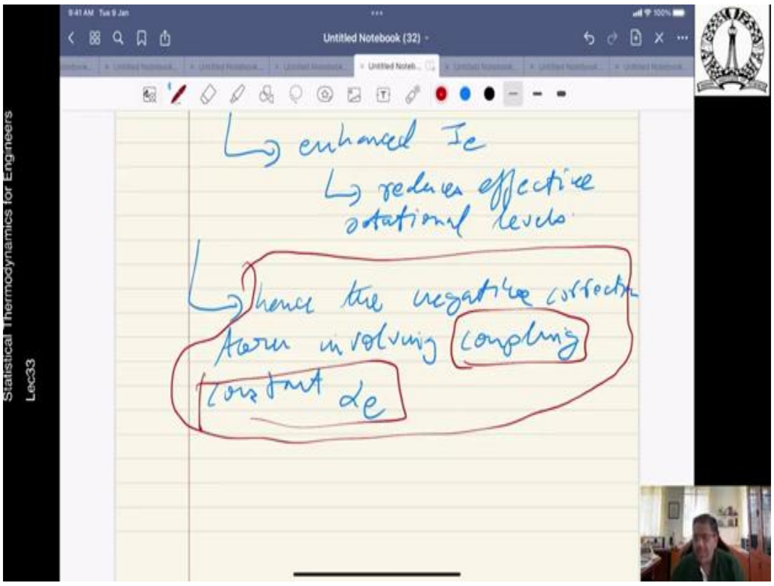


Be many vibrations per rotation but no rotational events per vibration.

Increasing bond length with rising vibrational quantum numbers

↳ enhanced I_e

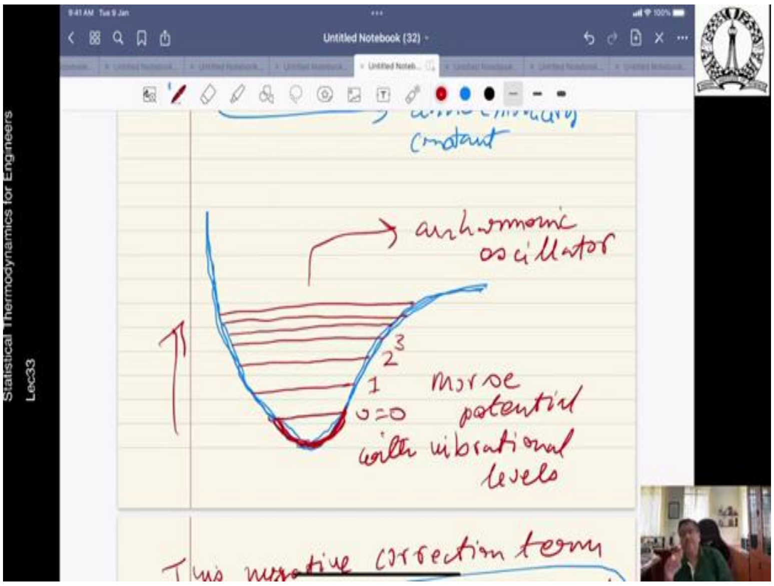
↳ reduces effective rotational levels



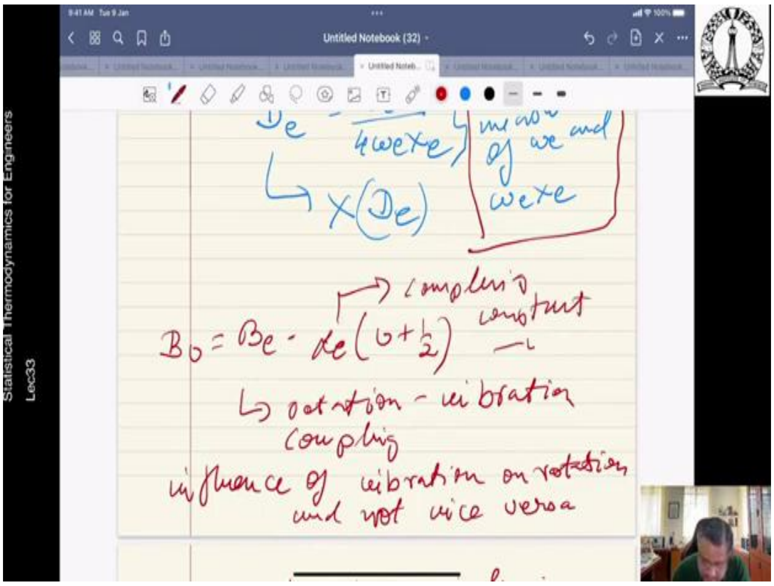
↳ enhanced I_e

↳ reduces effective rotational levels

↳ hence the negative correction term involving coupling constant α_e



This negative correction term



D_e … $4\omega_e x_e$) in terms of ω_e and $\omega_e x_e$

$\hookrightarrow x(D_e)$

$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right)$ → coupling constant

↳ rotation - vibration coupling

influence of vibration on rotation and not vice versa

So, finally if you look at B v equal to B e minus alpha e into v plus half this expression, so this represents what we call the rotation vibration coupling, here the coupling comes from the influence of vibration and rotation, so it is the one-way basically influence of vibration on rotation and not vice versa. In other words this essentially translates to a one-way coupling.

So, omega e by B e values are at the order of 100 to 1000, implying many vibrations per rotation but no rotational events per vibration. The controlling effect of vibration on rotation is also given in this particular diagram if you look at it carefully which portrays an increase increasing bond length with the rising vibrational quantum number is increasing bond length leads to an increase in the enhanced moment of inertia which reduces the effective rotational levels.

So, that is the negative correction term involving the coupling constant alpha, so again alpha e is a negative correction term. So, it is called a coupling constant, alpha e for the coupling constant again it is negative in nature. So, just to write it if you look at the Morse potential you will see that increasing bond length leads with rising vibrational quantum numbers, this further leads to enhanced moment of inertia enhanced Ie, Ie therefore reduces effective rotational levels.

So, hence we get hence the negative correction term involving coupling constant, so this is what we get. So, we saw that therefore we in this particular lecture we saw that how the Morse potential can be used now to depict a more complex model for diatomic molecules, next time we will do what we call the Ro-vibrational spectroscopy.

We also saw the effect of vibrational and harmonicity, the centrifugal stretching, the row vibrational coupling all these things we saw in this lecture, we will use all these things in the next lecture to investigate more into the row vibrational spectroscopy using the complex model. So, see you in the next lecture.