Statistical Thermodynamics for Engineers
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Lecture 31
The rotational and vibrational energy mode for a diatomicmolecule

Welcome to lecture number 21 on the statistical thermodynamics' sources for engineers. We are going to have companion tutorial sessions on spherical coordinates on the linear Hermitian operators as well as on Eigen values and Eigen functions and we are also going to have a brief idea about the ODEs, the different forms of ODEs because we are using some of them. So, this will be mainly as a recap or recollection of the courses that you have taken earlier. So, so far, we have as we know we have done an extensive piece of work in analyzing the rotational energy mode and how is it represented by the Legendre's polynomial.

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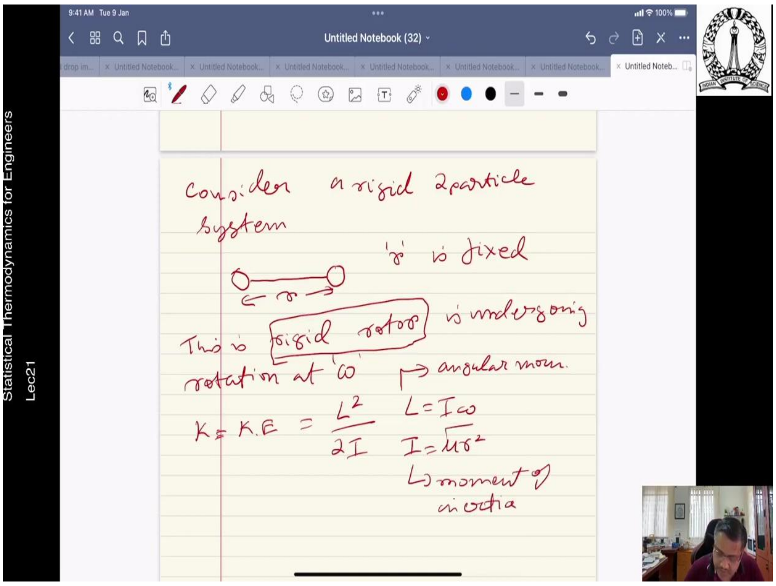

Consider a rigid 2particle system

'r' is fixed

$\leftarrow r \rightarrow$

This is $\boxed{\text{rigid rotor}}$ is undergoing rotation at 'ω'

$\rightarrow$ angular mom.

$K = K.E = \frac{L^2}{2I}$ $L = I\omega$

$I = \mu r^2$

$\hookrightarrow$ moment of inertia

Now, let us consider a rigid 2 particle system. So, assuming that this is the 2 particle, this is r and we are assuming that this r is fixed. So, this is rigid rotor, is undergoing rotation at omega. So, this is a rigid rotor therefore, undergoing rotation omega. So, we are still in the rotational analysis. So, K being the kinetic energy, is given as L square by 2I where L is I omega, so L is angular momentum I. It is also given as mu r square where I is the moment of inertia and the mu was the reduced mass. This part was well understood before.

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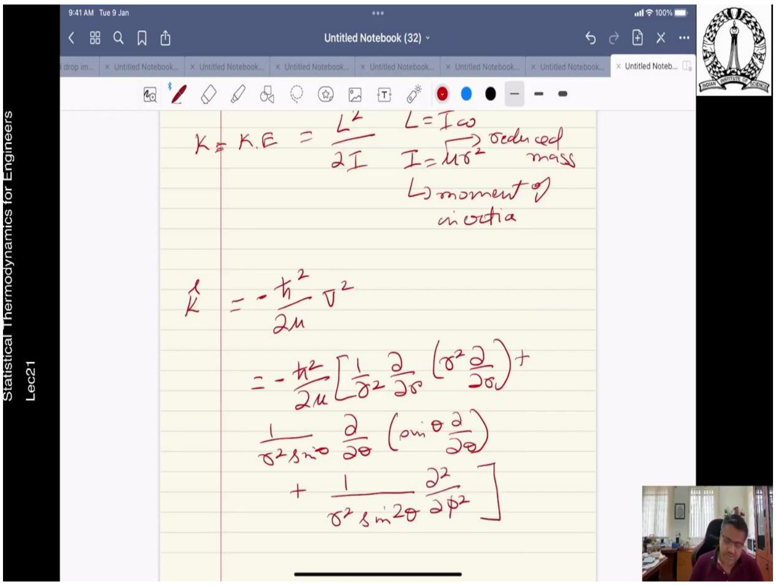

$K = K.E = \frac{L^2}{2I}$ $L = I\omega$

$I = \mu r^2$ → reduced mass

↳ moment of inertia

$$\hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

So, a operator for the kinetic energy is basically h bar square by 2 mu v2 this, which is h square by 2 mu 1 over r square d by dr r square d by dr plus 1 over r square sin theta d by d theta by sin theta optional theta plus 1 over r square sin square theta square, that is the total expression you recall.

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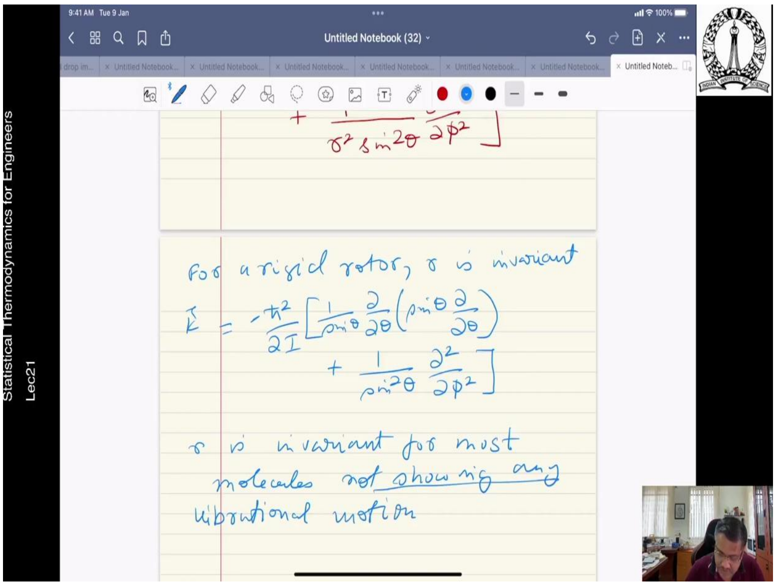

For a rigid rotor, r is invariant

$$\hat{K} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

r is invariant for most molecules not showing any vibrational motion

So, for a rigid rotor, r is invariant. That means it is fixed. So, the k operator it will become, so, there is no differential with respect to r. h square by 2 I, 1 over sin theta d by d theta plus 1 over square theta, R is invariant for most molecules. Molecules not showing any vibrational motion. So, that is what it is.

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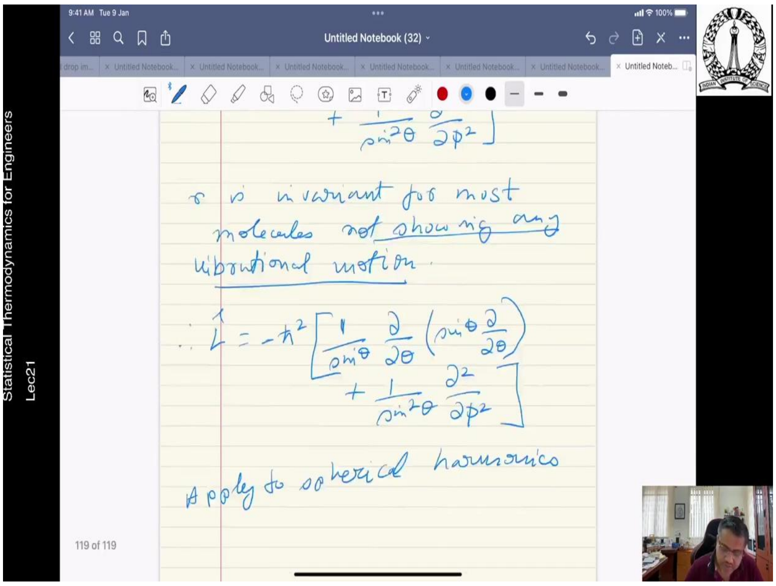

$$+ \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]$$

r is invariant for most molecules not showing any vibrational motion.

$$\therefore \hat{L} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Apply to spherical harmonics

So, therefore, this operator L hat is equal to minus h bar square 1 over sin theta d by d theta sin theta d by d theta plus 1 over sin squared theta d square... So, remember this was the I omega, L was I omega. So, this is the operator or the quantum mechanical operator for L. So, apply to the spherical harmonics, what were the spherical harmonics?

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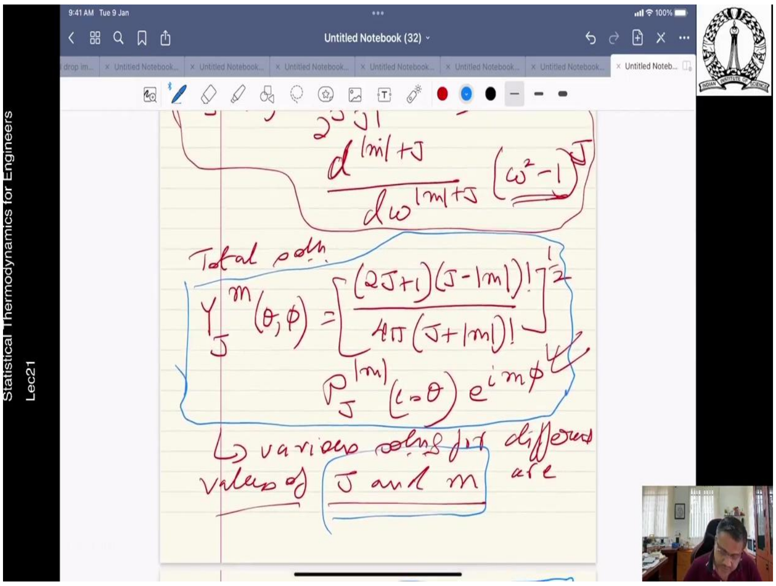

$$\boxed{\frac{d^{|m|+J}}{d\omega^{|m|+J}}\left(\omega^2-1\right)^J}$$

Total soln.

$$\boxed{Y_J^m(\theta,\phi) = \left[\frac{(2J+1)(J-|m|)!}{4\pi(J+|m|)!}\right]^{\frac{1}{2}} P_J^{|m|}(\cos\theta)\, e^{im\phi}}$$

↳ various solns for different values of J and m are

Let us just recall that the spherical harmonics these were the spherical harmonics.

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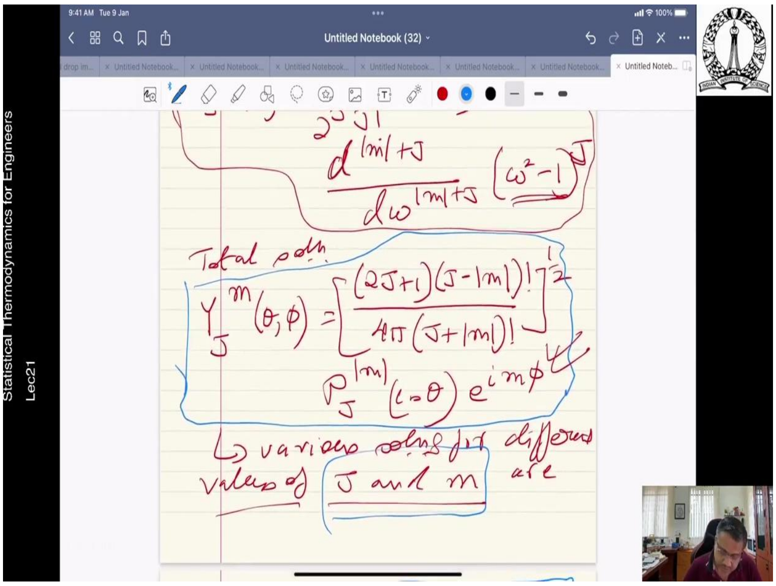

$$\frac{d^{|m|+J}}{d\omega^{|m|+J}}\left(\omega^2-1\right)^J$$

Total soln.

$$Y_J^m(\theta,\phi) = \left[\frac{(2J+1)(J-|m|)!}{4\pi(J+|m|)!}\right]^{\frac{1}{2}} P_J^{|m|}(\cos\theta)\, e^{im\phi}$$

↳ various solns for different values of J and m are

So, we apply a operator to the spherical harmonics. So, L hat square Y theta comma phi is equal to minus h square 1 by sin theta d by d theta sin theta dy d theta plus 1 over sin square theta d square y by d theta square is equal to alpha h square y.

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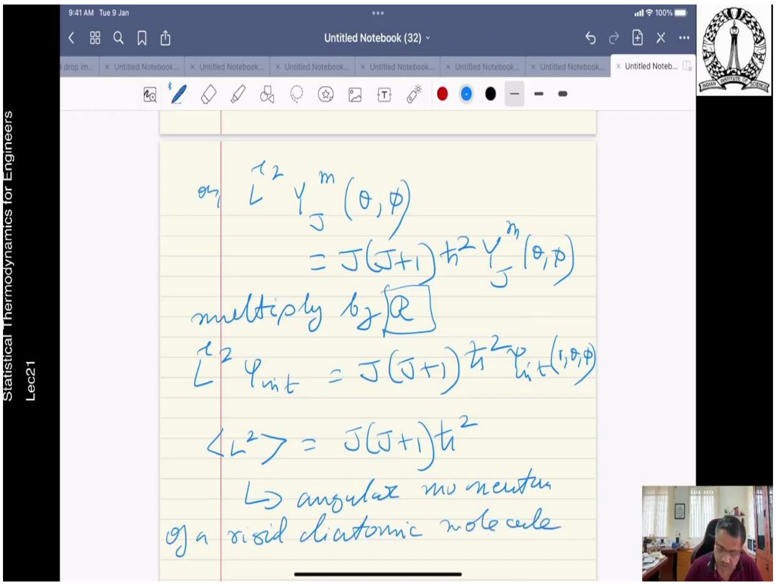


or $\hat{L}^2 Y_J^m(\theta,\phi)$

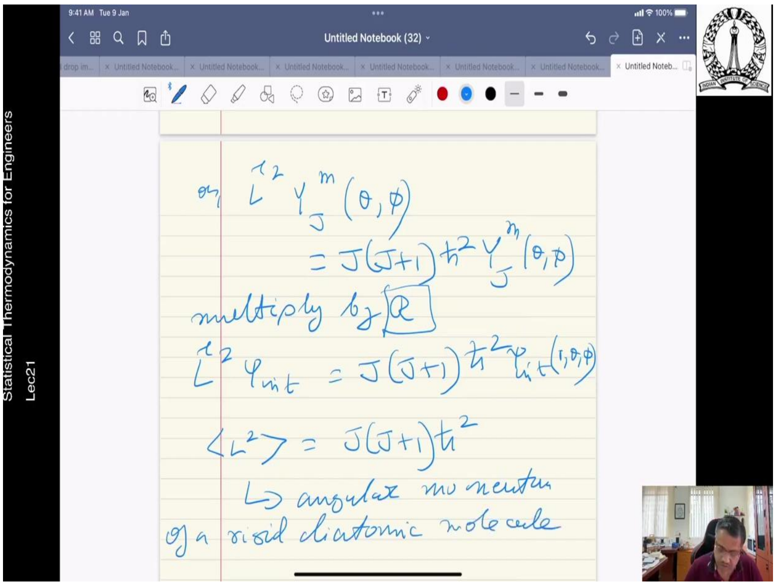
$$= J(J+1)\hbar^2 Y_J^m(\theta,\phi)$$

multiply by $\boxed{R}$

$$\hat{L}^2 \psi_{int} = J(J+1)\hbar^2 \psi_{int}(r,\theta,\phi)$$

$$\langle L^2\rangle = J(J+1)\hbar^2$$

↳ angular momentum of a rigid diatomic molecule



or $\hat{L}^2 Y_J^m(\theta,\phi)$

$$= J(J+1)\hbar^2 Y_J^m(\theta,\phi)$$

multiply by $\boxed{R}$

$$\hat{L}^2 \psi_{int} = J(J+1)\hbar^2 \psi_{int}(r,\theta,\phi)$$

$$\langle L^2 \rangle = J(J+1)\hbar^2$$

↳ angular momentum of a rigid diatomic molecule

So, in other words L square YJ m theta, phi is equal to J into J plus 1 h bar square Yjm. So, multiply by R, equal to j into j plus 1 h bar square chi theta, phi alright. So, that is what it is. So, this R is basically was the separation of variables that we did earlier variable. So, this was what it was. So, therefore, L square bar equal to J into J plus 1 h bar square.

So, this is the angular momentum of a rigid diatomic molecule… and the energy of rotation assuming it is a rigid rotor is J into J plus 1 by 2I h bar square. In wave number units, we have number space, you can write it as FJ is E rotation divided by hc J into J plus 1 into BE where J is equal to 0, 1, 2, and Be is h divided by 8 pi square 2c H pi square Ie Ie is equal to mu re square, we will we will take a look at what it is.

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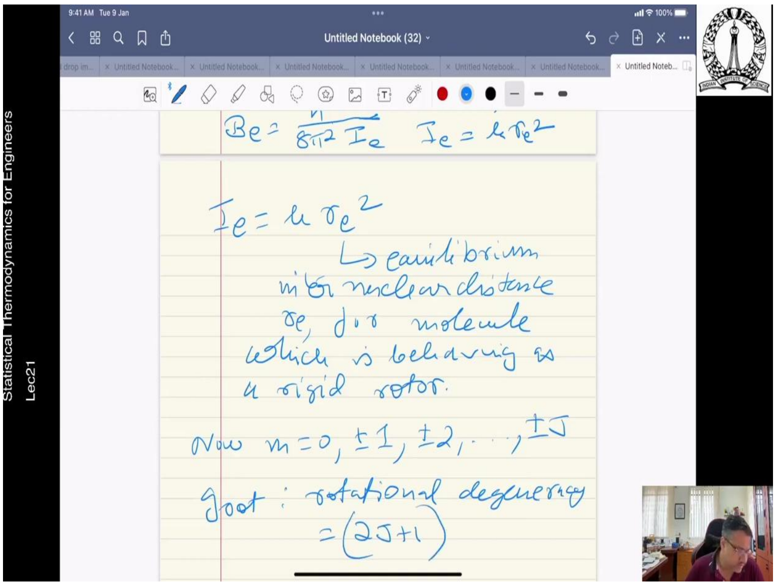


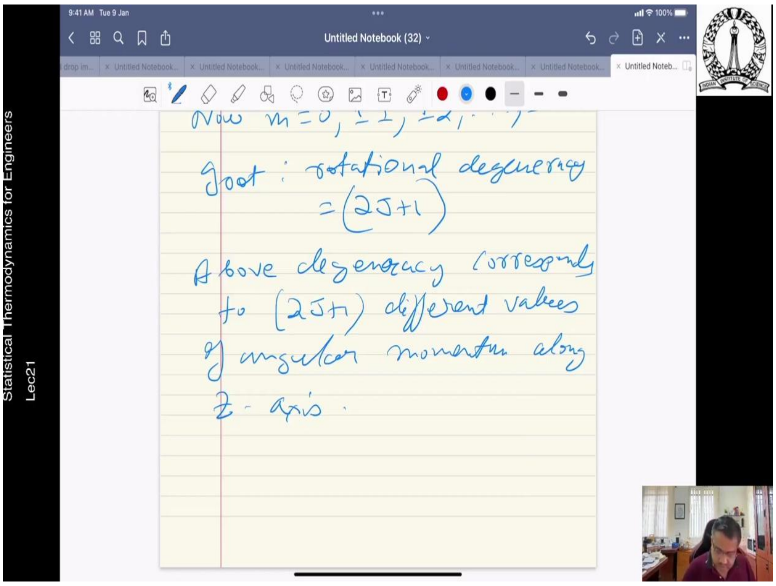
$B_e = \frac{h}{8\pi^2 I_e}$ $I_e = \mu r_e^2$

$$I_e = \mu r_e^2$$

↳ equilibrium inter nuclear distance r_e, for molecule which is behaving as a rigid rotor.

Now $m = 0, \pm 1, \pm 2, \ldots, \pm J$

g_{rot} : rotational degeneracy $= (2J+1)$



Now $m = 0, \pm 1, \pm 2, \ldots,$

g_{rot} : rotational degeneracy $= (2J+1)$

Above degeneracy corresponds to $(2J+1)$ different values of angular momentum along z-axis.

So, i e equal to mu r square, now this is the equilibrium, re is the equilibrium inter nuclear distance re or molecule which is behaving as a rigid rotor. Now, m is equal to 0 plus minus 1 plus minus 2 up to j. So, the degeneracy or the G rotation is also called the rotational degeneracy is given as 2J plus 1.

So, that means the above degeneracy received corresponds to 2J plus 1, different values of angular momentum, angular momentum along the z axis, something like that. So, this is what we have. So, let us see if there is anything that I missed. The Z quantity, it is basically the z component to them. So, for z equal to 2, let us show it with a simple figure.

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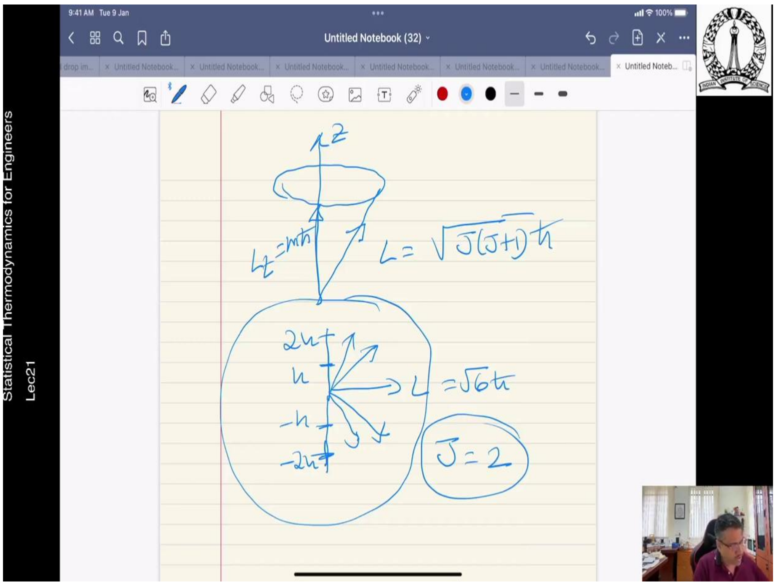

So, this is the Z axis. So, LZ of two mh bar it is like this. So, this is basically L j into j plus 1 h bar. So, this is how, if this is actually equal to 2 then you can have, so, let us do basically probably a problem to navigate some of this. So, this is how the quantization occurs along the z axis. So, the z component of the angular, so, this is this if you look at figure 612 from the book you will get a much fairer idea. So, it is like this L equal to root over say 6 h bar. So, therefore, this was minus h this is minus 2 h, this is plus h, this is plus 2h. So, this is how the degeneracy part actually happens.

It is 2j plus 1 as you can see that there are 5 degeneracy level here, j is equal to 2. So, 2 plus 3 so, J is equal to 2 and this is how the quantization actually happens. So, I think this is a useful way of doing that what the degenerate levels are. So, this is for a rigid rotor and found out that what will be the corresponding degeneracy levels. Now, you are going to go and take a look at the vibrational energy mode.

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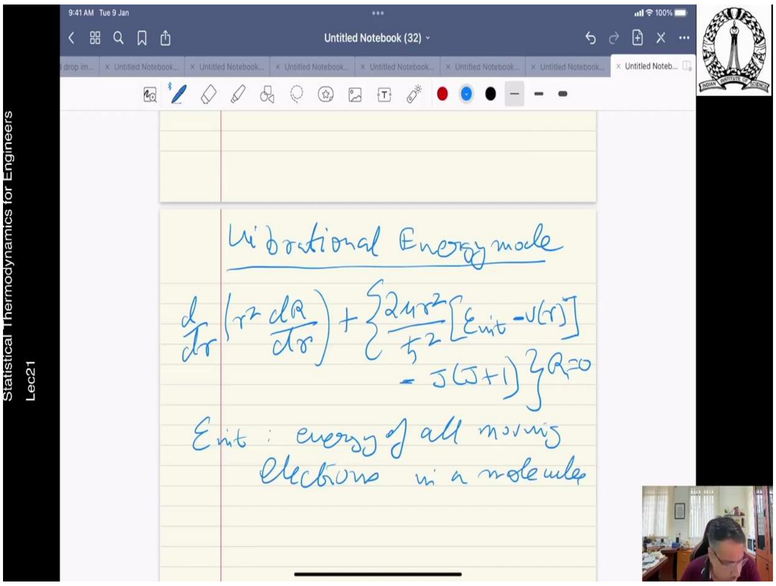

Vibrational Energy mode

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left\{\frac{2\mu r^2}{\hbar^2}\left[\varepsilon_{int}-V(r)\right]-J(J+1)\right\}R=0$$

ε_{int} : energy of all moving electrons in a molecule

Alright, the vibrational energy mode up next. So, we have still the r component when we separate it by 2, so this is d by dr square dr by small r 2 mu R square by H bar square E internal minus Vr minus j into j plus 1 into r is equal to 0. So, this is the internal energy, A of all moving electrons in a molecule. Not a single r coordinate per se.

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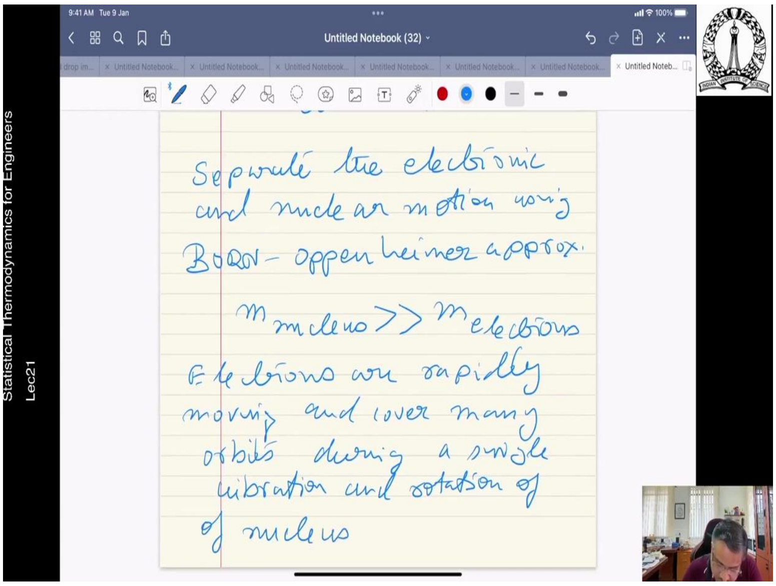

Separate the electronic and nuclear motion using Born-Oppenheimer approx.

$m_{nucleus} >> m_{electrons}$

Electrons are rapidly moving and cover many orbits during a single vibration and rotation of of nucleus

So, separate the electronic and the nuclear motion, we can separate, separate the electronic and nuclear motion using Born-Oppenheimer approximation. So, that means obviously, the mass of the nucleus is much greater than the mass of the electrons. This we know. So, the electrons are rapidly moving. So, electrons are rapidly moving and cover many orbits during a single vibration and rotation of nucleus.

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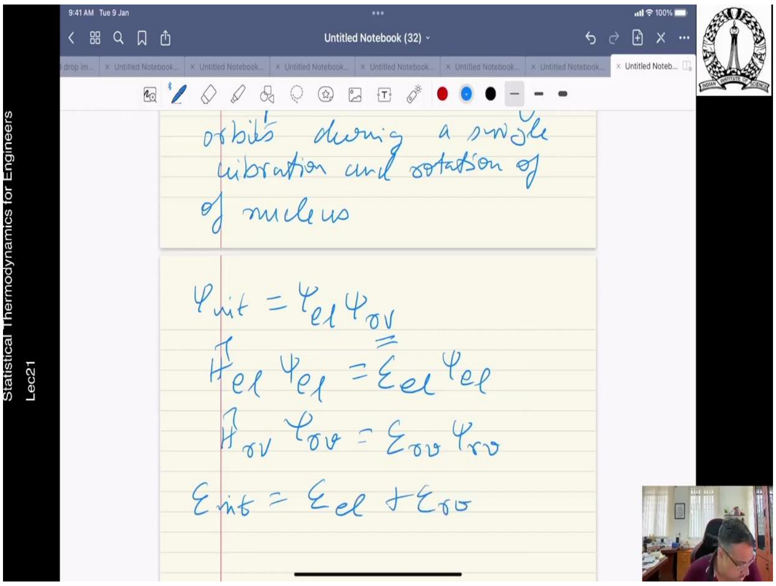

orbits during a single vibration and rotation of of nucleus

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

$\hat{H}_{el}\psi_{el} = \varepsilon_{el}\psi_{el}$

$\hat{H}_{rv}\psi_{rv} = \varepsilon_{rv}\psi_{rv}$

$\varepsilon_{int} = \varepsilon_{el} + \varepsilon_{rv}$

So, the internal therefore is written as electronic into ro-vibrational, rotational vibration. So, this is rovibrational, rotation and vibration. So, this is the Hamiltonian for the electronic, this is electronic is equal to energy electronic into the wave function and then of course, you have the rovibrational multiplied by the row vibrational wave function, this is rovibrational rv. So, and of course the internal energy is written as E electronic plus E ro vibration.

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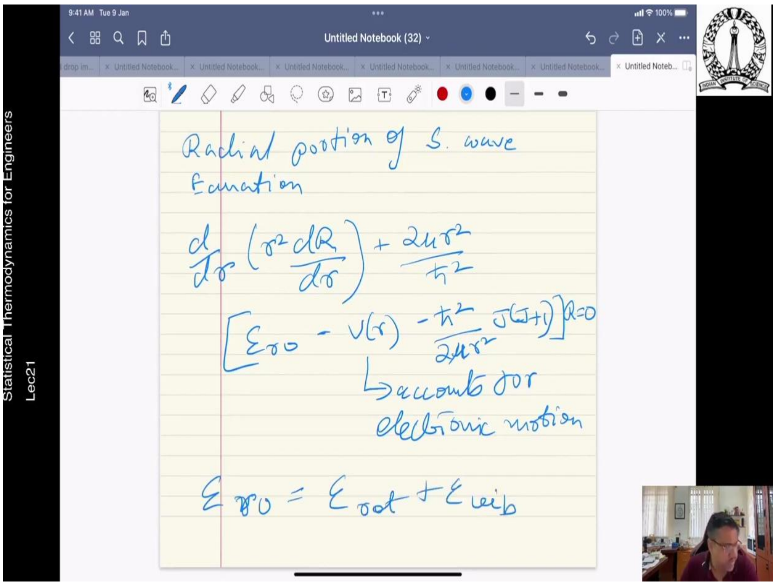

Radial portion of S. wave Equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left[E_{ro}-V(r)-\frac{\hbar^2}{2\mu r^2}J(J+1)\right]R=0$$

accounts for electronic motion

$$E_{ro}=E_{rot}+E_{vib}$$

So, now, if we do this the radial portion of the Schrodinger’s wave equation that becomes d r square plus 2 mu square h bar square, then I am writing whatever goes in the bracket E rovibrational minus Vr is h bar square by 2 mu r square is 2 mu r square J into J plus 1 r equal to 0, this part accounts for electronic motion. So, this part accounts for the electronic motion. So, now further, E rovibrational is written as E rotational plus E rovibrational.

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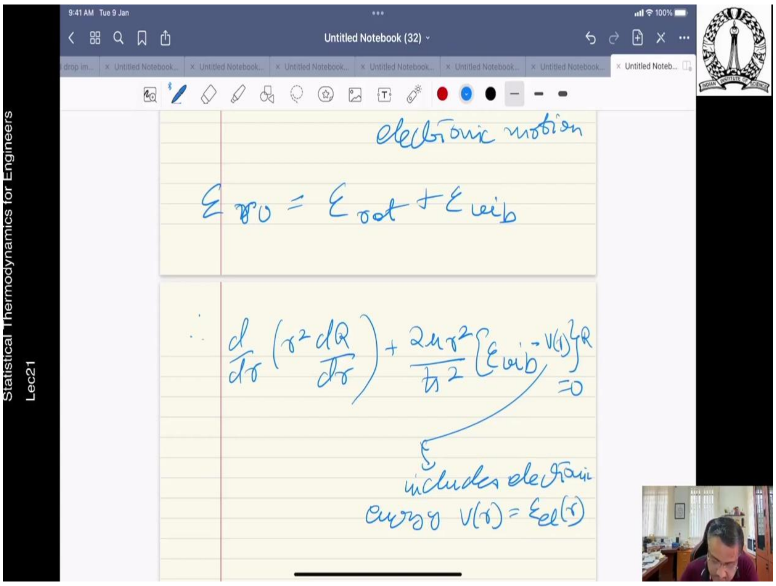
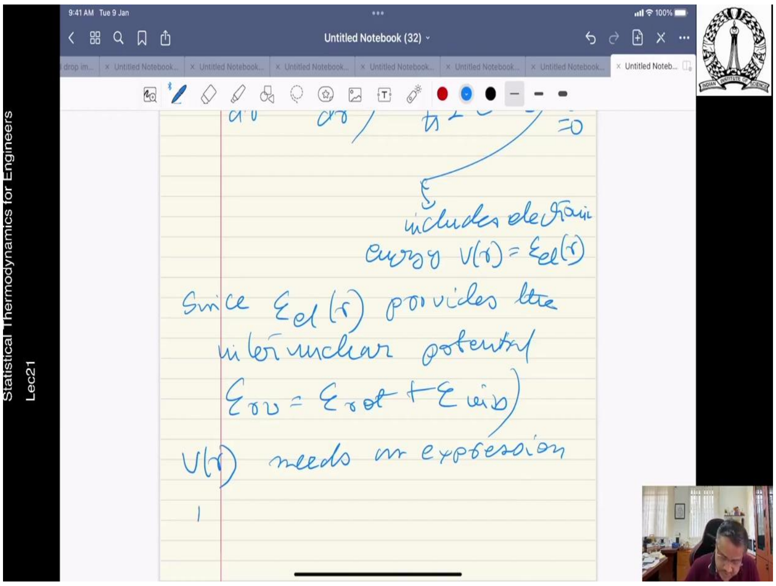


electronic motion

$$E_{ro}=E_{rot}+E_{vib}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left\{E_{vib}-V(r)\right\}R=0$$

includes electronic energy $V(r)=E_{el}(r)$



$=0$

includes electronic energy $V(r) = \varepsilon_{el}(r)$

Since $\varepsilon_{el}(r)$ provides the internuclear potential

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

$V(r)$ needs an expression

So therefore, d by dr r square dr by dr plus 2 mu square h bar E vibrational minus Vr into R is equal to 0, this basically includes electronic energy... So, since electronic r provides the inter nuclear potential E rovibrational is E rotation plus E vibration. So, VR needs an expression, at this point we need to have an expression for VR. So, VR which is basically nothing but includes electronic potential needs an expression.

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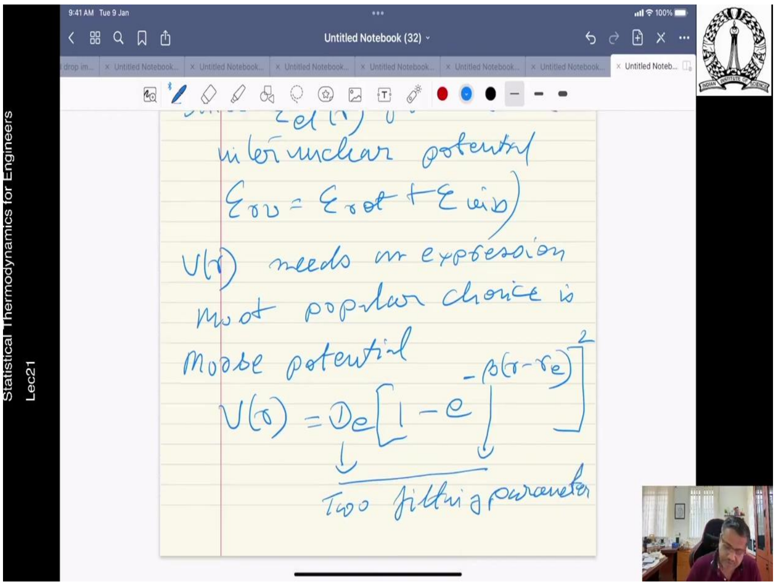


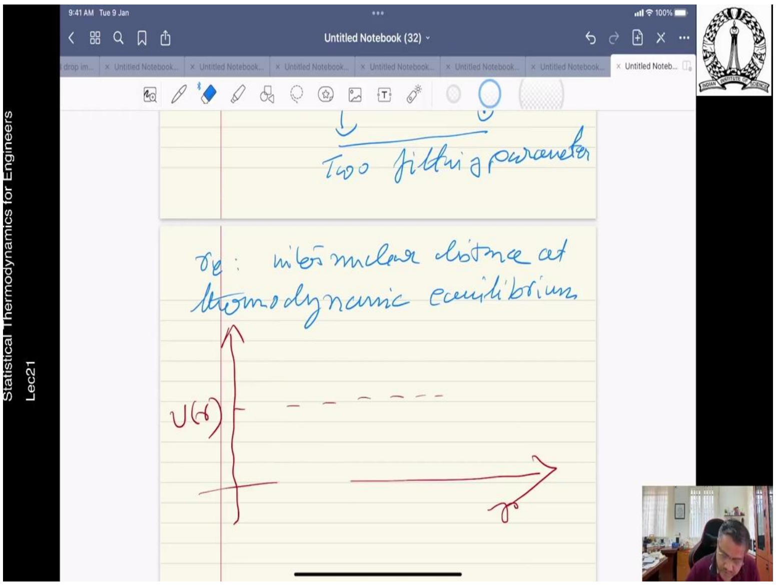
internuclear potential

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

$V(r)$ needs an expression

Most popular choice is Morse potential

$$V(r) = \underbrace{D_e\left[1 - e^{-\beta(r-r_e)}\right]^2}_{\text{Two fitting parameter}}$$



Two fitting parameter

re: internuclear distance at thermodynamic equilibrium

Before we move any further, the most popular choice is called the morse potential. so, morse potential is something like this, it is written as Vr is equal to De, we will come across what De is, 1 minus e minus beta r minus re, re remember is the mean, the equilibrium eeta nuclear distance A square. So, De and beta are basically 2 fitting parameters, re is the internuclear distance, re is the inter nuclear distance at thermodynamic equilibrium.

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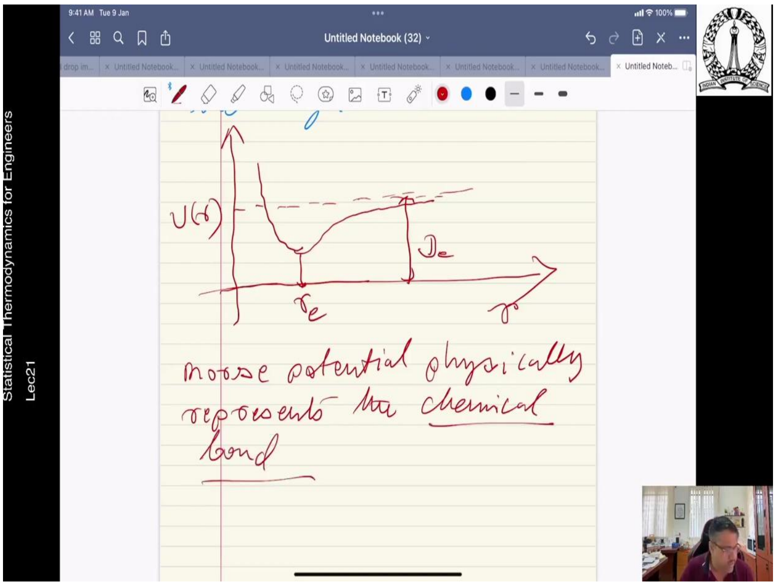
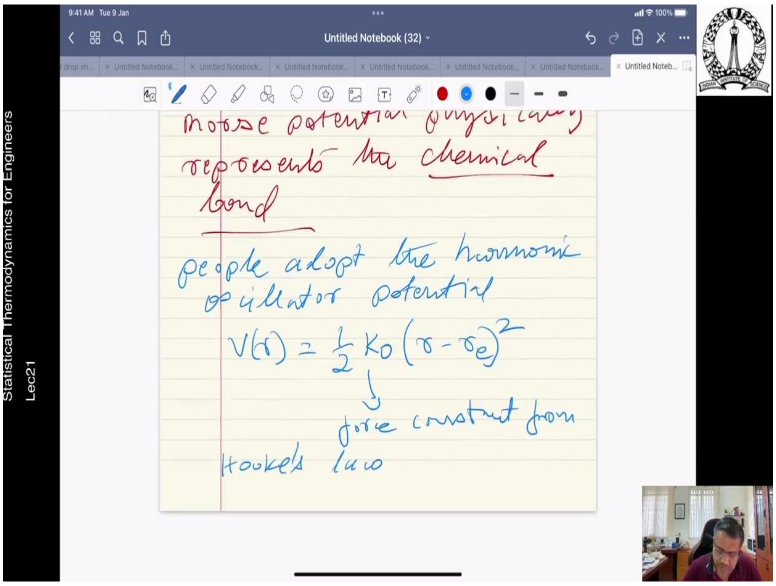


morse potential physically represents the chemical bond



morse potential physically represents the chemical bond

people adopt the harmonic oscillator potential

$$V(r) = \frac{1}{2} K_0 (r - r_e)^2$$

force constant from Hooke's law

So, let us look at this. This is the r. So, this is re, this is basically your Da. So, you need a fitting parameters actually or it is internuclear distance. So, the morse potential basically what does morse potential actually mean? So, morse potential physically represents the chemical bond. But it is hard to deal with. So, people adopt something which is a little bit easier to handle. So, people adopt the harmonic oscillator potential. It is easier to handle so to say. So, it is much easier to handle. So, VR is therefore written as half K naught r minus re square is K is like a spring constant, force constant. So, this is like a force constant K naught which comes from hooke's law.

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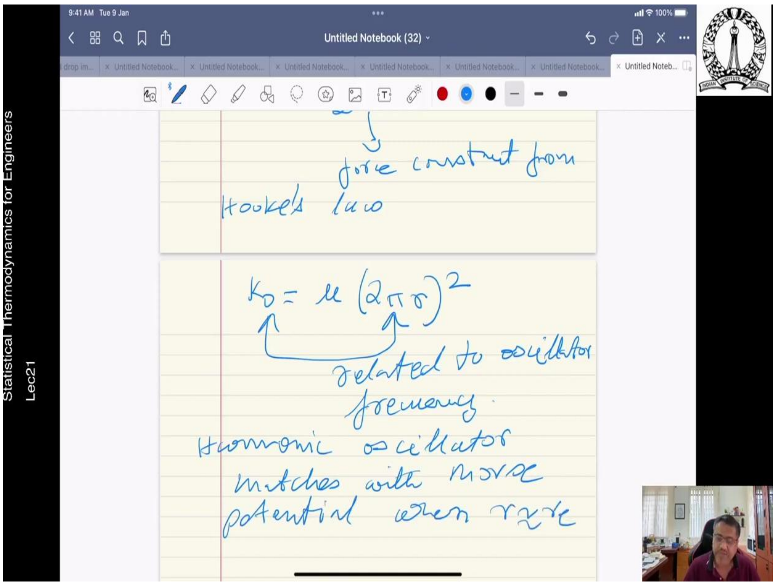

force constant from Hooke's law

$$K_0 = \mu (2\pi r)^2$$

related to oscillator frequency

Harmonic oscillator matches with morse potential when $r \approx r_e$

So, hooke's law means K not, now given as mu 2 pi r square. So, this is actually related to the oscillator frequency. So, the harmonic oscillator matches with the morse potential. So, this harmonic oscillator matches with Morse potential, when r is closer to re. So, around the equilibrium intramolecular distance, so, this is that.

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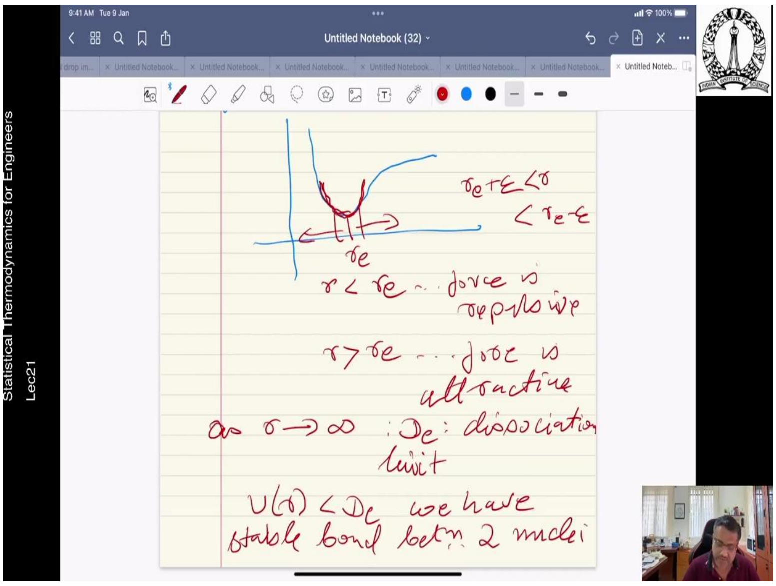

$r_e + \varepsilon < r < r_e - \varepsilon$

$r < r_e$ … force is repulsive

$r > r_e$ … force is attractive

as $r \to \infty$: D_e : dissociation limit

$U(r) < D_e$ we have stable bond betn 2 nuclei

So, this is the morse potential, harmonic oscillator will somewhat like here. So, in this zone, which is around re, it is going to be valid. So, re plus epsilon r is less than, something like that. So, this is valid. So, what we can see is that if r is less than re, the force is repulsive. When you go to this direction, force is repulsive; when r is greater than re you go in this particular direction, force is attractive and as r goes to infinity then we reach the which is called dissociation limit. That means, the bond is broken, dissociation limit, the bond is basically broken. So, if your Vr is less than De, we have stable bond between 2 nuclei.

Do you understand the nuclei? So, here it is repulsive, here it is attractive. So, if you go beyond a certain level right around here, it is lead to dissociation limit. So, normally when your Vr or your potential energy is less than d, d remember is that value is actually much less than d, we have a stable bond between 2 nuclei. So, when you supply excessive energy what happens is that you carry the risk of dissociation.

And we are dealing with a harmonic oscillator which only agrees within a small space around this equilibrium internuclear distance and that is represented by essentially a spring constant type of thing. So, and this is required because we need an expression for the potential function. So, in the next class we are going to see where this activity leads us, in the subsequent chapters, in the subsequent classes we will see where does it lead us. Thank you.