Statistical Thermodynamics for Engineers
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Lecture 32
Hermite Polynomials as Vibrational Energy Mode Solution

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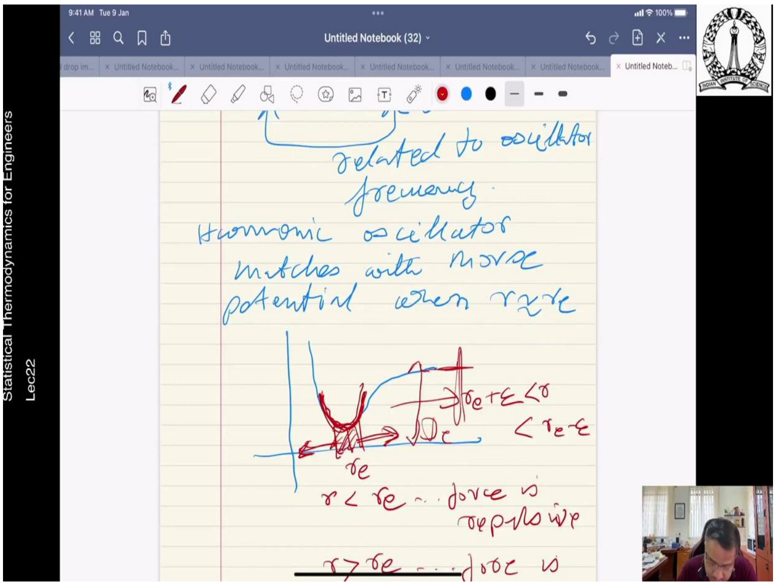
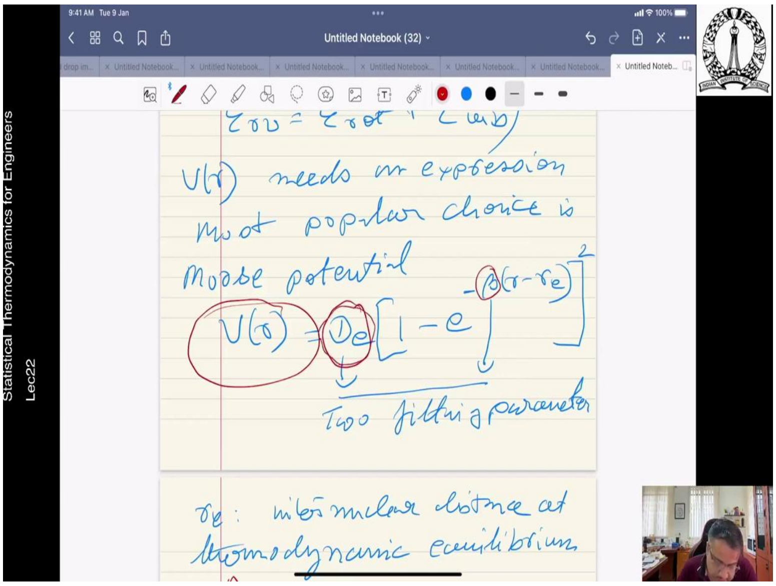


related to oscillator frequency.

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

$r < r_e$ … force is repulsive

$r > r_e$ … force is



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

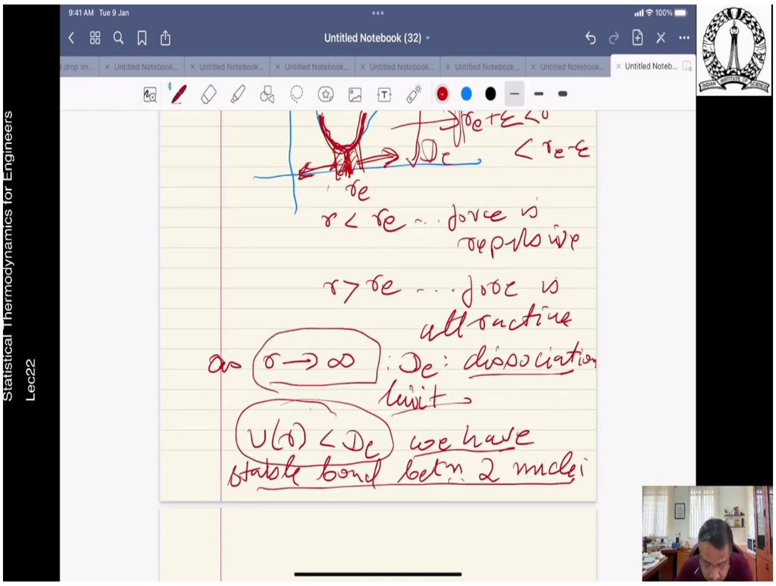
V(r) needs an expression

Most popular choice is Morse potential

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

Two fitting parameter

r_e: internuclear distance at thermodynamic equilibrium



$r < r_e$ ... force is repulsive

$r > r_e$ ... force is attractive

as $\boxed{r \to \infty}$: D_e : dissociation limit

$\boxed{U(r) < D_e}$ we have stable bond betn 2 nuclei

Welcome to lecture number 22 of this Statistical Thermodynamics for Engineers. So, previously in the previous section we found out that when you analyze the vibrational mode of energy we can use something called harmonic oscillator which is close to the actual morse potential. In the morse potential if you recall is given by these two fitting parameters out of that this parameter De is particularly important because it designates the dissociation potential.

So, the harmonic oscillator works very well when the distance r is within a particular band of the equilibrium inter nuclear radii in the nuclear distance and when r goes to infinity you have the dissociation. So, normally when your potential is less than De we have a stable bond between the two nuclei concerned.

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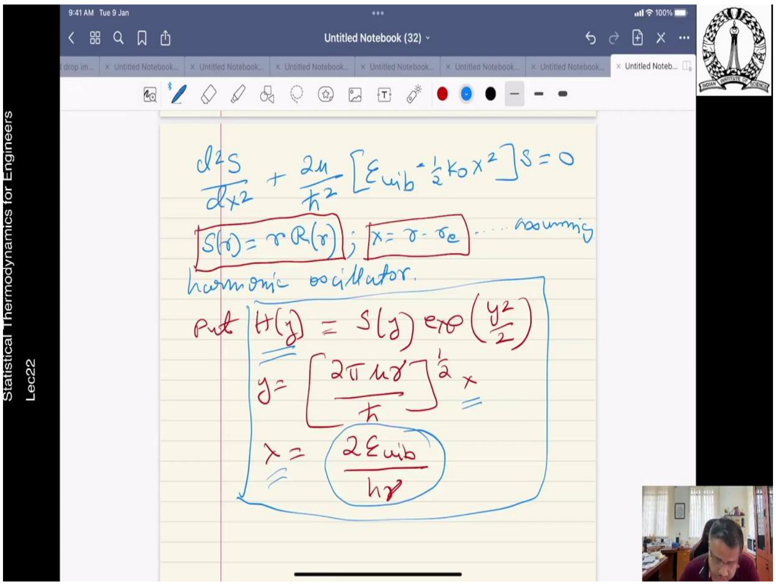


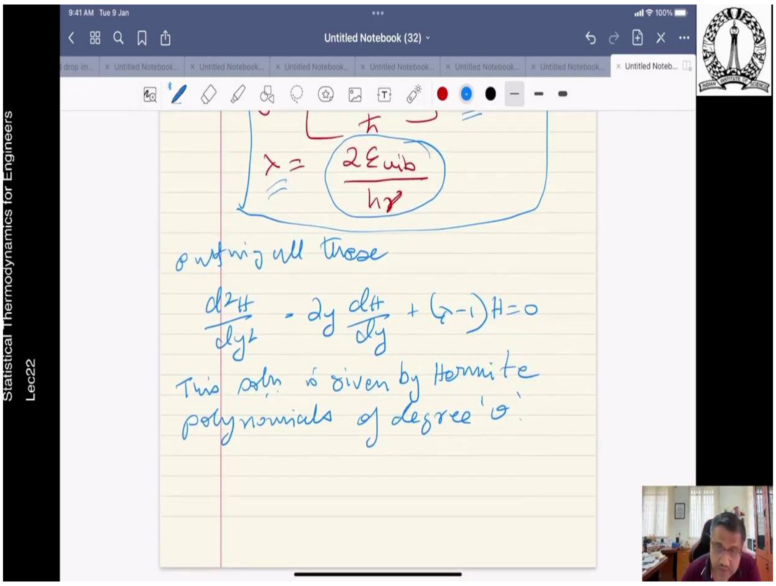
$$\frac{d^2S}{dx^2} + \frac{2\mu}{\hbar^2}\left[\mathcal{E}_{vib} - \frac{1}{2}k_0 x^2\right]S = 0$$

$\boxed{S(r) = rR(r)}$; $\boxed{x = r - r_e}$ …. assuming harmonic oscillator.

Put $H(y) = S(y)\exp\left(\frac{y^2}{2}\right)$

$$y = \left[\frac{2\pi\mu\nu}{\hbar}\right]^{\frac{1}{2}} x$$

$$\lambda = \boxed{\frac{2\mathcal{E}_{vib}}{h\nu}}$$



putting all these

$$\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (\lambda - 1)H = 0$$

This soln is given by Hermite polynomials of degree 'v'

So, let us now analyze the vibrational mode. So, this is given as d square dx(())(01:16) square plus 2 mu h square bar E vibrational minus half k naught into x square into S is equal to 0 where S is capital R. And x is r minus r e this is all assuming harmonic oscillator. So, we assume harmonic oscillator and therefore this is the expression that we will write. So, this is basically your Sr and this is basically your x. So, now put Hy is equal to Sy exponential y square by 2. So, y is equal to 2 pi mu r divided by h bar half into x and lambda is equal to 2 E vibrational divided by h mu.

So, if we put all these things now in these expression. So, you have now we proposed three things. We have proposed that H is equal to S y into exponential we have put y is equal to 2 pi mu frequency divided by h bar into x and then we have put lambda is equal to this. So, this is like a wavelength so lambda is equal to this. So, as you can see over here now putting all these things together you have d square H by d y square minus 2 y d H by d y plus lambda minus 1 into H is equal to 0. So, this is the expression which is the reduced form of expression after we applied all the variable changes. So, this solution is given by hermite polynomials of degree let us assume v.

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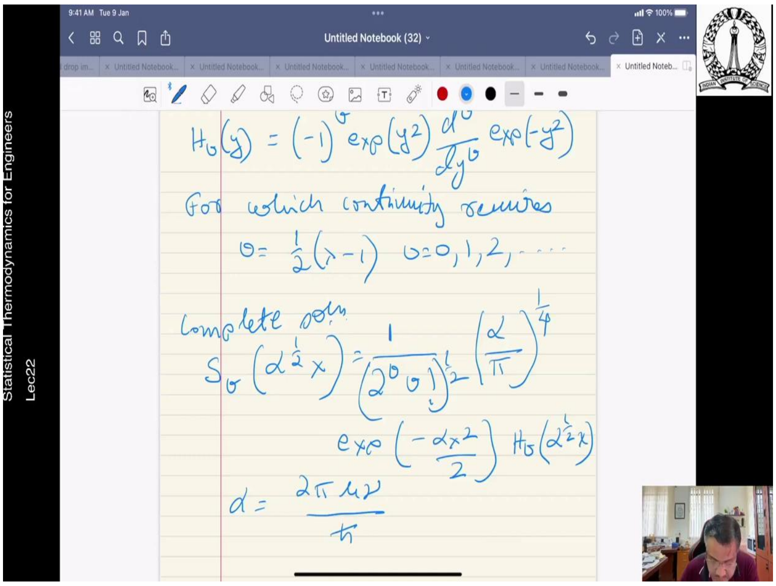


$H_v(y) = (-1)^v \exp(y^2) \frac{d^v}{dy^v} \exp(-y^2)$

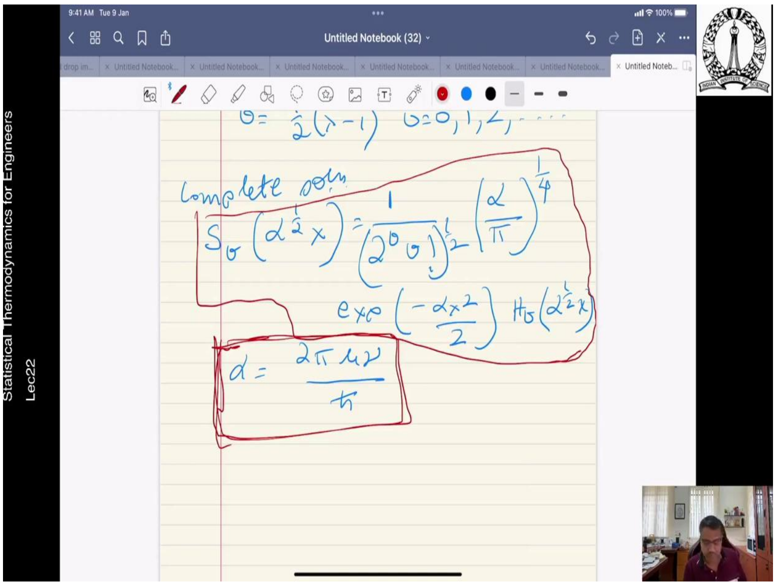
For which continuity requires

$v = \frac{1}{2}(\lambda - 1) \quad v = 0, 1, 2, \ldots$

Complete soln

$S_v(\alpha^{\frac{1}{2}} x) = \frac{1}{(2^v v!)^{\frac{1}{2}}} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\alpha x^2}{2}\right) H_v(\alpha^{\frac{1}{2}} x)$

$\alpha = \frac{2\pi \mu \nu}{\hbar}$



$v = \frac{1}{2}(\lambda - 1) \quad v = 0, 1, 2, \ldots$

Complete soln

$S_v(\alpha^{\frac{1}{2}} x) = \frac{1}{(2^v v!)^{\frac{1}{2}}} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\alpha x^2}{2}\right) H_v(\alpha^{\frac{1}{2}} x)$

$\alpha = \frac{2\pi \mu \nu}{\hbar}$

So, the solution to this particular equation is again ODE second order. So, Hv y minus 1 v exponential y square d v divided by y v exponential minus y square, for continuity for which continuity requires v equal to half lambda minus 1, v equal to 0, 1, 2 dot, dot. So, this is called the hermite polynomials of degree v.

So, the complete solution is S v lambda half into x 1 over 2 v v factorial into half alpha by pi raise to the power one forth exponential alpha x square by 2 multiplied by hermite polynomial alpha half x where alpha is given as 2 pi nu gamma divided by h bar. So, this is the total expression that you get and this is the expression for your alpha where alpha is 2 pi nu frequency divided by h bar. So, we get the point now.

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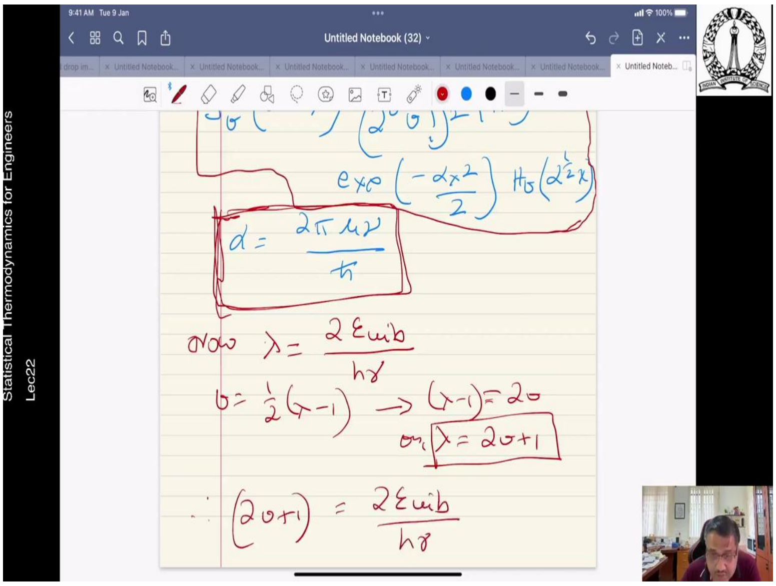


$$\exp\left(-\frac{\alpha x^2}{2}\right) H_v\left(\alpha^{\frac{1}{2}} x\right)$$

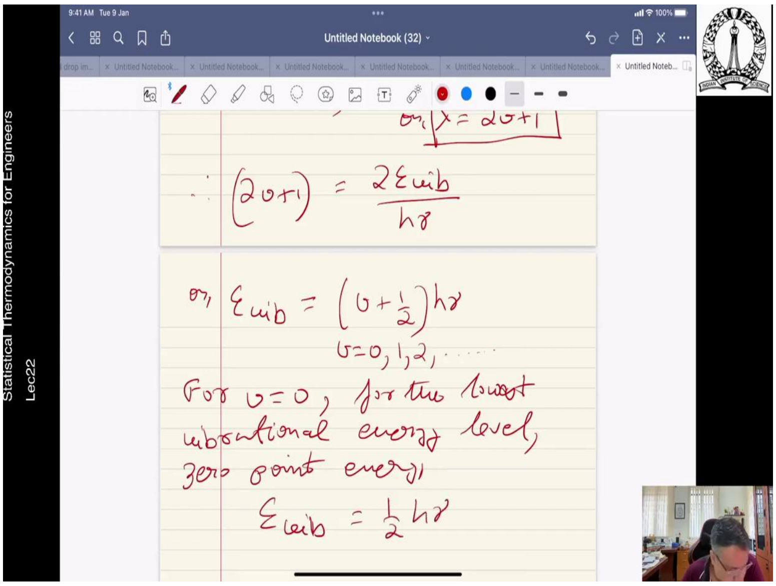
$$\boxed{\alpha = \frac{2\pi\mu\nu}{\hbar}}$$

now $\lambda = \frac{2\varepsilon_{vib}}{h\nu}$

$v = \frac{1}{2}(\lambda - 1) \rightarrow (\lambda - 1) = 2v$

or, $\boxed{\lambda = 2v+1}$

$\therefore (2v+1) = \frac{2\varepsilon_{vib}}{h\nu}$



$\therefore (2v+1) = \frac{2\varepsilon_{vib}}{h\nu}$

or, $\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu$

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

For $v = 0$, for the lowest vibrational energy level, zero point energy

$\varepsilon_{vib} = \frac{1}{2} h\nu$

So, now your lambda is 2 vibrational level divided by h nu. So, v is equal to half lambda minus 1 which leads to the facts that lambda minus 1 is equal to 2 v or lambda equal to 2 v plus 1. So, therefore 2 v plus 1 is equal to 2 vibrational divided by h nu or E vibrational is equal to v plus half h nu v is equal to 0, 1, 2 dot, dot. So, for v is equal to 0 that is for the lowest vibrational energy level zero-point energy is E vibrational into half h nu.

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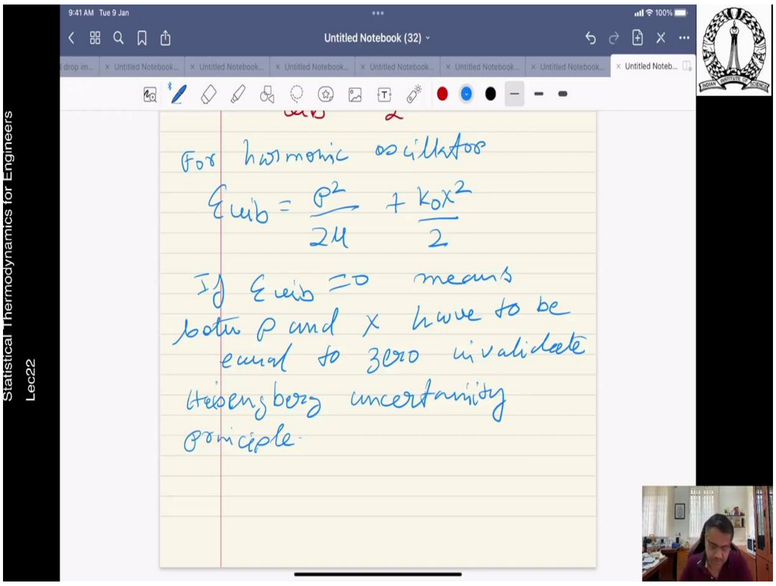
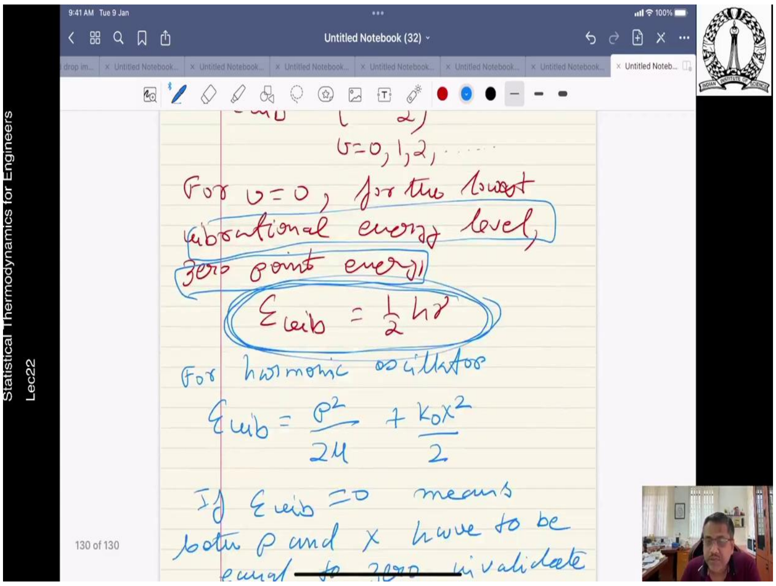


For harmonic oscillator

$\varepsilon_{vib} = \frac{p^2}{2\mu} + \frac{k_0 x^2}{2}$

If $\varepsilon_{vib} = 0$ means both p and x have to be equal to zero invalidate Heisenberg uncertainity principle



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

For $\upsilon = 0$, for the lowest vibrational energy level, zero point energy

$\boxed{\varepsilon_{vib} = \frac{1}{2}h\nu}$

For harmonic oscillator

$\varepsilon_{vib} = \frac{p^2}{2\mu} + \frac{k_0 x^2}{2}$

If $\varepsilon_{vib} = 0$ means both p and x have to be equal to zero invalidate

So, for the harmonic oscillator E vibrational is equal to p square by 2 mu plus K naught x square by 2. Now, if E vibrational was equal to 0 say for example means both p and x both have to be equal to 0, if that was true then this will invalidate Heisenberg’s uncertainty principle so that is why the vibrational energy cannot be equal to 0. So, the zero-point energy if you look at it for the lowest vibrational level is always half h mu.

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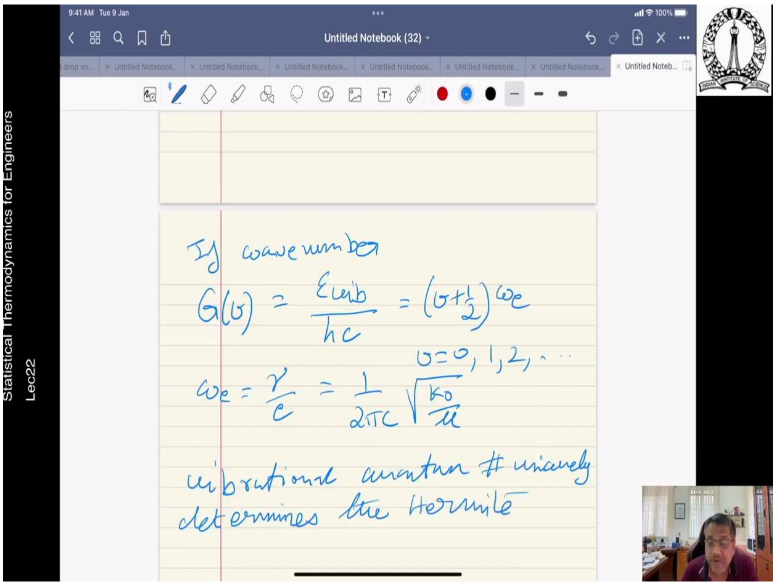


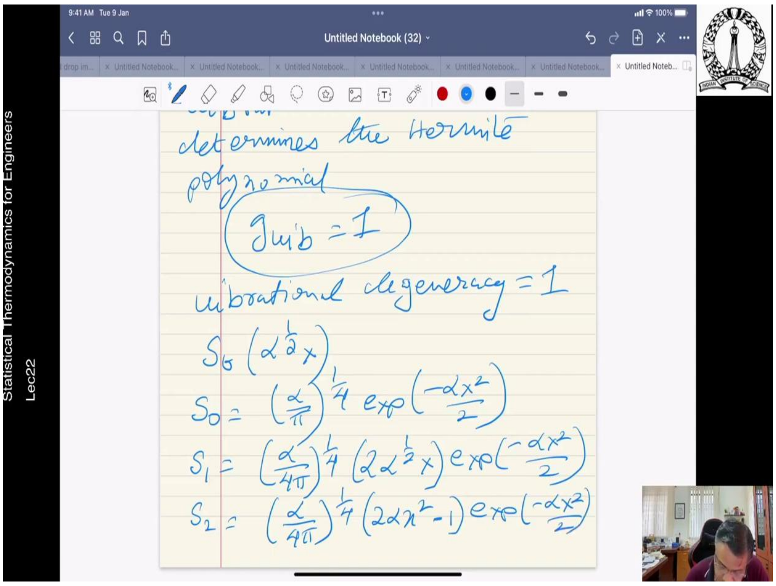
In wavenumber

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

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

$$\omega_e = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}}$$

vibrational quantum # uniquely determines the Hermite



determines the Hermite polynomial

$$\boxed{g_{vib} = 1}$$

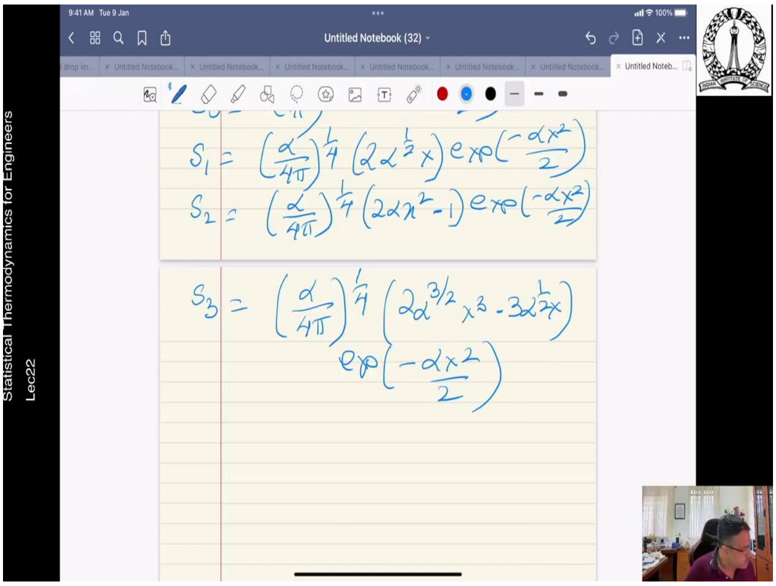
vibrational degeneracy = 1

$$S_v\left(\alpha^{\frac{1}{2}}x\right)$$

$$S_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(\frac{-\alpha x^2}{2}\right)$$

$$S_1 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \left(2\alpha^{\frac{1}{2}}x\right) \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$S_2 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \left(2\alpha x^2 - 1\right) \exp\left(\frac{-\alpha x^2}{2}\right)$$



$$S_1 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}}\left(2\alpha^{\frac{1}{2}}x\right)\exp\left(-\frac{\alpha x^2}{2}\right)$$

$$S_2 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}}\left(2\alpha x^2-1\right)\exp\left(-\frac{\alpha x^2}{2}\right)$$

$$S_3 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}}\left(2\alpha^{3/2}x^3-3\alpha^{\frac{1}{2}}x\right)\exp\left(-\frac{\alpha x^2}{2}\right)$$

So, if wave number is G v let us put it as G v vibrational divided by h c that is equal to v plus half into omega e v equal to once again 0, 1, 2 dot, dot. Omega e is equal to gamma by c which is nothing, but the frequency k naught is like the spring constant equal to that. So, this is in the wave number space. So, vibrational quantum number uniquely determines the hermite polynomial or in other words the g vibration is equal to 1.

That essentially means that the degeneracy is 1 vibrational degeneracy is equal to 1. There is only one type of way that you can have a vibrational world. So, if you look at now few of these vibrational solutions of is v of a half into x if you look at some of the solutions like for example S naught. S naught will be alpha by pi one forth exponential minus alpha x square by 2 S 1 which is alpha by 4 pi one forth that is equal to 2 alpha by half into x exponential minus alpha x square by 2.

S 2 is equal to alpha by 4 pi into one forth then 2 alpha x square minus 1, exponential minus alpha x square by 2 and S 3 is equal to alpha by 4 pi one forth into 2 alpha 3 by 2 x cube minus 3 alpha half into x exponential minus alpha x square by 2. So, these are the few solutions of this vibrational, first few solutions for the harmonic oscillator model. So, now let us look at the kind of a roadmap.

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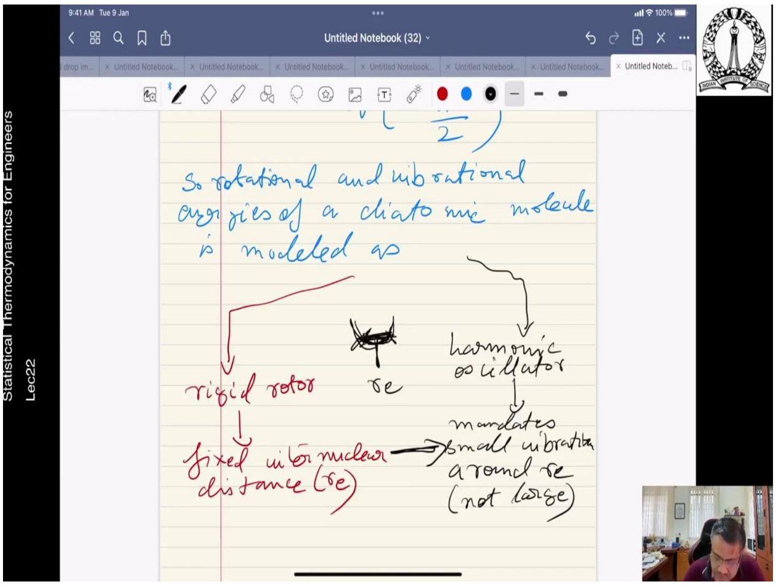


So rotational and vibrational energies of a diatomic molecule is modeled as

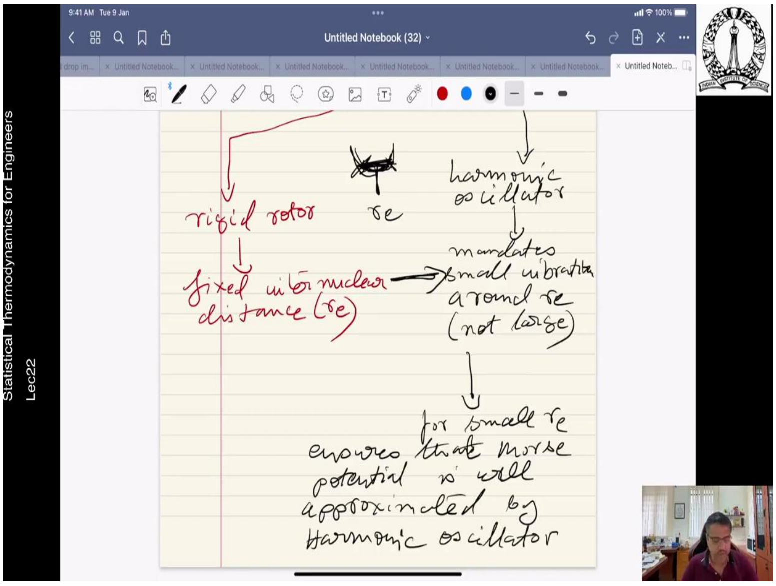
rigid rotor

re

harmonic oscillator

fixed inter nuclear distance (re)

mandates small vibration around re (not large)



rigid rotor

re

harmonic oscillator

fixed inter nuclear distance (re)

mandates small vibration around re (not large)

for small re ensures that morse potential is well approximated by harmonic oscillator

So, rotational and vibrational energies of a diatomic molecule is modeled as... We can have this (())(15:07). So, this is the rigid rotor which translates to fixed inter nuclear distance is re and on the other side you have the harmonic oscillator which basically it mandates what is this mandate? Mandate small vibration around re, remember small vibrations not large. So, this fits nicely into that.

Around re if this is re this is the well… so it is just vibrates around this particle level within a particular band. So, what it implies is that small re for small re ensures that most potentials is well approximated by a harmonic oscillator and that is in general that is it ties very well with the rigid rotor model because r is fixed invariant and therefore there is only a small amount of oscillations about r that is what ensures that it is oscillation is kind of well behaved.

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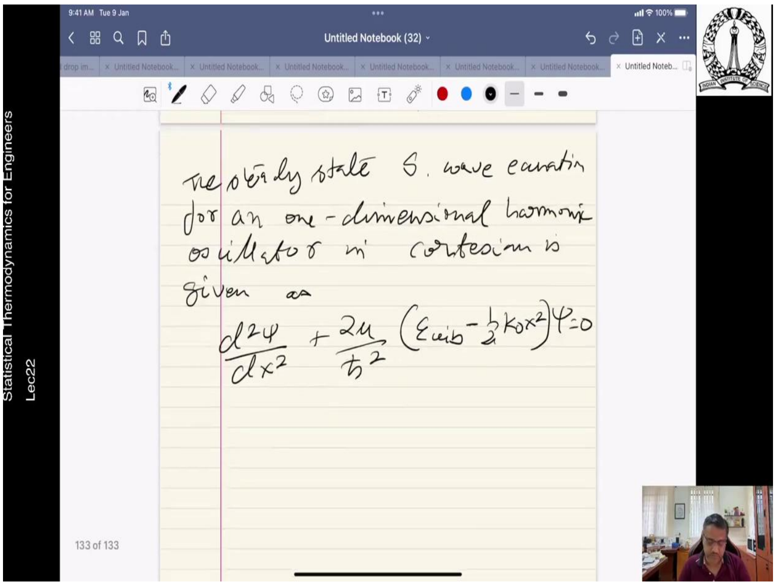
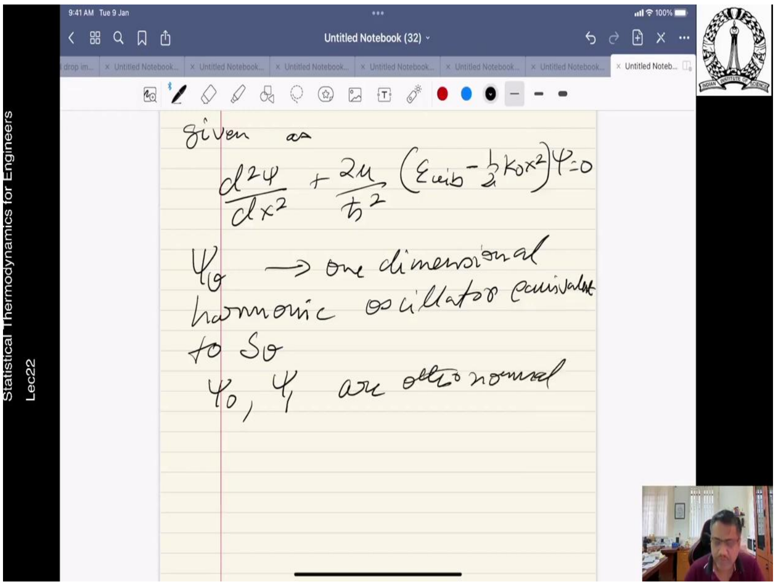


The steady state S. wave equation for an one-dimensional harmonic oscillator in cartesian is given as

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(\varepsilon_{vib} - \frac{1}{2}k_0x^2\right)\psi = 0$$

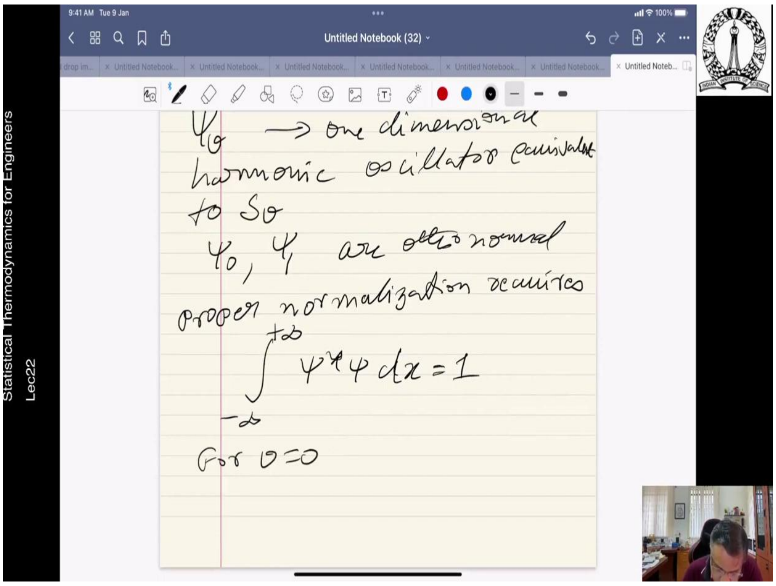


given as

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(\varepsilon_{vib} - \frac{1}{2}k_0x^2\right)\psi = 0$$

ψ_θ → one dimensional harmonic oscillator equivalent to S_θ

ψ_0, ψ_1 are orthonormal



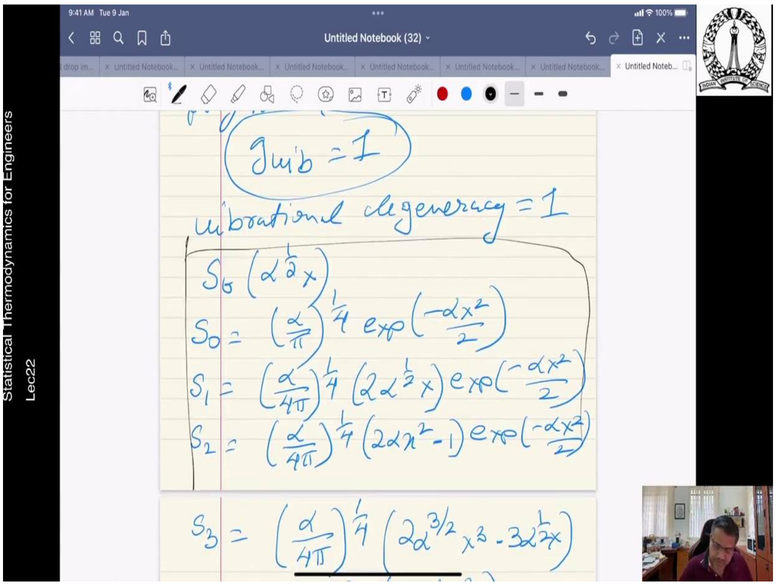
$\psi_v \rightarrow$ one dimensional harmonic oscillator equivalent to S_v

ψ_0, ψ_1 are orthonormal

proper normalization requires

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dx = 1$$

For $v=0$



$\boxed{g_{vib} = 1}$

vibrational degeneracy = 1

$S_v(\alpha^{\frac{1}{2}} x)$

$S_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\alpha x^2}{2}\right)$

$S_1 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \left(2\alpha^{\frac{1}{2}} x\right) \exp\left(-\frac{\alpha x^2}{2}\right)$

$S_2 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \left(2\alpha x^2 - 1\right) \exp\left(-\frac{\alpha x^2}{2}\right)$

$S_3 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \left(2\alpha^{3/2} x^3 - 3\alpha^{\frac{1}{2}} x\right)$

So, that brings us… we will do one more small example say for a one dimensional the steady state so it will be a wave equation or for an one dimensional harmonic oscillator in Cartesian is given as one degree of freedom one dimensional psi divided by x square plus 2 mu h bar E vibrational minus half k naught x square psi is equal to 0.

So, hence the wave function is basically sigma v describing the one dimensional a harmonic oscillator. It describes the one-dimensional harmonic oscillator equivalent to S v. So, we want you to show that psi naught and psi 1 are orthogonal. So, first and foremost proper normalization requires minus infinity to plus infinity psi star psi d(())(19:58) x which is equal to 1. So, if you just look at the numbers that we just pulled out these numbers you just look at those numbers over here what you have for v is equal to 0.

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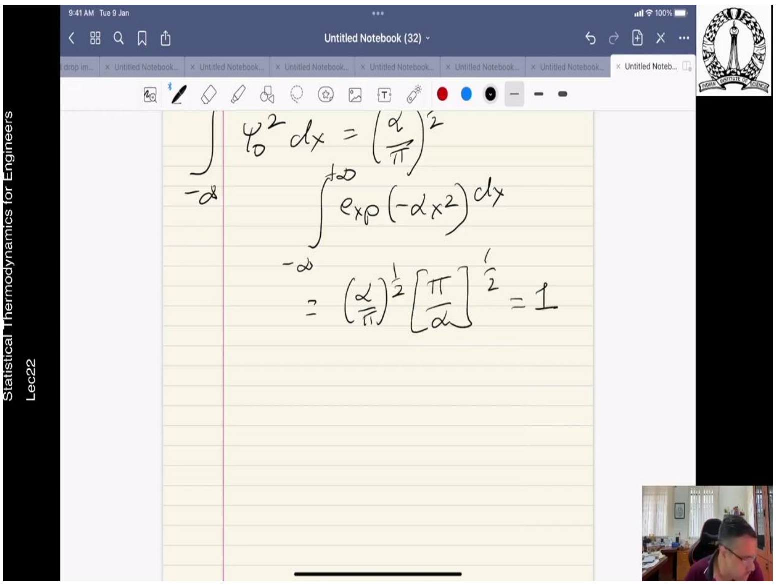
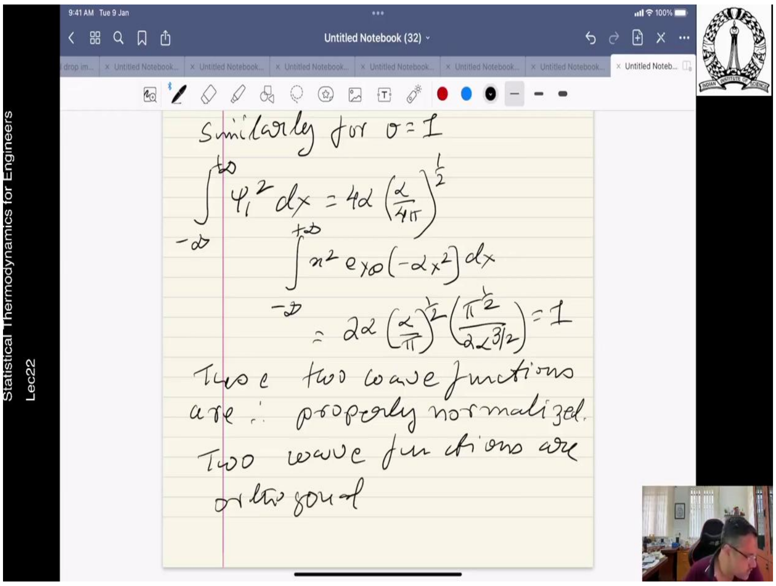


$$\int_{-\infty} \psi_0^2\,dx = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \exp(-\alpha x^2)\,dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \left[\frac{\pi}{\alpha}\right]^{\frac{1}{2}} = 1$$



Similarly for $v = 1$

$$\int_{-\infty}^{+\infty} \psi_1^2\,dx = 4\alpha\left(\frac{\alpha}{4\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2)\,dx$$

$$= 2\alpha\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\left(\frac{\pi^{\frac{1}{2}}}{2\alpha^{3/2}}\right) = 1$$

These two wave functions are $\therefore$ properly normalized.

Two wave functions are orthogonal

Integral will be psi square d x which is equal to alpha divided by pi into half. Writing the integral below plus infinity exponential minus alpha x square d x. So, this translates to if we do the integration of alpha by pi half pi by alpha half this is equal to 1. Similarly, for v is equal to 1 that is the second wave function that is minus infinity to plus infinity psi 1 square d x equal to 4 alpha by 4 pi raise to the power half. Again, we are writing the integral next line minus infinity to plus infinity x square exponential minus x square into d x.

This is equal to 2 alpha by pi half pi half 2 alpha 3 by 2 equal to 1. So, the two wave functions are properly normalized. So, now they are least two wave functions are therefore properly normalized that is good. So, now we recall that if two wave functions are orthogonal if they are orthogonal.

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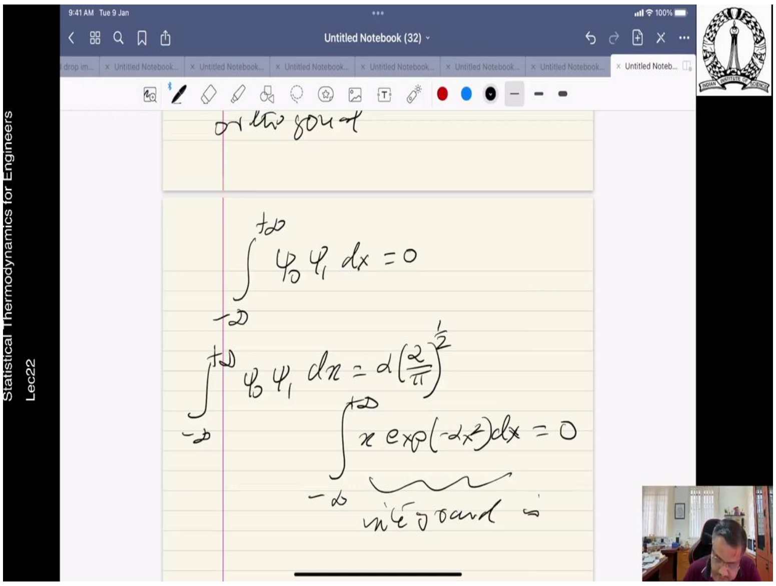
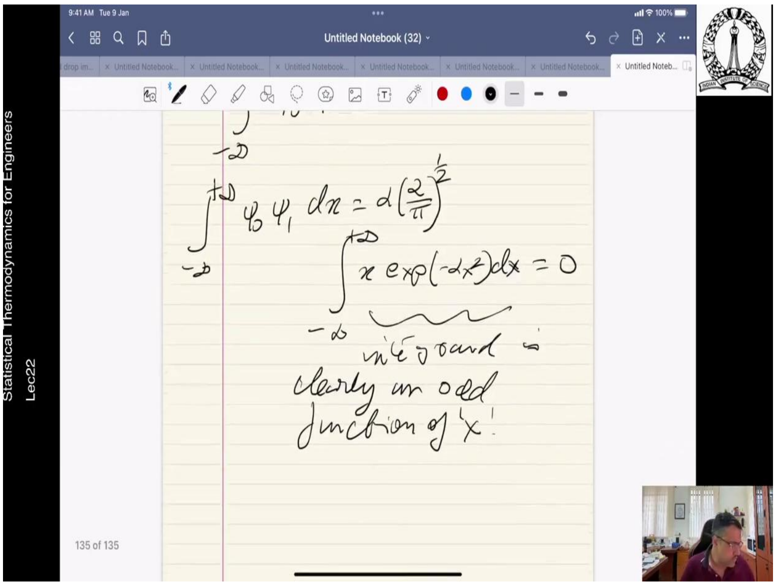


or the ground

$$\int_{-\infty}^{+\infty} \psi_0 \psi_1 \, dx = 0$$

$$\int_{-\infty}^{+\infty} \psi_0 \psi_1 \, dx = \alpha \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \underbrace{x \exp(-\alpha x^2)}_{\text{integrand is}} dx = 0$$



$$\int_{-\infty}^{+\infty} \psi_0 \psi_1 \, dx = \alpha \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \underbrace{x \exp(-\alpha x^2)}_{\text{integrand is}} dx = 0$$

clearly an odd function of 'x'!

So, if you take the product the two bringing this case that means from minus infinity to plus infinity it should be 0 psi 1 into d x should be equal to 0. So, what we can do is therefore multiply the wave functions. So, therefore we evaluate plus minus psi naught into psi 1 x which is equal to now alpha 2 by pi raise to the power of half you know I am writing the integral in the next line plus minus infinity exponential x into exponential minus half by x square into d x is therefore equal to 0 if we can validate this integrand is what is clearly a odd function x with the integrand is clearly an odd function of x. So, this kind of shows that this is how you analyze. So, we have seen that how the vibrational energy and the rotational energy and the translational energy can be done.

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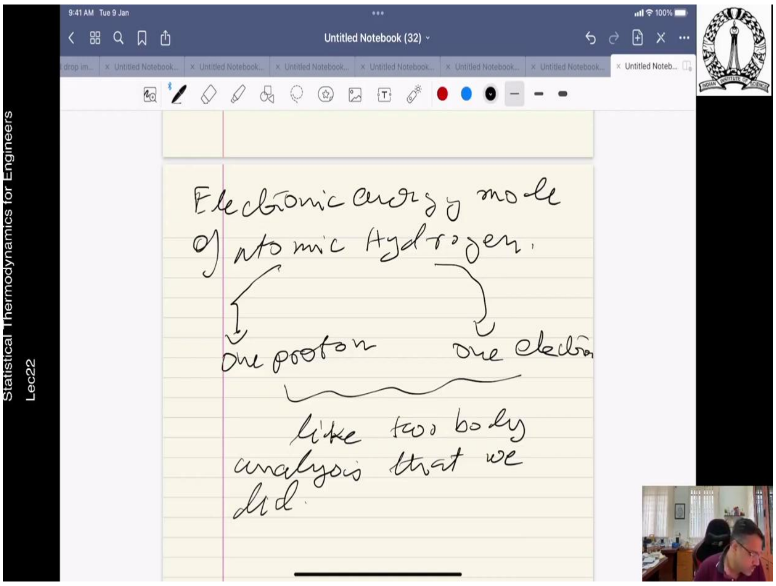
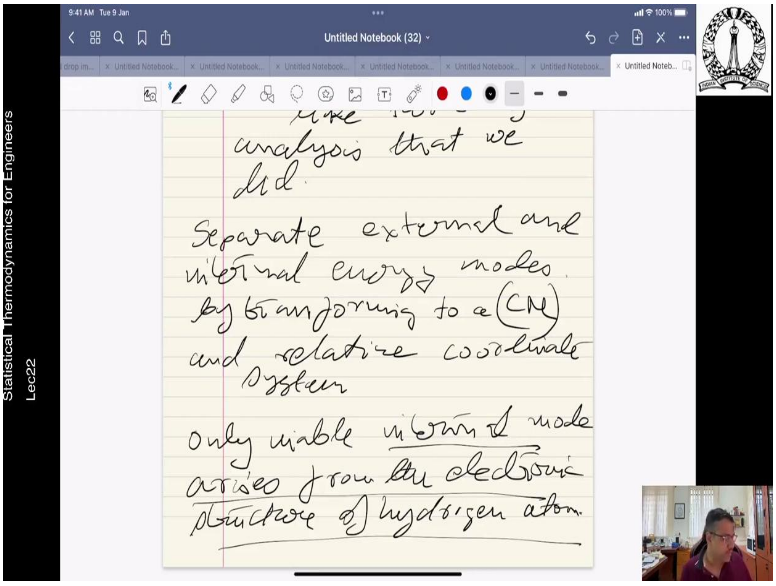


Electronic energy mode of atomic Hydrogen.

One proton

One electron

like two body analysis that we did.



analysis that we did.

Separate external and internal energy modes by transforming to a (CM) and relative coordinate system

Only viable internal mode arises from the electronic structure of hydrogen atom.

Now, we can extend this kind of an analysis for the electronic energy mode of atomic hydrogen extended. So, atomic hydrogen you know that you have now this rigid rotor, harmonic oscillator the degeneracy you know the energy level you know basically everything.

Now, atomic hydrogen is composed of what? One proton and you have one electron. So, it is almost like the two-body analysis that we did. Therefore, we can again separate the external and the internal energy by transforming to a center of mass and relative coordinate system except here the only viable electronic internal mode arises from the electronic structure of that atomic hydrogen.

So, here also we can do the same thing. We can separate the external and internal energy modes by transforming to a center of mass type of a system and relative coordinate system except you should just note here that one thing that happens that the only viable internal mode arises for the electronic structure of atomic hydrogen, electronic structure of hydrogen atom. So, in the next class what we are going to see we are going to introduce the same separation of variables and kind of try to justify that how this thing can be attained, how this thing can be analyzed further using our knowledge that we gained from the previous analysis. Thank you.