Statistical Thermodynamics for Engineers
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Lecture 33
Equivalent Two Body Model of Atomic Hydrogen

Welcome to lecture number 23 of the Statistical Thermodynamics course for engineers. Now, our analysis of the diatomic molecule as we said earlier has led to very important expressions for the allowed energy levels of the degeneracies which is what is important for the stack of perspective. Now, we begin that how about taking the electronic energy mode and if we take a prototypical system like hydrogen atom, this is a little easier because hydrogen has one proton and an electron and as a matter of fact this is almost we can replicate a very similar analysis like we did for the diatomic counterpart.

Because now, it is also a particle system, it is a two-body analysis. So, again we can separate the external and the internal energy modes by using the centre of mass concept and the relative coordinate system. Except here the only viable internal energy mode arises out of the electronic structure of the hydrogen atom.

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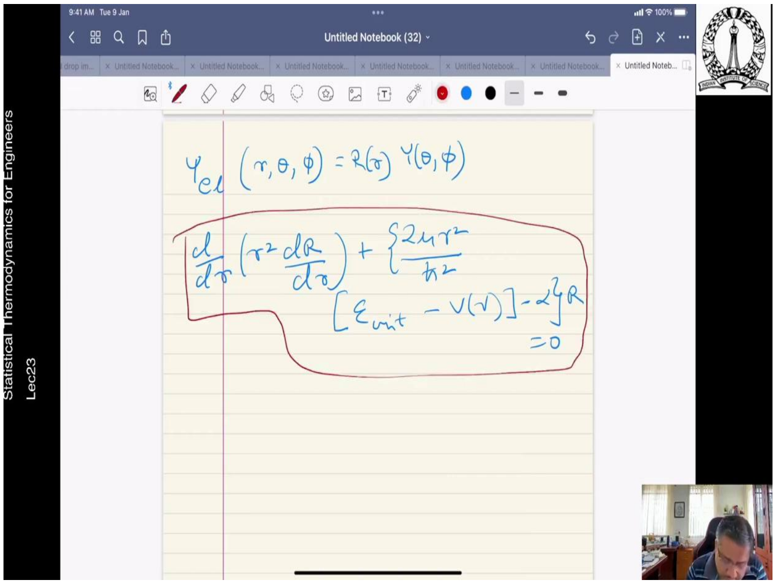

$$\Psi_{el}(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

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

So, what we do now, if you go through the motion that electronic mode which is given as r theta phi, again can be split into two parts R, y eta, phi. Such that once we have done this, we can also now revisit the same equation that we did earlier. So, which is basically let me just recopy the equation over here, because it is easier for everybody to understand. If we looked at this was the parent equation if you recall r square dR by plus here we(())(02:07) brought in the concept of the reduced mass square internal minus Vr minus alpha into R is equal 0. So, this was R equation. This equation now can be reduced in a similar form, we just we can replicate the similar form.

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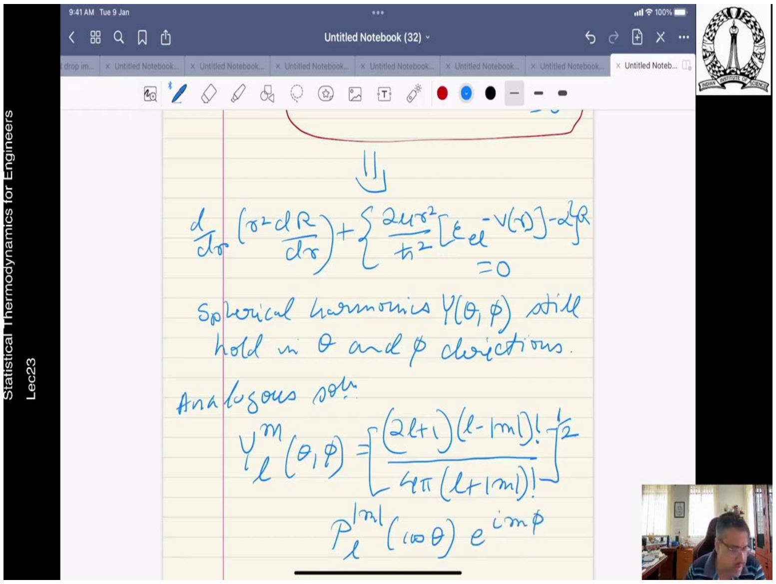

$$\Downarrow$$

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

Spherical harmonics $Y(\theta,\phi)$ still hold in θ and ϕ directions.

Analogous solⁿ:

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

So, this kind of becomes d by dr square dR by dr plus 2 mu r square by h bar square e electronic minus V r minus alpha into R equal to 0. So, here of course, the spherical harmonics Y theta comma phi still hold in theta and phi directions. So, what will happen is that we obtain analogous solution Y.

So, that solution analogous so, what we did for the diatomic particles so, analogous solution it becomes Y ml theta comma phi is equal to 2l plus 1 l minus mod m factorial divided by 4 pi and l plus modulus of m factorial is whole thing is raised to the power half P mod m l cos theta e i m phi. So, this is the analogous solution.

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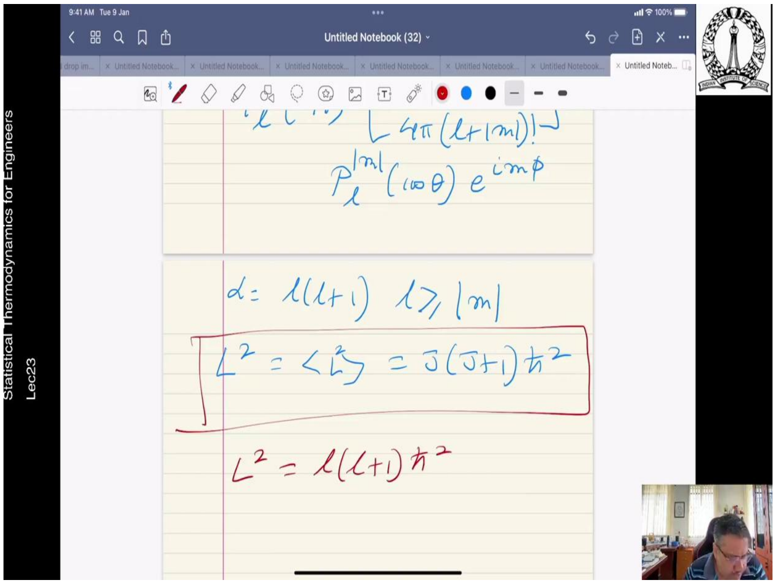


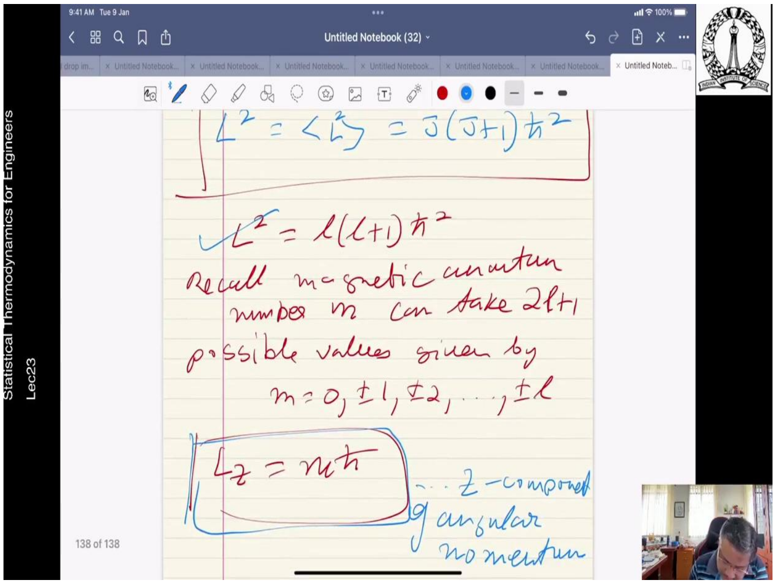
$$[4\pi(l+|m|)!]$$

$$P_l^{|m|}(\cos\theta)\, e^{im\phi}$$

$\alpha = l(l+1)$ $l \geq |m|$

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

$$L^2 = l(l+1)\hbar^2$$



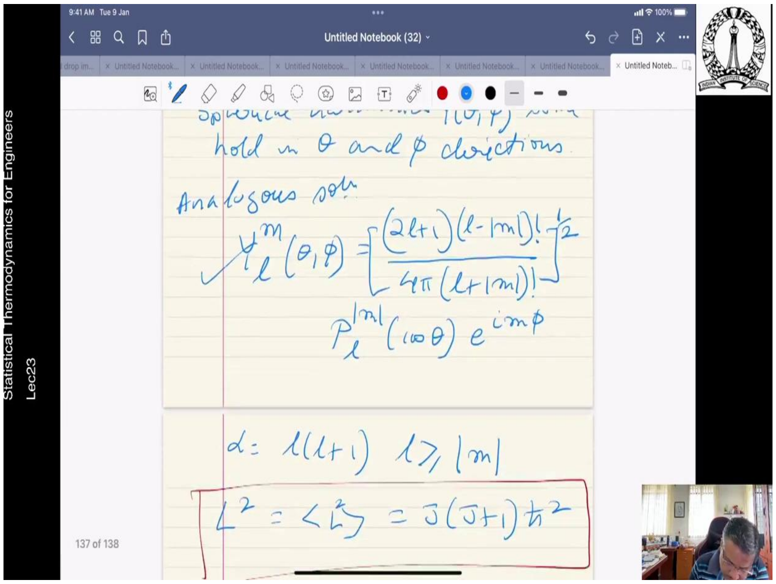
$$\boxed{L^2 = \langle L^2 \rangle = J(J+1)\hbar^2}$$

$$L^2 = l(l+1)\hbar^2$$

Recall magnetic quantum number m can take 2l+1 possible values given by

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

$$\boxed{L_z = m\hbar}$$ … z-component of angular momentum



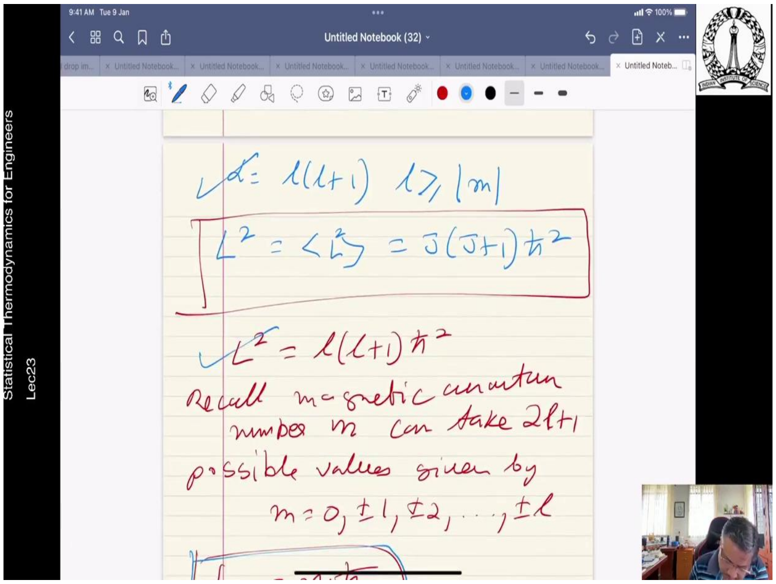
hold in θ and ϕ directions

Analogous soln

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

$\alpha = l(l+1) \quad l \geq |m|$

$$\boxed{L^2 = \langle \hat{L}^2 \rangle = J(J+1)\hbar^2}$$



$\alpha = l(l+1) \quad l \geq |m|$

$$\boxed{L^2 = \langle \hat{L}^2 \rangle = J(J+1)\hbar^2}$$

$L^2 = l(l+1)\hbar^2$

Recall magnetic quantum number m can take $2l+1$ possible values given by

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

And similarly, alpha is equal to l into l plus 1 where l is greater than equal to the mod of m. So, similarly, we introduce the concept of orbital angular momentum by invoking the equations that we did earlier, I will begin recopy the equation, if you recall that L square is L hat square was given as J into J plus 1 into h square bar recall this was from the diatomic counterpart.

So, invoking similar type of equation here now, it will be elsewhere l into l plus 1 into h bar square. So, it is very similar. And we recall that the magnetic quantum number m can take 2l plus 1 possible values given by m equal to 0 plus minus 1, plus minus 2 da da da continue up to plus minus l. So, this was if you recall this also we did it. So, if you recall equation and in from the book it is 6.56.

So, that equation we can replicate. So, again by using the previous forms and once again if you go that your if you recall that we define Lz equal to mh, if you recall this is what we did that the z component of angular momentum. So, this led to the quantization along the z axis if you recall. So, but this time for atomic hydrogen, so, this time it is the same thing now, for atomic hydrogen that we define the z component of the angular momentum and that is quantized in that particular way.

So, based on the above development, the distinctive mathematical feature for atomic hydrogen as compared to diatomic molecule is the radial component of the Schrodinger wave equation. So, let us look at the radial component of the Schrodinger wave equation and see what is new because after this point it is more or less the same this is almost analogous this is absolutely analogous, this is also analogous and the quantization along the z axis is also similar.

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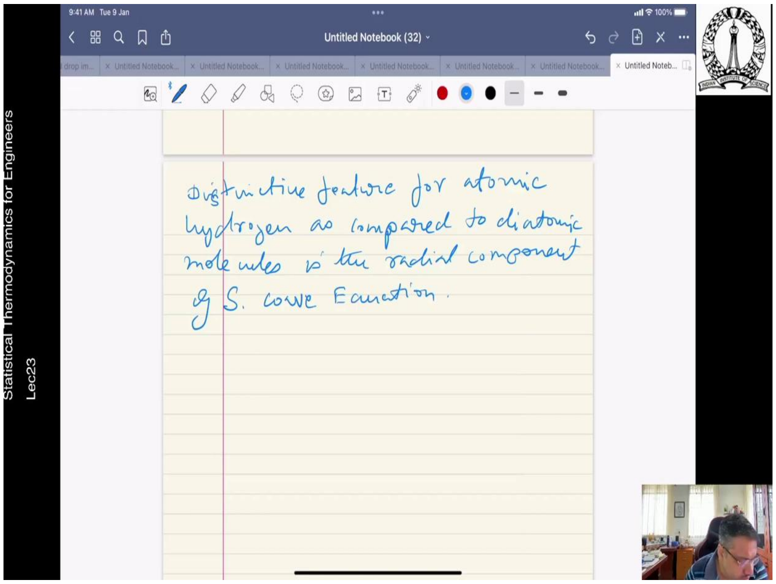
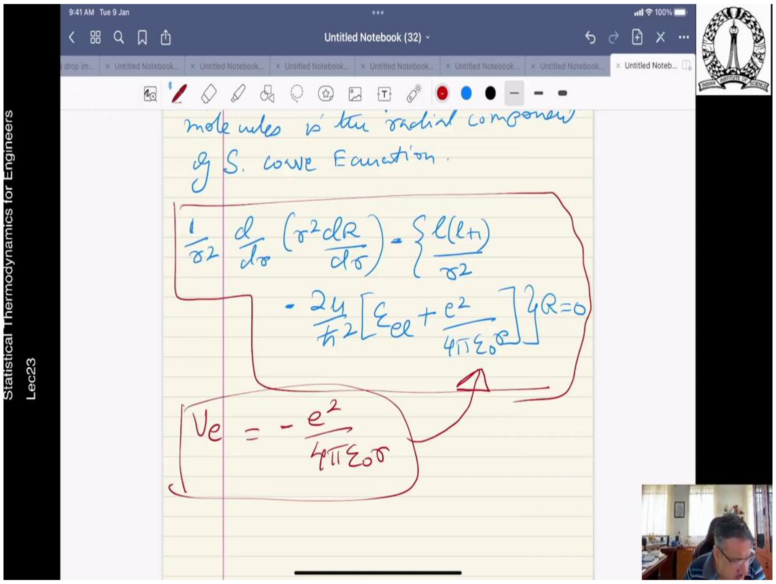


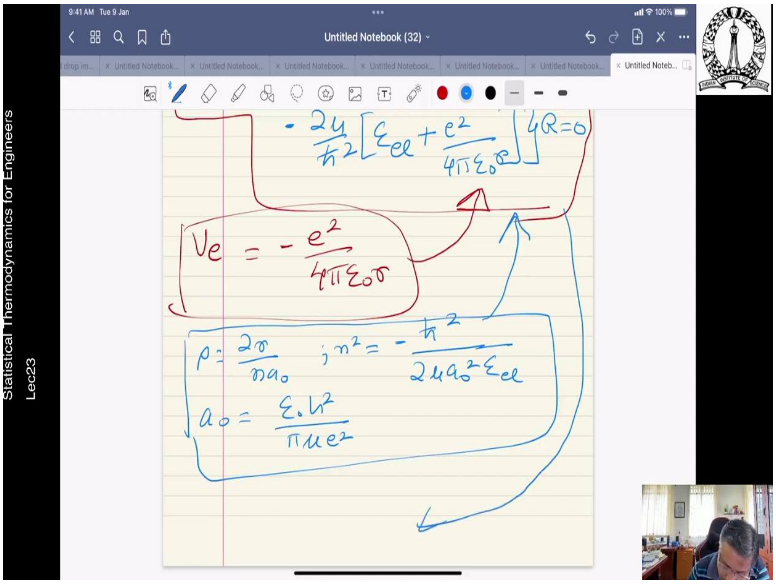
Distinctive feature for atomic hydrogen as compared to diatomic molecules is the radial component of S. wave Equation.



molecules is the radial component of S. wave Equation.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \left\{\frac{\ell(\ell+1)}{r^2} - \frac{2\mu}{\hbar^2}\left[\varepsilon_{el} + \frac{e^2}{4\pi\varepsilon_0 r}\right]\right\}R = 0$$

$$V_e = -\frac{e^2}{4\pi\varepsilon_0 r}$$



$$-\frac{2\mu}{\hbar^2}\left[\varepsilon_{el} + \frac{e^2}{4\pi\varepsilon_0 r}\right]\Bigg\}R = 0$$

$$V_e = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$\rho = \frac{2r}{n a_0}\ ;\ n^2 = -\frac{\hbar^2}{2\mu a_0^2 \varepsilon_{el}}$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2}$$

So, there is no difference between this and diatomic molecule at this particular point. But the distinctive feature comes from the radial component. So, if we write it distinctive feature for atomic hydrogen as compared to two diatomic molecules is the radial component of Schrodinger wave equation. So, what was that. It is d by dr square capital dR by dr minus l into l plus 1 h divided by r square minus 2 mu by h bar square electronic energy plus e square 4 pi r(())(09:54) is equal to 0 this(())(10:01) expression.

So, this expression you can also revisit the previous chapter essential find simply copy this (())(10:17) that if you recall the Ve was equal to minus e square 4 pi epsilon into r. This is what has been used to operate here(())(10:38) that is the potential energy. Because that was a electronic potential energy. So, now so this is a complicated expression now, you can do a few transformations of this equation we are not going to go into the details, but we are going to define a few variables which will kind of make this equation a little bit easier to deal with.

Let us, defined rho is not density it is 2r by n a naught. Then we define n square is equal minus h bar square 2 mu a naught square by the electronic energy and a naught finally is given is this mu square. So, these are the three variables we define and then we use these variables here and transform this equation, how do we transform this equation?

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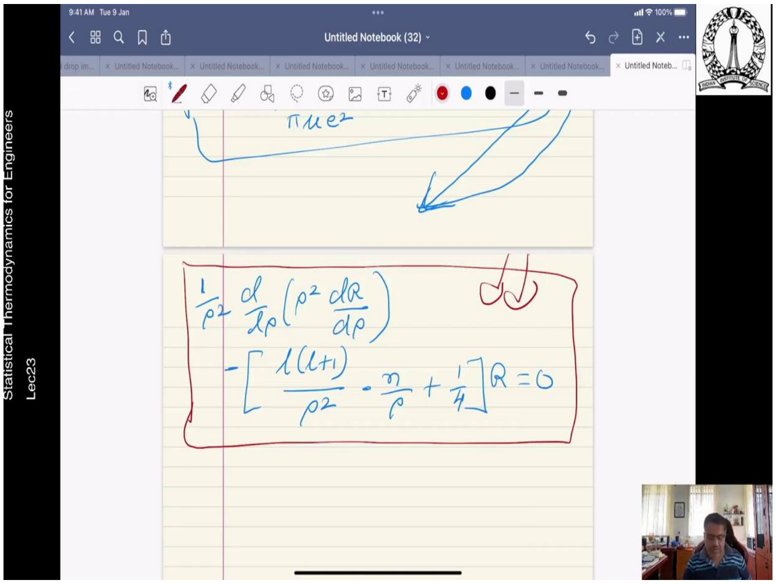
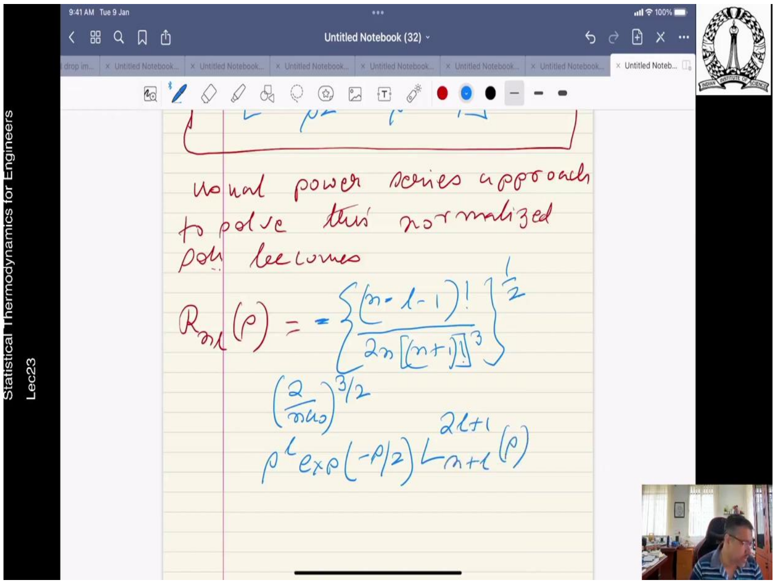
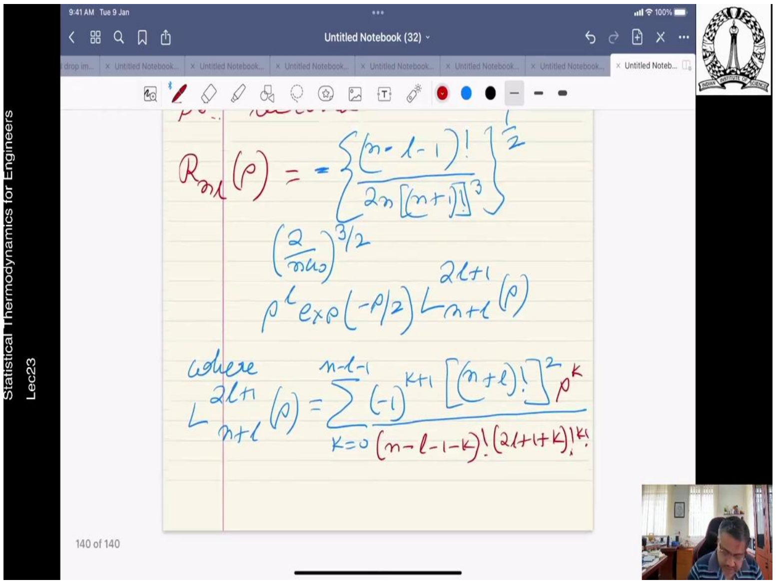


$$\boxed{\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) - \left[\frac{l(l+1)}{\rho^2} - \frac{n}{\rho} + \frac{1}{4}\right]R = 0}$$



usual power series approach to solve this normalized soln becomes

$$R_{nl}(\rho) = -\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{\frac{1}{2}} \left(\frac{2}{na_0}\right)^{3/2} \rho^l \exp(-\rho/2) L_{n+l}^{2l+1}(\rho)$$



$$R_{nl}(\rho) = -\left\{\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{\frac{1}{2}} \left(\frac{2}{na_0}\right)^{3/2} \rho^l \exp(-\rho/2) L_{n+l}^{2l+1}(\rho)$$

where

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1}[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

This equation now become 1 by rho square d by d rho, rho square dR(())(11:52) minus l into l plus 1 rho square minus n by rho plus 1 4th into R is equal to 0. So, this is after a few transformations we use these variables here and then this equation kind of reduces is something like this it reduce to something like this. So, now, what we can do is that we can use the usual power series approach to solve this the normalized solution becomes nl is equal minus this is long expression once again l minus 1 factorial divided 2n into n plus 1 factorial this is raise to the power 3 and then this entire thing is raised to the power half.

In the second term (())(13:52) n a naught raise to the power of 3 by 2 then you have rho l exponential minus rho by 2 L 2l plus 1 m plus l rho where. So, this is a solution where L 2 l plus 1 n plus l rho is equal to summation k equal to 0 n minus l minus 1 minus 1 k plus 1. So, n plus l factorial square divided by n minus l minus 1 minus k factorial 2l plus 1 plus k factorial k factorial and this raise to the power of k.

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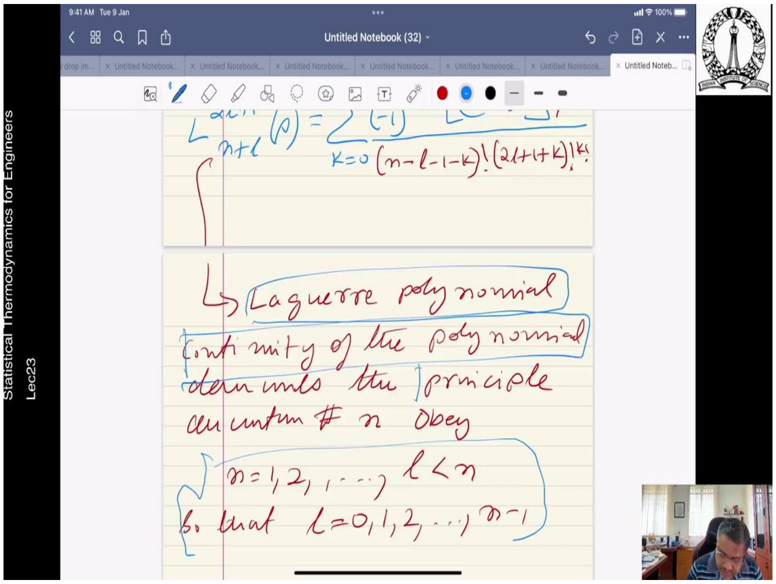


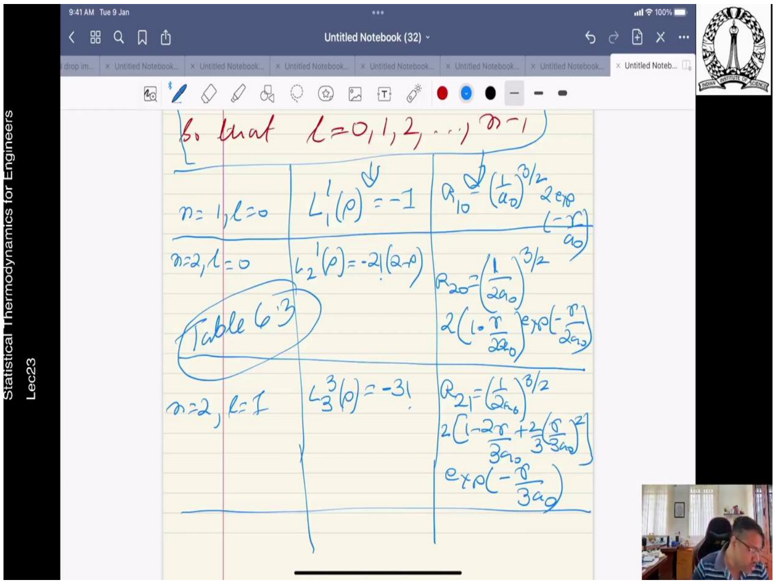
$$L^{2l+1}_{n+l}(\rho) = \sum_{k=0} \frac{(-1)}{(n-l-1-k)!\,(2l+1+k)!\,k!}$$

↳ Laguerre polynomial

Continuity of the polynomial determines the principle quantum # n obey

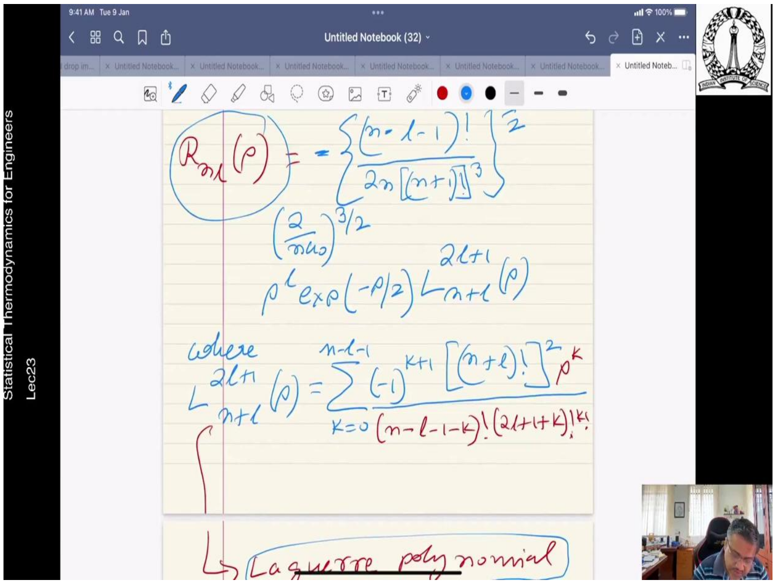
$n = 1, 2, \ldots,\ l < n$

so that $l = 0, 1, 2, \ldots, n-1$



so that $l = 0, 1, 2, \ldots, n-1$

$n = 1, l = 0$	$L^1_1(\rho) = -1$	$R_{10} = \left(\frac{1}{a_0}\right)^{3/2} 2\exp\left(-\frac{r}{a_0}\right)$
$n = 2, l = 0$ Table 6.3	$L^1_2(\rho) = -2!(2-\rho)$	$R_{20} = \left(\frac{1}{2a_0}\right)^{3/2} 2\left(1 - \frac{r}{2a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$
$n = 2, l = 1$	$L^3_3(\rho) = -3!$	$R_{21} = \left(\frac{1}{2a_0}\right)^{3/2} 2\left[1 - \frac{2r}{3a_0} + \frac{2}{3}\left(\frac{r}{3a_0}\right)^2\right] \exp\left(-\frac{r}{3a_0}\right)$



$$R_{nl}(\rho) = -\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2} \left(\frac{2}{na_0}\right)^{3/2} \rho^{l} \exp(-\rho/2) L_{n+l}^{2l+1}(\rho)$$

where

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

$\hookrightarrow$ Laguerre polynomial

This is called this L is called Laguerre Polynomial. The continuity of this polynomial, continuity of the polynomial demands that principal quantum number n obey n equals 1, 2 da da da to l which is less than n. So, l so that l is equal to 0, 1, 2. So, this is what the Laguerre this is given by the Laguerre Polynomial as we said at the continuity of the polynomial demands the principal quantum number obey this set of rules(())(16:49).

So, now, let us look at the table. So, that we can you know first associated the Laguerre Polynomial and the radial functions can be given as. So, this is the radial function, so, n equal to 1, l equal to 0, L which is a Laguerre polynomial 1 1 rho is equal to minus 1 and R 10 is given as 1 over a naught 3 by 2 into two exponential minus r by a naught.

That is a first one so make a table like this, and then n equal to 2, l equal to 0 L 2 1 rho equal to minus 2 factorial 2 minus rho and R 2 0 is given as 1 over 2 a naught to raise to the power of 3 by 2 into 1 minus r by 2 a naught exponential minus by 2 a naught. So, this is the first one, this is the second one.

Similarly, I am just writing one more. So, n equal 2, l equal to 1. So, L 3 3 rho equal to minus 3 factorial and it is given as R 21 which is basically equal to again 1 over 2 a naught 3 by 2 into 2 1 minus r 2r 3 a naught plus two third (())(19:29) r by 3 a naught square and exponential minus 3 r by 3 a naught. So, long and so forth you can compile all these numbers which is also given in the book which is table 6.3.

So, you have what we have done is that we have compile the Laguerre polynomial and the corresponding radial function in this particular way. This is the first few radial we can compile up to a lot of these numbers. As expected that each tabulated radial function has been normalized by integrating with respect to the radial portion of that differential equation.

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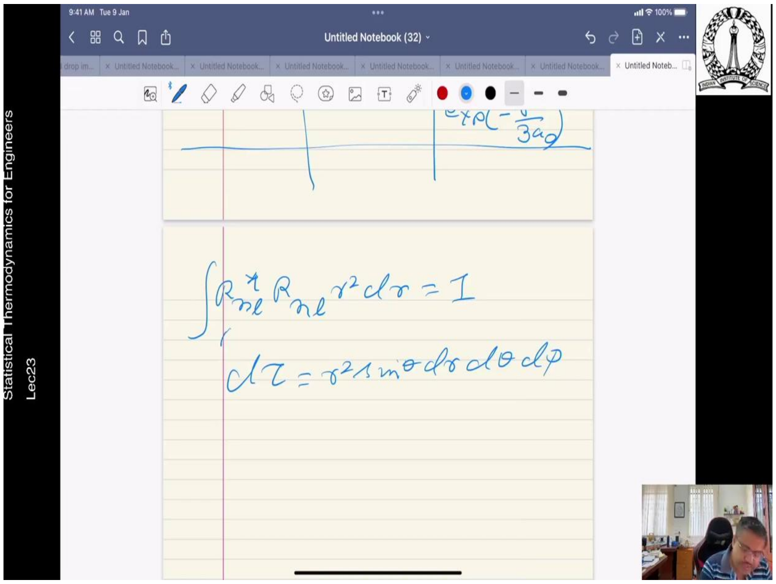

$\exp\left(-\frac{r}{3a_0}\right)$

$$\int R^*_{nl} R_{nl} r^2 dr = 1$$

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

So, this is to assure Rnl star into Rnl r square dr this is equal to 1. Because your d tau r square sin theta dr d theta d phi. So, the probability density function associated with table 6 point that is the table that we just now presented is also shown in the figure in the book which is 6.4 urge you to take a look at it. So, but I will just compile, we tried to draw a few for the sake of understanding.

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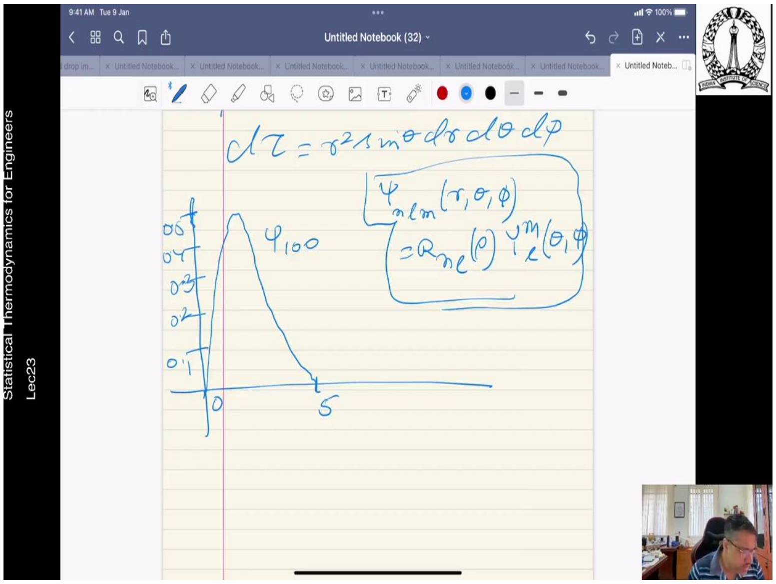

So, this is 0 this is say 5, 0.1, 0.2 0.3, 0.4, 0.5 so, this function is something like this (())(21:27) like this. So, we see so this is psi 100. So, we can on the other hand just to reiterate the psi n l m r theta phi is actually therefore, written as Rnl rho multiplied by Yml theta comma phi this was a total solution. So, this is basically with respect to n equal to 1, l equal to 0, m equal to 0. So, that is the first you know a cloud.

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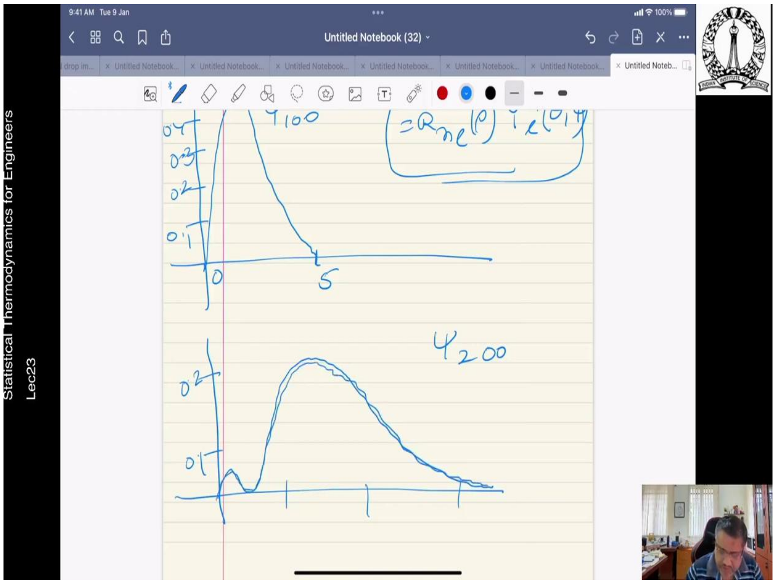

Now, similarly, we can draw a second one just to give a pictorial feel the whole thing 0.1, 0.2. So, this is psi 200. So, this is got a smaller peak else and then and tremble a little bit like these peaks then goes like this. So, this is the psi 200.

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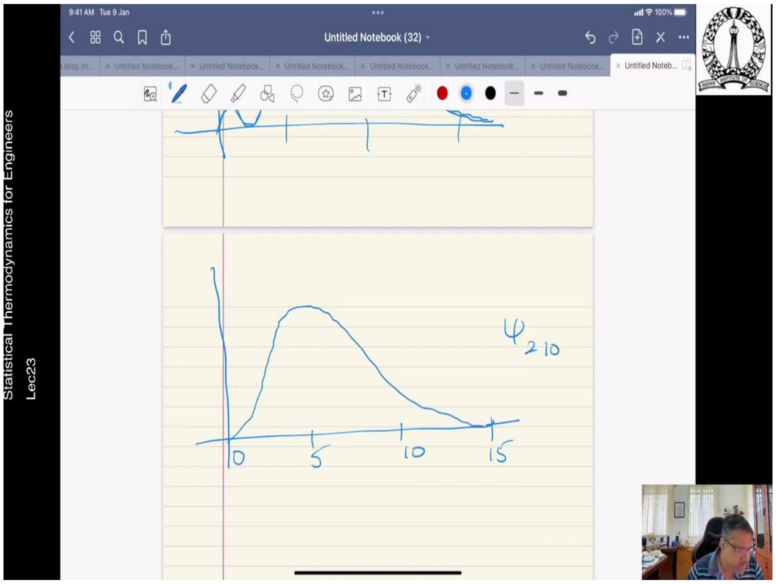

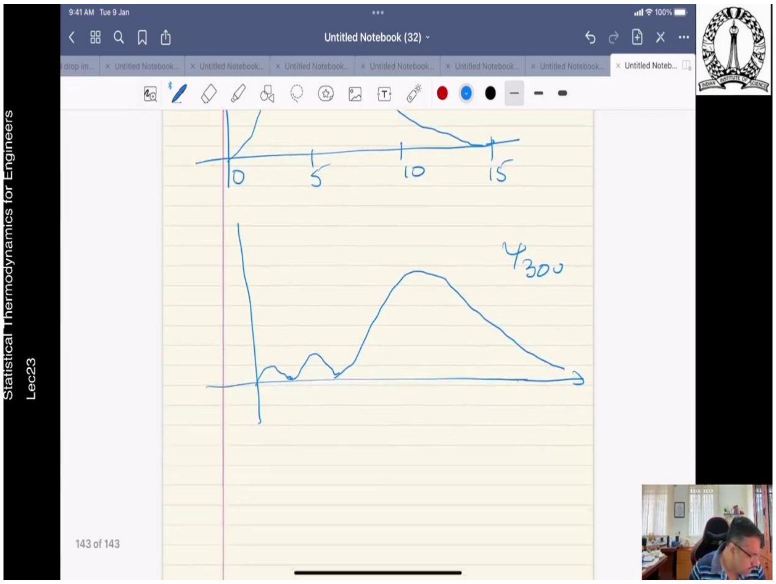

And then you write it the second one (())(23:09) 0, 5, 10, 15 stuff like that this psi 210 set. So, this is (())(23:24)… So, that is one and then if you go on further you can go on doing this basically. So, that psi 300 will be equal to this this something like that 300. Now, you could do 310 and so on and so forth.

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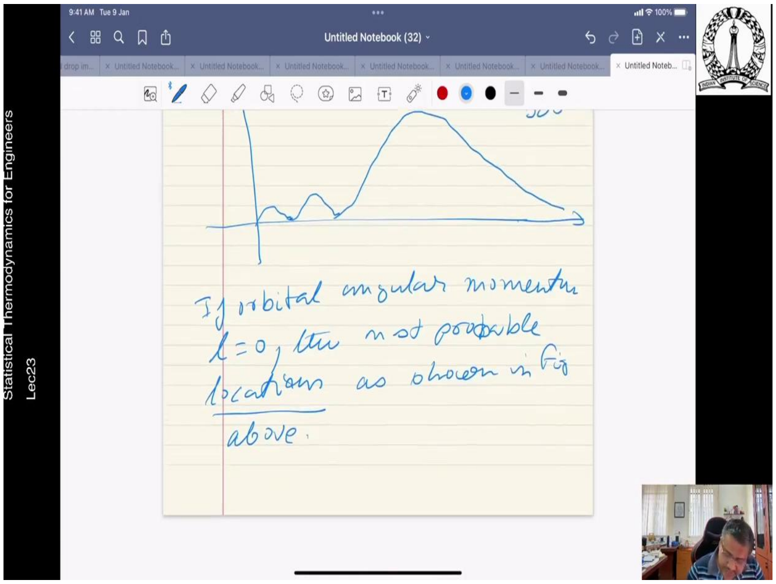
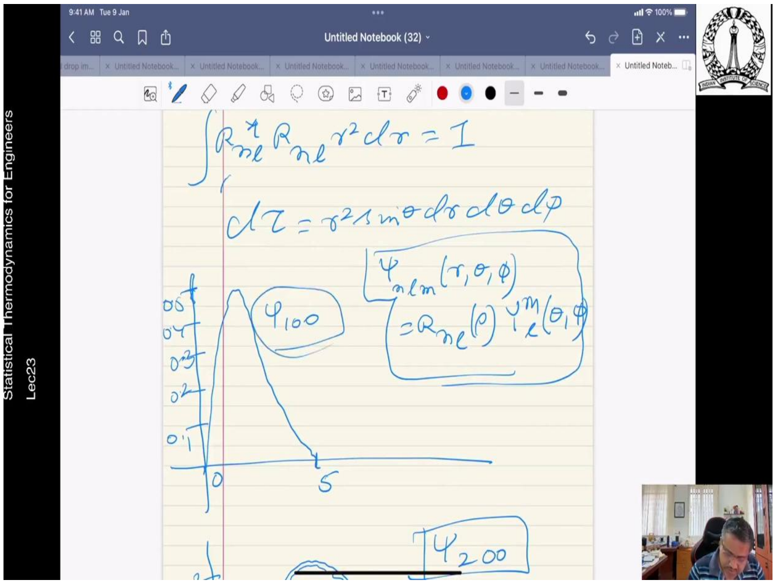


If orbital angular momentum $l=0$, the most probable locations as shown in fig above.



$$\int R^*_{nl} R_{nl} r^2 dr = 1$$

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$\boxed{\psi_{nlm}(r,\theta,\phi) = R_{nl}(\rho) Y^m_l(\theta,\phi)}$$

So, if the angular orbital angular momentum. Now, if the orbital angular momentum l is equal to 0. The most probable locations are depicted as we saw. So, these are the most probable locations. So, probable locations is suggested and they actually are as shown in the figure basically shown in figure above and also in the book.

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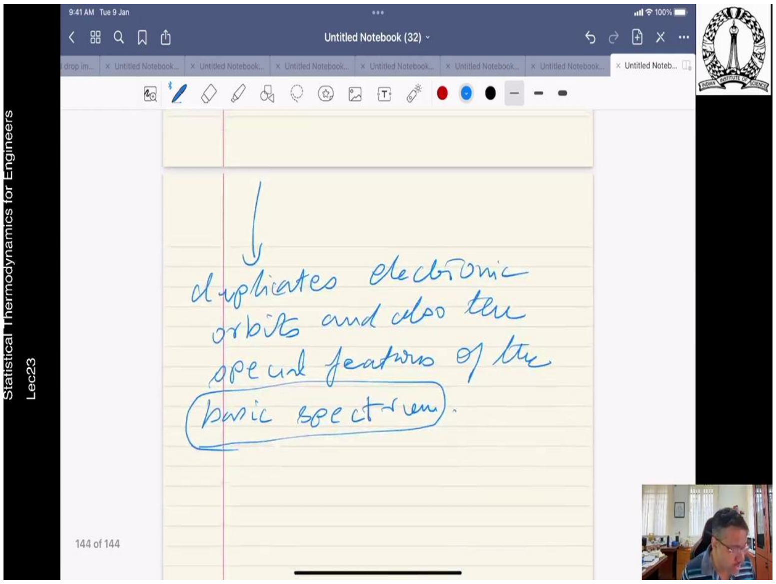
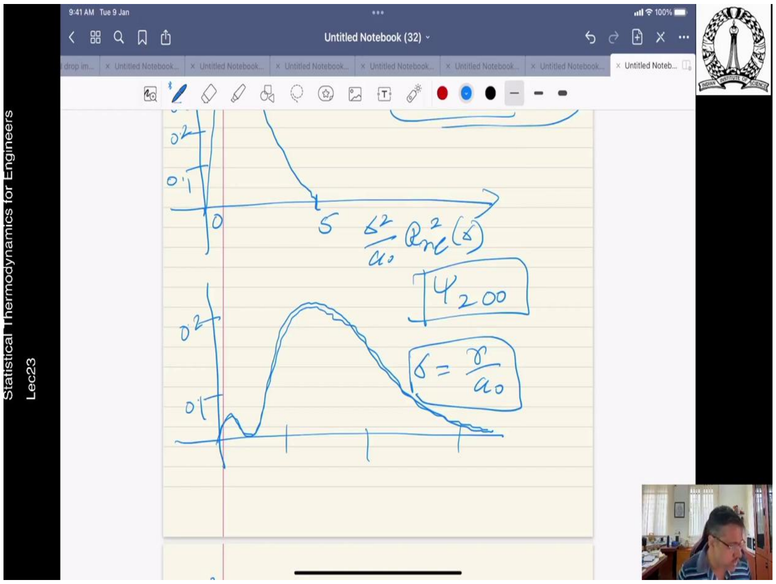
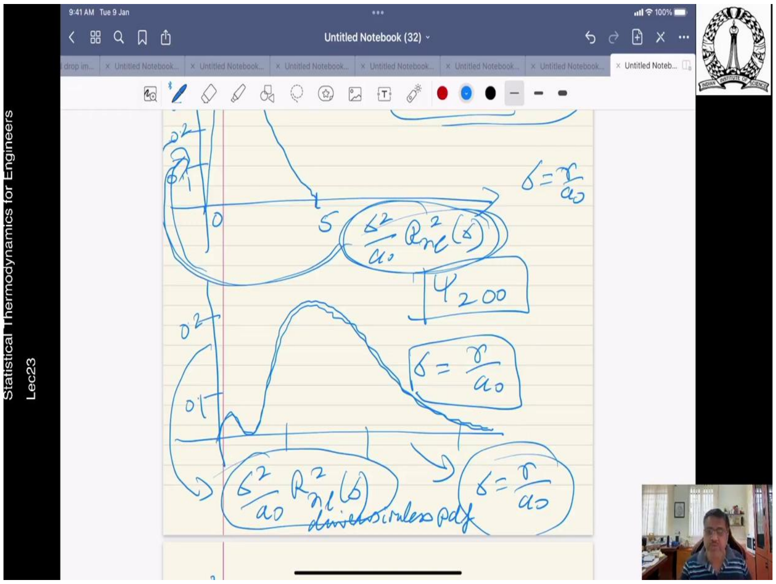
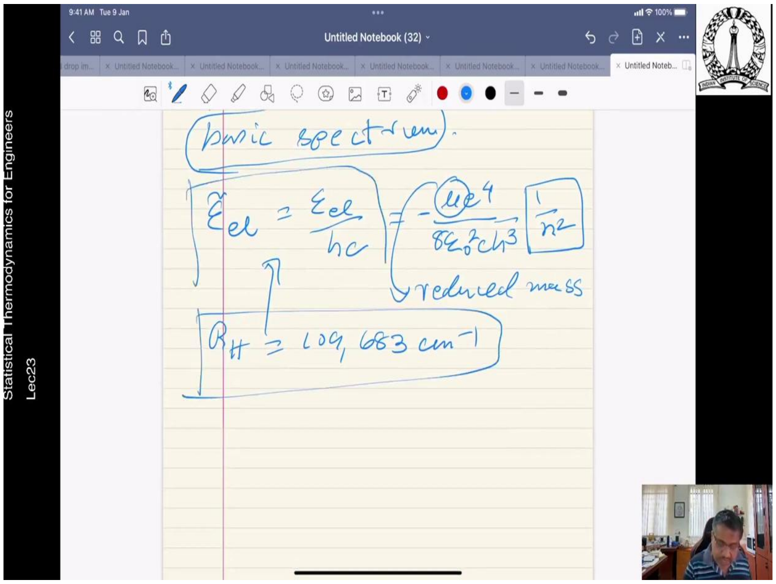


duplicates electronic orbits and also the special features of the basic spectrum.







basic spectrum.

$$\tilde{\mathcal{E}}_{el} = \frac{\mathcal{E}_{el}}{hc} = -\frac{\mu e^4}{8\varepsilon_0^2 c h^3} \boxed{\frac{1}{n^2}}$$

reduced mass

$$\boxed{R_H = 109,683\ \text{cm}^{-1}}$$

Now, this has got a particular charm, this act this is this duplicates this kind of you know replicates duplicates, this kind of duplicates with the basic spectral features of the duplicate the electronic orbits and also the special features of the features of basic spectrum as suggested by the Bohr model, but obviously, this adds more value, because now you can see that how the wave function will look like for different types of quantum numbers. So, that is a very interesting you know, so its adds a value to the basic model that was suggested by Niels Bohr.

So, in other words, also, we can see that, you know, if you look at the figures that you can see the electron cloud can be very radially stretched, it can be found in multiple radial locations as well, it is like a wide zone that is presented over there. So, spermatids special distribution is much more complicated. But at the same time, one can see that, using these features that we have outlined over here even predicted how the basic electron cloud is going to perhaps reply.

So, from the perspective of stat thermo we now are able to get an idea about energies at the degeneracies the allowable(())(26:42) energies and the degeneracies. So, the electronic energy is hc minus e 4 8 e naught square ch cube into 1 over n square. So, this is different from Bohr except that we have used the reduced paths. So, that is the difference with Niels Bohr… And this enables us to calculate the Rydberg constant if you remember.

So, Rydberg constant when they it is calculated from this is 109683-centimetre inverse, this is very close to it is experimentally measured value. So, you recognize that in addition to equations these two (())(27:30) equation that you see over here, we have now developed a robust model from the Schrodinger wave equation and then hence it can be applied to more complicated molecules and atoms, because it explains the Bohr spectrum and more, when you look at the probability distribution for these different types of fix.

Here of course, what I forgot to write over here, the axis are basically given as sigma square divided by a naught A naught R nl square in to sigma. So, this is basically the radial function sigma is basically r by a naught. So, it is some kind of dimensionless probability function associated with the radial portion the wave function, dimensionless probability distribution function. So, this is what we have plotted here with respect to the associated with the radial portion which is sigma equal to r by a naught. So, this is what has been plotted with respect to the dimensionless radius (())(28:53).

So, in other words, this axis is sigma square a naught Rnl square into sigma whereas, the x axis is basically sigma equal to r by a naught is like a dimensionless radius and this is the dimensionless PDF. So, this is a dimensionless PDF associated with the radial portion of various wave functions. So, this allows you to measure the extent of the electronic cloud spread or the probability of that what is zone that the electronic cloud may be available.

So, that is what it is shown in this particular figure. So, and we have also know that now the Rydberg constant is pretty robust. And this is how we have calculated the electronic energy levels also. So, next class we are going to do a sample problem and then move on and see what else is there in store for us. So, see you till next class.