Statistical Thermodynamics for Engineers
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Lecture 34
The Electronic Energy Mode for Atomic Hydrogen

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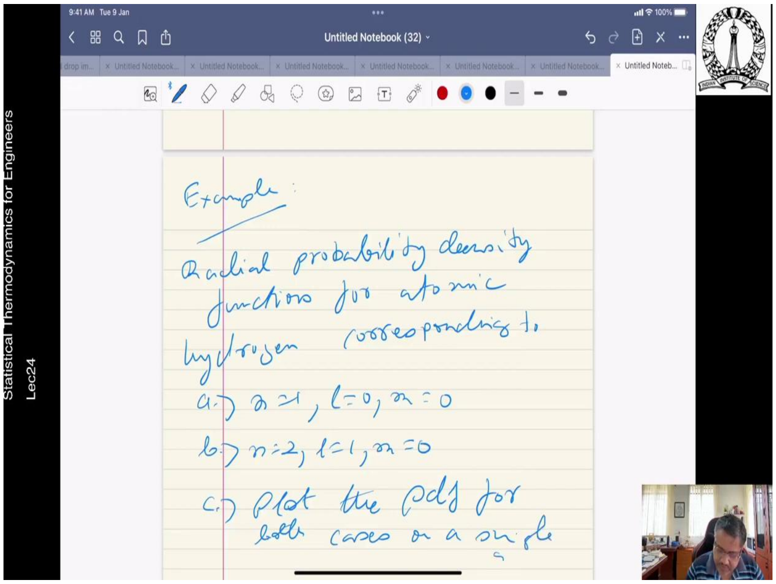


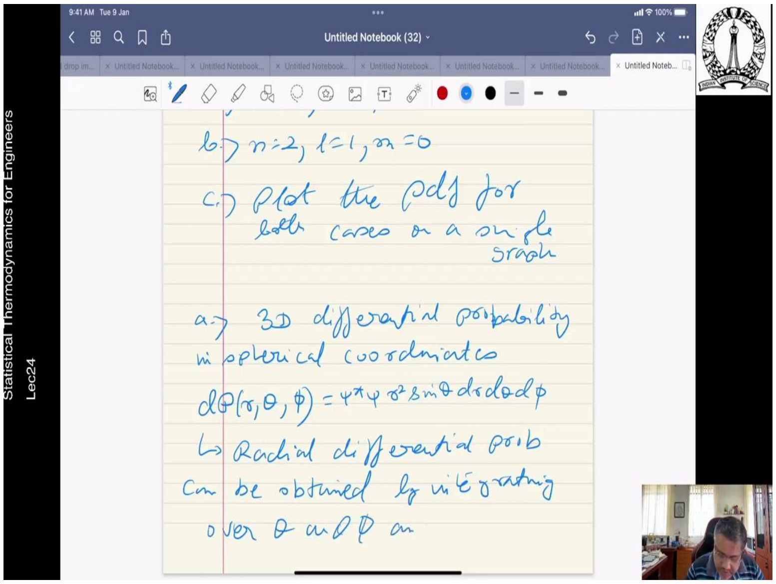
Example :

Radial probability density functions for atomic hydrogen corresponding to

a.) $n=1, l=0, m=0$

b.) $n=2, l=1, m=0$

c.) Plot the pdf for both cases on a single



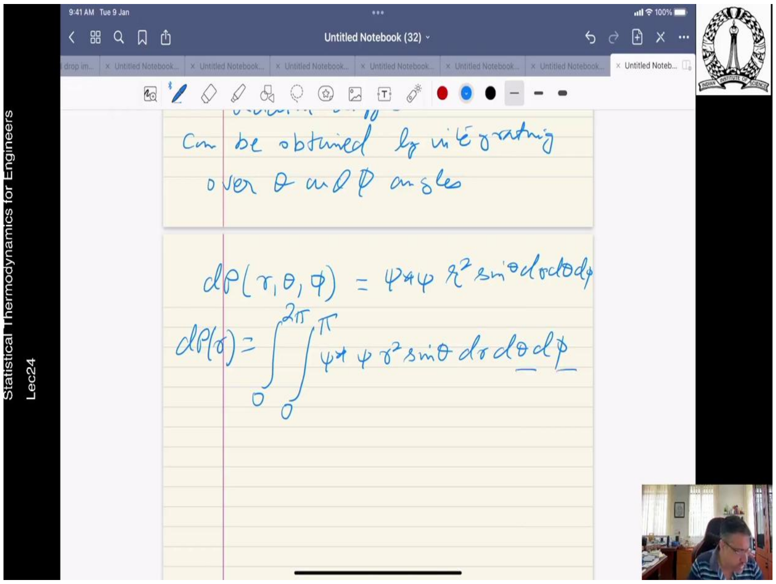
b.) $n=2, l=1, m=0$

c.) Plot the pdf for both cases on a single graph

a.) 3D differential probability in spherical coordinates

$d\mathcal{P}(r,\theta,\phi) = \psi^*\psi\, r^2 \sin\theta\, dr\, d\theta\, d\phi$

↳ Radial differential prob can be obtained by integrating over θ and ϕ an



can be obtained by integrating over θ and ϕ angles

$$dP(r,\theta,\phi) = \psi^* \psi\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$dP(r) = \int_0^{2\pi}\int_0^{\pi} \psi^* \psi\, r^2 \sin\theta\, dr\, \underline{d\theta}\, \underline{d\phi}$$

So, welcome to lecture number 24 of the course statistical thermodynamics. So, we in the last class, we covered the spectrum of hydrogen and what will be the what were the different quantum numbers associated with it. So, this time we are first going to start with an example problem and then take it further.

So, the question is find out the radial probability distributions probability density function for atomic hydrogen corresponding to a n equal to 1, l equal to 0, m equal to 0, b n equal to 2, l equal to 1, m equal to 0 and C plot the probability the PDF for these two cases or both cases on a single graph.

So, that is the problems the first 1 if you want to answer question a. So, the 3-dimensional probability in differential probability 3D differential probability in spherical coordinates given as dP r theta phi is given as (())(02:06) the wave function square theta dr d theta phi that is the differential probability spherical coordinate for volume element. So, the radial differential probability now, how can we get to the radial differential probability? Just have to integrate our theta and phi.

The radial differential probability actual probability can be obtained by integrating over theta and phi angles that is what it is. So, dP r comma theta comma phi we write one more time(())(03:13) this is psi r square theta d theta d phi. Therefore, dP r it becomes if you integrate out the other 2 variations 0 to 2 pi, 0 to pi, psi star psi square sin theta dr d theta d phi. So, this is the radial differential probability, which is attain by integrating out theta and phi.

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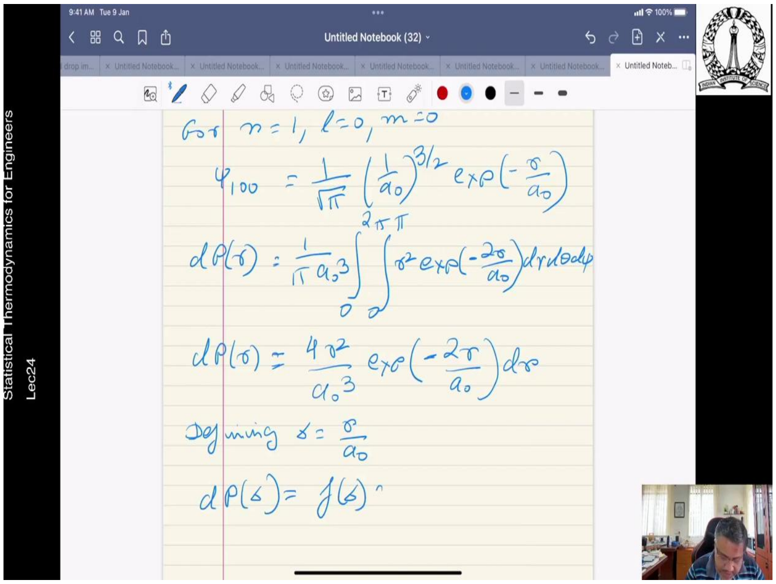


For $n=1,\ l=0,\ m=0$

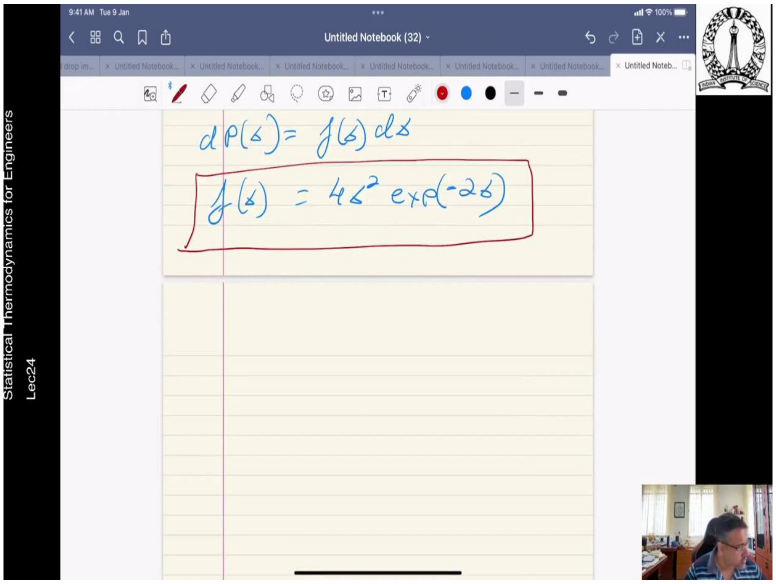
$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\exp\left(-\frac{r}{a_0}\right)$$

$$dP(r) = \frac{1}{\pi a_0^3}\int_0^{2\pi}\int_0^{\pi} r^2\exp\left(-\frac{2r}{a_0}\right)dr\,d\theta\,d\phi$$

$$dP(r) = \frac{4r^2}{a_0^3}\exp\left(-\frac{2r}{a_0}\right)dr$$

Defining $\sigma = \frac{r}{a_0}$

$$dP(\sigma) = f(\sigma)$$



$$dP(\sigma) = f(\sigma)\,d\sigma$$

$$\boxed{f(\sigma) = 4\sigma^2\exp(-2\sigma)}$$

So, for n equal to 1, l equal to 0, m equal to 0. We can obtain and we can look up the table in this particular case the tables that we just now did. So, that is 100 is given as 1 over pi 1 by a naught 3 by 2 exponential r by a naught. So, dPr now you substitute this 1 over pi a naught cube 0 to 2 pi integration 0 to pi integration square exponential minus 2r by a naught dr d theta d phi.

Therefore, dP r is equal to 4 r square a naught cube exponential minus 2r by a naught dr. So, now define sigma equal to r by a naught what we can do is that we write now dP sigma equal to f sigma into d sigma. Where f sigma (())(05:54) equal to 4 sigma square exponential minus 2 sigma. Similarly, this the first expression.

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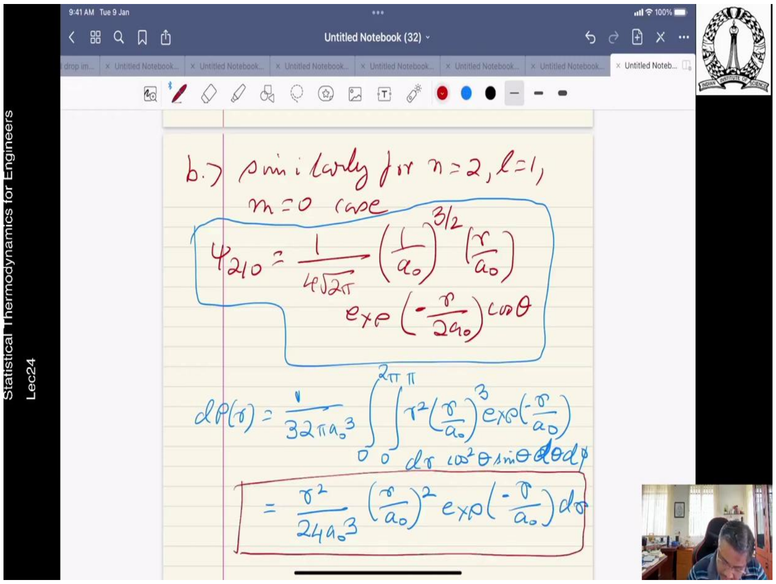
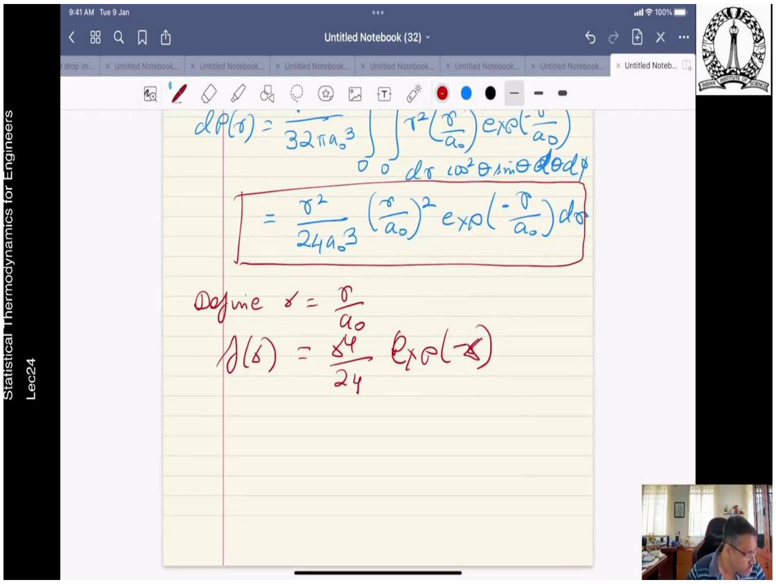


b.) Similarly for $n=2, l=1,$
$m=0$ case

$$\boxed{\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\cos\theta}$$

$$dP(r) = \frac{1}{32\pi a_0^3}\int_0^{2\pi}\int_0^{\pi} r^2\left(\frac{r}{a_0}\right)^3 \exp\left(\frac{r}{a_0}\right) dr\, \cos^2\theta \sin\theta\, d\theta\, d\phi$$

$$\boxed{= \frac{r^2}{24 a_0^3}\left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right) dr}$$



$$dP(r) = \frac{1}{32\pi a_0^3}\int_0\int_0 r^2\left(\frac{r}{a_0}\right)^3 \exp\left(\frac{r}{a_0}\right) dr\, \cos^2\theta \sin\theta\, d\theta\, d\phi$$

$$\boxed{= \frac{r^2}{24 a_0^3}\left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right) dr}$$

Define $\sigma = \frac{r}{a_0}$

$$f(\sigma) = \frac{\sigma^4}{24}\exp(-\sigma)$$

Similarly, for say n equal 2 which was other condition l equal to 1, m equal to 0 case, what will happen is this would be psi 2, 1, 0. Again you can look up on the table 4 by 2 pi 1 by a naught 3 by 2 r by a naught exponential minus r 2 a naught into cos theta. So, this is the other expression. So, similarly thus dPr becomes 1 over(())(07:24) 32 pi a naught cube 0 to 2 pi 0 to pi r square r by a naught cube exponential minus r by a naught dr cos square theta then(())(07:58) sin theta d theta which is equal to now r square by 24 a naught cube r by a naught square and exponential minus r a naught dr. Define sigma equal to r a naught. So, this becomes f sigma and this becomes sigma to the power 4 24 exponential minus sigma. So, this will be the two expression for the two minus sigma this is sigma.

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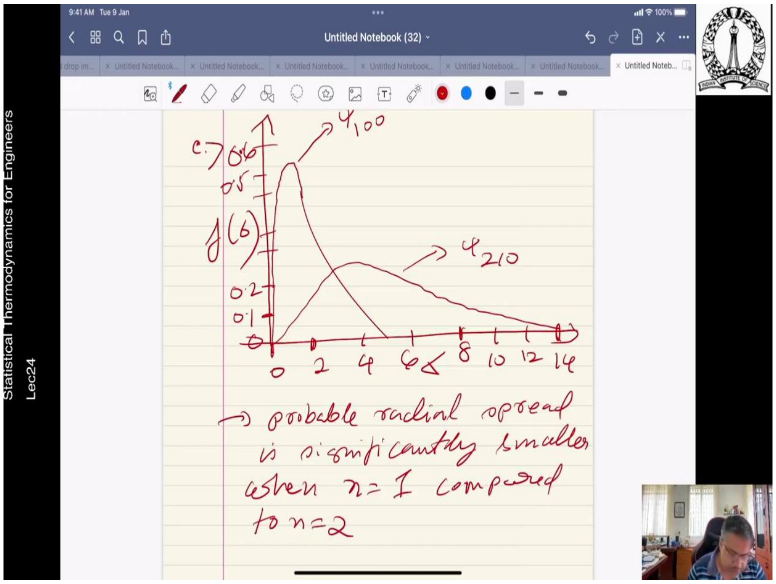
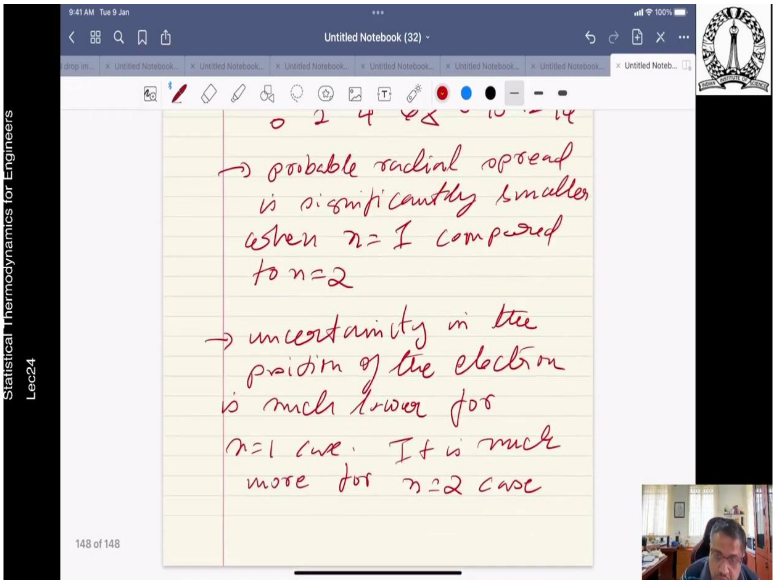
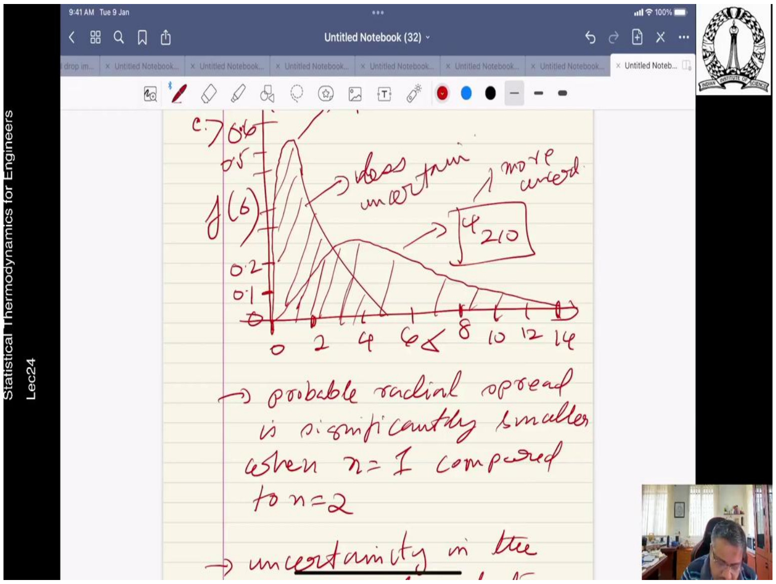


→ probable radial spread is significantly smaller when $n = 1$ compared to $n = 2$



→ probable radial spread is significantly smaller when $n = 1$ compared to $n = 2$

→ uncertainty in the position of the electron is much lower for $n = 1$ case. It is much more for $n = 2$ case



→ probable radial spread is significantly smaller when n = 1 compared to n = 2

→ uncertainity in the

So now, we are in a position to plot the 2 cases. So, sigma this axis (())(09:17) f sigma here. Let us put some numbers this is 0, this is 2, this is 4, 6, 8, 10, 12, 14 and you have 0 here 0.1, 0.2, above 0.6. So, something like that. So, this is psi 100 and another one is like this which is psi 210. So, this is if you plot the 2 functions it will be like that.

Now, as expected probable radius is significantly smaller. Probable radius spread basically is significantly smaller when n equal to 1 compared to n equal to 2. So, the uncertainty in the position therefore, this means uncertainty in the position of the electron is much lower for n equal to 1 case and it is more it is much more for n equal to 2 case as we can see, is the much more wider spread it to this.

So, this obviously carries more uncertainty compared to this less uncertainty. So, these are the 2 cases that we have pointed out over here. So, these are the 2 radial distributions which signifies the position of the electron for the radial position of the electron is actually given(())(12:47) by that. So, this should put at rest that what we mean by the by this trend.

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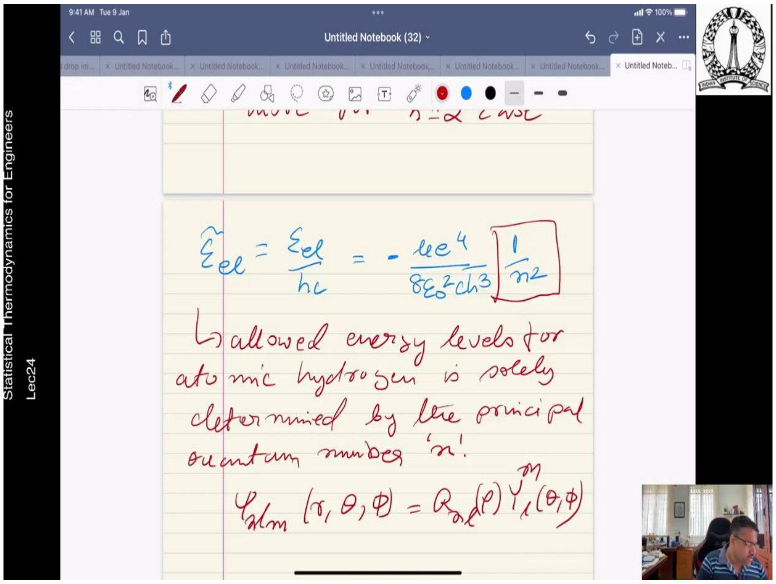
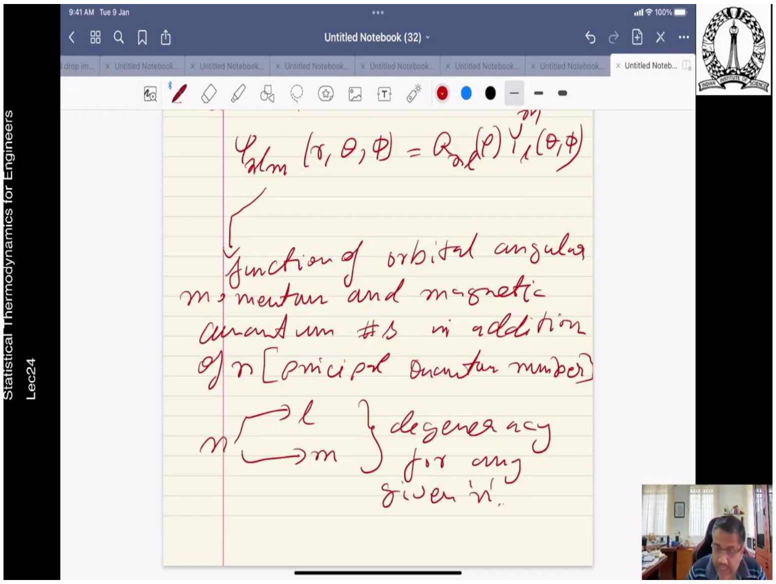


$$\tilde{\mathcal{E}}_{el} = \frac{\mathcal{E}_{el}}{hc} = -\frac{\mu e^4}{8\varepsilon_0^2 ch^3}\boxed{\frac{1}{n^2}}$$

↳ allowed energy levels for atomic hydrogen is solely determined by the principal quantum number 'n'!

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(\rho)\,Y_l^m(\theta,\phi)$$



$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(\rho)\,Y_l^m(\theta,\phi)$$

function of orbital angular momentum and magnetic quantum #s in addition of n [principal quantum number]

$n \to l,\ m$ } degeneracy for any given 'n'.

So, also one other thing to note over here and this time this is beyond the example now, that if you now relook at equation which is this Eel is given by Eel by hc which is equal to minus mu e to the power of 4 divided by 8 psi naught square ch cube into 1 over n square. So, what you decide from here is as follows and this equation demonstrates that allowed energy levels energy levels for atomic hydrogen is solely determined by the principal quantum number n. So, now, on the other hand if you look at the equation and I will just write the equation. If you write nlm this was a total wave function is r theta phi that is given as Rnl rho Y ml theta comma phi.

So, that was the other wave function that was the complete(())(14:51) function for the hydrogen. Now, if you look at that particular wave function associated wave function this wave function is a function of both orbital angular momentum and magnetic quantum numbers in addition to n, which is principal quantum number.

So, hence the possible values of l and n corresponding to any particular value of n must general define the degeneracy. So, for n you will have a possible value of l and m. So, these together should determine the degeneracy for any given n. So, these are like the energy states that we learned previously.

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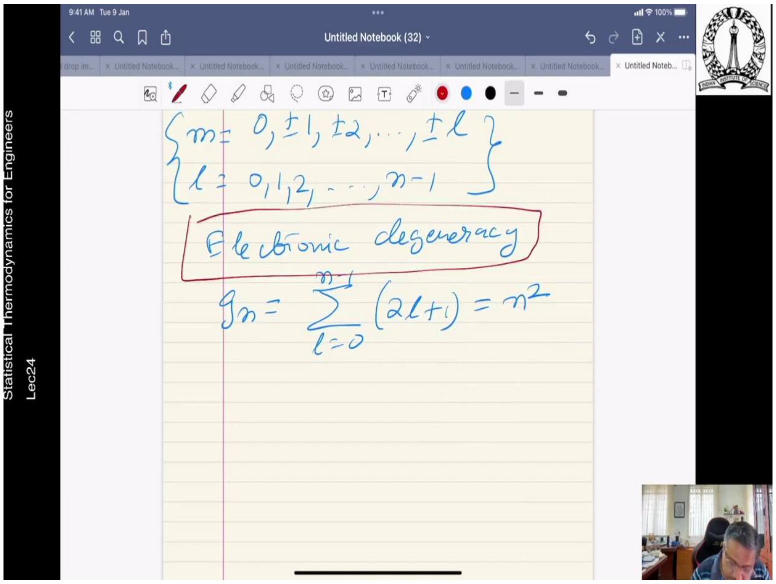
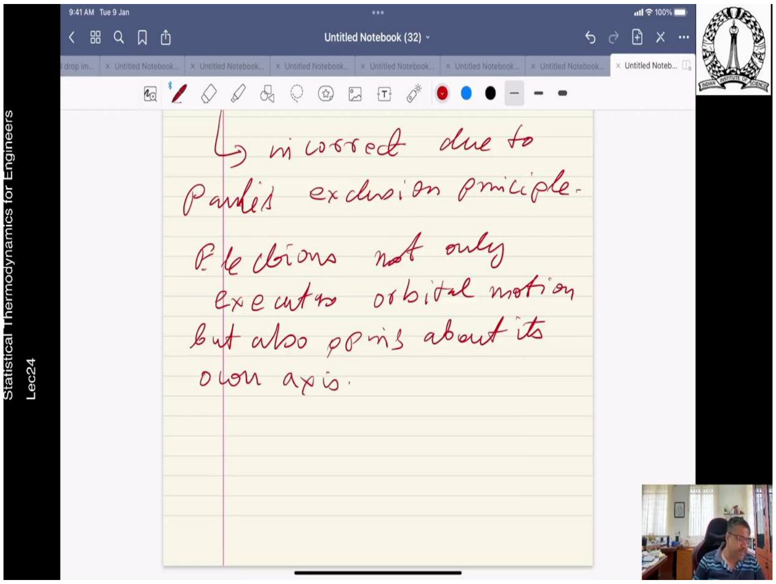


$$\left\{ \begin{array}{l} m = 0, \pm 1, \pm 2, \ldots, \pm l \\ l = 0, 1, 2, \ldots, n-1 \end{array} \right\}$$

Electronic degeneracy

$$g_n = \sum_{l=0}^{n-1} (2l+1) = n^2$$



↳ incorrect due to Pauli's exclusion principle.

Electrons not only executes orbital motion but also spins about its own axis.

So, now, we know m is equal to 0 plus minus 1 plus minus 2 da da da up to plus minus l and l is equal to 0 1 2 da da da n minus 1 is to we knew we know. So, the electronic degeneracy therefore is given by gn say which is summation l equal to 0 to n minus 1 then this is 2l plus 1 which is equal to n square.

So, that is the electronic degeneracy that we are proposing. There is however a fatal flaw in this. Because this is incorrect due to Pauli's exclusion principle. Because the electron as execution not only orbital motion, but it also spins about its own axis. So, apart from moving around the orbit, it also spins around its own axis right. So, the electrons not only execute orbital motion but also spins about its own axis.

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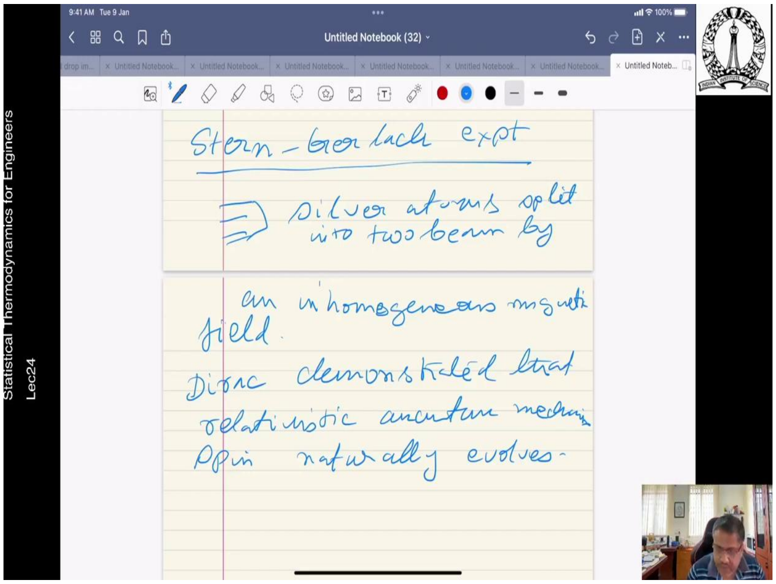
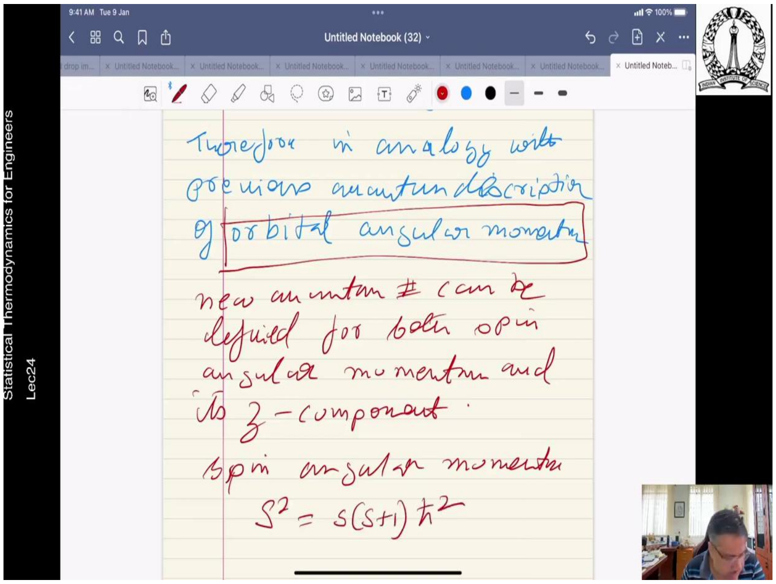


Stern-Gerlach expt

⇒ silver atoms split into two beam by an inhomogeneous magnetic field.

Dirac demonstrated that relativistic quantum mechanics spin naturally evolves.

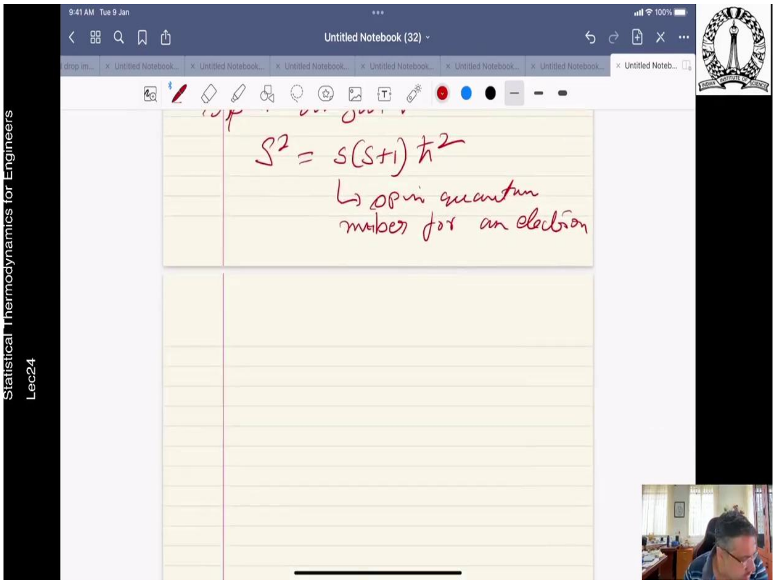


Therefore in analogy with previous quantum description of orbital angular momentum

new quantum # can be defined for both spin angular momentum and its z-component.

spin angular momentum

$$S^2 = s(s+1)\hbar^2$$



$$S^2 = s(s+1)\hbar^2$$

↳ spin quantum number for an electron

So, this intrinsic spin is also you know, if you come for the spins then you could also explain what we call the Stern–Gerlach experiment. So, what the Stern–Gerlach experiment actually did? So, what happened was that a beam of silver atoms its like a beam of silver atoms could be split into 2 beams by a magnetic field split into 2 beams by an inhomogeneous magnetic field.

So, Dirac also did and this is beyond the scope. So, Dirac demonstrated that if we account for relativistic effects, so, from relativistic quantum mechanics spin naturally evolves or comes out. So, here we are not going to do that exactly so, we are going to take some analogy and we are going to see what the spin actually does.

Therefore, in analogy with our previous arguments, in analogy with previous quantum description of orbital angular momentum, new quantum number can be defined for both spin angular momentum because of its rotation about its own axis angular momentum and it can be twisted also(())(21:30) and it is z component which we did in the case of your orbital angular. So, the spin angular momentum becomes we are taking an analogy spin angular momentum becomes S square is equal to all small s plus 1. So, it is written in analogy with a previous argument. So, S nothing but the spin quantum number for an electron.

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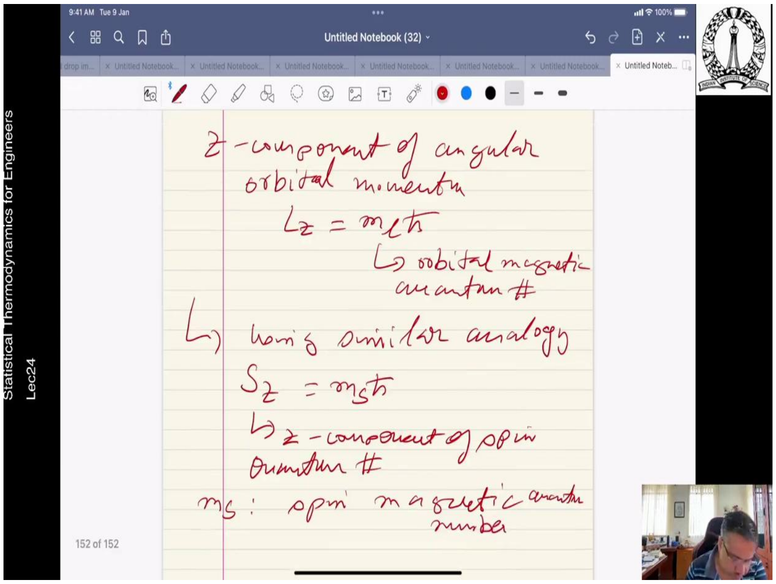


z-component of angular orbital momentum

$L_z = m_l \hbar$

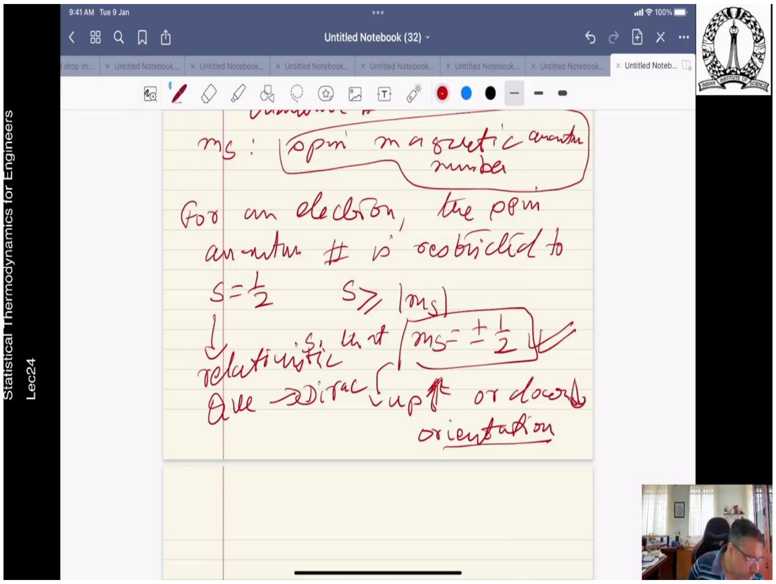
↳ orbital magnetic quantum #

↳ having similar analogy

$S_z = m_s \hbar$

↳ z-component of spin quantum #

m_s : spin magnetic quantum number



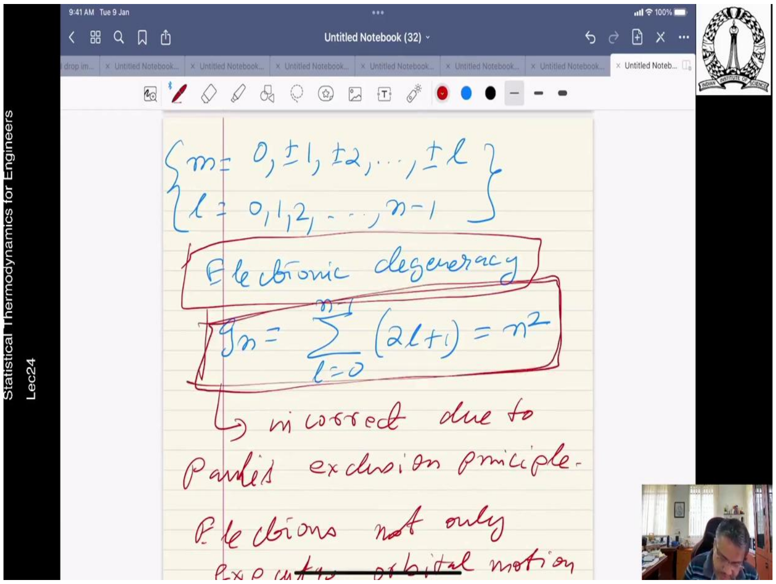
m_s : spin magnetic quantum number

For an electron, the spin quantum # is restricted to

$s = \frac{1}{2}$ $s \geq |m_s|$

↓ relativistic limit $\boxed{m_s = \pm \frac{1}{2}}$ ✓

Que → Dirac {up ↑ or down ↓ orientation



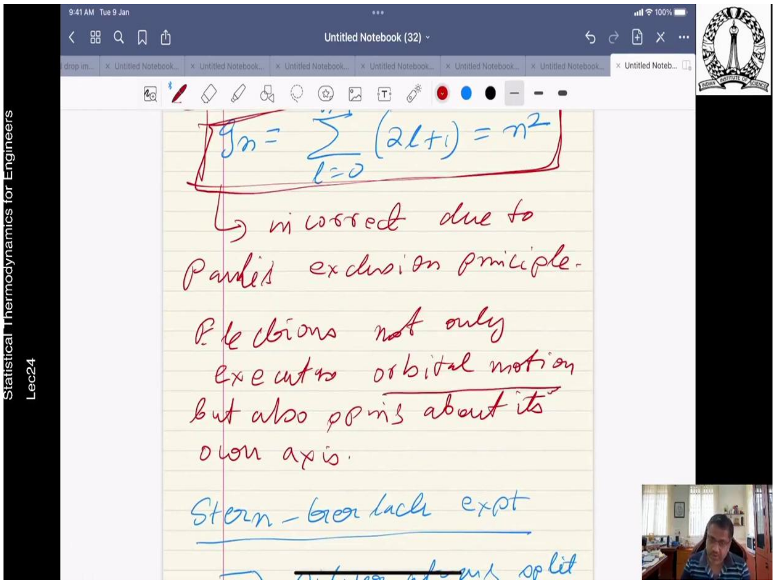
$$\left\{ m = 0, \pm 1, \pm 2, \ldots, \pm l \right\}$$
$$\left\{ l = 0, 1, 2, \ldots, n-1 \right\}$$

Electronic degeneracy

$$\boxed{g_n = \sum_{l=0}^{n-1} (2l+1) = n^2}$$

↳ incorrect due to Pauli's exclusion principle.

Electrons not only executes orbital motion



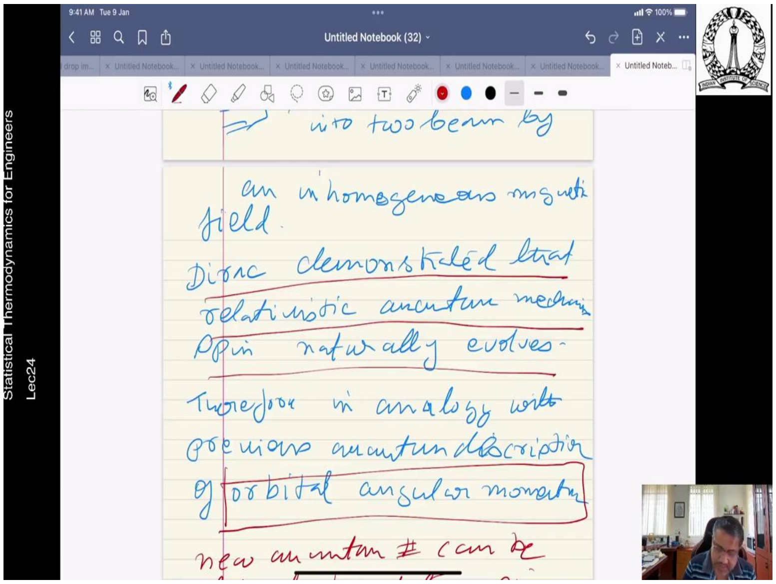
$$\boxed{g_n = \sum_{l=0}^{n-1} (2l+1) = n^2}$$

↳ incorrect due to Pauli's exclusion principle.

Electrons not only executes orbital motion but also spins about its own axis.

Stern-Gerlach expt

→ split



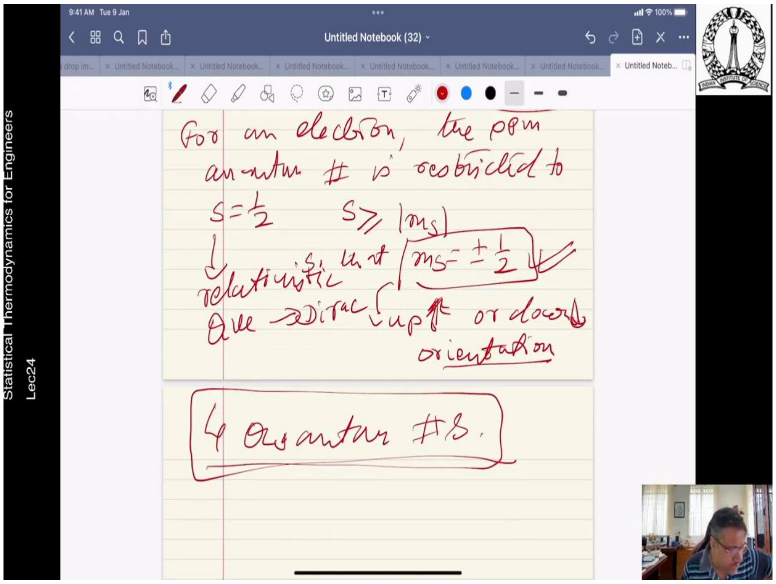
into two beam by

an inhomogeneous magnetic field.

Dirac demonstrated that relativistic quantum mechanics spin naturally evolves.

Therefore in analogy with previous quantum description of orbital angular momentum

new quantum # can be



For an electron, the spin quantum # is restricted to

$s = \frac{1}{2}$ $s \geq |m_s|$

relativistic Que → Dirac

so that $\boxed{m_s = \pm\frac{1}{2}}$

up ↑ or down ↓ orientation

4 Quantum #s.

So, the z component of the orbital angular, so, the z component of orbital angular momentum was basically Lz equal to ml into h bar where ml was the orbital magnetic quantum number by analogy simply using similar analogy we have a z component of the spin quantum number so this is the z component of spin quantum number as ms into h bar, where ms is called the spin magnetic quantum number.

Now, or an electron the spin quantum number is restricted to S is equal to half and since S has to be greater than equal to the mod of ms. So, that ms is a equal to plus minus half it is like an up or down orientation. And this also satisfy the Pauli exclusion principle because no 2 electrons therefore will have all the four quantum numbers to be the same. So, now that we have so, this ms therefore is plus minus half. This comes from relativistic Quantum mechanics courtesy(())(24:56) Dirac.

So, what we got here is that not this is not the right degeneracy value. Because of all Pauli exclusion principle and because of the fact that the electrons not only execute orbital motion spins about its own axis. So, this was also in accordance to the Gerlach experiment and Dirac demonstrated that relativity quantum mechanics can use to naturally evolve this. Therefore, in analogy with a previous quantum description of orbital angular momentum, new quantum number has to be defined, which is basically the spin angular momentum and from there out pops the spin magnetic quantum number with a value of plus minus half.

So, this is an up configuration or a down orientation depending on Dirac (())(25:59). So, in the next class what we are going to do, we are going to then look at multielectrode species and also what does the quantum numbers all designate. All we have now got four quantum numbers altogether four quantum numbers, what are they? Just a recap of what are those four quantum numbers and if we now go to a multi electron species kind of a system, can we just use the same set of equations to describe it? So, that is what we are going to do in our next class.