Statistical Thermodynamics for Engineers
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Lecture 36
The Four Quantum Numbers and Multielectron System

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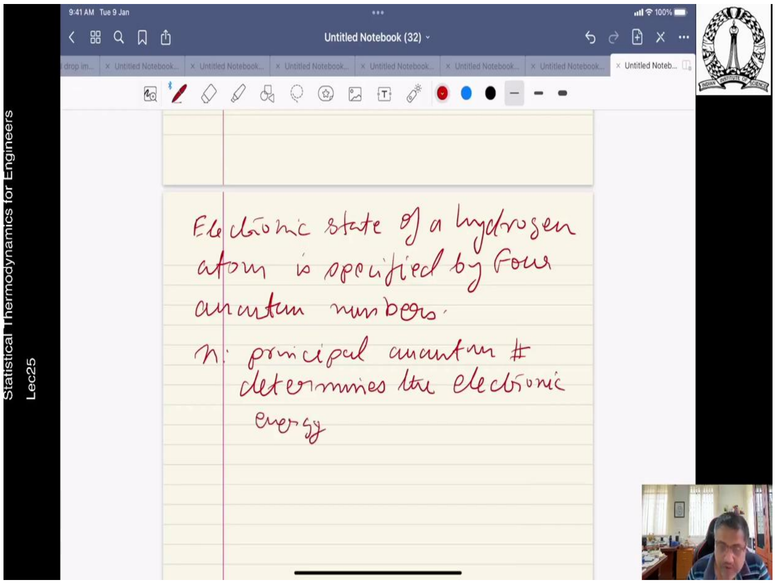
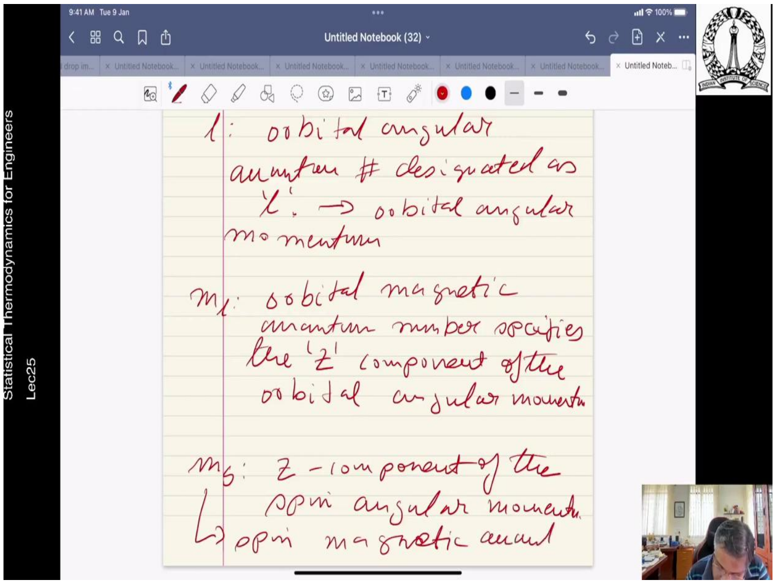


Electronic state of a hydrogen atom is specified by Four quantum numbers.

n: principal quantum # determines the electronic energy

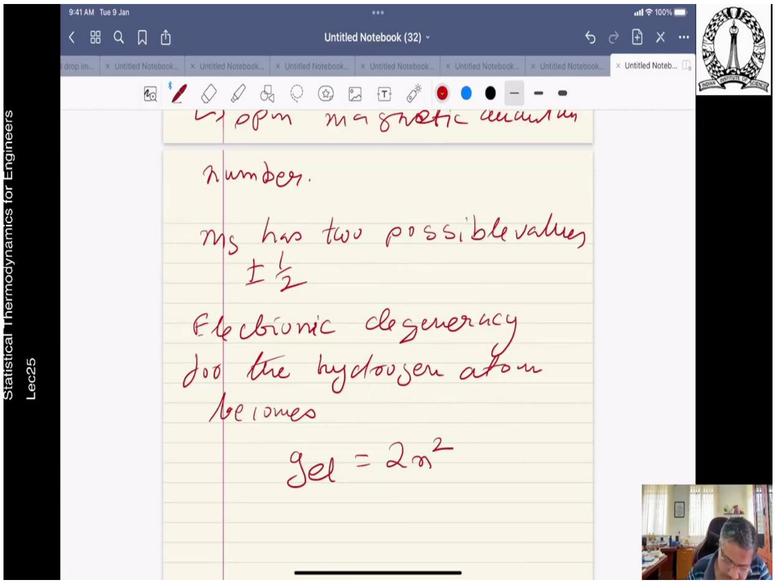


l: orbital angular quantum # designated as 'l'. → orbital angular momentum

m_l: orbital magnetic quantum number specifies the 'z' component of the orbital angular momentum

m_s: z-component of the spin angular momentum

↳ spin magnetic quant

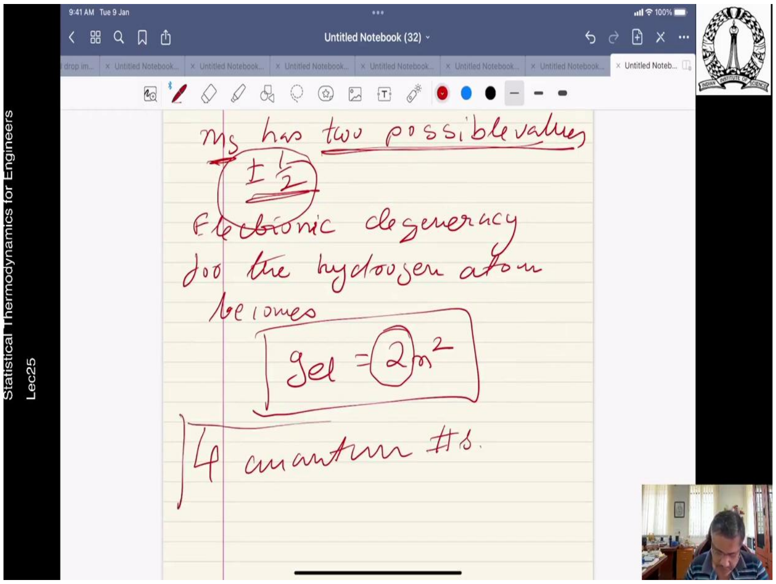


is spin magnetic quantum number.

m_s has two possible values $\pm\frac{1}{2}$

Electronic degeneracy for the hydrogen atom becomes

$$g_{el} = 2n^2$$

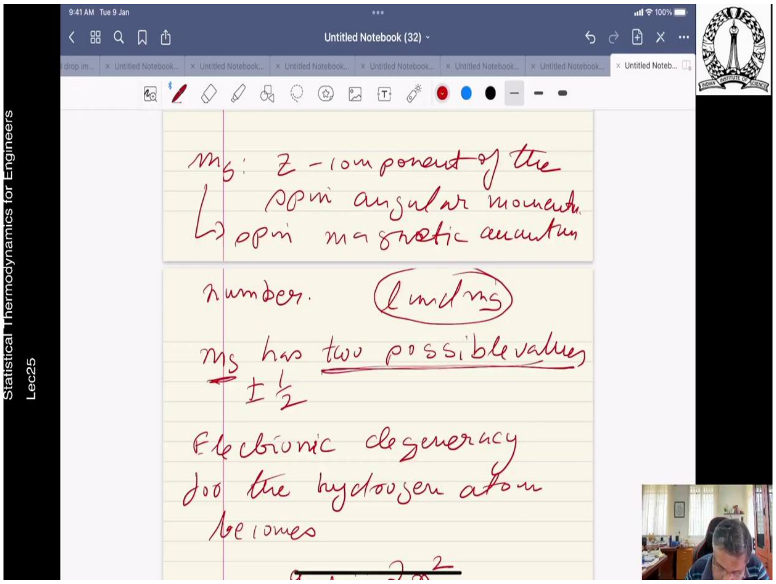


m_s has two possible values $\boxed{\pm\frac{1}{2}}$

Electronic degeneracy for the hydrogen atom becomes

$$\boxed{g_{el} = \boxed{2}n^2}$$

4 quantum #s.

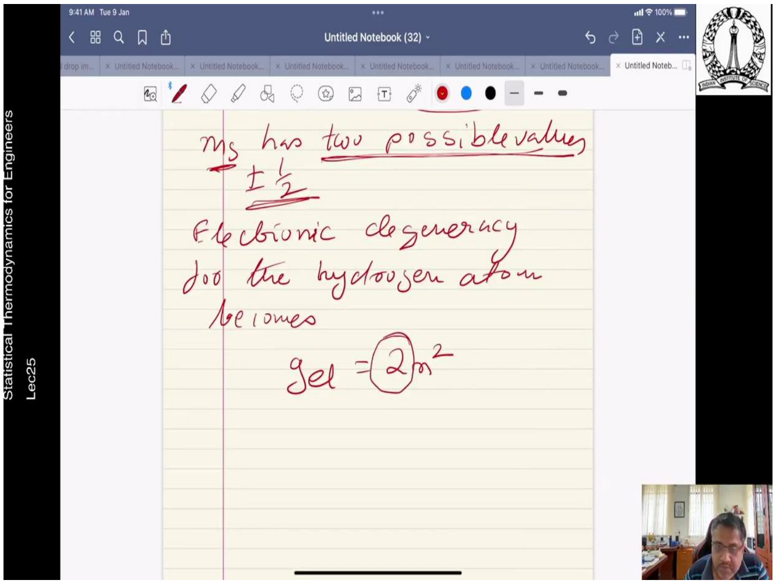


m_s: z-component of the spin angular momentum

↳ spin magnetic quantum number. (l and m_s)

m_s has two possible values $\pm\frac{1}{2}$

Electronic degeneracy for the hydrogen atom becomes



m_s has two possible values $\pm\frac{1}{2}$

Electronic degeneracy for the hydrogen atom becomes

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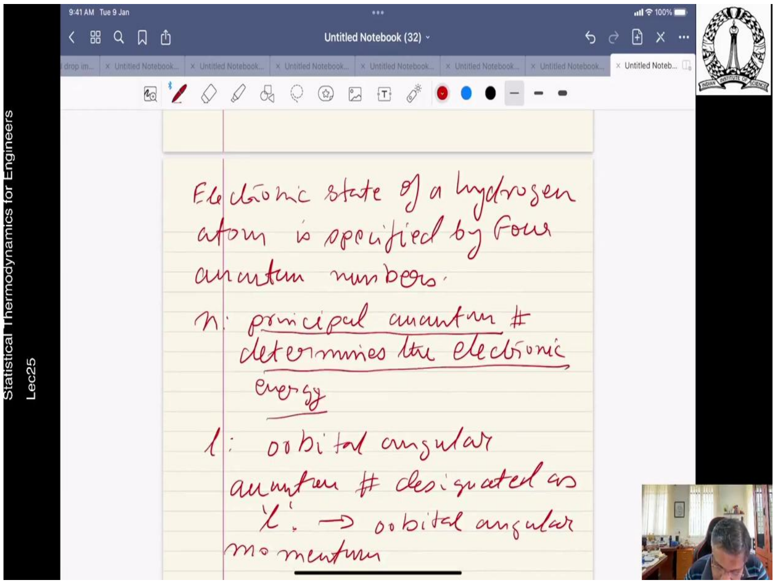
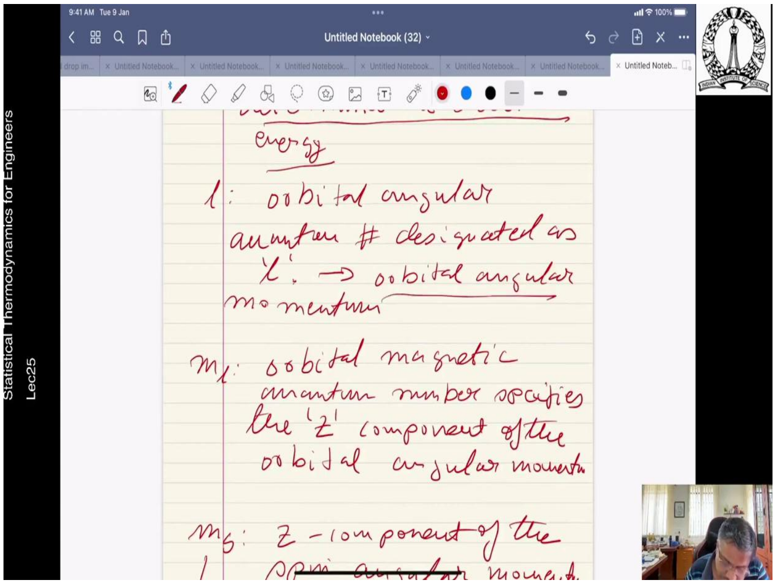


Electronic state of a hydrogen atom is specified by four quantum numbers.

n: principal quantum # determines the electronic energy

l: orbital angular quantum # designated as 'l'. → orbital angular momentum

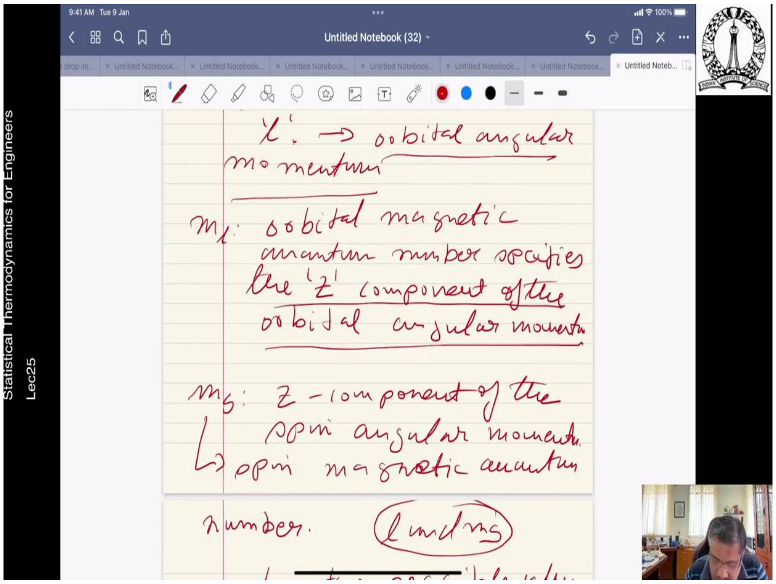


energy

l: orbital angular quantum # designated as 'l'. → orbital angular momentum

m_l: orbital magnetic quantum number specifies the 'z' component of the orbital angular momentum

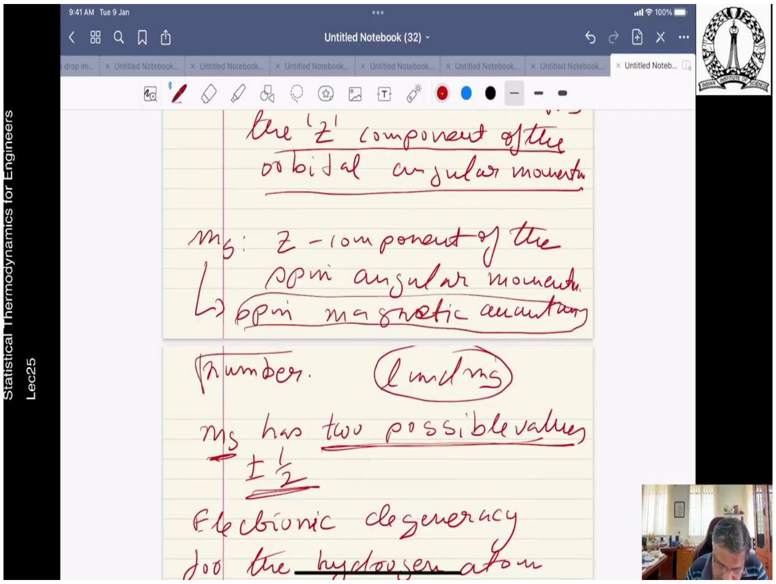
m_s: z-component of the spin angular moment



l: → orbital angular momentum

m_l: orbital magnetic quantum number specifies the 'z' component of the orbital angular momentum

m_s: z-component of the spin angular momentum
→ spin magnetic quantum number. $(l\ m_l\ m_s)$

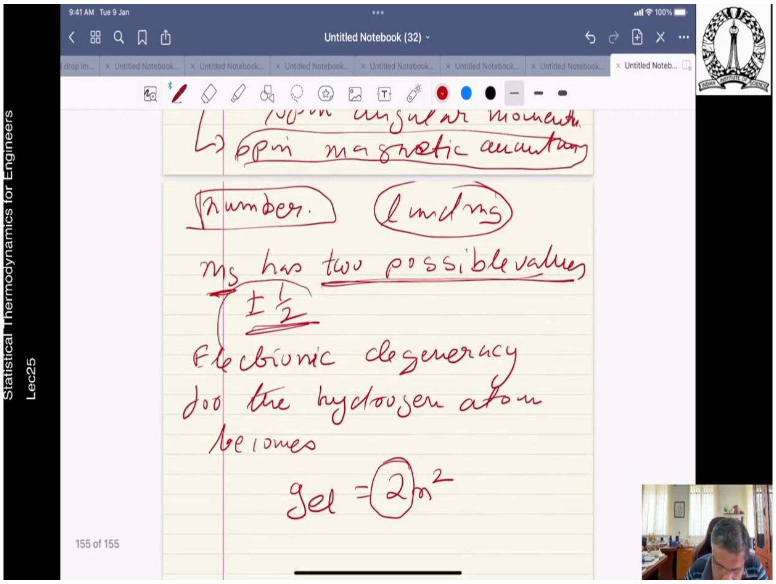


the 'z' component of the orbital angular momentum

m_s: z-component of the spin angular momentum
→ spin magnetic quantum number. $(l\ m_l\ m_s)$

m_s has two possible values
$\pm\frac{1}{2}$

Electronic degeneracy for the hydrogen atom



spin angular moment.
↳ spin magnetic quantum
number.
$l\ m_l\ m_s$
m_s has two possible values
$\pm \frac{1}{2}$
Electronic degeneracy
for the hydrogen atom
becomes
$g_{el} = \boxed{2} n^2$

So, welcome to lecture number 25 of the Statistical Thermodynamics course. So, as we told in the previous lecture that the electronic state, electronic state of an atom, of a hydrogen atom, hydrogen atom is specified, specified by four quantum numbers. So, of this let us see which quantum number does what, and which is also the principal quantum, number quantum number, and determines the electronic energy, determines electronic energy.

Now, orbital l is basically the orbital, angular orbital, angular quantum number designated as l. So, it defines the orbital angular momentum. So, this particular number is basically, this, it is totally for designating the orbital angular momentum. Now, then comes m l which is called the orbital magnetic quantum number, magnetic quantum number. That is, m l. It specifies basically, specifies the z component, the z component of the orbital angular momentum.

Lastly, we have m s, which is the z component of the spin quantum number, of spin angular momentum. So, this is called the spin magnetic number magnetic number, magnetic quantum number. So, already you see that the quantum states are defined by l and m l. Now, there are two possible values of the fourth quantum number. So, m s has two possible values, plus and minus half.

So, the electronic degeneracy therefore, electronic degeneracy for the hydrogen atom, the hydrogen atom becomes g electronic is equal to 2 n square. The n is the principal quantum number. So, basically we already have seen that l and m s was the two quantum numbers that was used to generate the degeneracy. Now, you add the fourth quantum number which is has got two possible values, plus minus half. So, therefore n gets multiplied by this factor 2 because of these two possibilities.

So, this is the four quantum numbers therefore. n, principle quantum number which determines electronic energy, l is the orbital angular quantum number which designates the orbital angular momentum, then m l is basically the orbital magnetic quantum number which specifies, in essence, the z component of the orbital angular momentum. And m s is the z component of the spin angular momentum also called the spin magnetic quantum number.

So, these four quantum numbers, and m s has got two possible values. So, this actually completes the total degeneracy, how to calculate the total degeneracy for the hydrogen atom. So, there are four quantum numbers. And all four are basically required to designate the electronic state. And of course, obviously the energy, energy is dependent on the principle quantum number. So, this completes this, for the hydrogen atom.

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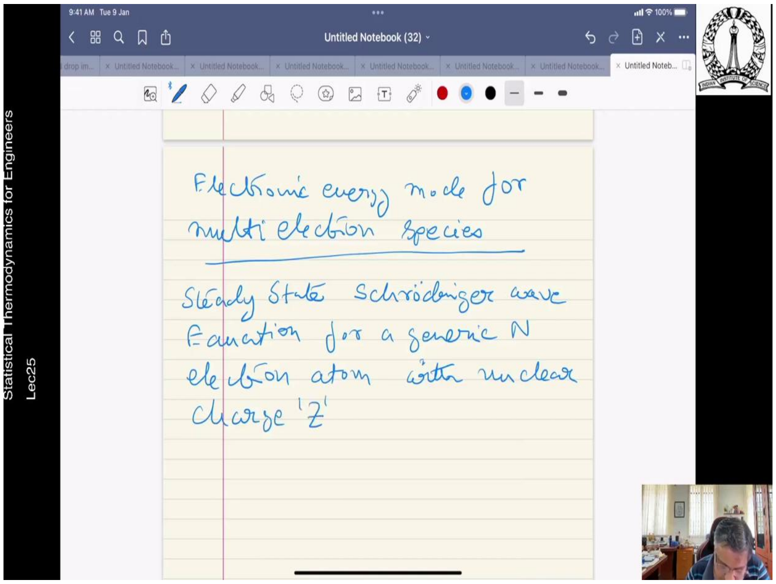
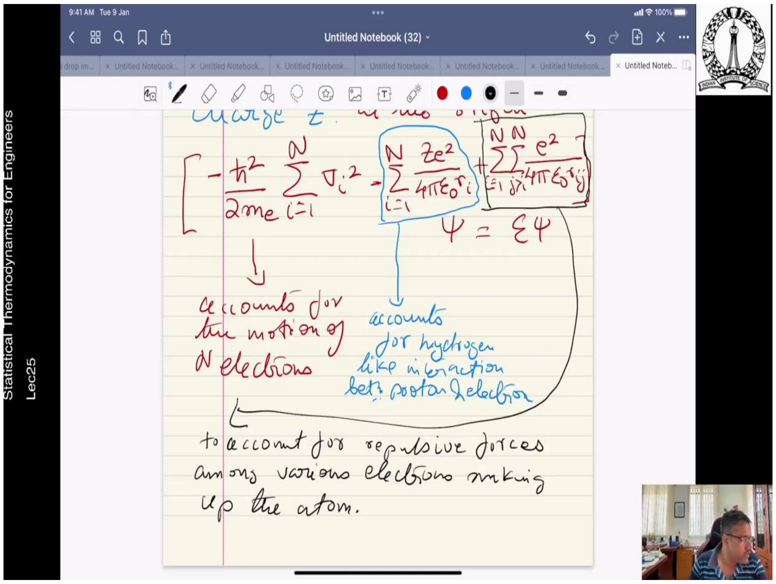


Electronic energy mode for multi electron species

Steady State Schrödinger wave Equation for a generic N electron atom with nuclear charge 'Z'

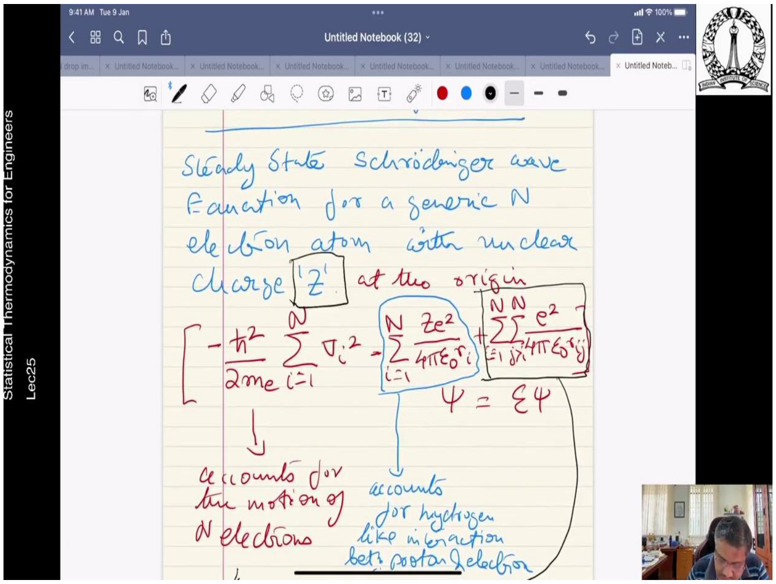


$$\left[-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2-\boxed{\sum_{i=1}^{N}\frac{Ze^2}{4\pi\epsilon_0 r_i}}+\boxed{\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0 r_{ij}}}\right]\psi=\epsilon\psi$$

accounts for the motion of N electrons

accounts for hydrogen like interaction betn proton & electron

to account for repulsive forces among various electrons making up the atom.



Steady State Schrodinger wave Equation for a generic N electron atom with nuclear charge $\boxed{'Z'}$ at the origin

$$\left[-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2-\boxed{\sum_{i=1}^{N}\frac{Ze^2}{4\pi\epsilon_0 r_i}}+\boxed{\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0 r_{ij}}}\right]\psi=\epsilon\psi$$

accounts for the motion of N electrons

accounts for hydrogen like interaction betn proton & electron

Now we move on to the electronic energy mode for multielectron species. So, electronic energy mode or multielectron species. So, again for doing this, we write a steady state, steady state Schrodinger wave equation, wave equation for a generic N electron atom with nuclear charge Z. So, this is the, this is the equation that we are going to write, z at the origin.

So, minus h bar square divided by 2 m e summation i equal to 1 to N del i squared minus summation I equal to 1 to N, Z e squared divided by 4 pi epslion nought r i plus summation I equal to 1 to N summation j greater than I e square divided by 4 pi epsilon nought r i j. This entire thing is multiplied by psi. Now, the first term that you see over here, first term accounts for the motion, accounts for the motion of N electrons. This is the Term 1. The second term, this particular term, this term accounts for hydrogen like interaction, interaction between proton and electron.

And last term, this i over here, this particular term you see over here, the last term, the third term is for, to account for repulsive forces, forces, repulsive among the various electrons making. So, these are the. So, this is the steady state Schrodinger wave equation which has got a charge of Z at the center of the origin.

So, this is the total, this is how you write that total equation form. So, first one is to account for the motion, second one is to account for the proton electron reaction, the interactions, and the third is to basically to account for the repulsive forces. So, this entire thing is multiplied by the wave function is equal to this. So, this is the Schrodinger's steady state wave equation, to begin with.

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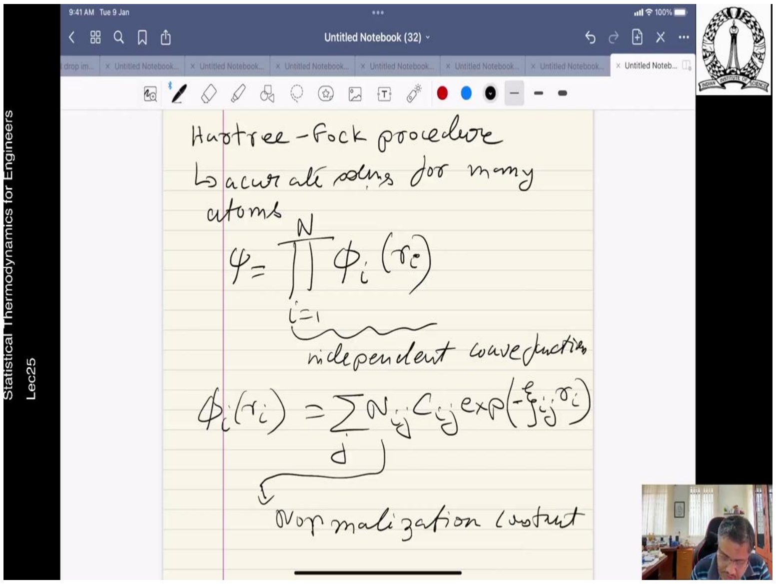
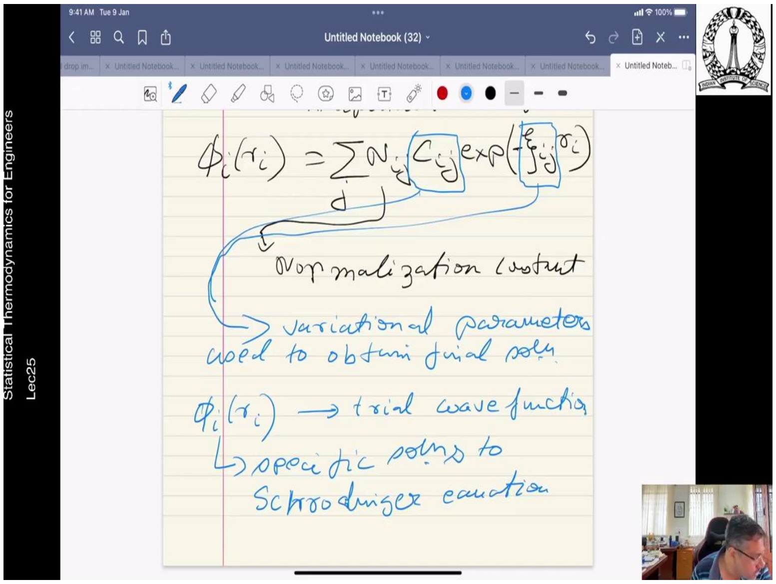


Hartree-Fock procedure

↳ accurate solns for many atoms

$$\psi = \underbrace{\prod_{i=1}^{N} \phi_i(r_i)}_{\text{independent wavefunction}}$$

$$\phi_i(r_i) = \sum_j \underbrace{N_{ij}}_{\text{Normalization constant}} C_{ij} \exp(-\xi_{ij} r_i)$$



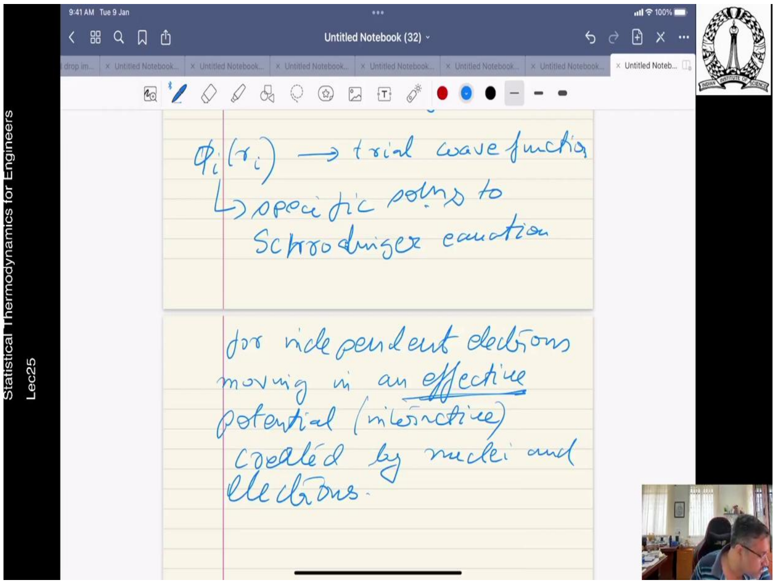
$$\phi_i(r_i) = \underbrace{\sum_j N_{ij}}\boxed{C_{ij}}\exp(-\boxed{\xi_{ij}}r_i)$$

Normalization constant

→ variational parameters used to obtain final soln.

$\phi_i(r_i)$ → trial wave function

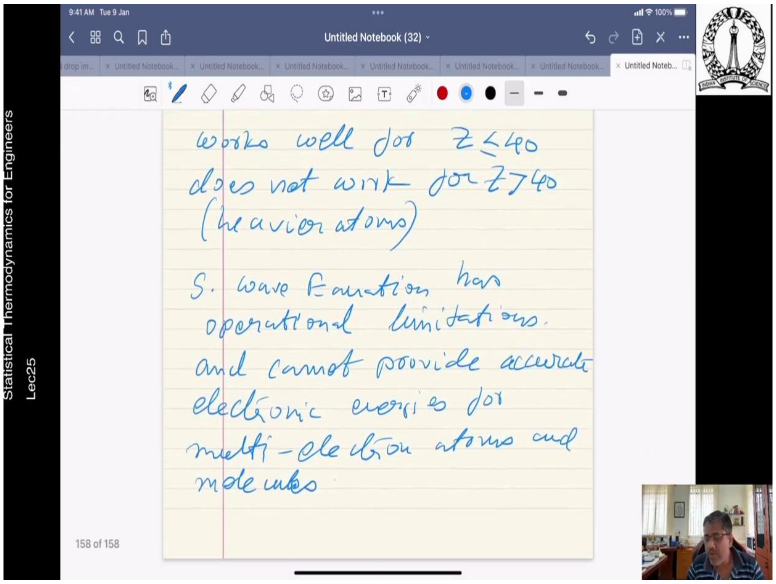
↳ specific solns to Schrodinger equation



$\phi_i(r_i)$ → trial wave function

↳ specific solns to Schrodinger equation

for independent electrons moving in an effective potential (interactive) created by nuclei and electrons.

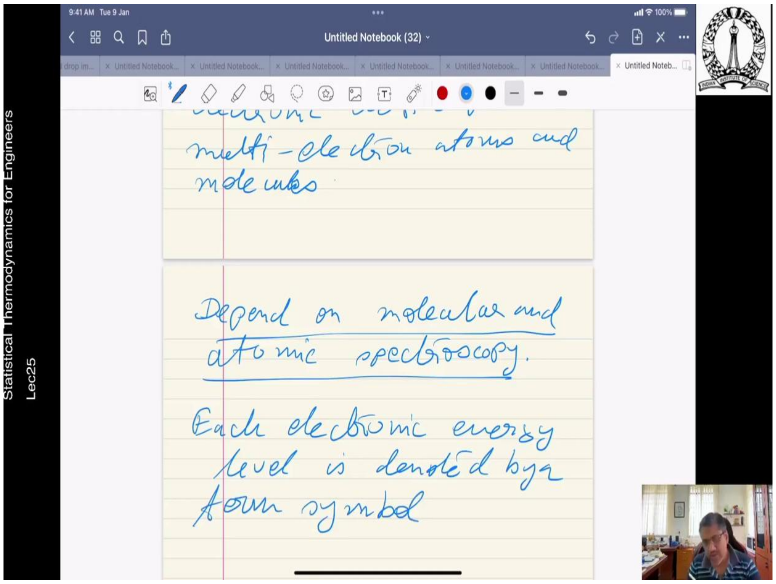


works well for $Z \leq 40$

does not work for $Z > 40$

(heavier atoms)

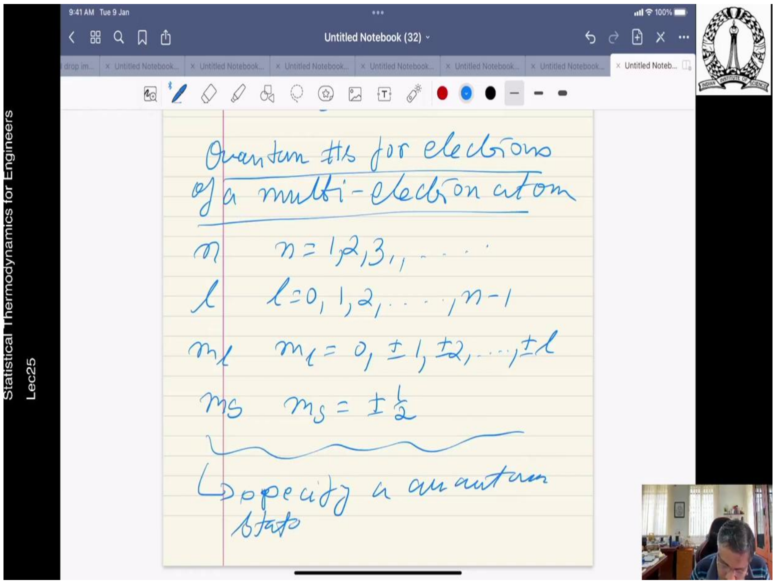
S. wave function has operational limitations and cannot provide accurate electronic energies for multi-electron atoms and molecules



multi-electron atoms and molecules

Depend on molecular and atomic spectroscopy.

Each electronic energy level is denoted by a term symbol



Quantum #s for electrons of a multi-electron atom

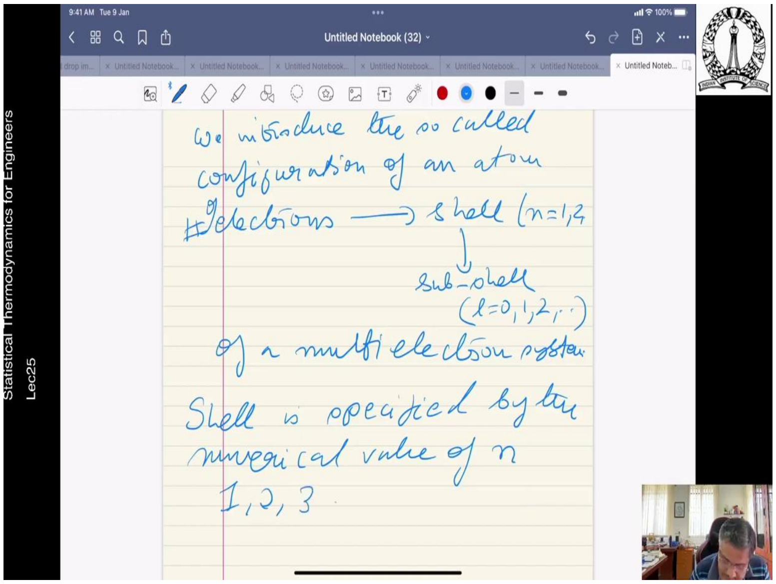
n $n = 1, 2, 3, \ldots$

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

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

m_s $m_s = \pm \frac{1}{2}$

$\hookrightarrow$ specify a quantum state



We introduce the so called configuration of an atom

# of electrons → shell ($n = 1, 2$

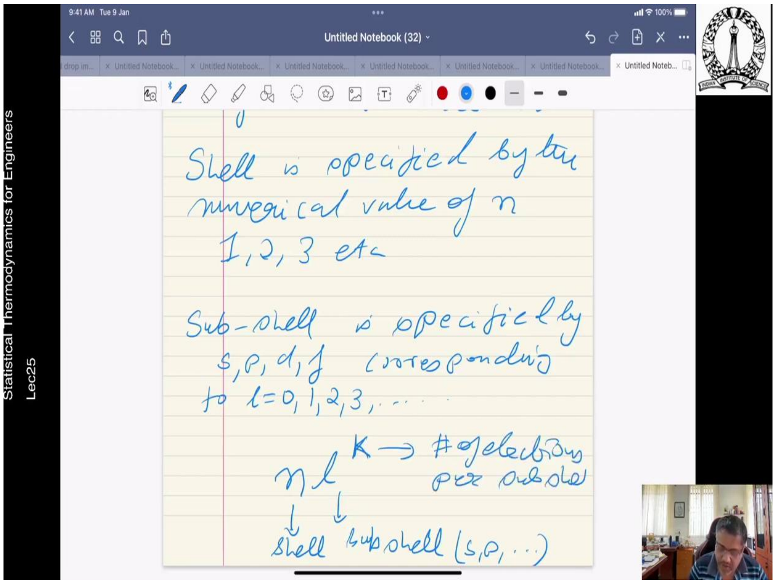
↓

sub-shell ($l = 0, 1, 2, \ldots$)

of a multielectron system

Shell is specified by the numerical value of n

1, 2, 3

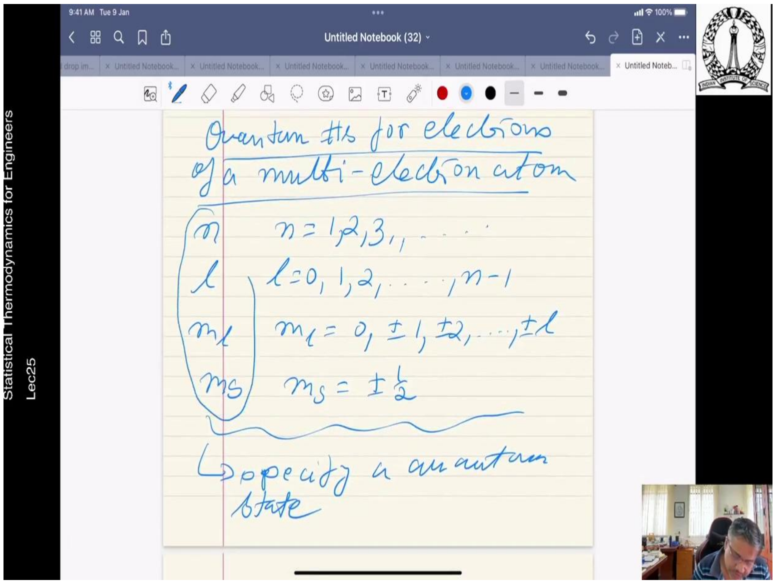


Shell is specified by the numerical value of n

1, 2, 3 etc

Sub-shell is specified by s, p, d, f corresponding to $l = 0, 1, 2, 3, \ldots$

$$\underset{\text{shell}}{\underset{\downarrow}{n}}\;\underset{\text{subshell }(s,p,\ldots)}{\underset{\downarrow}{l}}^{K} \quad K \rightarrow \#\text{ of electrons per subshell}$$



Quantum #s for electrons of a multi-electron atom

n $n = 1, 2, 3, \ldots$

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

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

m_s $m_s = \pm \frac{1}{2}$

↳ specify a quantum state

So, it is kind of not always easy to find out solutions to this. So, there is a process called Hartree-Fock procedure. So, what does this procedure actually do? So, Hartree-Fock procedure, we use this procedure to basically find out accurate solutions, solutions for many atoms, many. So, it is usually done like this.

So, the psi, the wave function, the total wave function is multiplied i equal to 1 to N, and this is represented by some element, phi. So, overall wave function is a product of independent wave functions. And especially this phi i, is given a summation of N i j sum over j C i j exponential j r. So, this is a normalization constant, optimization constant. These are, this and this, these two, these two are variational parameters.

These two are variational parameters used to obtain the final solution, solution. So, these are also called, phi i r i are also called the trial wave functions. So, what the solution, so this trial wave functions represent basically specific solutions to, specific solutions to the Schrodinger's wave equation, Schrodinger equation. Or independent electrons moving in an effective potential.

Trial Solutions, these are specific solutions to the Schrodinger's equation for independent electrons moving in an effective potential, mind the word effective potential, this is which is interactive in nature basically, interactive, created by nucleus, nucleus, by the nuclei, by nuclei, actually, by nuclei and electrons. Nuclei and electrons

So, final solution is obtained by iteratively guessing the values of this above new parameters and so on until we get some convergence. So, you, you, what you do is that basically you guess values and then you see that whether it converges. So, many, so, it is like an iterative kind of a solution, iterative solution. So, it works very well, works well for Z less than equal to around 40.

Does not, does not work or Z greater than 40, that means heavier atoms, it does not work at all. So, it works but similar calculations for larger atoms and for diatomic molecules, it does not really work that way. So, therefore we can infer that Schrodinger wave equation, wave equation, equation has operational limitations, operational limitations, operational limitations.

And cannot provide accurate electronic energies, and cannot provide accurate electronic energies, energies for atoms and molecules or multielectron basically, multielectron molecules. So, these are operational limitations. So, you principally depend on, depend on molecular and atomic spectroscopy, atomic and molecular spectroscopy.

So, each electronic level is also characterized by an associated term symbol from which we can, we can extract the electronic degeneracy which is required for the statistical thermodynamics, statistical mechanical calculations. So, so each electronic, electronic energy level, each electronic energy level, energy level is denoted by a term symbol, so which is required for the stat-thermo calculations that we are going to perform later on.

So, we have to develop an appreciation for these term symbols, what they actually mean and how they can be used et cetera et cetera. So, as we saw that how Hartree-Fock orbital procedure can do a lot of stuff, it can give very accurate solutions not only for smaller more compact atoms even for the multielectron kind of a system. Now, let us see that we know now that there are four quantum numbers for the electrons of a multielectron atom.

So, the, so the quantum numbers, let us put it like that, quantum numbers for electrons, of a multielectron, multielectron. So, the first one is n, n equal to, n equal to 1, 2, 3, da, da, da. Then of course, it is l, l equal to 0, 1, 2, dot, dot, dot, n minus 1. Then there is m l, which we know m l is equal to 0, plus minus 1 plus minus 2 dot, dot, dot. plus minus l. Then that is m s which is equal to, m s equal to plus minus half.

So, these are the four sets of quantum numbers. So, all four sets of quantum numbers must specify, all these should specify a quantum state. Furthermore, say only one electron can occupy any given quantum state. This comes from Exclusion Principle. Therefore each electron of a multielectron atom can be identified by a unique combination of these four quantum numbers. So, there is only a unique combination of these four quantum numbers that can identify an electron in a multielectron kind of a setting.

So, we introduce the so called configuration of an atom, we introduce the so called configuration of an atom which is a convenient fashion, the number of electrons occupying each shell and sub-shell. That means, so this actually says the electrons, the number of electrons occupying each shell, shell is basically n, 1, 2, et cetera and then the corresponding sub-shell which is basically equal to l equal to 0, 1, 2, dot, dot, dot, so, for multielectron system, multielectron system.

The shell is specified by the numerical values. So, the shell is specified by the numerical value, the numerical value of n, which is basically 1, 2, 3, et cetera. The sub-shell which is orbital quantum number, is specified by s, p, d, f, s, p corresponding to l equal to 0, 1, 2, 3. So, given this nomenclature, so we have identified that the electron should be specified by n and then the corresponding option in which they are residing.

So, this is given in the format n lk. So, n is the principal quantum number which tells you the shell, l is the sub-shell or s, p, d, f, and k is nothing but the number of electrons per sub-shell, number of electrons per sub-shell. So, that is the configuration that we have.

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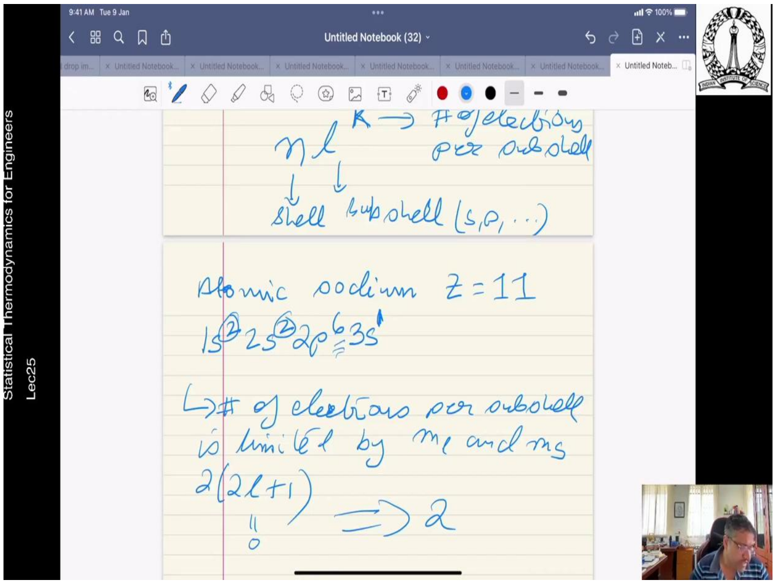


$n\,l\;k \rightarrow$ # of electrons per sub shell

$n \downarrow$ shell, $l \downarrow$ sub shell (s, p, ...)

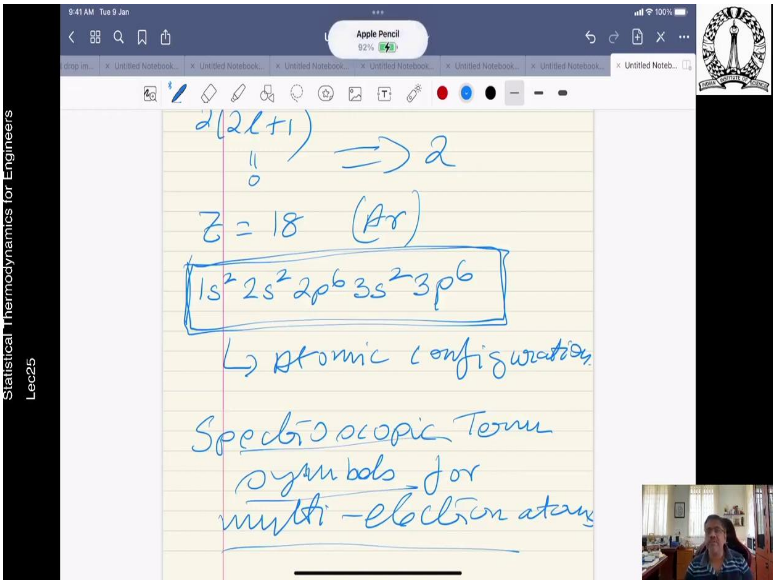
Atomic sodium $Z = 11$

$1s^2 2s^2 2p^6 3s^1$

↳ # of electrons per subshell is limited by m_l and m_s

$2(2l+1) \Rightarrow 2$

$\overset{\|}{0}$



$2(2l+1) \Rightarrow 2$

$\overset{\|}{0}$

$Z = 18$ (Ar)

$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6}$

↳ atomic configuration

Spectroscopic Term symbols for multi-electron atom

So, n represents the sub-shell number. As an example, if you take, take atomic sodium, let us say atomic, atomic sodium for which the Z is equal to 11, the configuration for the ground electronic state will be 1s2 2s2 2p6 3s. So, the number of electrons, but however you see the number of electrons, electrons per sub-shell, sub-shell is limited by, limited by ml and ms, which is 2 into 2 l plus 1.

So, for example when you are at s, s is equal to 0, so there are only two electrons that are possible. When l is equal to 1, so that means the number becomes 3. 3 into 2, 6 electrons are possible in that particular sub-shell so on and so forth. So, you understand when s means l equal to 0, so that means if you put l equal to 0 here, so the number of ways this can be counted is 2. So, that is why you have the number 2.

And you cannot have, because if you see, l varies up to n minus 1. So, at n is equal to 1, l can only be 0, l can only be 0 when n is equal to 1. Correct. So, that is why we have 1 s 2, because there is no p when, when n is equal to 2, l can be 0 and 1, respectively. That means s and p. So, when it is s, when l equal to 0, this is 2, when l is equal to 1, this is actually 3 into 2, 6.

Similarly, you can have 3 s but then we exhaust. So, it is like 2, 2, 6, 10 and 11. So, this is, this is 1, actually. It is what it is. So, in this configuration, in this particular way, you can basically do any kind of, any kind of elements. For example, let us take the example of the Z is equal to say 18. This is Ar. So, what will be the configuration over here? So, first you write 1s2, then 2s2 2p6, out of this, these are common, this is basically common for all of these things.

And then of course you write 2p6 and then what? 2p6, and then what comes after that? Then you have 3s2, n is the same. Now you have like s p d now. So, then it becomes 6 once again. So, this completes the configuration 18. So, you understand, you get a good idea that how this variations is. It basically because of this right and because of this, and because of this right. And of course, this is still the principle quantum number. So, even for a multi-electron system, we can represent how the atomic configuration is.

So, this is how the atomic configuration is, atomic configuration can be written in this succinct kind of a way for this. And then you can do it for n number of these things. So, next class, we are going to do what we call spectroscopic term symbols, term symbols, symbols for multielectron atoms, multielectron. Because these symbols are very important. Some of these symbols you already know from your undergraduate. So, no harm in actually seeing it one more time. Thank you.