**Statistical Thermodynamics for Engineers**
**Professor Saptarshi Basu**
**Indian Institute of Science, Bengaluru**
**Lecture 37**
**Spectroscopic Term Symbols for Multielectron Atoms**

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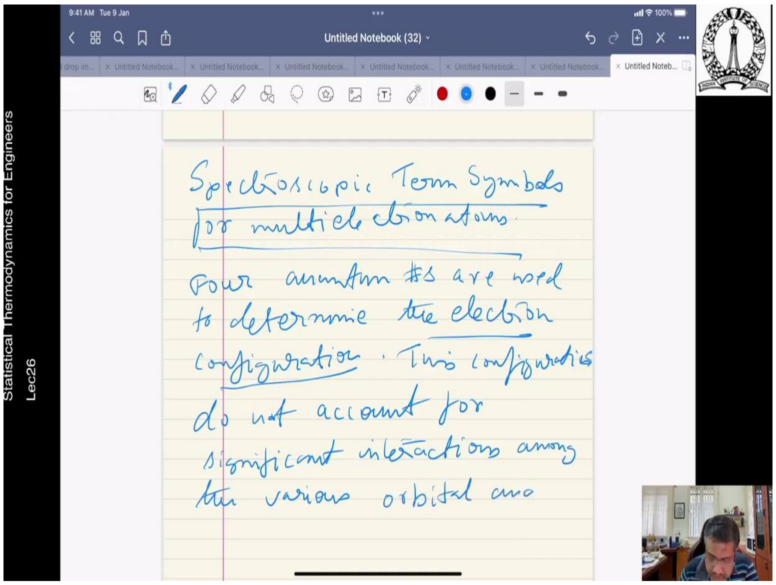


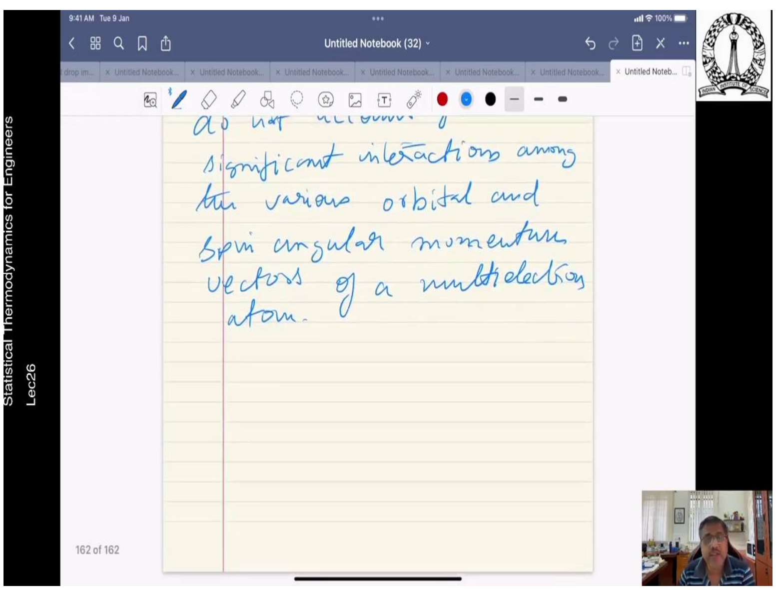

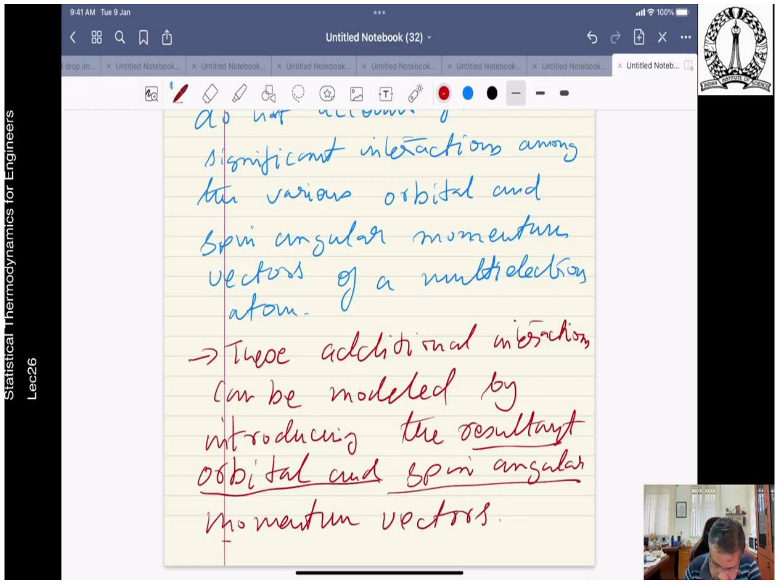


Welcome to lecture number 26 of this Statistical Thermodynamics course. So, this time our main focus will be on spectroscopic, spectroscopic term symbols, symbols for multielectron atoms, electron atoms. So, that would be the first thing that we will do here. So, the electronic configuration, now, let us look at it now in a little bit more details. So, that, so we can, in this lecture.

So, so basically four quantum numbers, quantum numbers quantum numbers are used, used to determine, used to determine the electron configuration, electron configuration. But that is what we saw in the last lecture. But however, however this configuration, this configuration, configuration it does not count for, do not account, this configuration do not account for significant interactions, significant interactions, interactions among the various orbital and spin angular momentum vectors, vectors of the multielectron atom.

So, though the four quantum numbers are essential and they are used to determine the electronic configuration, but they are not enough because there are significant interactions around the various orbital and the spin angular momentum vectors.

So, these interactions can be therefore modeled with additional interactions, these additional interactions, interactions can be modeled, can be modeled by introducing, by introducing the resultant, mark the word resultant orbital, and spin angular momentum vectors, with the resultant orbital and spin angular momentum vectors.

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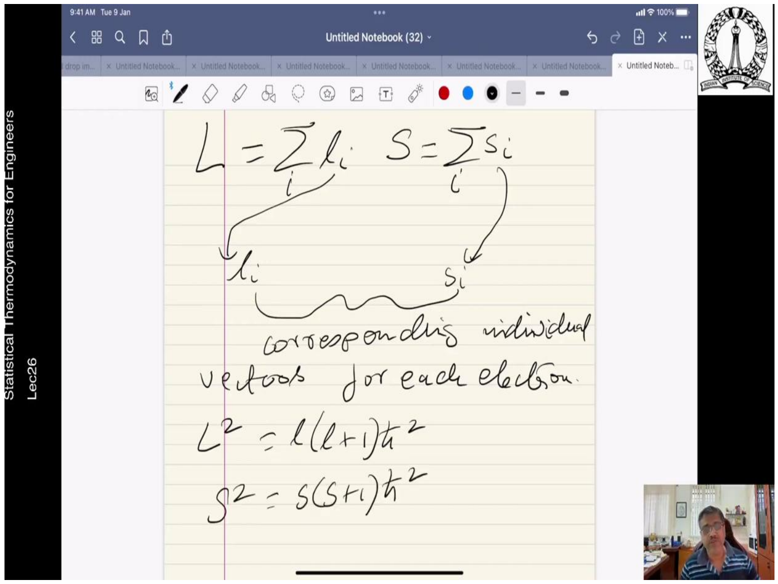


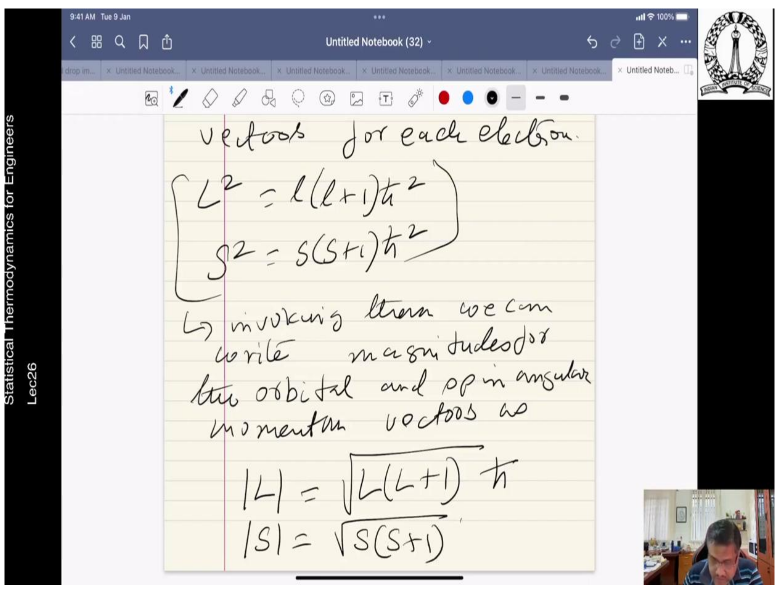

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$$|L| = \sqrt{L(L+1)}\,\hbar$$

$$|S| = \sqrt{S(S+1)}\,\hbar$$

where L and S are the resultant orbital and spin angular momentum quantum numbers respectively.

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Spin-orbit (Russell-Saunders) coupling which dominates for multielectron atom with $Z < 40$.

Total angular momentum vector as

$$J = L + S$$

coupling which dominates for multielectron atom with $Z < 40$.

Total angular momentum vector as

$$J = L + S$$

Spin-orbit coupling ~~f~~ orbital, spin and total angular momentum vectors exercise

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momentum vectors exercise

pronounced effect on the allowed energy levels and consequently the spectrum of a multielectron atom.

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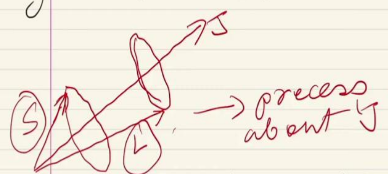


precession affects the electronic energy of a multielectron atom.

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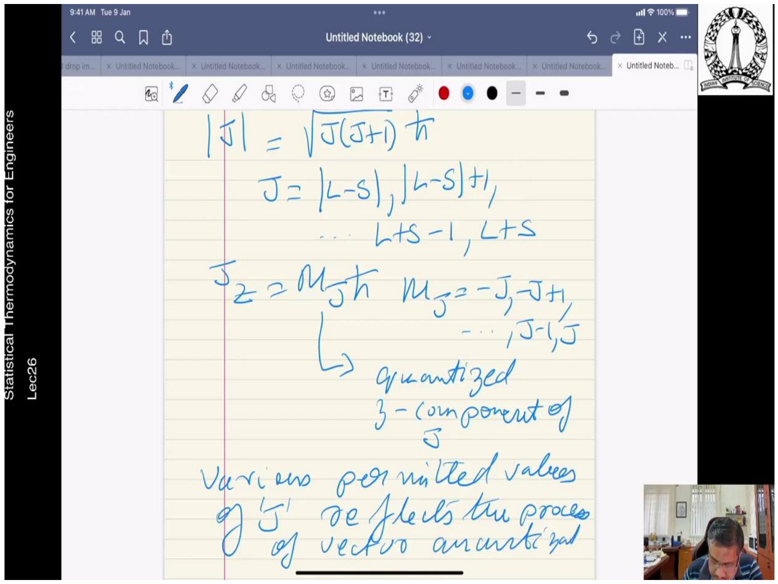
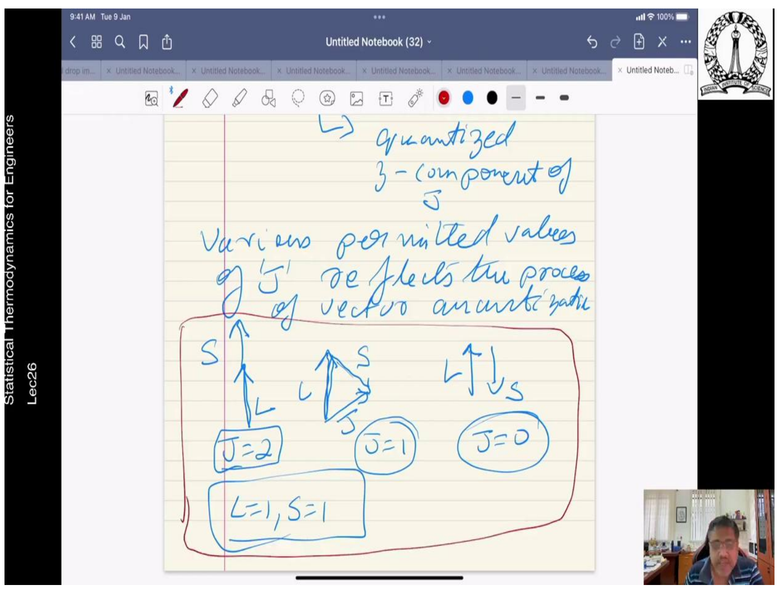
precession affects the electronic energy of a multielectron atom.

Because of this coupling, the total angular momentum vector becomes quantized.




So, this means this means L is summation of l i over i, S is summation of a s i over i, where l i and S i, what do they indicate? They indicate the corresponding, the corresponding individual vectors, individual vectors, vectors, for each, for each electron, which we already know. So, now, so this is the, this is the first step that we did. Now, we can draw an analogy from, if you look at equations, let me rewrite equation once again.

So, if you if you recall that L square equal to l into l plus 1 into h bar square, and, and, and S square equal to s into s plus 1 h bar square. So, if you recall these two. So, therefore, now using these two or invoking them, invoking them, we can say, write with the magnitudes, the magnitudes for the orbital spinning angular momentums, momentum vectors  momentum vectors as h bar and S equal to s s plus 1 h bar. So, where L and S are the resultant orbital and spin angular, angular momentum quantum numbers respectively.

Now, if we introduce the, introduce the spin-orbit coupling, spin-orbit, which is also called Russell-Saunders coupling, which dominates, which dominates, dominates for multielectron atoms with Z less than 40. So, we can write the total, total angular momentum vector as J equal to L plus S.

So, because of this coupling, because of the spin-orbit coupling, because of the spin-orbit coupling, the orbital spin and total angular momentum exercise a pronounced effect on the allowed energy levels, and thus, the spectrum.

So, because of this and the orbital, because of the spin orbital coupling, the orbital then spin and total angular momentum, angular momentum vectors, vectors exercise pronounced effect, pronounced effect on the allowed energy levels, energy and consequently the spectrum. The spectrum, the spectrum of a multielectron, multielectron atom. So, the spectroscopic classification is a nomenclature basically and it provides a scheme for labeling these energy levels.

So, if you just look at the Russell-Saunders what we mean, so this is like, let us show it like this. This is J. So, this is L, so this is like the vector model for this Russell-Saunders model. So, the coupling. So the coupling can be also understood that a coupling between such vectors. So, it is basically between such vectors, it introduces what we call a natural torque. So, n l and s will precess about J. So, L and S, as you can see this is S.

So, and L will precess about, precess about J. This induced precession, this, because of this precession, precession is like this, so it produces this precession because of this coupling and because of this precession. So, this precession affects, this precession affects the electronic energy, electronic energy of multielectron system, electron atom.

Got it? So, because of this, so because of this coupling, the total angular momentum vector becomes quantized. Because of this coupling, coupling, the total angular momentum, momentum vector becomes quantized. So, J is equal to L minus S, L minus S plus 1, L plus S minus 1, all the way up to L plus S.

J z which is basically, we will see what that is, M J h bar, M J is minus J minus J plus 1, J minus 1, J. So, J is the total angular momentum. M J is obviously, is obviously the quantized Z component, J. So, various permitted values of J, various permitted values of J, values of J reflect the process of vector quantization, reflects the process of vector quantization. And we can give a picture to demonstrate that.

So, let us look at this picture. So, J is equal to 2, L, this is S. So, this is for L equal to 1, S is equal to 1. Then J equal to 1. So, L is this, S would be like that. This is J. Then J equal to 0, it is like this. So, this is like additive because these two are unity. So, this is two, same direction. These are all unity.

So, therefore, this is J equal to 1, and this is J equal to 0. So, this is how the L and S, if they are all unity, so, this is the way the vector quantization actually happens.

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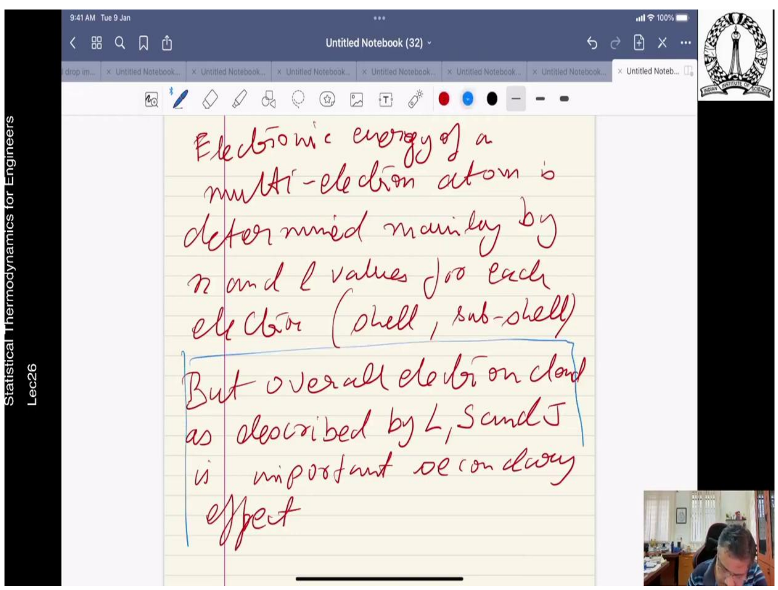

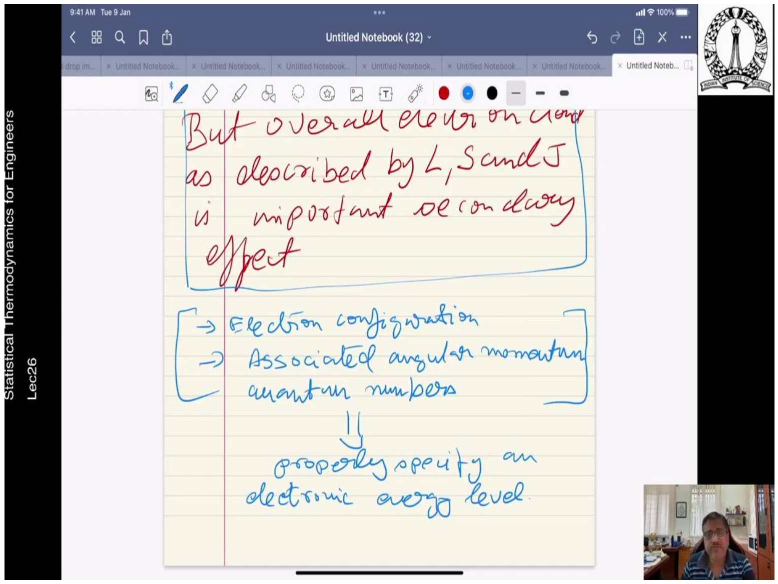


So, the electronic energy of a multielectron system is primarily determined. So, we can, we can say that the electronic energy, electronic energy of a multielectron system, multi-electronic atom is determined by, is determined mainly by n and l values for each, each electron, which was the shell and sub-shell concept that we had, that spdf.

But overall, but overall, overall, electron cloud, electron cloud, if we consider the electron cloud as described by L, S, and J. This is important secondary, secondary effect. So, this is an important secondary effect on the electron cloud. Therefore both, so what we require? We require the electron configuration, electron configuration and also the associated, and the associated angular momentum quantum numbers, angular momentum quantum numbers, quantum numbers.

To, these two are required to basically properly specify, properly specify an electronic, electronic energy level. These two are required for specifying the electronic energy level.

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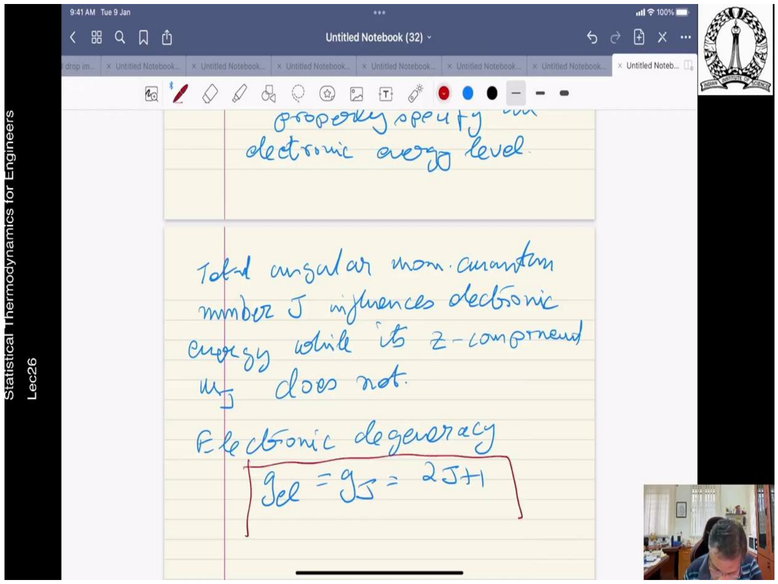


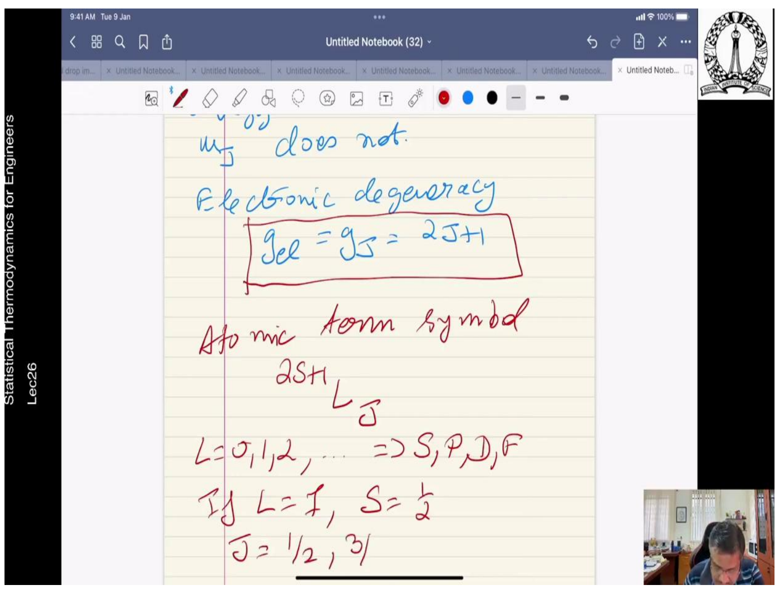

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Term symbols

$^2P_{\frac{1}{2}}$ $^2P_{3/2}$

doublet P states.

↳ characteristic of all alkali metals like Sodium and Potassium.

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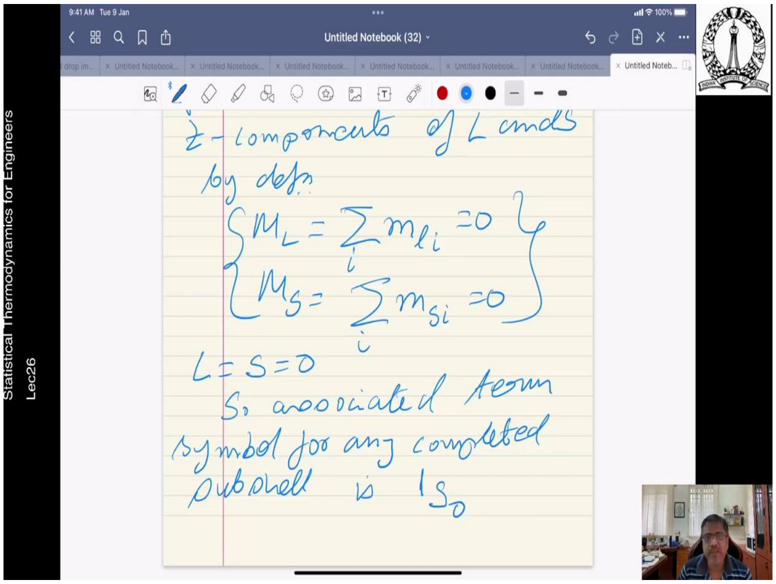
Sodium and Potassium.

for any completed subshell z-components of L and S by defn

$$\left\{\begin{array}{l} M_L = \sum_i m_{l_i} = 0 \\ M_S = \sum_i m_{s_i} = 0 \end{array}\right\}$$

$L = S = 0$




Moreover, the, it should be noted now that the total angular momentum angular momentum quantum number J, quantum number J influences electronic energy while its Z component, Z component m J does not, while its other component does not. The electronic degeneracy, degeneracy g el is equal to g J is equal to 2 J plus 1. The term classification for the electronic state of a multi electron atom is predicted by the need to specify L, S and J.

So, in general atomic term symbol is given in this form, 2 S plus 1 L J. So, L equal to 0, 1, 2, da, da, da is equivalent to say S, P, D, F. So, if L equal to say 1, and S is equal to plus half, then what will be J? J will be half and 3 by 2. J, we already have designated what is J going to be here, that is your J. So, that is the J. And therefore, the total degeneracy is also 2 J plus 1. So, J is this.

Hence, the relevant term symbols would be, term symbols will be for this particular case is 2 P half, and then 2 P 3 by 2. So, in other words this has also has got a fancy name, this is called the doublet, doublet P states. So, this is the characteristic of, characteristic of all alkali metals, alkali metals like, like sodium, sodium and potassium. So, the electronic level of an atom requires a specific term symbol.

So, for completeness, now if we take the, if we write the ground electronic state for all the 18 elements that were there in the book, Table 6.6 can be consulted, we know that for any completed, for any completed, completed sub-shell, sub-shell, the Z-components, the

Z-components of L and S, this is the sum total by definition, M L is equal to summation m l i, which is 0, and M S summation over i m s i equal to 0.

As a result of this, L is equal to S is equal to 0. So, the associated term symbol for any, so associated term symbol, term symbol for any, any completed sub-shell, any completed sub-shell is 1 S 0 because that is 0, L equal to 0. And if you look at the nomenclature, S equal to 0. So, that is 1, and then J obviously is, J is obviously equal to 0 as well.

So, therefore, we may safely ignore all quantum numbers affiliated with completely filled inner sub-shells, when determining the relevant term symbol. So, for the relevant term symbols, we just need the un-filled, un-filled, inner unfilled sub-shells, so to say.

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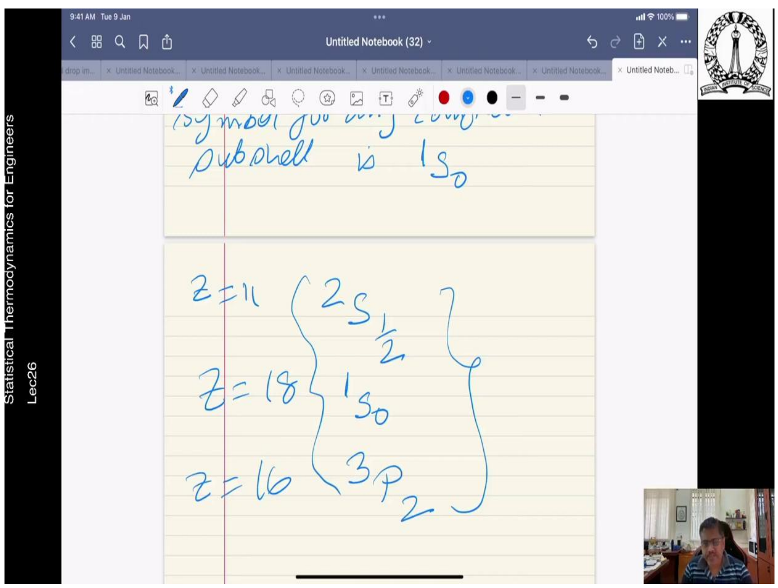

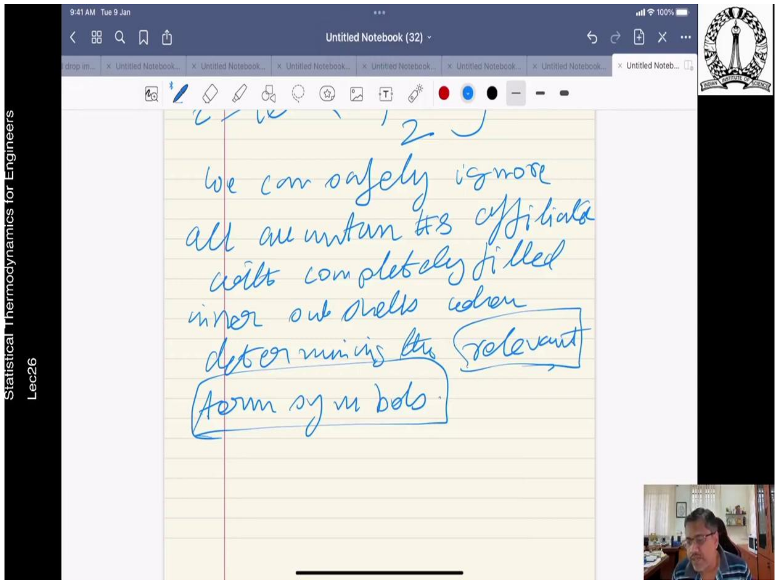


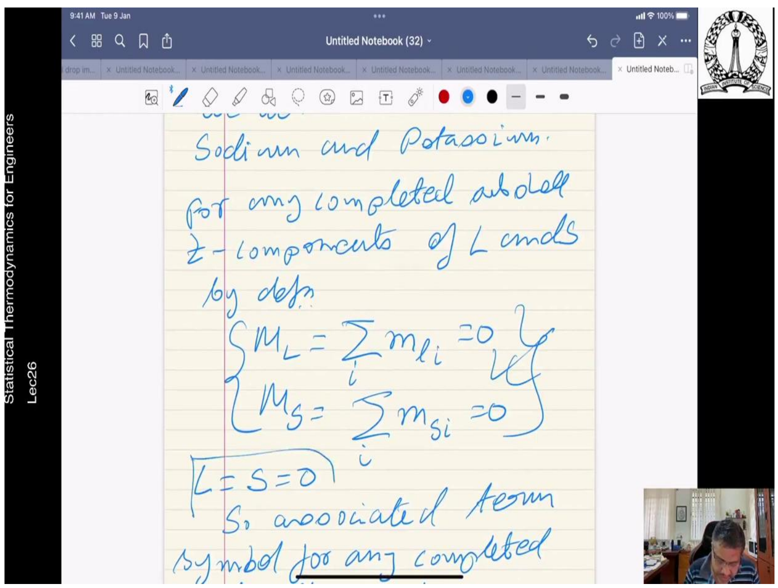


So, this is also given. For example, let us take an example, let us say for Z equal to 11, so that was sodium. So, the term symbol in this case will be 2 S half. Similarly, if Z is equal to say 18, the term symbol will be 2 S, sorry, term symbol will be 1 S 0. Similarly, if it is Z equal to say, 16, the term symbol will be 3 P 2. These are the different term symbols that, that we can write because of this.

The empirical rules for all these things, so you can, so as I said earlier that if we take safely, ignore, let me write it here that we can safely ignore, ignore all quantum numbers, all quantum numbers affiliated with completely filled, filled inner sub-shells, inner sub-shells when determining, when determining the relevant terms symbols. So, you can, I have shown a few examples of it here that this is what it is.

And therefore, the term symbols can be, can be associated in the way that we talked about. So, in the next one, we will do the electronic energy levels and the degeneracy for atoms. But before that, just take a look that for any completed sub-shell, this particular relationship is valid, which leads to L equal to S equal to 0.

So, that means you do not need to consider those field inner shells when you determine the relevant term symbols. So, in the next class we will take a look about but what are the other, what is the electronic energy levels and the degeneracy for atoms, and we will take it forward from there. Thank you.