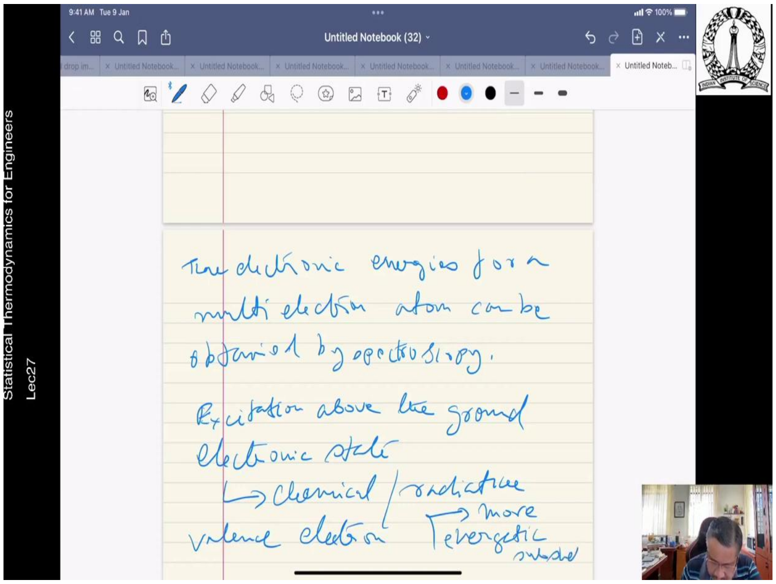
Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 38
Electron Energies for Multielectron Systems

(Refer Slide Time: 00:01)

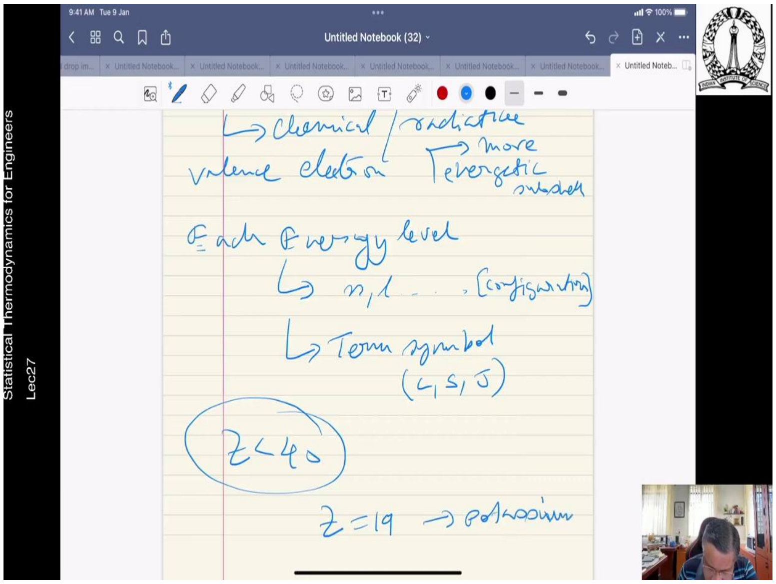


The electronic energies for a multi electron atom can be obtained by spectroscopy.

Excitation above the ground electronic state

↳ Chemical / radiative

valence electron | → more energetic subshell



↳ Chemical / radiative

valence electron | → more energetic subshell

Each Energy level

↳ $n, l, \ldots$ [configuration]

↳ Term symbol (L, S, J)

$\boxed{Z < 40}$

$Z = 19$ → potassium

Welcome to lecture number 27 of the Statistical Thermodynamics course. So, let us see. So, in this lecture we are going to cover how the electronic energies or electronic energy levels and degeneracies of atoms can be typically written for a multielectron technical system. So, let us look at, so we are going to take a look at the corresponding definitions and how this can be best written.

So, in the previous class also we provided quite a bit of information that that how term symbols can be written. Here, the electronic energies, the electronic energies, the electronic energies, energies for a multielectron, multielectron atom can be obtained, it can be obtained by spectroscopic methods by spectroscopy. This, we already told earlier that it is developed from spectroscopy.

So, typically excitation about the ground electronic state occurs due to chemical or radiative processes that excites a signal valence electron to a more energetic sub-shell. So, what happens is that excitation, excitation above the ground electronic state, ground electronic state is usually determined by chemical or radiative process, chemical slash radiative process. What it does is that it takes a valence electron, electron, and promotes it, promotes it to a more energetic, energetic sub-shell.

Now we already know that each energy level, let us take each energy level, now those energy levels are designated by, the configuration part is designated by n l et cetera, this is the configuration part, atomic configuration. That is why we know the 2s2, 2p6 and stuff like that. And then you have the term symbol which takes into account the interactions which is L, S and J.

So, the term symbol and the electronic energy, so those are kind of, can be listed. So, similar for simple elements which is below Z equal to 40, below Z equal to 40 can be written in this particular form. So, let us take Z equal to 19, which is basically nothing but potassium. So, let us look at how the energy actually looks like

(Refer Slide Time: 03:40)

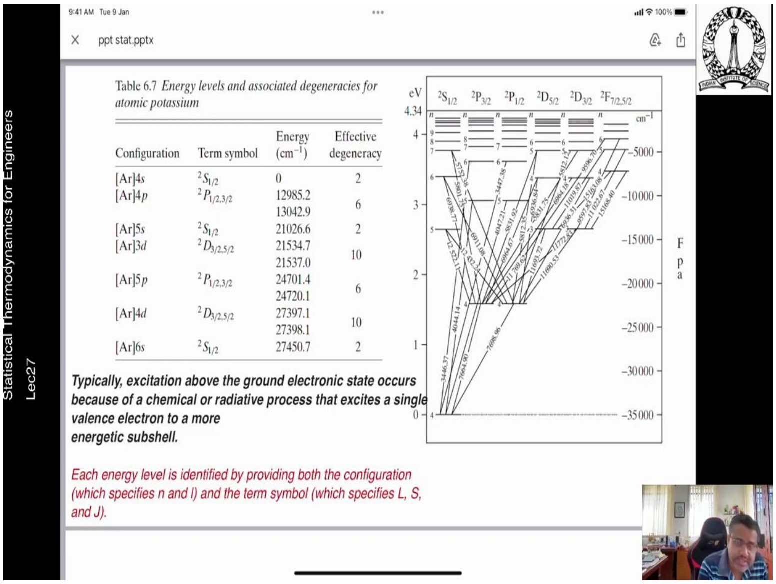


Table 6.7 *Energy levels and associated degeneracies for atomic potassium*

Configuration	Term symbol	Energy (cm^{-1})	Effective degeneracy
[Ar]4*s*	$^2S_{1/2}$	0	2
[Ar]4*p*	$^2P_{1/2,3/2}$	12985.2 13042.9	6
[Ar]5*s*	$^2S_{1/2}$	21026.6	2
[Ar]3*d*	$^2D_{3/2,5/2}$	21534.7 21537.0	10
[Ar]5*p*	$^2P_{1/2,3/2}$	24701.4 24720.1	6
[Ar]4*d*	$^2D_{3/2,5/2}$	27397.1 27398.1	10
[Ar]6*s*	$^2S_{1/2}$	27450.7	2

Typically, excitation above the ground electronic state occurs because of a chemical or radiative process that excites a single valence electron to a more energetic subshell.

Each energy level is identified by providing both the configuration (which specifies n and l) and the term symbol (which specifies L, S, and J).

So, so the energy for potassium is written in this particular fashion. So, this is, these are the energy levels and the associated degeneracies for atomic potassium. So, as you can see that the configuration, when it is, this is, that in the argon configuration and 4s. The term symbol is written as 2 S half. And so, and this is the -- and the effective degeneracy is given by 2. We will come to the point that what is actually called effective degeneracy in just a little bit.

So, similarly, when you look at the other configuration, the electronic energies of potassium, so these are the electronic energy levels of potassium, level diagram. So, and then each energy level as we can see is provided by both the configuration which is n and l, and the terms symbols which provides L, S and J. So, that is why you have a doublet state here with a degeneracy of 6.

So, these are the different energy levels, and if you look at the diagram, if you look at the diagram on the right hand side, if we look at the diagram, this is also portrayed by the, by the allowable transitions over here. So, the transition part also you could see that allowable transitions that can happen. So, this is basically the energy diagram, this is basically the corresponding figure, figure which shows, which is a more graphical description.

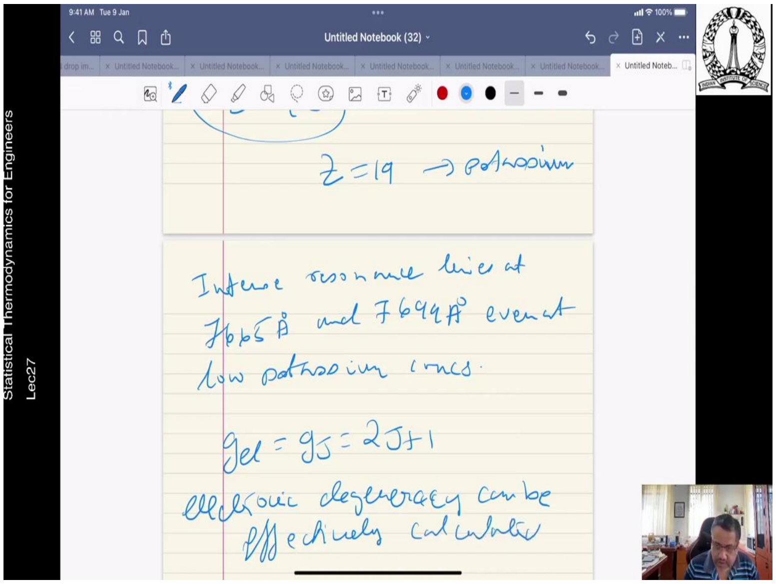
And it also indicates the allowable energy transitions including the wavelengths of the resultant spectral lines. So, that is what is actually given in angstrom. So, if you look at the units, they are given in angstrom. So, the intense, you can see a few things, there are some intense resonance lines at 7665 and 7699. These are observed even at very low potassium concentrations, 7655 and 7699.

These are the resonant, these are the two resonant lines that are readily available. So, you can see there, you can see a couple of them, especially here. So, if you look at the lower part, here you can see the lines. And so, that is a couple of lines which is, which is of interest. So, much can be learned between this relationship between this electronic energy levels and the atomic spectroscopy with the relationship between the two.

So, so also figure 6.8 indicates that potassium is characterized by doublets. There is a lot of doublets as you can see over there. Just look at the term symbol, you will get an idea that there are a lot of doublets. Typical spectral features of other atoms however can include triplets, quartets, quintets and sextets. So, in fact these are quite possible and we will see what the effective degeneracy is. This is something that we have not covered so far. We will do that in a in a minute.

But as you can see potassium, this is a typical energy level diagram for potassium, and this indicates that what are the allowable energy levels and what are the allowable energy transitions that you can have. As a result of that, as a result of that you can, you can also construct diagrams in which you can see which are the allowable energy levels as well. So, that is an important feature of this particular, this particular thing.

(Refer Slide Time: 07:40)

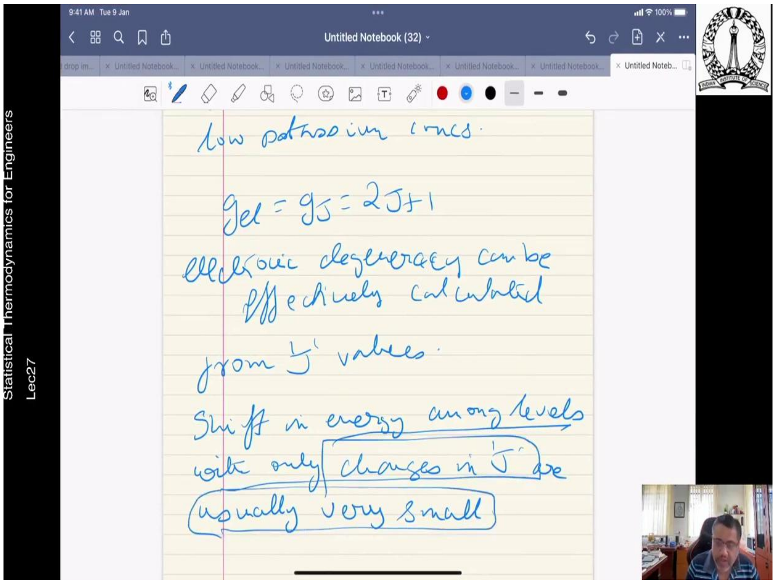


Z = 19 → potassium

Intense resonance lines at 7665 Å and 7699 Å even at low potassium concs.

$g_{el} = g_J = 2J+1$

electronic degeneracy can be effectively calculated

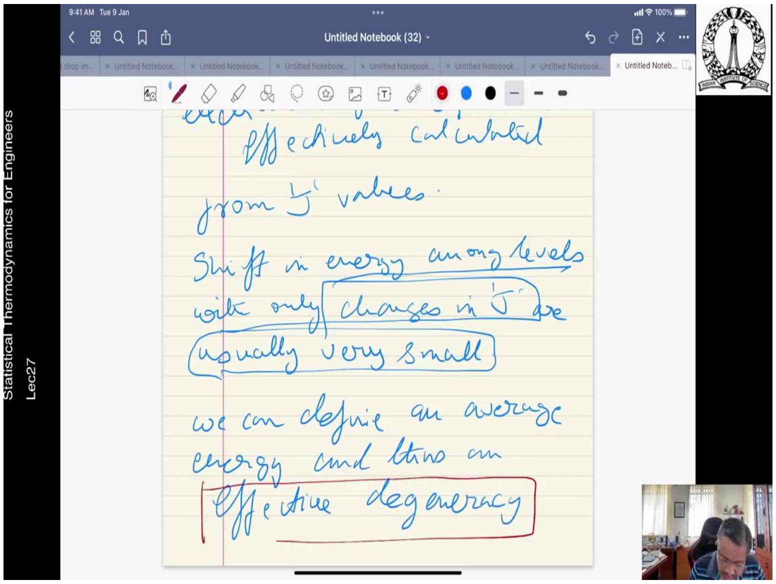


low potassium concs.

$g_{el} = g_J = 2J+1$

electronic degeneracy can be effectively calculated from 'J' values.

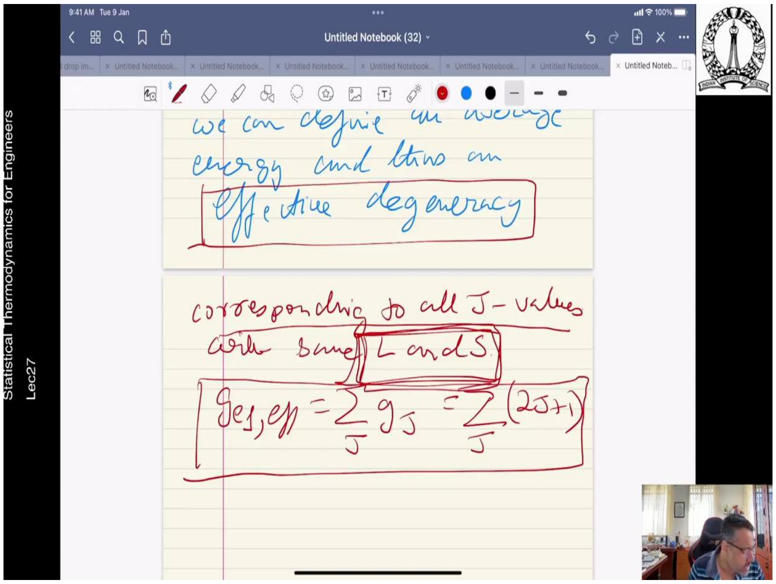
Shift in energy among levels with only changes in 'J' are usually very small



effectively calculated from 'J' values.

Shift in energy among levels with only changes in 'J' are usually very small

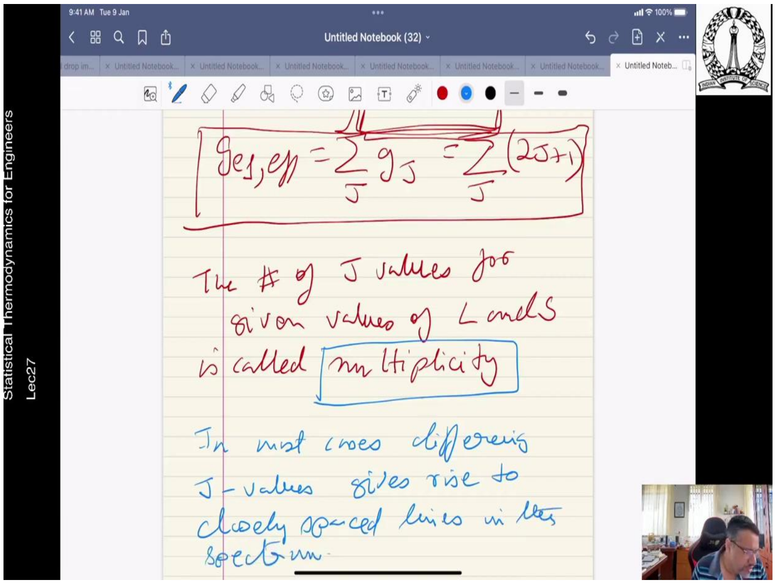
we can define an average energy and thus an effective degeneracy



we can define an average energy and thus an effective degeneracy

corresponding to all J-values with same L and S.

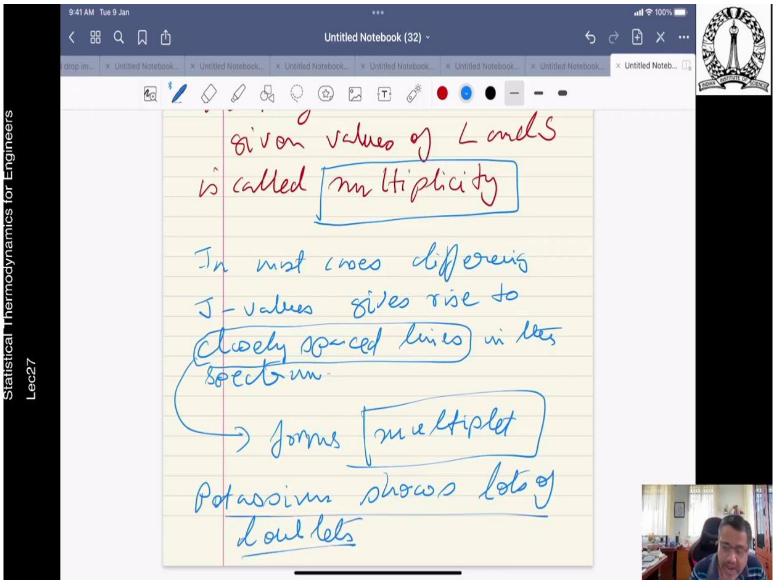
$$\boxed{g_{el,eff} = \sum_J g_J = \sum_J (2J+1)}$$



$$\boxed{g_{el,eff} = \sum_J g_J = \sum_J (2J+1)}$$

The # of J values for given values of L and S is called $\boxed{\text{multiplicity}}$

In most cases differing J-values gives rise to closely spaced lines in the spectrum.



given values of L and S is called $\boxed{\text{multiplicity}}$

In most cases differing J-values gives rise to closely spaced lines in the spectrum.

→ forms $\boxed{\text{multiplet}}$

Potassium shows lots of doublets

So, just writing down a few things. So, you can see intense resonance lines at 7665 angstrom and 7699 angstrom even at low potassium, potassium concentrations, these lines they are available. So, now let us look at, now let us look at what is meant by effective degeneracy. Now, we already know that g el is equal to g J is equal to 2 J plus 1. So, this is something that we already know.

So, the electronic degeneracy can be effectively calculated from the J values. So, the electronic degeneracy, degeneracy can be effectively, effectively calculated, calculated from J values. However, if you look, if you recall the table that I just showed, the shifts in energy levels, so the shift in energy among levels, among levels with only changes in J, changes J are usually very small.

This is also given in the table that you can just now see. The change in the value, the change in the value of the energies because it is like for example 2154.37, 2153.7. So, this, this variation in energy is very, very low in the case of when there is only changes in J. If you do not recall, this is let us just go back to the to the diagram.

As you can see over here, look at the doublet state P12 and P32, or look at D 3 by 2 and 5 by 2. As you can see, the change in energy is very, very low. For example, it is 3 in the case of this D, 3 by 2 5 by 2. So, as you can see, so therefore, what we have written over here, that the shift in energy among levels with only changes in J is usually very small, very, very small.

So small that we can define, we can define an average, we can define an average energy, because the differential is very small. And thus an effective degeneracy, corresponding to all J-values with same L and S. So g el effective is basically sum overall J g J, which is basically J equal to sum over J 2 J plus 1.So, it just summed over all the things. So, in the same way, so you can understand the corresponding to all J values with the same L and S, remember, with the same L and S, that is mandated.

So, those two, once they are kept the same, we can define an average energy which is basically the average energy of among the different J values, and an effective degeneracy which corresponds to all the, all the J values for the same elements. And this is how you calculate the effective degeneracies. We calculate the effective degeneracy. So, in some cases when the J value is just 1, so it is basically, you can make an estimate that what will be the effective degeneracies in those kind of cases.

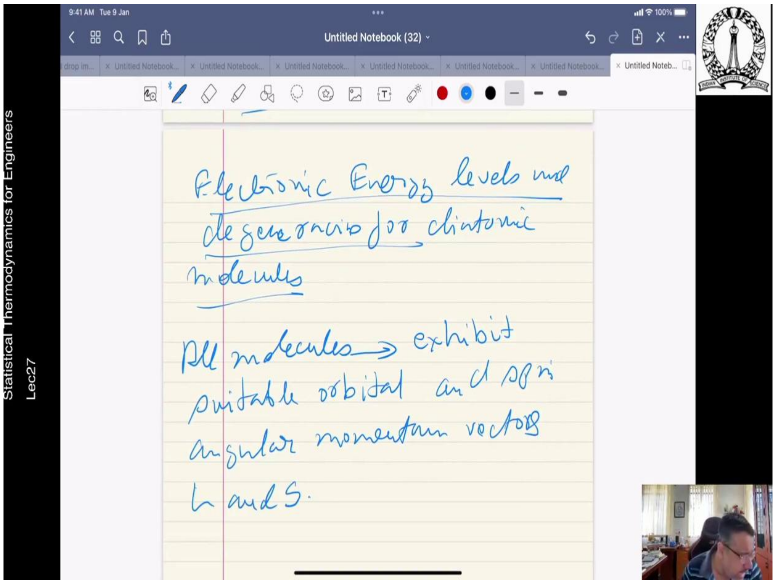
So, so in this case, so let us look at the figure once again because I think that would give us a better idea. So, let us take a look at the degeneracy of the first term, which is given as 2. So, the J value is half. So, 2 into half is 1 plus 1 which is basically gives you 2. Let us look at the second one, which is half and 3 by 2. These are the two J values.

So, 2 into J, 2 into J, so that is basically, and we are summing over all J, remember, we are summing over all J, so you can put half, so it is once again, that is the same as 2, and then you have the other J value also, so which is basically 2 into 3 by 2, which is 3. So, 2 1 plus 3 plus 2. So, that gives you, gradients will be 6. So, this is how you can calculate the effective degeneracies among the multiple levels.

So, the number of J values, the number of J values, values for given values of L and S is called multiplicity, called multiplicity. In most cases, in most cases, in most cases, differing, differing J values or the number of J values or the different J-values gives rise, gives rise to closely spaced, closely spaced lines in the spectrum, which is something that you saw in the figure.

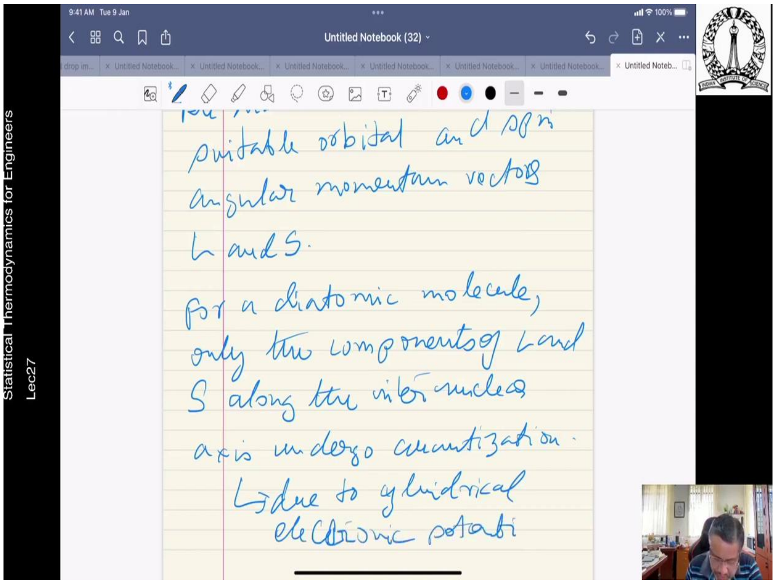
So, as we can, so different J values and which together, these, these closely spaced lines together forms what we call multiplet. So, this is now you can understand that potassium, potassium shows lots, shows lots of doublets. Similarly, there can be other atoms and molecules which can show other kind of symbols as well.

(Refer Slide Time: 15:30)



Electronic Energy levels and degeneracies for diatomic molecules

All molecules → exhibit suitable orbital and spin angular momentum vectors L and S.



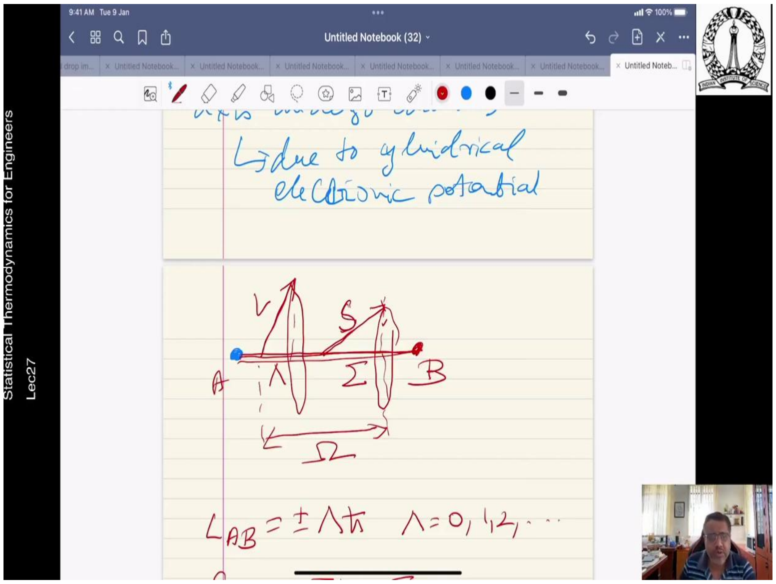
suitable orbital and spin
angular momentum vectors
L and S.
For a diatomic molecule,
only the components of L and
S along the inter nuclear
axis undergo quantization.
↳ due to cylindrical
electronic potenti

So, this is the first thing that we have done. So, we have, we now know that what is effective degeneracy, what is the, what are the kind of transitions that are allowed, and how to, so a particular atom in a multielectron kind of a system is specified not just by the electronic configuration but also, but also by the term symbol. So, these two are important.

So next, what we do is that we look at, we now look at the degeneracies or the electronic energies, so electronic energy levels, energy levels and degeneracies, degeneracies before diatomic molecules. Now, diatomic molecule is a little bit different. So, all molecules exhibit, so let us write all molecules exhibit, exhibit suitable, suitable orbital, orbital and spin, spin angular momentum vectors, vectors L and S, momentum vectors L and S however.

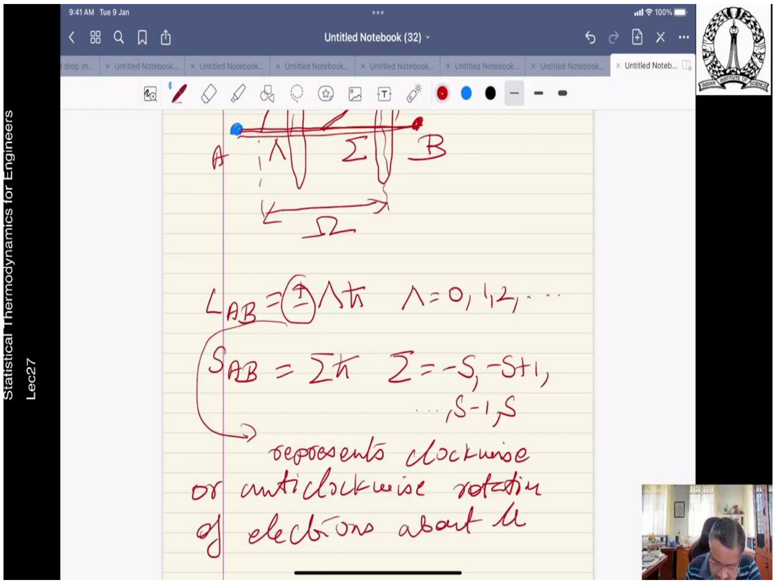
So, it exhibits that kind of a vector, so suitable orbital angular momentum vectors, L and S. However, however, for a diatomic molecule, for a diatomic molecule only the components, only the components of L and S along the inter nuclear axis, along the inter nuclear axis, axis, undergo quantization, undergo quantization. This is primarily due to the cylindrical, rather spherically symmetric electronic potential, due to cylindrical electronic potential.

(Refer Slide Time: 18:20)



↳ due to cylindrical electronic potential

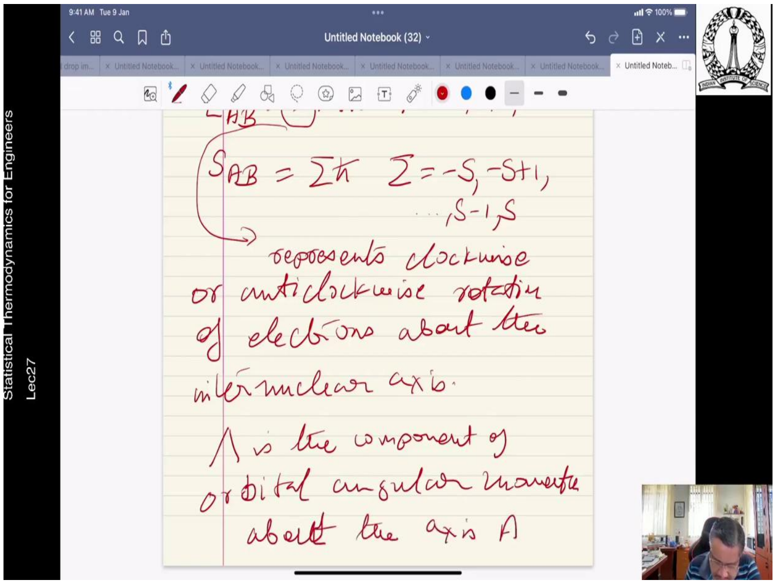
$L_{AB} = \pm \Lambda \hbar \quad \Lambda = 0, 1, 2, \ldots$



$L_{AB} = \boxed{\pm} \Lambda \hbar \quad \Lambda = 0, 1, 2, \ldots$

$S_{AB} = \Sigma \hbar \quad \Sigma = -S, -S+1, \ldots, S-1, S$

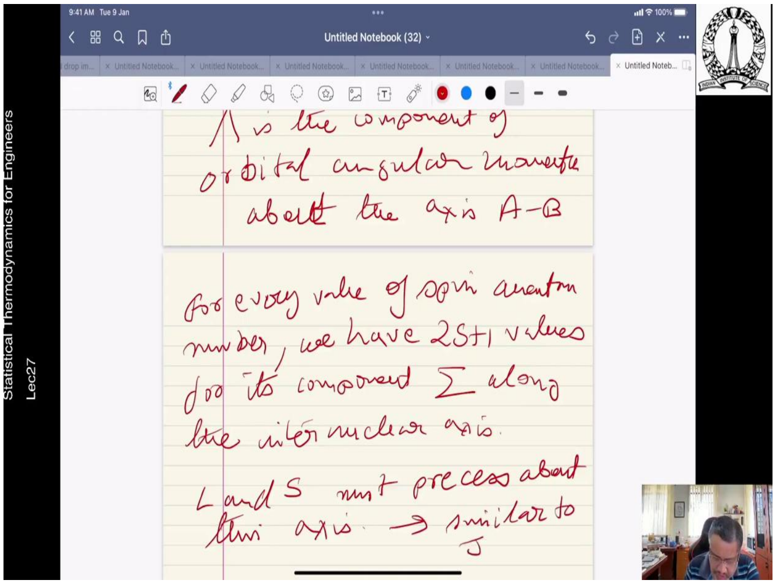
→ represents clockwise or anticlockwise rotation of electrons about it



$$S_{AB} = \Sigma\hbar \quad \Sigma = -S, -S+1, \ldots, S-1, S$$

represents clockwise or anticlockwise rotation of electrons about the internuclear axis.

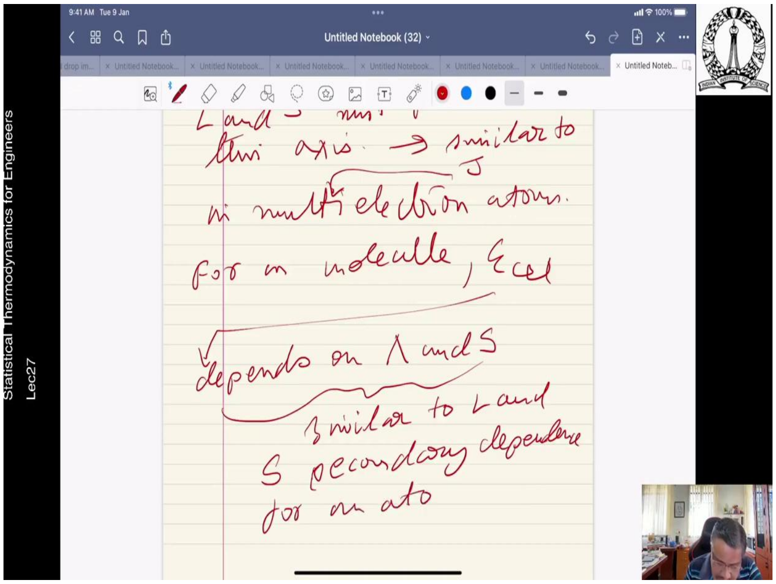
Λ is the component of orbital angular momentum about the axis A



Λ is the component of orbital angular momentum about the axis A-B

For every value of spin quantum number, we have 2S+1 values for its component Σ along the internuclear axis.

L and S must precess about this axis. → similar to J



L and

this axis. → similar to J

in multielectron atoms.

For an molecule, ε_{el}

✓ depends on Λ and S

similar to L and S secondary dependence

for an ato

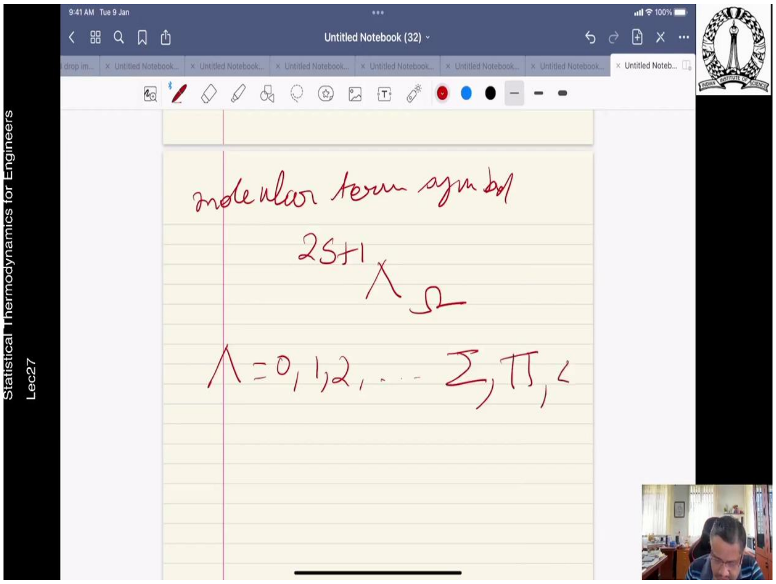
So, if you look at now, a simple figure, so this is going to tell. So, this is say, A, this is say, B. These are the two atoms. This is their inter nuclear distance, A and B, and they say this is your L, and this is your S. So, we are going to take positions along this inter nuclear axis. So, when this is precessing, but this is the part this is written as gamma. So, you can, maybe sigma. And, so this is omega. So, these are the Greek symbols.

So, this is how this is written, primarily. So, that, so your L AB, is plus-minus gamma h bar is equal to 0, 1, 2, dot, dot, dot. S AB, which is the spin is given as summation or basically sigma h bar. So, not summation, minus S, minus S plus 1 up till S minus 1, S. So, the plus-minus term that you see over here, this indicates or represents clockwise or anti-clockwise, clockwise or anti-clockwise rotation, rotation or circulation, circulation of electrons about the inter nuclear axis, not present in the case of spin.

So, this is the component, component of, of orbital angular momentum, orbital angular momentum about the axis A-B, which I drew in this particular figure, A-B, from this axis. So, similarly, similarly in equation, in the equation for S that we wrote, for every value of spin quantum number, for every value of spin quantum number, spin quantum number, we have this 2 S plus 1values for its component, component along the inter nuclear axis, inter nuclear axis.

So, we recognize that L and S, they must precess about this axis similar to, similar to J in multielectron, in multielectron atoms. So, J for multielectron atoms this is L and S, they precess, they precess about the inter nuclear axis. So, for a molecule, so for a molecule, molecule, the electronic energy, e electronic, electronic, it depends on the quantum numbers, depends on these two quantum numbers. This is very similar to the L. This is similar to L and S secondary dependence, secondary dependence, dependence for an atom.

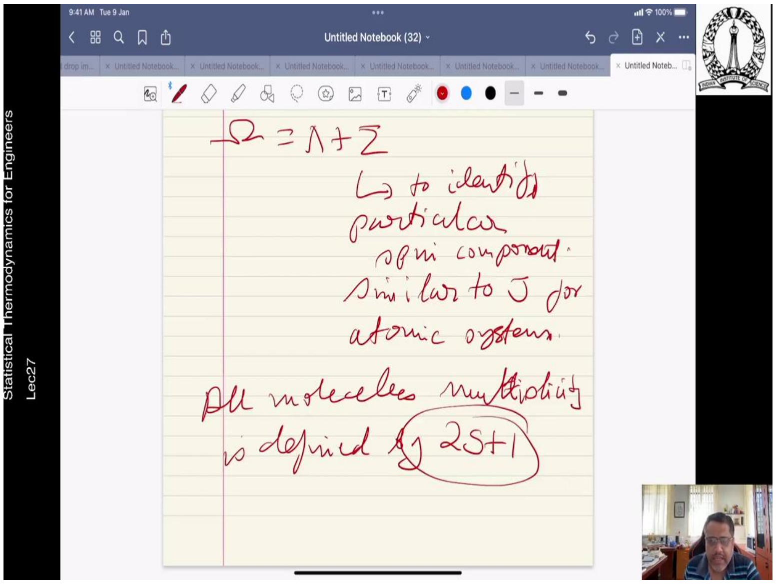
(Refer Slide Time: 23:43)



molecular term symbol

$$^{2S+1}\Lambda_{\Omega}$$

$\Lambda = 0, 1, 2, \ldots$ $\Sigma, \Pi, <$



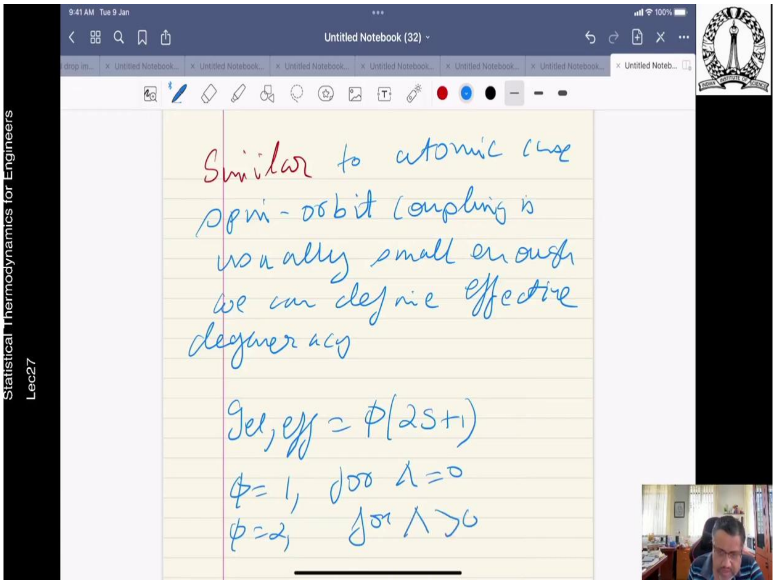
$\Omega = \Lambda + \Sigma$

↳ to identify particular spin component. Similar to J for atomic systems.

All molecules multiplicity is defined by $\boxed{2S+1}$

So, therefore the molecular term symbol, molecular term symbol molecular is 2S plus 1 omega. So, this is 0, 1, 2, represented by, the is represented by summation pi delta et cetera. The subscript omega is equal to sum total of these two, this is basically appended to identify, identify spin component, particular spin component, particular spin component similar to, similar to J for atomic systems, similar to J for atomic systems. For all molecules, all molecules multiplicity, multiplicity is defined by 2S plus 1.

(Refer Slide Time: 25:10)

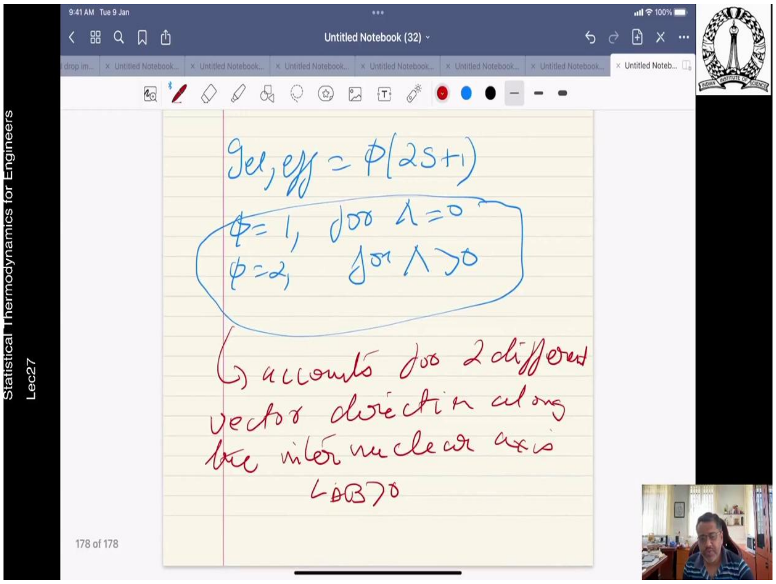


Similar to atomic case spin-orbit coupling is usually small enough we can define effective degeneracy

$g_{el,eff} = \phi(2S+1)$

$\phi = 1$, for $\Lambda = 0$

$\phi = 2$, for $\Lambda > 0$



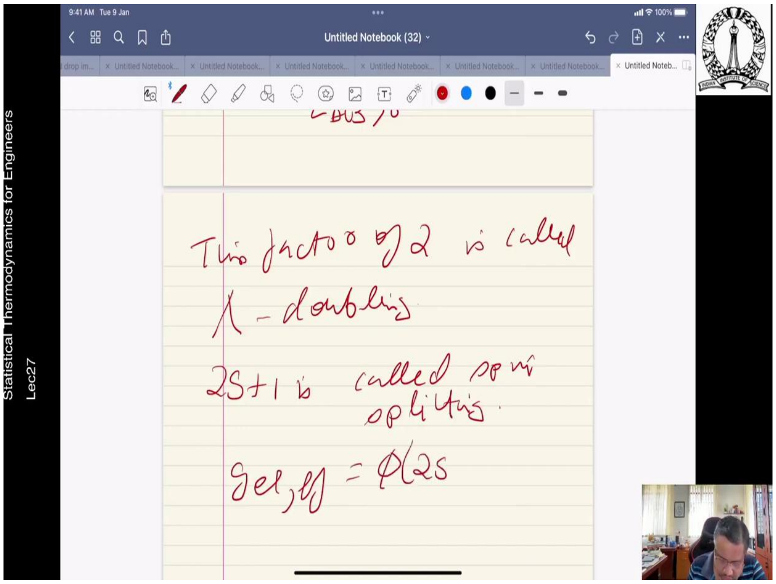
$g_{el,eff} = \phi(2S+1)$

$\phi = 1$, for $\Lambda = 0$

$\phi = 2$, for $\Lambda > 0$

↳ accounts for 2 different vector direction along the internuclear axis

$\langle AB > 0$

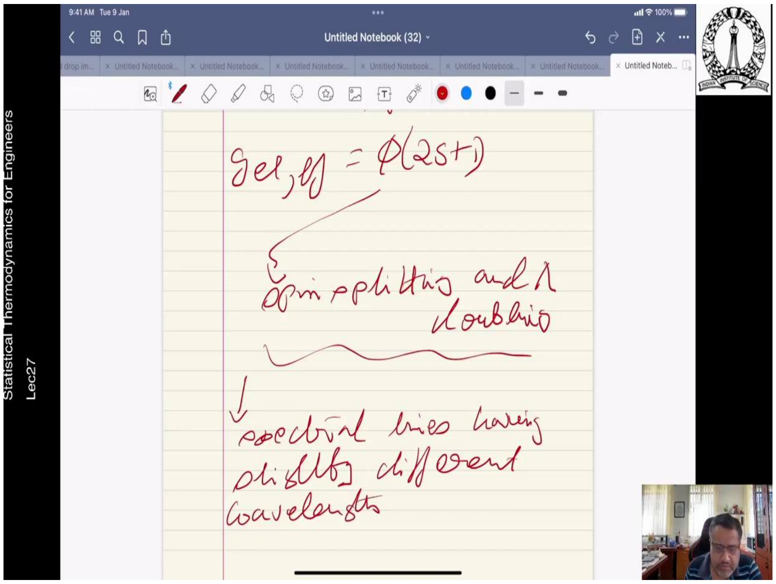


This factor of 2 is called

Λ - doubling

$2S+1$ is called spin splitting.

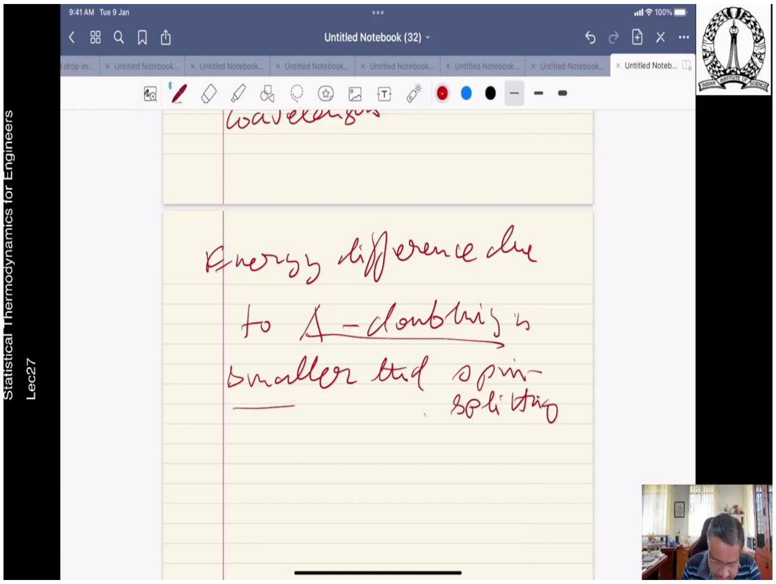
$g_{el,eff} = \phi(2S$



$g_{el,eff} = \phi(2S+1)$

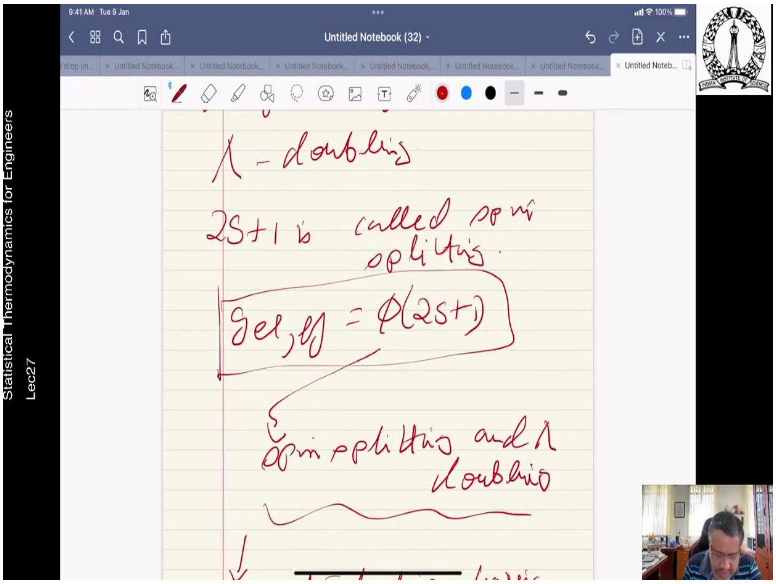
spin splitting and Λ doubling

spectral lines having slightly different wavelengths



wavelengths

Energy difference due to Λ-doubling is smaller than spin splitting



Λ-doubling

2S+1 is called spin splitting.

$\boxed{g_{el,eff} = \phi(2S+1)}$

spin splitting and Λ doubling

And in, like the atomic case, now similar to the atomic case, similar to atomic case, atomic case, where spin-orbit coupling, spin-orbit coupling is usually small, is usually small enough, so we can define, we can define very similarly, an effective degeneracy, effective degeneracy, degeneracy which is given as g el effective is phi into 2S plus 1. So, where phi is equal to 1 for gamma equal to 0 and phi equal to 2 for greater than zero.

Thus, accounting for, this basically accounts for the two possible vector directions along the inter nuclear axis. So, this counts for two different, different vector directions, vector directions along the inter nuclear axis when L AB is greater than 0. These two factors, this factor of 2, this factor of 2, this factor of 2 here is called gamma doubling. And 2S plus 1 is called spin splitting.

The degeneracy therefore is, is the degeneracy that is defined g el effective, phi into 2S plus 1, is clearly, is clearly effective, is the clearly effective as spin splitting, spin splitting and gamma doubling. So, this leads to, this leads to spectral lines, leads to spectral lines, having slightly different wavelengths, slightly different wavelengths. Although, the energy difference, but however one thing that you should note here that the energy difference, difference due to gamma doubling is smaller than spin splitting.

So, so this is akin to the atomic case, so the electronic energies for diatomic molecules are also typically derived from the spectroscopic measurements which we will cover in more details a little later, but these are the different term symbols and these are the different significances, these are the different degeneracy values that we have got out of this, out of this exercise.

So, next we will look at something which is a little bit more interesting, we would look at the combined energy modes for atoms and diatomic molecules. But before that, we are also going to look at the typical electronic energy levels for oxygen, say, for example. So, that we will do in the next class.