Introduction to Solid State Physics

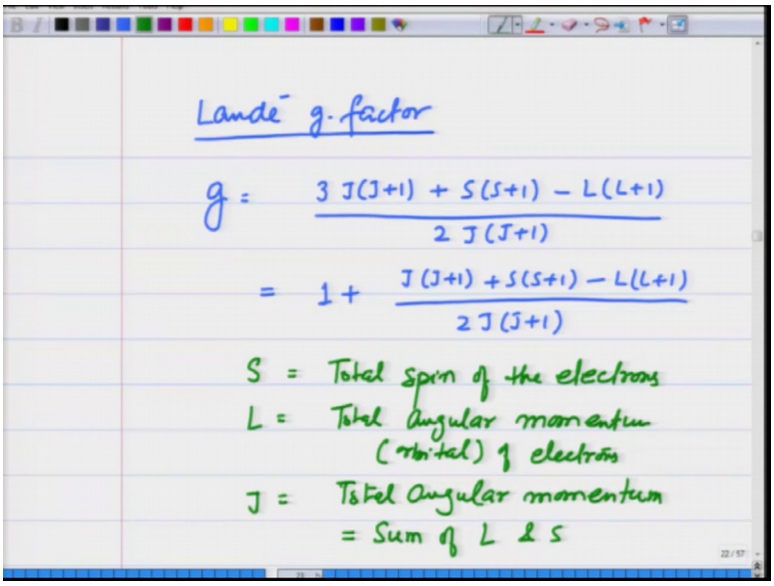
Prof. Manoj K. Harbola
Prof. Satyajit Banerjee
Department of Physics
Indian Institute of Technology, Kanpur

Lecture – 77

Hund's rules for calculating the total angular momentum J, orbital angular momentum L and spin angular momentum S for an atom

In the previous 2 lectures, we obtained expression for Lande g factor and the magnetic susceptibility of solid systems consisting of atoms and we considered that each atom itself develops a magnetic moment, that all together put all together gave a net magnetic moment to the solid. And, we assume that there is no interaction between the atoms, in this a quantity that we considered was the Lande g factor.

(Refer Slide Time: 00:53)



Lande g.factor

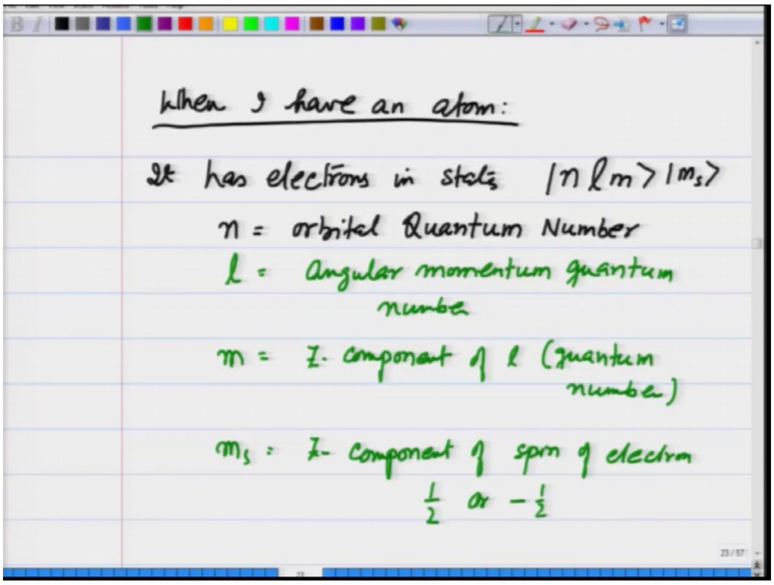
$$g = \frac{3\,J(J+1) + S(S+1) - L(L+1)}{2\,J(J+1)}$$

$$= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2\,J(J+1)}$$

S = Total spin of the electrons
L = Total angular momentum (orbital) of electrons
J = Total angular momentum = Sum of L & S

Or simply the g factor which was given as g equals 3 J J plus 1 plus S S plus 1 minus L L plus 1 divided by 2 J J plus 1 which is also equal to 1 plus J J plus 1 plus S S plus 1 minus L L plus 1 divided by 2 J J plus 1. And, the quantities S L and J are S is the total spin of the electrons. L is the total angular momentum which is due to the orbital motion, orbital angular momentum of electrons. And, J is total angular momentum which comes from the sum of L and S. In this lecture we consider how for an atom the quantities L, S and J are calculated.

(Refer Slide Time: 02:45)



When I have an atom:

It has electrons in states $|n\,l\,m\rangle|m_s\rangle$

n = orbital Quantum Number

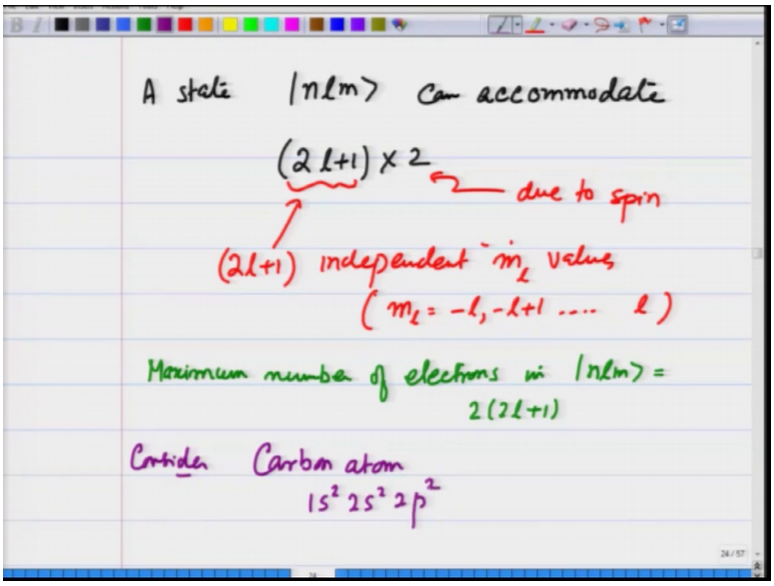
l = Angular momentum quantum number

m = Z- component of l (quantum number)

m_s : Z- component of spin of electron $\frac{1}{2}$ or $-\frac{1}{2}$

So, let us see when I have an atom it has electrons in states n l and m. And, then I can write m s where n is the orbital quantum number, l is the angular momentum quantum number, m is the z component quantum number of l quantum number. And, m s is the z component of spin of electron which can be either one-half in units of h cross or minus half.

(Refer Slide Time: 04:17)



A state $|n\,l\,m\rangle$ can accommodate

$$\underbrace{(2l+1)}\times 2$$

due to spin

$(2l+1)$ independent m_l values

$(m_l = -l, -l+1 \ldots\ldots l)$

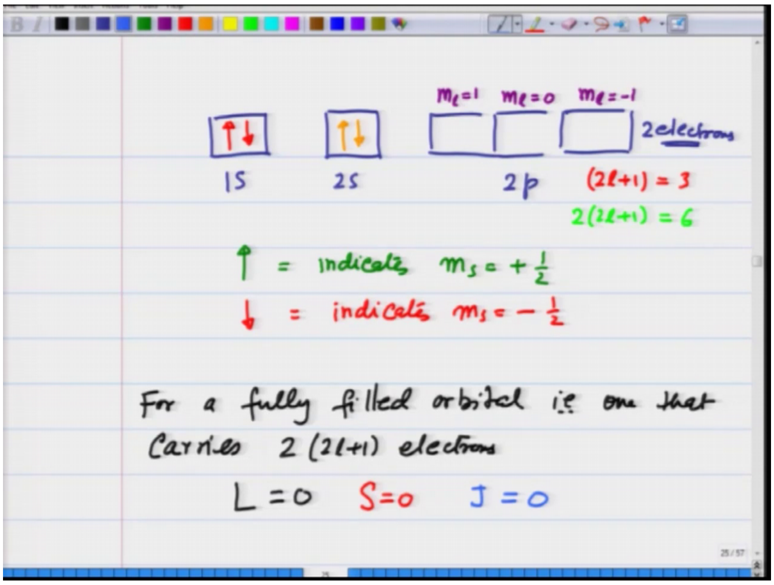
Maximum number of electrons in $|n\,l\,m\rangle = 2(2l+1)$

Consider Carbon atom

$1s^2\,2s^2\,2p^2$

Now, a state n l m that is only the orbital part can accommodate 2 l plus 1 times 2, where the second 2 comes due to spin. And, this is 2 l plus 1 independent m l values, these are from m l equals minus l minus l plus 1 and so on all the way up to l. So, it can accommodate 2 l plus 1 times 2 number of electrons. So, we can write maximum number of electrons in n l m is equal to 2 times 2 l plus 1. For example, consider carbon atom which has the electronic configuration 1 s 2 2 s 2 2 p 2.

(Refer Slide Time: 05:47)



$(2l+1) = 3$

$2(2l+1) = 6$

↑ = indicates $m_s = +\frac{1}{2}$

↓ = indicates $m_s = -\frac{1}{2}$

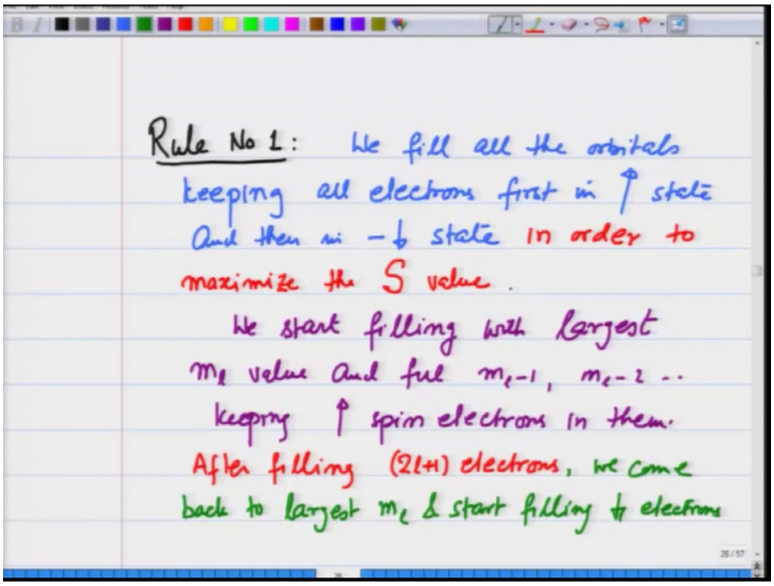
For a fully filled orbital i.e one that carries $2(2l+1)$ electrons

$L=0$ $S=0$ $J=0$

So, if I make these orbitals as these boxes, this is 1 s 2 s 2 p with the correspondence m l equals 1 m l equals 0 m l equals minus 1; then the maximum number of electrons that can come in 1 s are 2 1 with a spin plus half the other with spin minus half which I indicate by these arrows. So, let me also write it here this indicates m s equals plus one half and the down arrow indicates m s equals minus half. Similarly, in 2 s also I can have 2 electrons and 3 S the maximum number of electrons are 2 l plus 1 which in this case is 3 and 2 times 2 l plus 1 therefore, is 6. So, it can have maximum 6 number of electrons, but there are only 2 electrons how do we fill these.

So, this filling of 2 electrons here is to be done following something called the Hund's rules and that is what am going to state now. Before I state those and take up this example again, let me just make it clear that for a fully filled orbital that is one that carries 2 times 2 l plus 1 electrons. The L value comes out to be 0 because; you are feeling filling plus m l and corresponding minus m l. And similarly, all the electrons that are filled half of them have spin m s equals plus half and the other half has minus half. So, that also adds up to 0 and therefore, the S value is also 0 and the J value therefore, also is 0. So, fully filled orbitals are no problem, we are more concerned with the orbitals where number of electrons may not be completely filling the orbitals.

(Refer Slide Time: 08:33)



Rule No 1: We fill all the orbitals keeping all electrons first in ↑ state And then in $-\frac{1}{2}$ state in order to maximize the S value.

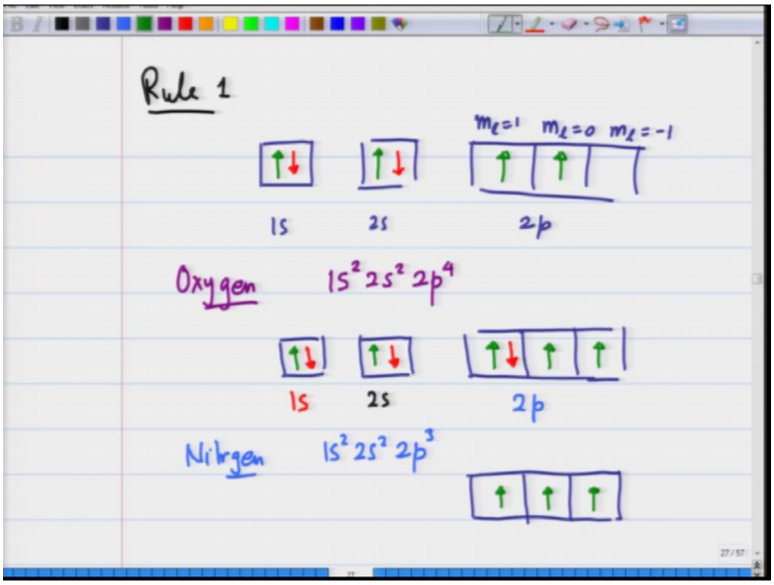
We start filling with largest m_l value And fill $m_l - 1$, $m_l - 2$ .. keeping ↑ spin electrons in them.

After filling $(2l+1)$ electrons, we come back to largest m_l & start filling $\frac{1}{2}$ electrons

So, rule number 1 is that we fill all the orbitals keeping all electrons first in plus half state and then in minus half state. It will be clear as I take up the examples and this is done in order to maximize the capital S value. And, how do we start filling? We start filling with largest m l value and then keeping the electron spin up we go to the next m l and so on.

And, fill m l minus 1 m l minus 2 etcetera keeping up spin electrons in them. Once they are filled; that means, 2 l plus 1 electrons are filled we start all over again. So, after filling 2 l plus electrons we come back to largest m l and start filling minus half spin electrons. So, this is done very systematically for example.

(Refer Slide Time: 11:03)



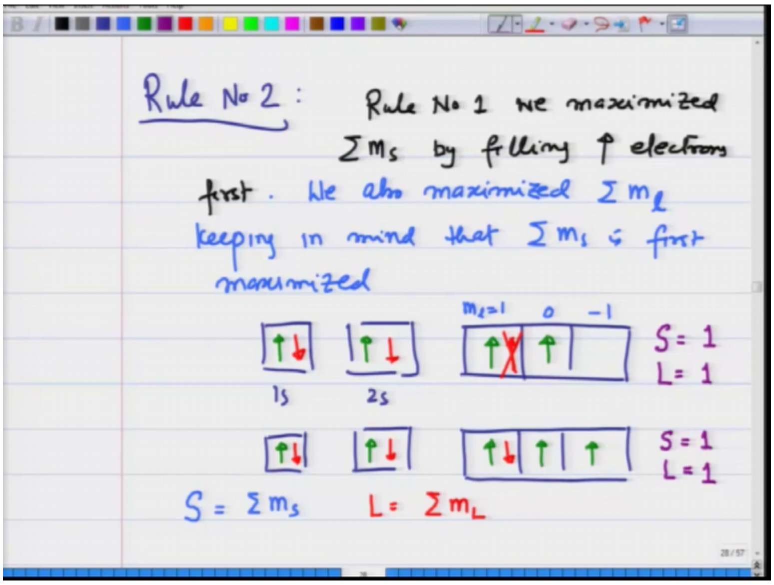
So, again we are still in rule 1 in the carbon system when I had 1 s orbital 2 s orbital and 2 p orbitals with 3 m l states 1 s 2 s 2 p, 1 s and 2 s are lower energy. So, I will fill the first electron with up spin and the next electron would not go to the higher level it will remain in the same level, but will be with the down spin. In the next orbital also the same thing up spin and then the down spin, in 2 p I have only 2 electrons.

So, I will first fill the largest m l value with the up spin, the next also I want to maximize summation over m s. So, next electron will go with up spin in m l equals 0 and that is it I have exhausted them all. If on the other hand, I had oxygen which has the configuration 1 s 2 s 2 2 p 4. In that case the way I will fill these orbitals will be again 1 s 2 s and 2 p; I am not writing now ml equals 1 0 and minus 1 it is understood.

So, I will first fill up electrons in 1 s and down in this is 1 S, in the 2 s I will fill the up electron first and then the down electron. And, in 2 p I will first fill the up electron in m l equals 1, then in m l equals 0, then in m l equals minus 1; I have tried to maximize m s as summation of m s as much as possible. Now, next electron up electron cannot go anywhere in these three orbitals. So, I have to fill the down electrons, but I start all over again the maximum value of m l and put the fourth one down here, this will be the configuration for oxygen.

So, I have given you two examples where the number of electrons is either larger than 2 l plus 1 that is a half-filled orbital or smaller than half filled orbital and how to fill these electrons. Of course, if I have something in between for example, nitrogen which has 1 s 2 2 s 2 and 2 p 3 electrons, the 2 p orbital 1 s 2s are filled just like we showed earlier, the 2 p orbital will be half filled. So, in this case the 2 p orbital will have only up spin electrons. So, this is how we fill the electrons after we fill them.

(Refer Slide Time: 14:05)



Rule No 2 : Rule No 1 we maximized $\sum m_s$ by filling ↑ electrons first. We also maximized $\sum m_\ell$ keeping in mind that $\sum m_s$ is first maximized

$S = \sum m_s$ $L = \sum m_L$

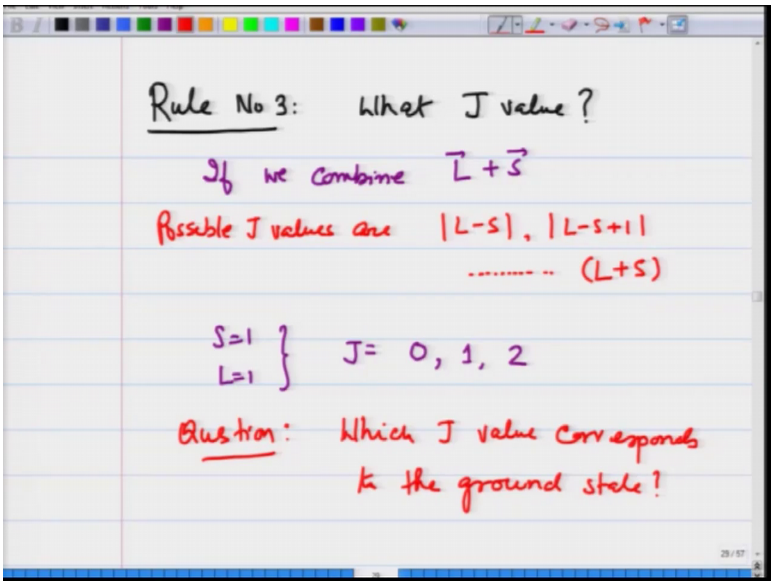
How do I calculate the m and s values? So, in rule number 1 we maximized summation m s by filling up electrons first. So, that I can get large as possible value of m s and side by side I also did one more thing. We also maximized summation m l keeping in mind that summation m s is first maximized, let me explain that. We first put all the up spin electrons so, that m s is maximized then only I took care of m l. So, for example, when I fill the carbon atom I had 1 s 2 s and these are filled orbitals.

So, I do not really discuss them anymore these have m s and the l n, s values to be 0 and when I come to the 3 2 p orbitals; the first electron went with up spin 2 m l equals 1, let me write this ml equals 1 0 and minus 1. Now, first thing I wanted to do was maximize m s and therefore, I will put only up spin electrons first. However, an up spin electron cannot go here, this I will cut it cannot go here by Pauli’s exclusion principle because no 2 electrons can have all the spins the same. And therefore, I put it in the next available m l, but keeping summation m l to be maximum. So, I cannot put it in m l equals minus 1, I will put it in m l equals 0. Similarly, in the oxygen atom the first 2 orbitals are filled anyway.

So, I do not really bring them into, the discussion the last 2 p orbital I first put first electron in m l equals 1, then I want to maximize m s first. So, I will put this in m l equals 0 again keeping in mind that I should maximize m summation m l and the next one again I want to maximize m s. So, I will put only the up spin electron so, it has to go into ml equals minus 1, I cannot suddenly put a down electron in m l equals 1. So, that m l is maximized, but m s is not and then I will put the down electron in m l equals 1 again. Once I fill it like this then the S value is given as summation m s and the L value is given as summation m L.

And let me now show these values for the carbon atom and the oxygen atom both, for the carbon atom the S value would be equal to 1 one half plus one half. And, the L value will be equal to 1 plus 0 1, similarly for the oxygen atom the S value would be equal to S equals 1 because, the first two up and down electrons cancel their spin and the other to give us equals 1 and the ml value adds up to 2 times 1 plus 0 plus minus 1. So, this comes out to be L equals 1 again. So, that is rule number 2 how we fill the orbitals and then calculate the capital S and capital L values. These of course, are related to the total spin angular momentum and the orbital angular momentum next rule number 3.

(Refer Slide Time: 18:33)



Rule No 3: What J value?

If we combine $\vec{L} + \vec{S}$

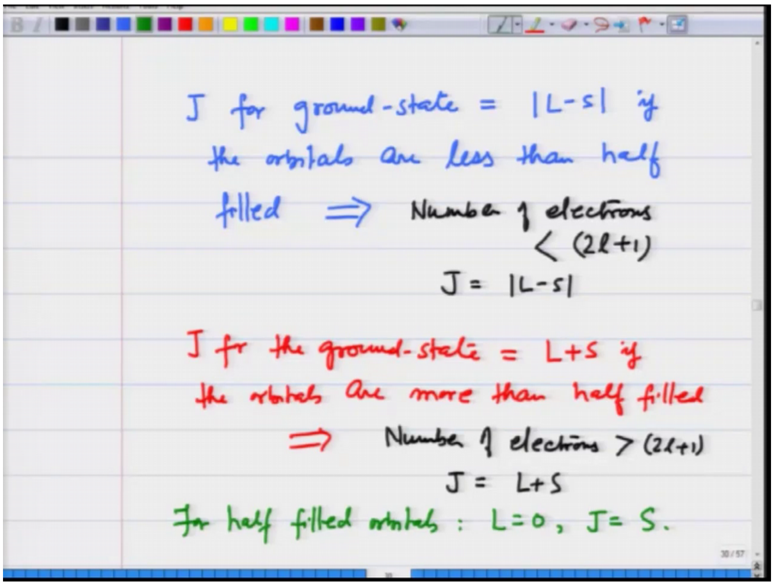
Possible J values are $|L-S|$, $|L-S+1|$ .... $(L+S)$

$\left.\begin{matrix} S=1 \\ L=1 \end{matrix}\right\}$ $J = 0, 1, 2$

Question: Which J value corresponds to the ground state?

This concerned with the J value because, remember from quantum mechanics I know if we combine L and S add them then the possible J values are from L minus S mod to L minus S plus 1 and so on, all the values differing by 1 to L plus S. Thus for example, if I have S equals 1 and L equals 1 I can have J equals 0 1 and 2. And, the question is which J value corresponds to the ground state because; all these 3 J values are differing at energies. This has again been calculated and then given in the form of the rule number 3.

(Refer Slide Time: 20:03)



J for ground-state = $|L-S|$ if the orbitals are less than half filled $\Rightarrow$ Number of electrons $< (2l+1)$

$J = |L-S|$

J for the ground-state = $L+S$ if the orbitals are more than half filled

$\Rightarrow$ Number of electrons $> (2l+1)$

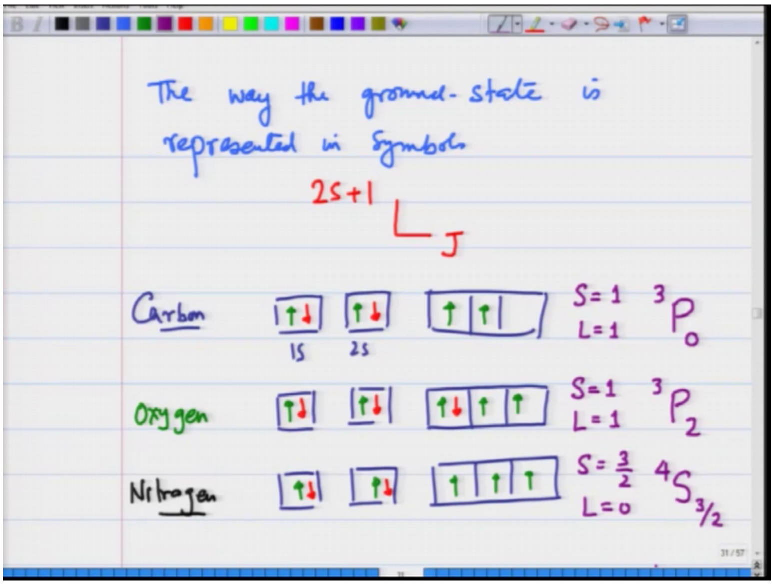
$J = L+S$

For half filled orbitals : $L=0$, $J=S$.

And, it says that the J for ground state is equal to mod L minus S if the orbitals are less than half filled. And that means, that if number of electrons is less than 2 l plus 1 then J equals mod L minus S.

On the other hand J for the ground state is equal to L plus S, if the orbitals are more than half filled which implies that if number of electrons is greater than 2 l plus 1 J equals L plus S and then for half filled orbitals L anyway comes out to be 0 because, the same number of plus and minus values of m l and J equals S. So, this is rule number 3. So, we have given 3 rules that give you the values for J, L and S and the way the ground state is represented.

(Refer Slide Time: 21:59)



The way the ground-state is
represented in symbols

$^{2S+1}L_J$

Carbon ↑↓ ↑↓ ↑ ↑ S = 1 L = 1 $^3P_0$
1s 2s

Oxygen ↑↓ ↑↓ ↑↓ ↑ ↑ S = 1 L = 1 $^3P_2$

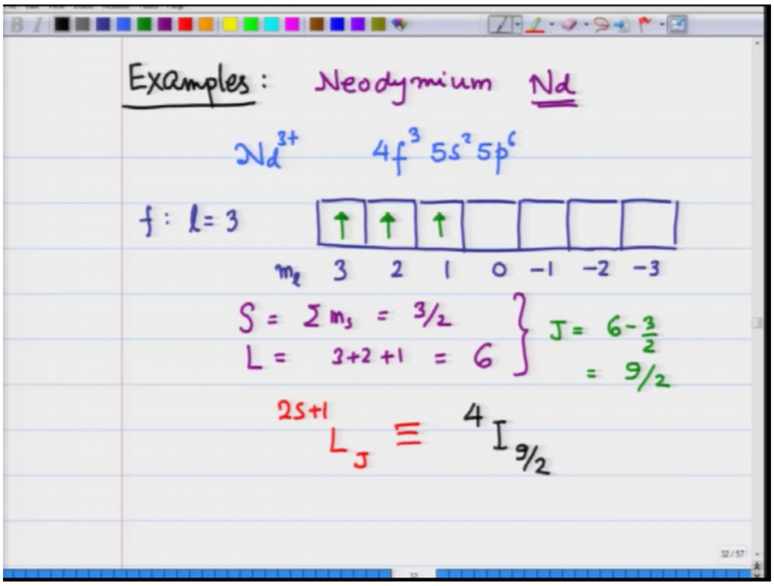
Nitrogen ↑↓ ↑↓ ↑ ↑ ↑ $S = \frac{3}{2}$ L = 0 $^4S_{3/2}$

So, let me write this clearly the way the ground state or for that matter any state is represented in symbols is that you write 2 S plus 1 value, then the symbol corresponding to the L value and J value here. So, let me now take examples carbon we had 1 s 2 s and 2 p, I did not really worry about 1 s and 2 s because they are filled orbitals. And therefore, I do not really get any L or S values from there they are 0 and the last orbital was like this. So, in this case we found that the S value was 1 and L value was 1.

So, L equals 1 corresponds to p and now we are going to write capital P symbol for this 2 s plus 1 is 3 and therefore, I write 3 on left top and J value now this is less than half filled orbital. So, J value is going to be the L minus S value. So, this is going to be 3 P 0, on the other hand for oxygen I am going to have 1 s completely filled and the 2 s completely filled and 2 p orbital like this and here also we had obtained S equals 1 L equals 1. So, again it is a P state; however, the J value correspond to the ground state is going to be now L plus S because, it is more than half filled; so, it is going to be 3 p 2.

If you wonder where these rules came from, these are done by calculating total energies of these electrons, taking in their interaction into account and last example I had done last time as in the previous slides was that of nitrogen. So, let me do that also and nitrogen had 7 electrons. So, I have these up electrons and 1 s and 2 s have these down electrons also. Now, this is half filled so, you can see that S comes out to be 3 halves L value is 0. So, this is going to be correspond to L equals 0, 2 s plus 1 gives me 4 and J value is only s so, this is 4 S 3 by 2. So, this is what explains these rules to you; let me take some examples that are directly concerned with magnetic systems.

(Refer Slide Time: 25:27)



Examples: Neodymium Nd

Nd^{3+} $4f^3 5s^2 5p^6$

f : $l = 3$

↑	↑	↑				

m_l 3 2 1 0 −1 −2 −3

$S = \sum m_s = 3/2$

$L = 3+2+1 = 6$

$J = 6 - \frac{3}{2} = 9/2$

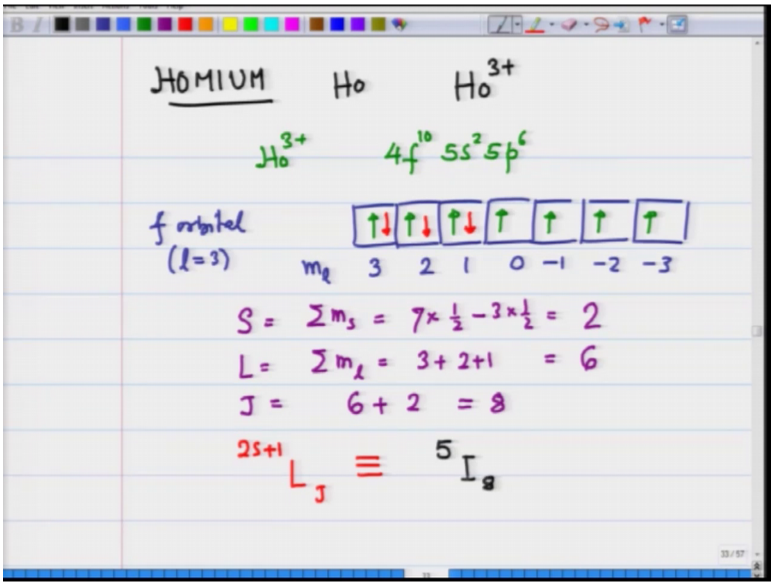
$^{2S+1}L_J \equiv {}^4I_{9/2}$

So, let me take examples for lanthanides which are concerned directly with magnetic systems. So, first example am going to take is that of neodymium represented as Nd. In the solid it comes in the state of Nd 3 plus and that gives rise to paramagnetism and its electronic configuration is 4 f 3 5 s 2 and 5 p 6, you can see that 5 s 2 and 5 p 6 orbitals are completely filled. And so, are the lower orbitals; they are going to give L equals type total L equals 0 total S equals 0. So, we are concerned only with the f state, f state as is s p d f. So, f state corresponds to l equals 3.

So, it is going to have m l values 7 of those 1 2 3 4 5 6 and 7. So, this is m l values of 3 2 1 0 minus 1 minus 2 and minus 3 and I have 3 electrons in this. So, all 3 are going to go starting with the highest m l value, I put an up spin electron. Since, I am maximizing m s first I still put a electron up spin electrons, keeping in mind that I still have to have maximum summation over m l so, it goes to m l equals 2 and the next one goes to m l equals 1. So, I applied rule number 1 and 2, now the S value is going to be equal to summation m s and this gives me 3 halves. L value is going to be 3 plus 2 plus 1 which is 6 and combining these 2 the J value is going to come out to be this is less than half filled. So, it is going to be 6 minus 3 by 2 which gives me 9 by 2. So, this state is going to be denoted by s p d f g h i; so, this is this has corresponding symbol i.

So, 2 s plus 1 L J will be equivalent to 2 s plus 1 gives me 4, L is equal to 6 that responds to I and J value is 9 by 2. Let me take another example which is more than half filled and this is homium denoted as Ho.

(Refer Slide Time: 28:19)



HOMIUM Ho Ho^{3+}

Ho^{3+} $4f^{10} 5s^2 5p^6$

f orbital ($l=3$)

	↑↓	↑↓	↑↓	↑	↑	↑	↑
m_l	3	2	1	0	−1	−2	−3

$S = \Sigma m_s = 7 \times \frac{1}{2} - 3 \times \frac{1}{2} = 2$

$L = \Sigma m_l = 3 + 2 + 1 = 6$

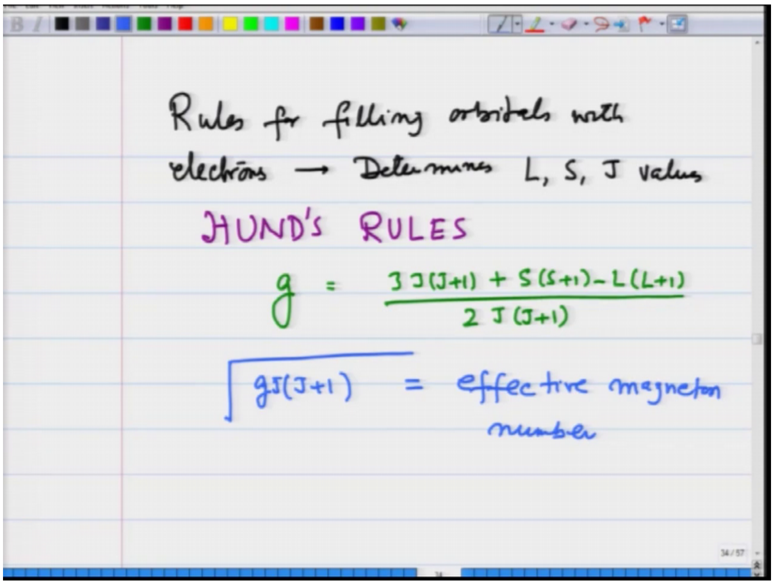
$J = 6 + 2 = 8$

$^{2S+1}L_J \equiv {}^5I_8$

And, this also occurs in the solid in 3 plus states and Ho 3 plus has the electronic configuration 4 f 10 5 s 2 5 p 6. So, again if I make the f orbital l equals 3 I have 7 boxes corresponds to m l value of 3 to 1 0 minus 1 minus 2 minus 3 and I have to put 10 electrons in it. So, first I exhaust all the up electrons maximizing summation m s right. Now, I do not really care about m l, but am taking care of that by filling m l values largest to lower values. Now I exhausted 7 electrons so, next 3 will go as down spin electrons in the largest m l possible values.

So, S which is given as summation m s is going to be 7 times one half minus 3 times one half so, that becomes 2. The L value is going to be summation m l and that is going to be 3 plus 2 plus 1, all the others cancel out and this is going to be 6. The J value for the ground state is going to be this time is more than half filled so, it is going to be 6 plus 2, L plus S which is going to be 8. And therefore, the term symbol for this which is 2 s plus 1 L J is going to be 5 L equals 6 corresponds to I J is 8.

(Refer Slide Time: 30:31)



Rules for filling orbitals with electrons → Determines L, S, J values

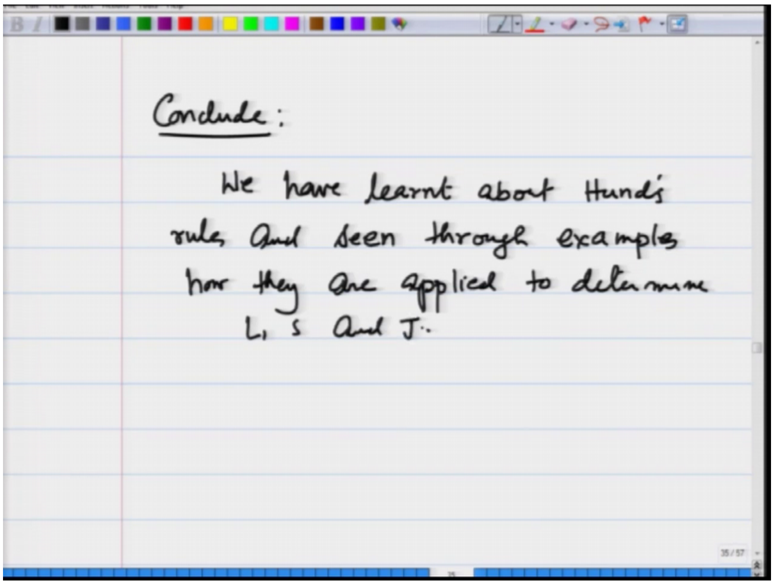
HUND'S RULES

$$g = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$\sqrt{gJ(J+1)}$ = effective magneton number

So, I have given you rules for filling orbitals with electrons and that determines L, S and J values. These rules are known as Hund's rules and once we know L, S and J values we can calculate the Lande g factor g as 3 J J plus 1 plus S S plus 1 minus L L plus 1 divided by 2 J J plus 1. Incidentally the value square root of g J J plus 1 is known as effective magneton number while, come back to this again. So, using Hund's rules we can fill these orbitals and get the effective magneton number.

(Refer Slide Time: 31:53)



Conclude:

We have learnt about Hund's rule and seen through examples how they are applied to determine L, S and J.

So, to conclude we have learned about Hund’s rules and seen through examples how they are applied to determine L, S and J.

Thank you.