Condensed Matter Physics
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Magnetism-Worked Examples (Continued)

Today, we continue to do few more examples on magnetism.

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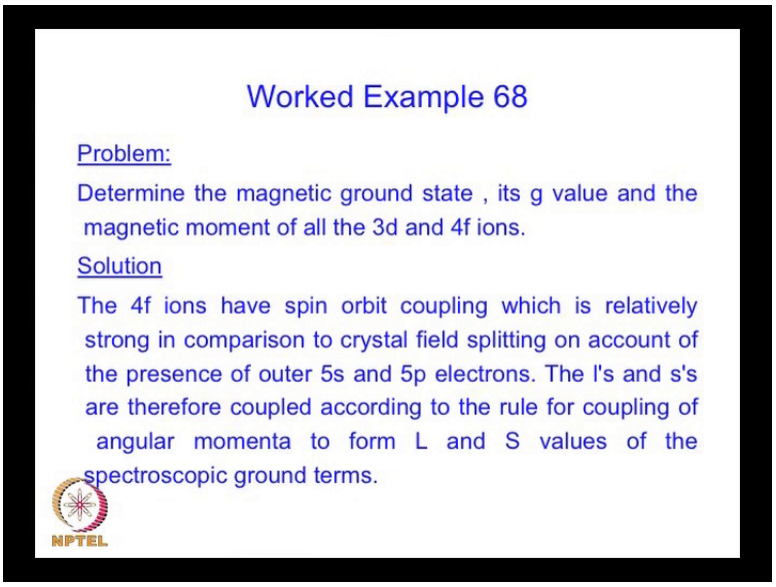

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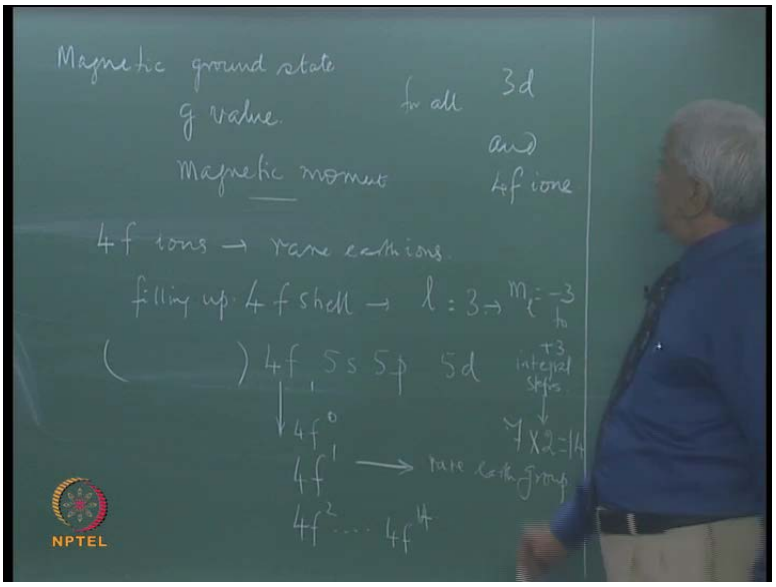

This is an important question, in which we are asked, determine the magnetic ground state, its g value of this ground state and the corresponding magnetic moment for all 3d and 4f ions. Some of these results, we have already used in our discussion of the basic ideas of magnetism in solids, but today we will work out the magnetic ground state, the corresponding g value and the magnetic moment.

In the case all the members of the 3d and 4f groups in the periodic table. We will consider the 4f first for reasons, which will become obvious very soon. 4 f ions, which are better known as more commonly known as rare earth ions.

The rare earth ions are a group of elements in the periodic table, which correspond to the successive filling up of the 4f shell. The 4f shell corresponds to an angular momentum of 3.

So, the electronic configuration is such that the outermost shell is or the 4f and then 5s, 5p and in some cases 5d shells. So, these are the outer electron configurations.

There are of course, close shells inside, which do not contribute anything to the magnetic moment. It is only the unpaired electrons in the unfilled shell, which give rise to magnetic moment. So, we have the possibility since l is 3, we have m l going from minus 3 to plus 3 in integral steps.

So, this corresponds to 7 and then there is a spin which can be plus or minus. So, there are 2 orientations. So, there are 14 electronic states, 14 electrons can occupy the 4f shell. So, corresponding to 4f 0, where there is no electrons in the 4f shell and then 4f 1, 4f 2 etcetera 4f 14, all the elements corresponding to these different values of the electron in the 4f shell form these are called rare earth group.

We will consider one by one. These elements and the reason why, we consider this first rather than the 3d is, because in the 4f group there are outer electrons in the 5s, 5p and 5d shells, which start of shield the inner 4f electron.

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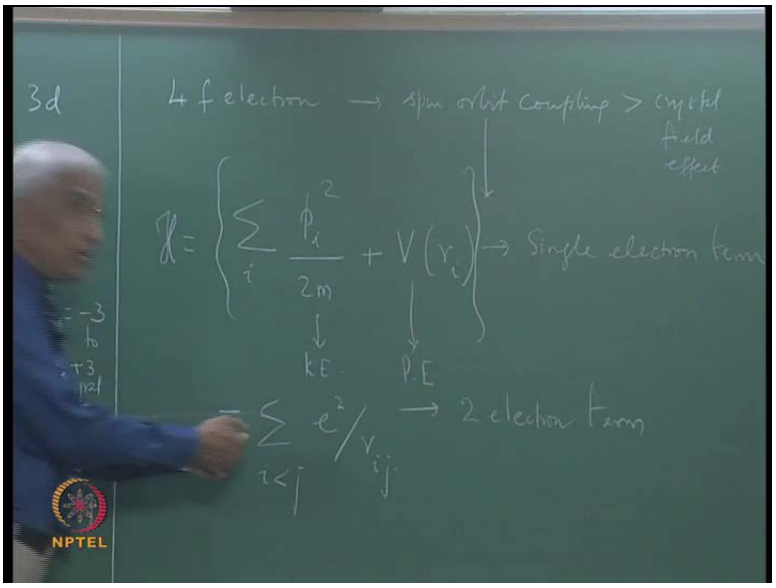

The spin orbit coupling is relatively strong in comparison to the crystal field effect. So, the spin orbit coupling is rather strong and therefore, if we wrote the free electron Hamiltonian. We have the single electrons states corresponding to the kinetic energy, there i, is going from one to the total number plus V of r i this is the kinetic energy, this is the potential energy the coulomb interaction energy between the ith electron and the nucleus.

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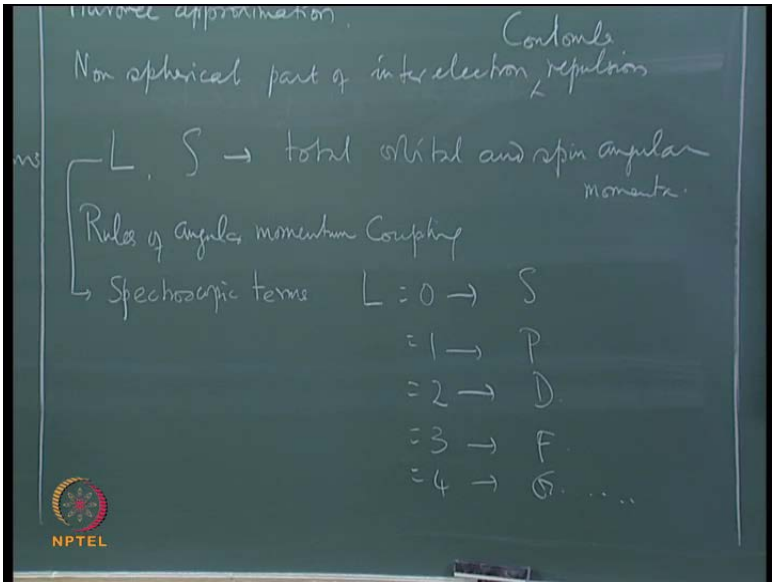

So, this is all single electron terms. These define the angular momentum and spin of every individual electron. In addition next in descending order of strength, we have the inter electron coulomb repulsion. This is a two electron term so, this couples the individual electrons ((Refer Time: 06.55)) and in the Hartree approximation.

Considers this spherical part of this inter electron repulsion and adds this on to the single electron potential energy. So, that we get hydrogen like ground state, but there will be a non spherical part coulomb repulsion. This non spherical part of the coulomb repulsive potential couples the individual l s and s s of the single electron and produces a total angular momentum orbital angular momentum L and the total spin angular momentum S. According to the rules of angular momentum coupling in quantum mechanics, it is these l s and s s which define is so, called the spectroscopic terms.

So, these spectroscopic terms are identified by the total value of the orbital angular momentum, if L is 0, we call it an S term, if L is 1, it is a P term, if L is 2, it is a D term, if L is 3, it is a F term and then 4, 5, etcetera, it is in alphabetical order G etcetera and so on. So, these are the terms symbols corresponding to the different angular momentum values, orbital angular momentum values.

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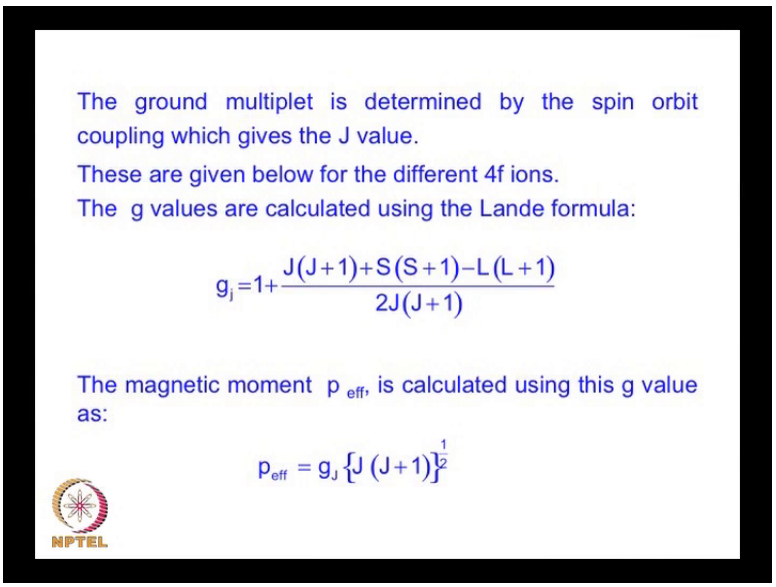

Once we know the individual total orbital and spin angular momentum corresponding to the ground term. It is the ground stage which matters in magnetic properties and therefore, we are interested in the ground term.

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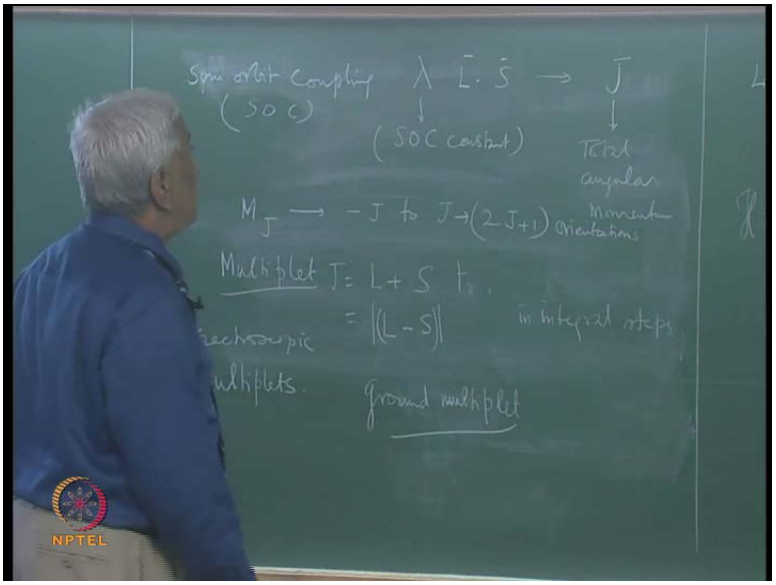

And this term now, is acted on by the spin orbit coupling, which is usually represented in the form lambda L dot S, where lambda is the spin orbit coupling constant. And this produces a coupling between these orbital and spin angular momenta to produce a total angular momentum which is usually represented by the symbol J.

Corresponding to a given value of J, you can have different values of M J, the magnetic quantum number which goes from minus J to plus J. There are 2 J plus 1 value, corresponding to different orientations of the spins magnetic moment of the ions with respect to an applied magnetic field. So, now, these correspond to so, called multiplet different J values correspond to different multiplet, when L and S are coupled. According to the rules of angular momentum coupling it can be coupled and the resultant angular momentum goes from J equal to L plus S to mod L minus S or S minus L depending on which is greater in integral steps that is all we get 2 J plus 1 values. Each of these J value corresponds to a different multiplet. So, this gives me the multiplet states, spectroscopic multiplet there are different multiplet corresponding to different values of J of which the ground multiplet is what matters for magnetic behaviour.

So, the magnetic ground state is determined by the multiplet which lies lowest on account of the fact that the excited states are normally not appreciably populated and are ordinary conditions of temperature and magnetic field. So, it is only the ground multiplet which determines the magnetic ground state and hence the magnetic behaviour.

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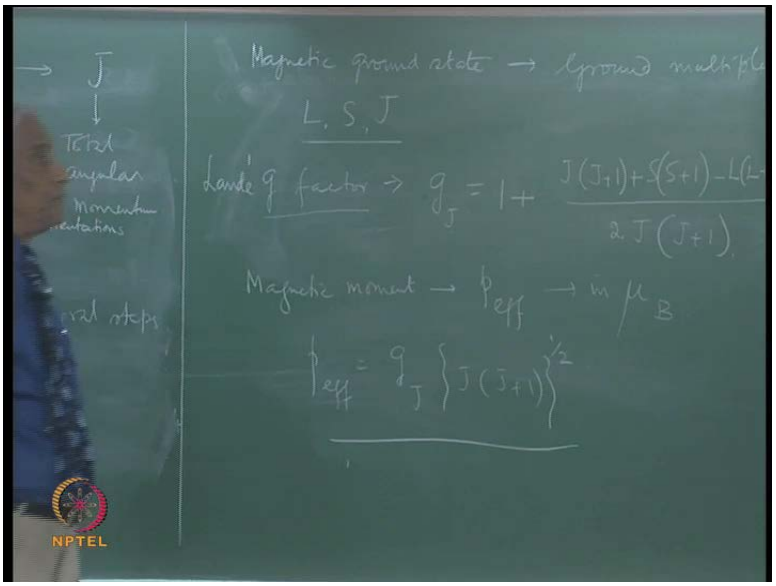

So, the magnetic ground state which we have been asked to determine corresponds to the ground multiplet state. This is what we have to determine now in the case of the different ions. Once we know the multiplet ground state and the corresponding J value. So, we now, know the L S and J values for a given multiplet. A given multiplet is characterised by different values of L S and J and then the g factor which is known as the Lande g factor is given by corresponding to a given multiplet state with a given J value is given by the Lande expression.

So, since we know L S and J for a given multiplet charactered by a particular value of J. We can immediately find the corresponding g value is also what we have to find out. Once we know g J the magnetic moment of corresponding to this ground state it is usually represented by the symbol P effective which is in Bhor magnetrons. So, this P effective is given by g J into J into J plus 1 to the power half. So, this gives the magnetic moment in units of the Bhor magnetron.

So, this is the procedure which we will adopt, in the case of all the 14 rare earth ions, belonging to the progressive filling up of the 4 f shells. Well if there are no electrons in

the 4 f shell there is no magnetic moment; obviously, because the shell is not occupied by any electron and therefore, the unpaired electron is necessary for it.

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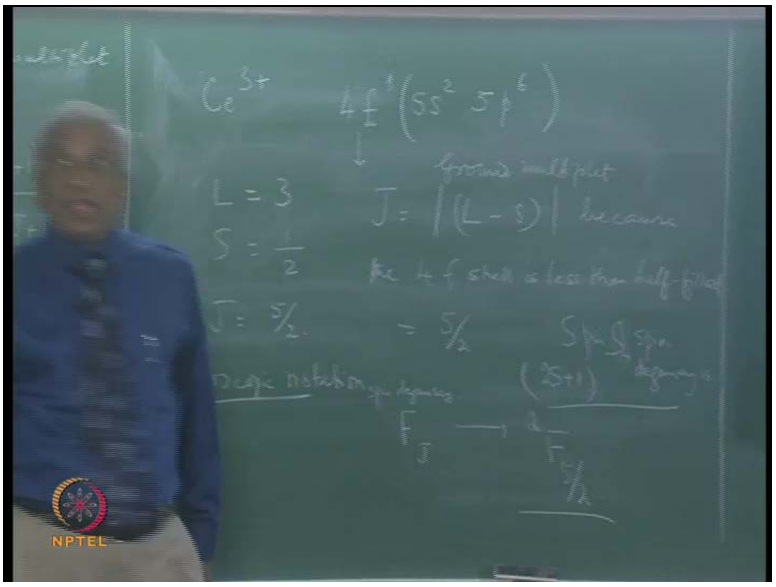

So, let us start from the first case, first rare earth ion, which is cerium 3 plus, which are the outer electron configuration of 4f 1 5s 2 and 5p 6. So, there are two electrons in the outer 5s shell and six electrons in the outer 5p shell and there is one unpaired electron in the 4f shell.

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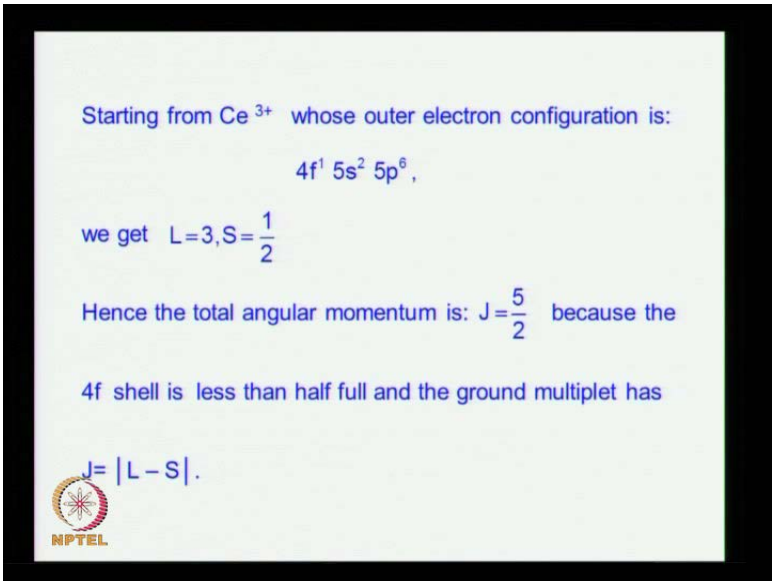

So, it is this which gives the magnetic behaviour. So, since there we have only one electron, the L value is since it is an electron in the f shell, L is 3. And since there is only one electron the spin value is also the total spin angular momentum is just that of one electron so, S is half. So, you have J which in this case big low lying multiplet corresponds to L minus S rather than L plus S because, the 4f shell is less than half filled.

So, this is the ground multiplet. So, in this case since L is 3 and S is half this will give you 5 by 2. So, the ground multiplet has L equal to 3, S equal to half and J is 5 by 2. There is a way of denoting this ground multiplet the spectroscopic notation for this ground multiplet. The spectroscopic notation usually proceeds by giving the ground term symbol which we already saw in this case since L is three it is an f term and it has a superscript which has these spin degeneracy and the subscript which gives the J value.

So, that is the standard notation for the ground multiplet. In this case the spin degeneracy is for a spin of S spin degeneracy is 2 S plus 1; obviously. So, we will have in this case S is half so, 2 S plus 1 is so, it is 2 f and the J value is 5 by 2. So, that is the notation for the ground multiplet for the cerium 3 plus ion, which is the first member in the rare earth group with unpaired electron.

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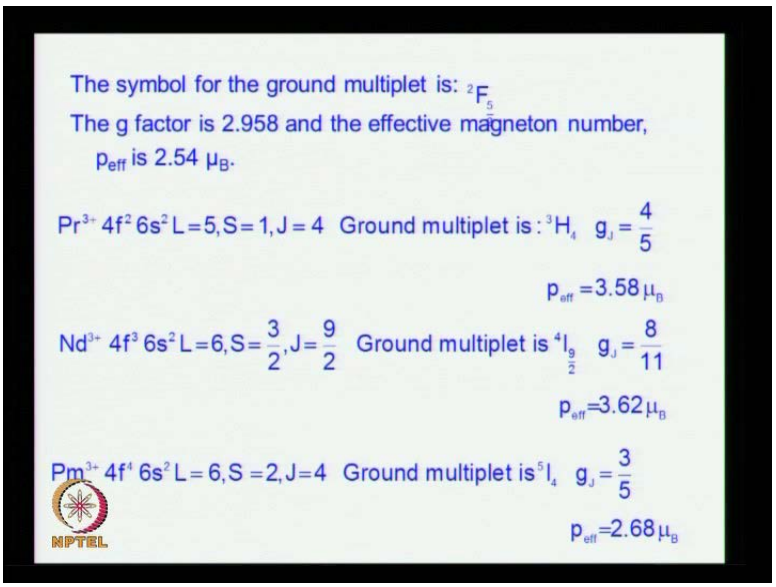

So, having found the ground multiplet, we use the expression for the Lande g factor to find g J, the g factor corresponding to this multiplet.

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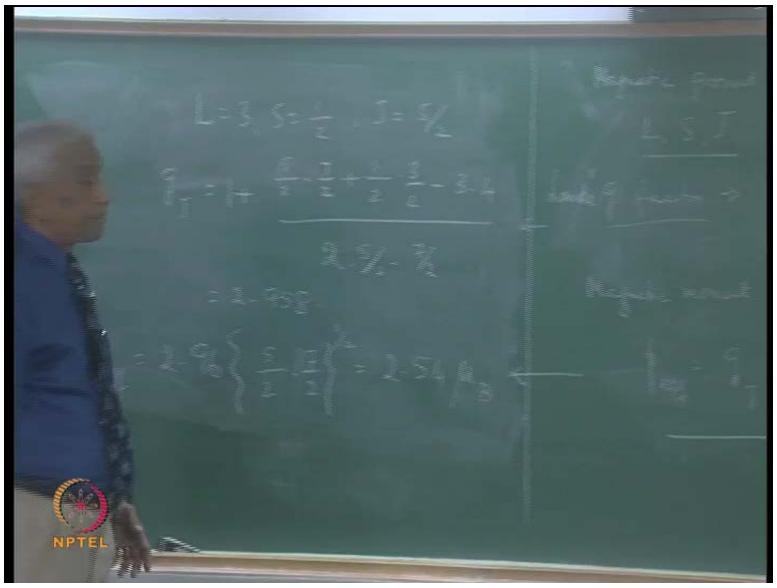

So, this has L equal to 3, S equal to half and J is 5 by 2. So, the Lande expression is for g J is 1 plus J into J plus 1, which is 5 by 2 into 7 by 2 plus S into S plus 1, which is half into 3 by 2 minus L into L plus 1, which is 3 into 4 divided by 2 J into J plus 1. This turns out to be 2.958 on simplification. The corresponding magnetic moment is given by this formula. So, we write P effective is this value for g J times 5 by 2 J into J plus 1 to the power half. So, this turns out to be 2.54 Bhor magnetron.

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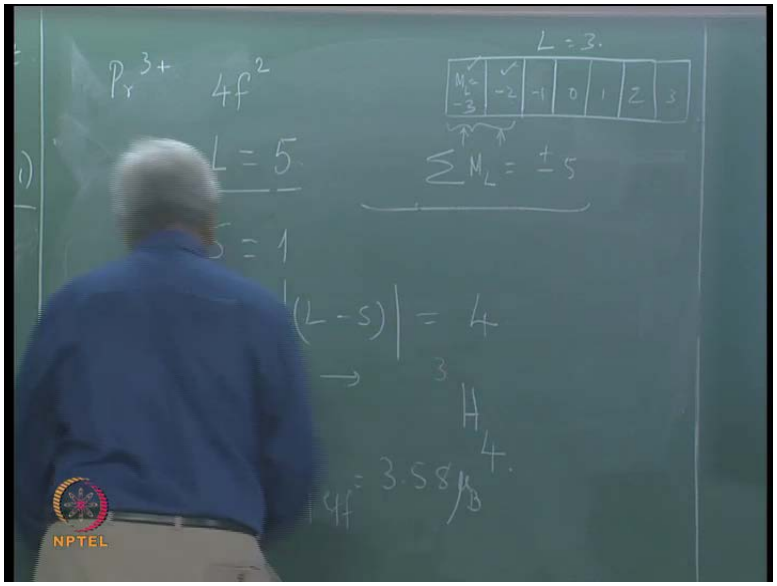

So, following the same procedure for the other ions, let us move on to the next ion in the rare earth group which has two electrons in the 4f shell this ion is praseodymium 3 plus. So, it has 4f 2 therefore, the corresponding L value is there are two electrons the Hunts rules tells you, if I have different values of a mell which I represent here. So, this is M L equal to minus 3, minus 2, minus 1, 0, 1, 2 and 3 corresponding to L equal to 3.

So, the Hunts rules tells us that the electrons will have a total M L value and hence a total L value due to the coupling, which will be correspond to the sum of the two stage which the electron occupies the corresponding M L values sigma M L corresponding to the two states such that this spin multiplicity is maximum. In other words the two electrons has spins parallel. So, these are the two states and therefore, we get minus 5 or it can also be here. So, it is plus or minus 5 and therefore, the corresponding L value is 5 since this summation is gives you M L as plus or minus 5, the only possibility for this is with L equal to 5.

So, that is the total orbital angular momentum of these two electrons and since there are two electrons the spins are parallel and therefore, S is 1 and J which is mod of L minus S because, it is still less than half filled. So, this will be 5 minus 1, 4. So, the ground multiplet in the case of the praseodymium 3 plus ion is has the L value 5, which means it is an H in the term and the spin multiplicity is 2S plus 1 for S equal to 1 is 3 and the J value is 4.

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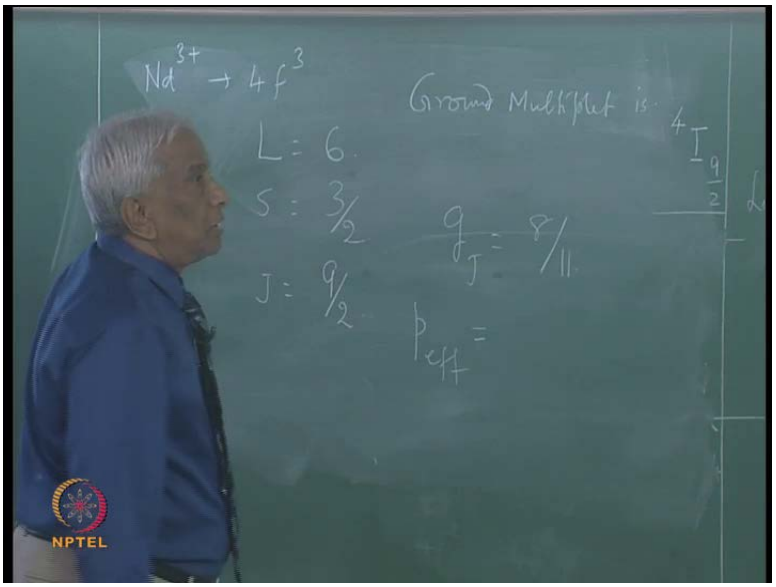

And if we substitute in the Lande g factor expression for this, the g J turns out to be 4 by 5 by substitution. And the corresponding effective magnetic moment is 3.58 Bhor magnetron. Adapting the same procedure for the next ion in the series, which is neodymium 3 plus, which has three electrons in the 4f shell and therefore following the same procedure sigma M L will be minus 3, minus 2 and minus 1. So, this will be minus 6.

So, L will be 6 and the S since there are three electrons all with spin parallel in order to maximise the spin. So, this will be 3 by 2 and therefore, J will be L minus S which is 9 by 2. So, the ground multiplet for neodymium 3 plus is, L equal to 6 which is an I term, 2 S plus 1 is 4 for S equal to 3 by 2 and the J is 9 by 2. So, this is the ground multiplet. All the rare earth ions have the valance is 3 plus the corresponding g J value in the Lande g factor expression works out to be 8 by 11. And the effective magnetic moment P effective is 3.62 Bhor magnetron.

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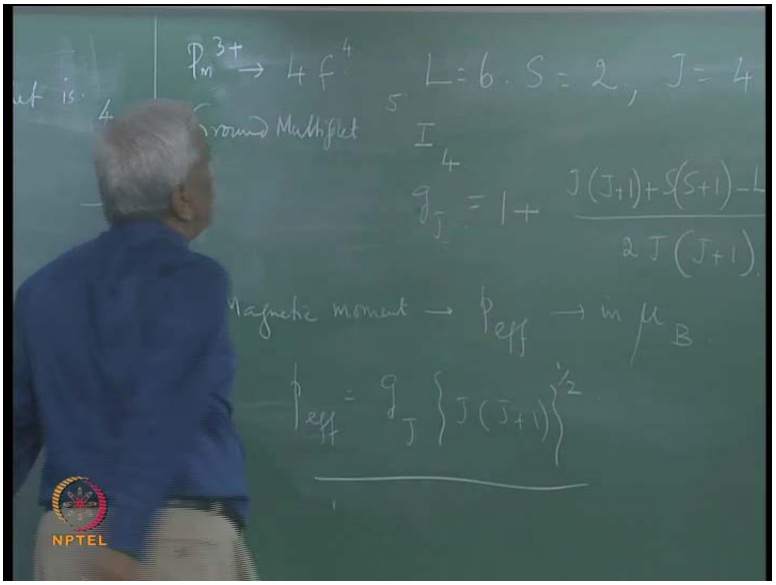

We then move on to promethium 3 plus, which is a short lived isotope. Still it is one with four electrons in the 4f shell. So, the corresponding L values since this would be four electron this would add zero to this. So, the L remains 6 and the S of course, becomes 2 since there are four electrons with parallel spins therefore, the J is 4.

So, the ground multiplet is again an I term, but with spin multiplicity 5, 2 S plus 1, 5 S equal to 2 and the J value is 4.

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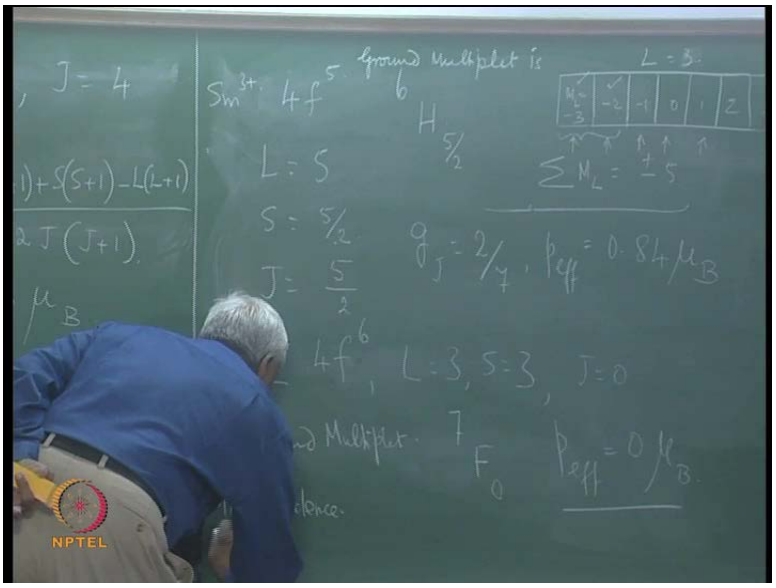

Next, we consider samarium 3 plus, which has a 4f 5 configuration therefore, the L now, there are five electrons so, the minus 1 and plus 1 will neutralise each other, leaving us with sigma M L equal to minus 5. So, that L is 5 and S for five electrons is still 5 by 2 because, all the electrons have parallel spins therefore, the J value is L minus S which is 5 by 2 and the g J has the value if ground multiplet is represented by L equal to 5.

So, it is again an H term with a spin multiplicity 6 corresponding to a spin of 5 by 2 and a J value of 5 by 2 this is the ground multiplet. And the corresponding g J value is 2 by 7 and the magnetic moment is having the value 0.84 Bhor magnetrons.

You go to europium 3 plus, which has 6 electrons in 4f shell. So, L is 3 by the same procedure S is also 3 because, six electrons with parallel spins. And So, J is 0. So, the ground multiplet is an F term with spin multiplicity 7 and a J value of 0. So, since this has J 0. So, the g value is 0 and the magnetic moment corresponding to that is also 0. Of course, europium 3 plus is nonmagnetic because, of this, but usually europium 3 plus also there is frequently you have a mixed valance with europium 2 plus, which contributes to some non zero magnetism, when europium 2 plus is present.

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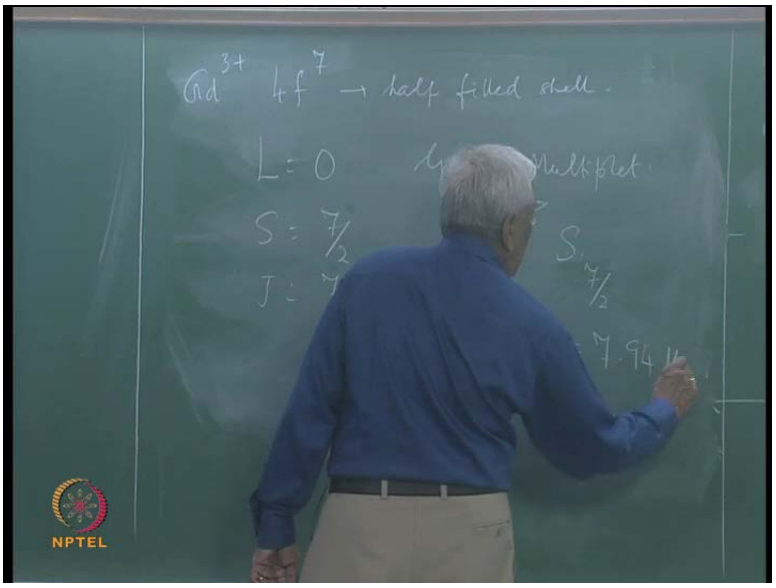

Next, we have gadolinium 3 plus which has seven electrons in the 4f shell, which can accommodate a total of fourteen electrons.

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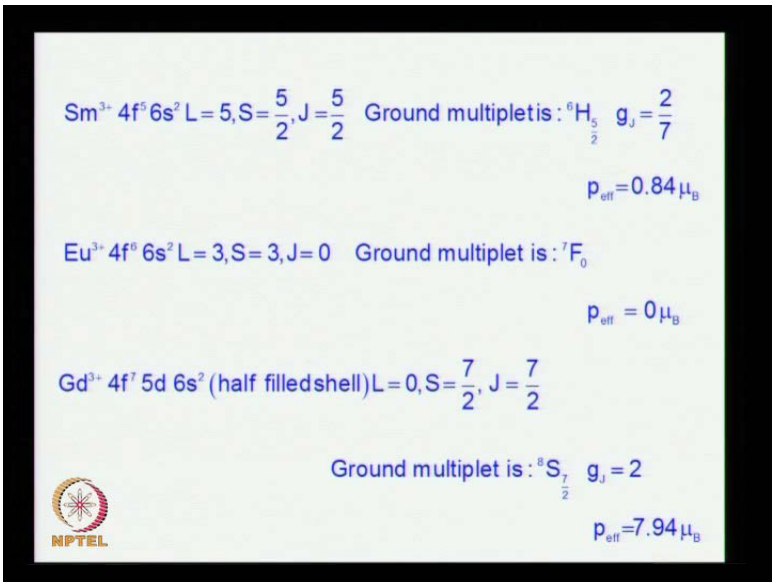

So, this is a half filled shell, the corresponding L value turns out to be 0, S is 7 by 2 and J is also 7 by 2. Since L is 0, the ground multiplet has a term symbol, which is that of an S term and therefore, this will be 8 S 7 by 2.

So, substituting these values of L S and J we get g J for gadolinium 3 plus as to we just this spin only value. Since it has only spin contribution, the orbital angular momentum is

0. So, it has a spin only g factor. And the corresponding magnetic moment has value of 7.94 Bhor magnetrons, in the same way we can work out the values for the other seven electrons.

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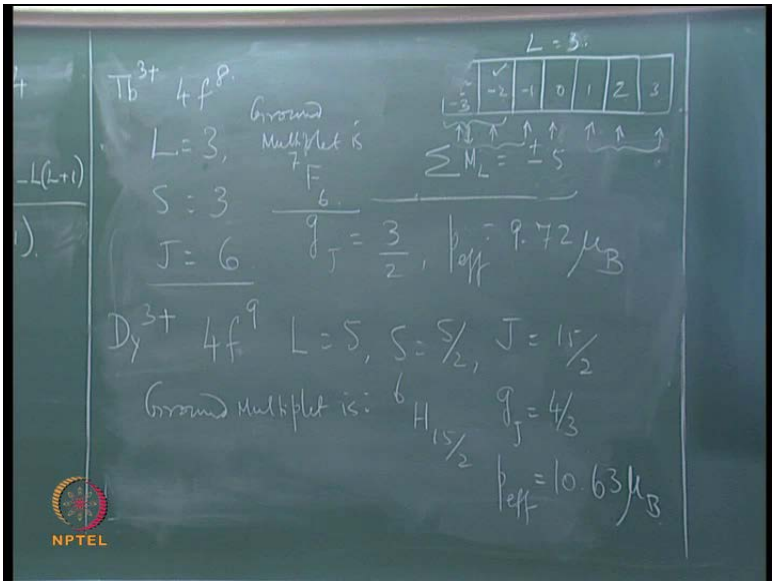

So, terbium 3 plus, which has eight electrons in the 4 f shell. So, L is 3, S is 3, J is 6.

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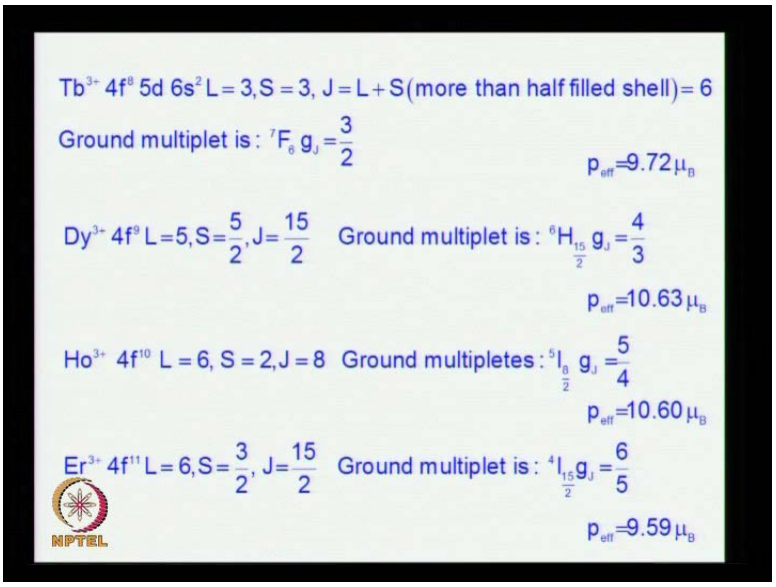

This case the S is 3 because, there are seven electrons with parallel spin and then the eighth electron goes to this. So, that we have plus 3 and minus 3 cancelling out leaving L equal to 3. The corresponding g J value since it is more than half L shell the ground

multiplet is corresponding to L equal to 3 it is an F term with the spin multiplicity of 7 and the J value of 6, the g J value is 3 by 2 and the effective magnetic moment is 9.72 Bhor magnetrons.

Similarly, we consider dysprosium 3 plus, which has 4f 9 configuration. The corresponding values are L equal to 5, S equal to 5 by 2 and J is 15 by 2. So, the ground multiplet is 6 H 15 by 2 and the g J value is 4 by 3. The magnetic moment is 10.63 Bhor magnetrons.

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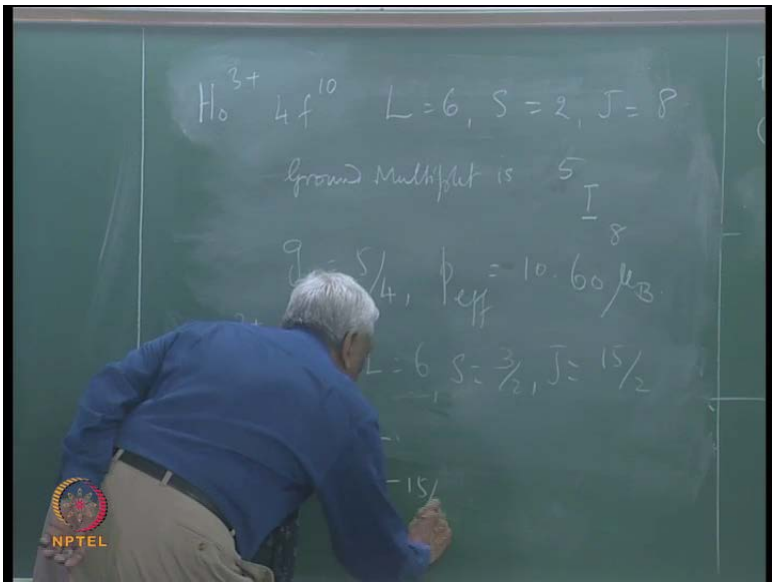

In the same way one can verify the cases of holmium 3 plus, which have 4 f 10 and the L value is 6, S value is 2, J value is 8. So, the ground multiplet is 6. So, it is an I term with the 3 no 5 8. So, the g J value is 5 by 4 in this case and the magnetic moment is 10.6 Bhor magnetrons.

Than we have erbium 3 plus, which has 4 f 11 and the corresponding L value is 6, S is 3 by 2 and J is 15 by 2. So, the ground multiplet is again an I term with 4 15 by 2, leading to a g J value of 6 by 5 and a P effective of 9.59 Bhor magnetrons.

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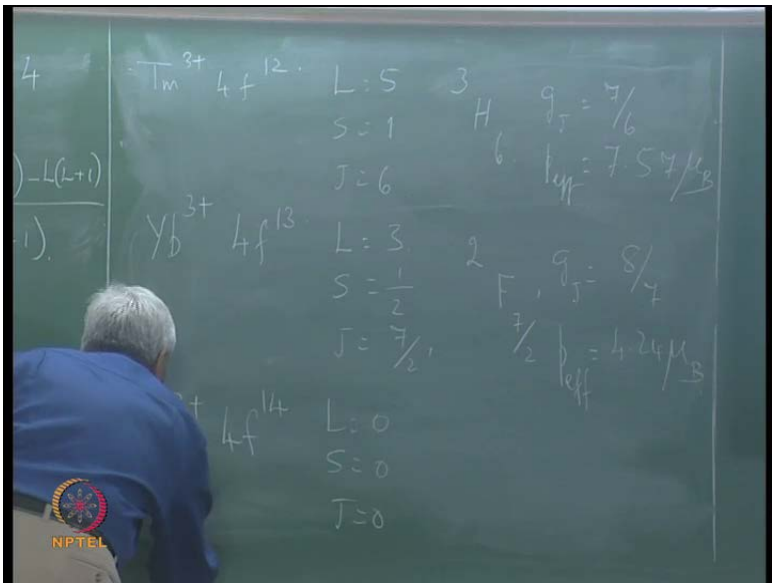

We next come to the case of thulium, which has 4 f 12. So, the L value is 5, S value is 1, J value is 6 and the ground multiplet is an H term with spin multiplicity 3, J equal to 6. So, the g J is 7 by 6 and the P effective is just 7.57 Bhor magnetrons. Lastly we have ytterbium 3 plus, which has thirteen electrons in the 4f shell and the corresponding values of L S J are, L equal to 3, S equal to half, J equal to 7 by 2 and the ground multiplet is F term because, L is 3 2 7 by 2. So, g J is 8 by 7 and P effective is 4.24 Bhor magnetrons. We of course, have the final case of lutetium which has the full shell filled with all the fourteen electrons.

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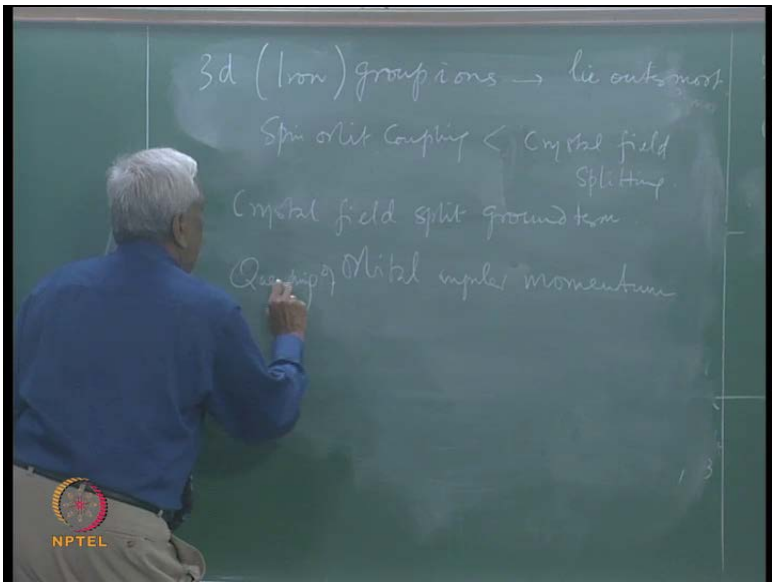

So, this corresponds to L equal to 0, S equal to 0, J equal to 0 because, it is a closed shell. And therefore, it is diamagnetic no Para magnetism no unpaired electrons. So, that completes the story about the rare earth ions. We now, move on to the iron group of 3 d group ions. The iron group corresponding to the progressive filling up of the 3 d shell.

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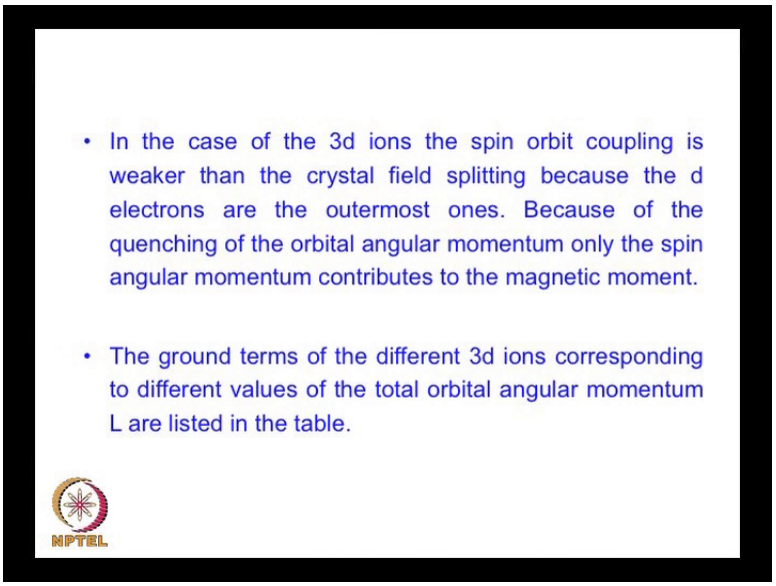

In this case the spin orbit coupling is weaker when crystal field splitting because; there is a crystalline electric field and the 3 d ions, which lie outer most there are no outer electron shielding them. So, they lie outermost and therefore, they experience the effect of the crystal field and therefore, the crystal field splitting is much stronger than the spin orbit coupling.

So, one has to determine the crystal field split ground term. Usually the crystal field is so; strong that the orbital angular momentum is completely quenched therefore, the only angular momentum which contributes to magnetism is the spin angular momentum. So, it is spin only magnetism. So, the g factor is that of the spin value.

Pure spin value two close to two and the corresponding magnetic moment is 2S into S plus 1 to the power half, where S is the spin angular momentum. So, with this prescription let us look at the ions in the 3 d shell.

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3d ion	Electron configuration	Ground term	$g = 2\{S(S+1)\}^{1/2}$ μ_B	Measured Magnetic moment(μ_B)
Ti^{3+}	$3d^1$	^2D	1.73	-
V^{4+}	$3d^1$	^2D	1.73	1.8
V^{3+}	$3d^2$	^3F	2.83	2.8
V^{2+}	$3d^3$	^4F	3.87	3.8
Cr^{3+}	$3d^3$	^4F	3.87	1.7
Mn^{4+}	$3d^3$	^4F	3.87	4.0
Cr^{2+}	$3d^4$	^5D	4.9	4.8
Mn^{3+}	$3d^4$	^5D	4.9	5.0
Mn^{2+}	$3d^5$	^6S	5.92	5.9
Fe^{3+}	$3d^5$	^6S	5.92	5.9
Fe^{2+}	$3d^6$	^5D	4.9	5.4
Co^{2+}	$3d^7$	^4F	3.87	4.8
Ni^{2+}	$3d^8$	^3F	2.83	3.2
Cu^{2+}	$3d^9$	^2D	1.73	1.9

So, we start with titanium 3 plus which has 3 d 1, one electron.

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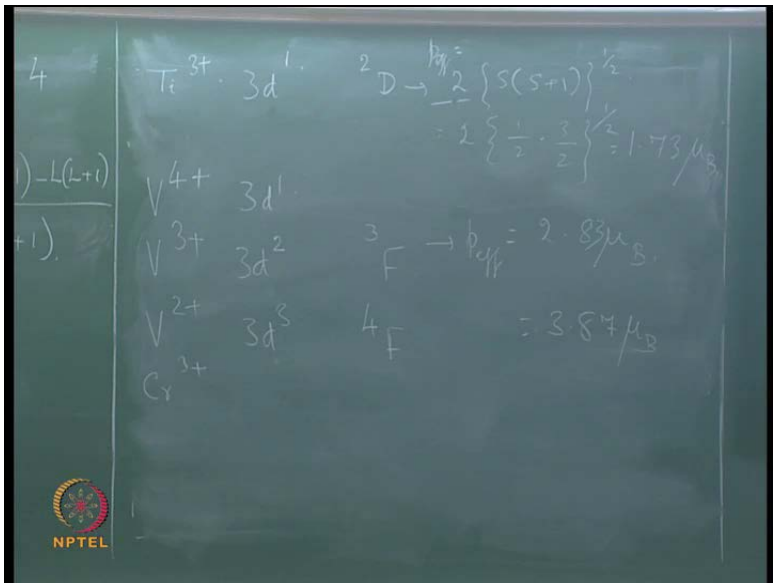

So, it has since it is a D electron the ground term is has the symbol D and it is a 2 D term, which is the ground term therefore, 2S into S plus 1 to the power half. In this case is 2 into half into 3 by 2 to the power half. This is value of the effective magnetic moment, this is g value.

So, this works out to be 1.73 then we have V 4 plus vanadium, which has also 3 d 1. So, its behaviour is similar then vanadium 3 plus has two electrons 3 d 2 and that

corresponds to a 3 F by the same reasoning as we did for the rare earth ions and the P effective in this case is 2.8. We can also have vanadium 2 plus, which is 3 d 3 and the spectroscopic ground term is 4 F and the P effective will be 3.87, 2.83 here.

Vanadium 2 plus as well as chromium 3 plus and manganese 4 plus all have the same electronic configuration of 3 d 3. And so, they have similar magnetic behaviour.

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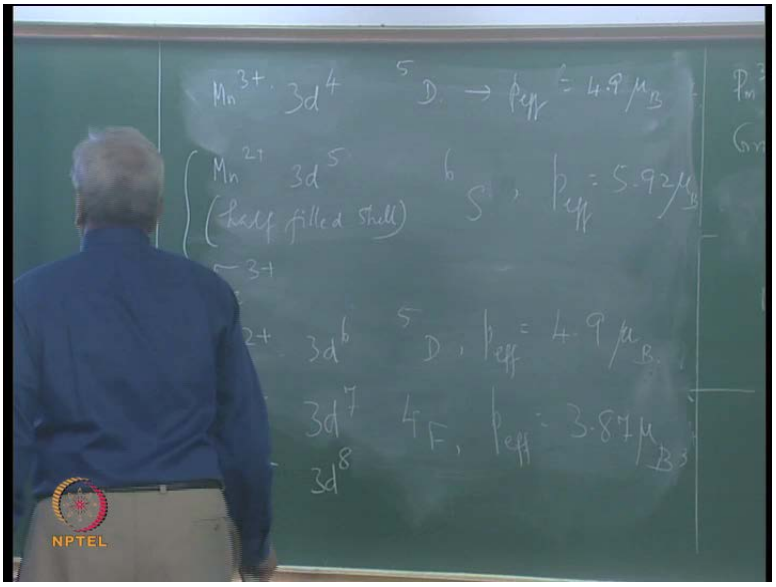

Then we move on to manganese 3 plus, which has four electrons in the 3 d shell and therefore, it has a 5 D term giving a magnetic moment of 4.9 Bhor magnet. Then Mn 2 plus which has five electrons. So, it is a half filled shell with a spectroscopic ground term of 6 S, it is an S state and so, the P effective since it is an s state. So, it will be 5.92 is also the case with iron 3 plus is identical isoelectronic. Then we go on to for s ion which has 3 d 6 configuration and again a 5 D ground term with a magnetic moment calculated magnetic moment of 4.9 as before. Then we have cobalt 2 plus, which is 3 d 7 and 4 F ground term P effective of 3.87. Then we have nickel 2 plus, which is 3 d 8 and so, a 3 F ground term and a magnetic moment of 2.83.

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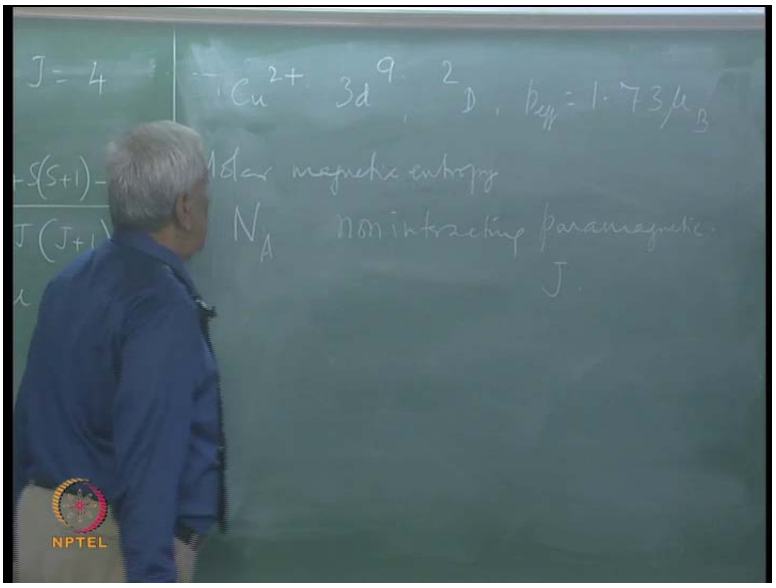

Finally, we come to copper 2 plus, cuprous ion which has a 3 d 9 configuration. So, it has a 2 D ground term with a P effective of 1.73 Bhor magnetrons. So, the experimental measured magnetic moments are given the last column in this table. So, you can see that the agreement with the spin only magnetic moment is fairly good.

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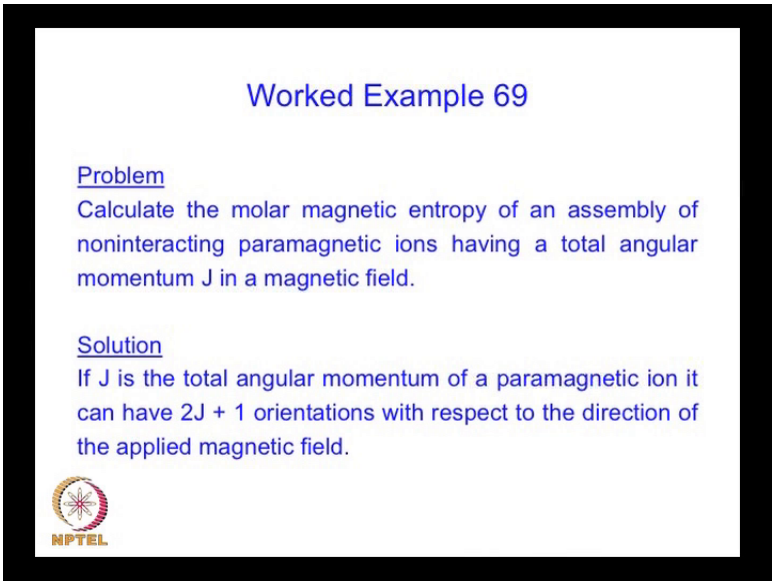

Next you are asked to calculate the molar magnetic entropy, of an assembly of non interacting paramagnetic ions. Molar means the number of spins is the Avogadro number. Each of these has a total angular momentum of J and a magnetic field is applied.

So, if you have a total angular momentum of J, there are 2 J plus 1 orientation possible for each ion with respect to the direction of the applied magnetic field.

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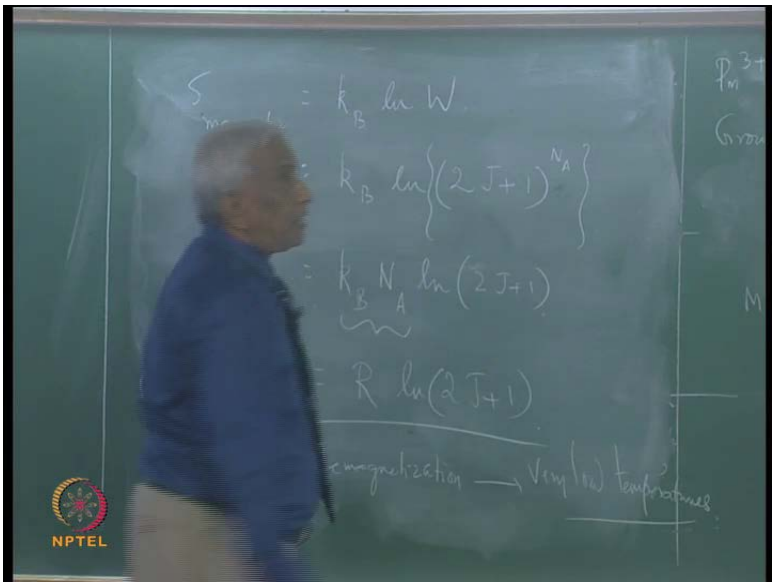

Therefore, the magnetic entropy can be calculated readily from the Boltzmann formula, which gives the magnetic entropy as K B log W, where K B is the Boltzmann constant and W is the number of different configurations.

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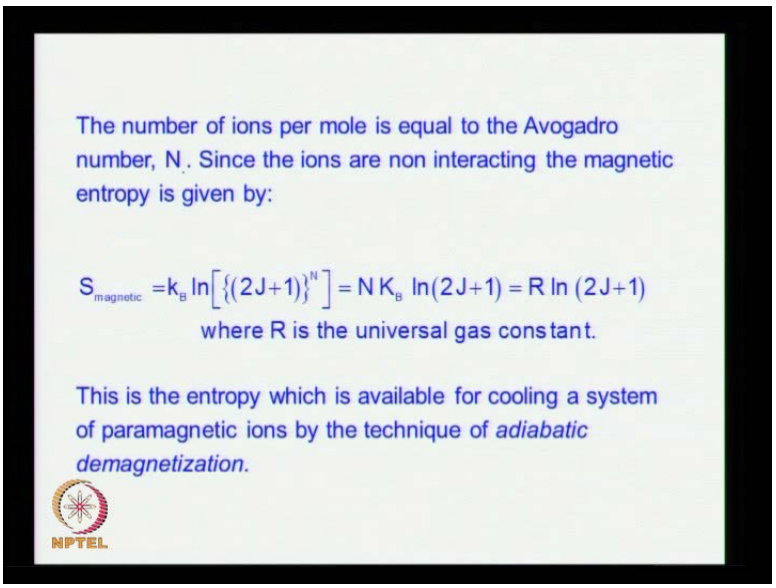

So, this will be in this case, since there are N ions, N A where N A is the Avogadro number and therefore, the total probability is K B log 2 J plus 1 to the power N A

therefore, since it is logarithm, it will be and we know that K B N A is just the universal gas constant R and therefore, it is R log 2 J plus 1.

So, this is the magnetic entropy that is available in a system of paramagnetic ions and in an applied magnetic field. So, you can have the technique of adiabatic de magnetisation by means of which we can remove the applied magnetic field suddenly keeping the spins in thermal isolation and this entropy causes a cooling of the spins or the paramagnetic ions by this technique, which takes these two very low temperatures. this technique has been used to achieve extremely low temperatures, it is a refrigeration technique.