Coordination Chemistry
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Lecture - 31
Magnetic Measurements

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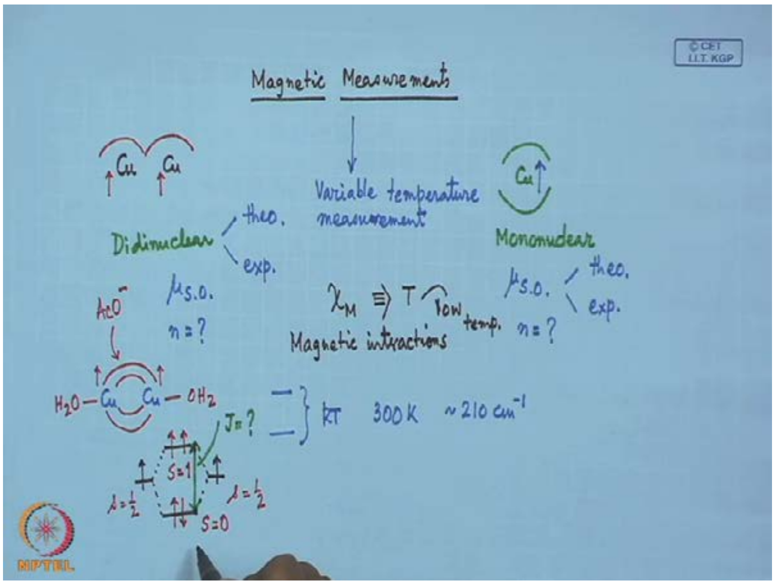

Good evening everybody. So, we are talking about the different types of magnetic properties of the metal complexes, and today we will see about the magnetic measurements where we can see how experimentally we can determine the different magnetic movements of these metal complexes.

And what we have seen in our previous classes that if we have 2 centers, and these 2 paramagnetic centers, it can be in any solid sample or it can be any biological sample also, such as that of in hemocyanin, where this particular centre is having one unpaired electron and the second is also having second unpaired electron. And this can be compared with some other species like that of our simple copper complex which is mono nuclear.

So, if we have a mono nuclear complex, and this is obviously a dinuclear one. And these 2 systems we can simply compare by knowing the corresponding magnetic movement values; if this is simply the corresponding spin only value, we can have one theoretically predicted value and another one is the experimentally determined quantity. Similarly, here also we can have the theoretically predicted one and the experimentally determined the corresponding one.

So, in this today’s class, when we go for this typical measurements, if initially we can consider that theoretically we can have some idea about the total magnetic movement it can be, in both these two cases only, the spin only, that means, the spin contribution we are only considering; then we can have some magnitude of these, depending upon the number of unpaired electrons. So, what are the unpaired electrons present in these two systems that can immediately tell us that what would be the corresponding magnetic movement.

So, based on these values, we basically get the corresponding theoretically predicted magnetic movement values. Then we will see how the different techniques, the physical techniques we can use to measure these magnetic movements starting from the simple mononuclear or dinuclear or tetranuclear complexes of any coordination compound containing the transition metal ions or the lanthanides or the actinides, and we can compare these values with that of the corresponding values what we get from the theoretical calculations. So, these theoretical calculations are very useful considering the number of unpaired electrons in these systems.

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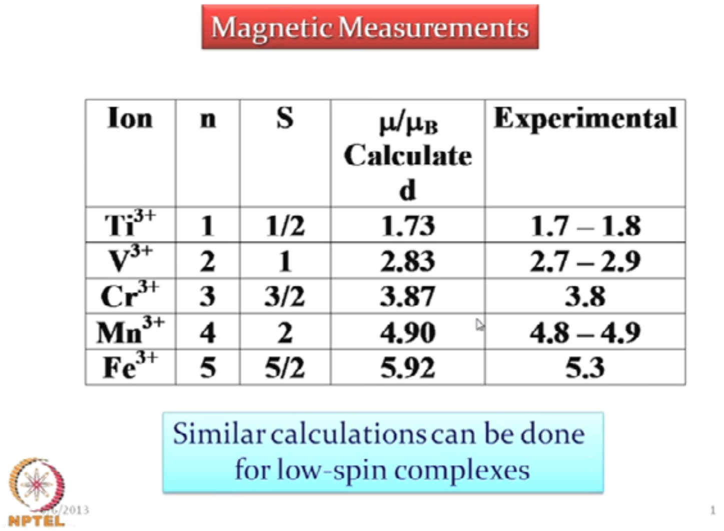

Magnetic Measurements

Ion	n	S	μ/μ_B Calculated	Experimental
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Fe^{3+}	5	5/2	5.92	5.3

Similar calculations can be done for low-spin complexes

So, these measurements basically give us some very good idea that, what are the different types of interactions we can have for the overall magnetic moment of the system.

So, this we have seen already that, when we have these number of unpaired electrons in the different metal ions, and these metal ions are bound to the ligand system, it can be to the biogenic ligand system like that of porphyrin or any other protein derived ligand system also. And then we just simply can focus our attention on the spin magnetic moment; so the spin magnetic moment basically giving all the corresponding spin only values which are ranging from 1.7 to 5.3 for a system having 1 unpaired electron to 5 unpaired electrons.

So, side by side, when we will see that, these 2 values, in this the values what we are getting in this column are the theoretically predicted values based on the number of unpaired electrons and they are corresponding spin values, total spin values. And on the right hand side, what we get, experimental one. So, the theoretically predicted one and the experimentally determined quantities always we should compare.

And, in some cases, we will see, afterwards that, there is some deviation from the theoretically predicted, calculated magnitude movement values with that of our experimentally determined values; then only we can assume that there is some mechanism operating, which can either increase the magnetic movement or decrease the magnetic movement, but we can predict from these theoretical calculations.

So, in some cases, we have, can see that the magnetic movement values are in excess of what we have calculated from the spin only values, then something else is contributing towards the total magnetic movement; and will find that if we just consider the orbital magnetic movement values together with the spin values, then only we can justify some of these excess amount of magnetic movements, particularly when we are considering a magnetically dilute system, where the system has the separated metal ions centers containing unpaired electrons which are isolated by the ligand environments. So, they are not close enough to each other, and they are not interacting to each other to give us a magnetically concentrated system, and we can have the other 2 types of interactions such as ferromagnetic as well as anti ferromagnetic interactions for these systems.

So, if we have these similar unpaired electrons for these systems, and when we have 5 unpaired electrons on a ferric iron giving rise to a magnetic movement value of 5.92, we simply say that the corresponding crystal field is not changing the presence of the unpaired electrons which are 5 in number. That means, we are considering a system which is simply the high spin system; that means, the crystal filled is not strong enough to go for any spin pairing.

So, the similar calculations considering the formula, we, what we are using depending on the end values for the mu in units of mu B, we can do for the other low spin complexes at the same time. So, we can have 2 values for, either the high spin complexes, or the low spin complexes. And we can find out that in some cases we can have the magnetic movement less, or in some other cases we can have a magnetic movement greater than what we theoretically predict.

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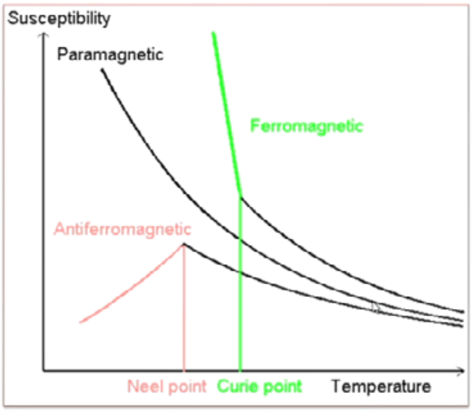

So, if we have a simple paramagnetic system, and we will take the help of the temperature dependence of the susceptibility term or the magnetic movement term, and if we can go for a variable temperature measurement for these values; so whatever magnetic measurements we can have, we can go for a variable temperature measurement where we can see that how the corresponding kai M values are changing with that of the change in the temperature. Because some of these magnetic interactions, some of these magnetic interactions are seen at a very low temperatures; when the low temperature domain or a low temperature resume, we see the corresponding interactions.

So, at this particular temperature, what we are talking in our last class that we can have the corresponding multiplied width, and if we go down with this temperature we are basically manipulating the corresponding thermal energy packet; that means, the corresponding kT values at which we are changing, which is at 300 Kelvin; that means, the room temperature is around 205 to 210 centimeter inverse. So, as we go down to either to a liquid helium temperature or a liquid nitrogen temperature, our kT values are changing, and we had a different types of populations for these different magnetic orbitals, with that of the available unpaired electrons on the complexes, whether if the complex is a mono nuclear one or a dinuclear or a higher nuclearity.

So, when we see that a simple paramagnetic species, it can be a biological species, it can be catalyst, it can be any solid state material, it basically give our some idea that when we go the change in temperature; that means, the when we go for increase in temperature the corresponding susceptibility; that means, the ground susceptibility values as well as the molar susceptibility values are decreasing. But this decrease is very much monotonous and we can have a some relationship with that of our kai M values, with that of our temperature, that we basically get from the Curie equation. And as a result, we can have also the corresponding constant for this type of plot of susceptibility versus temperature.

But, if we find in some other case, that a interaction is taking place between two or more centers, and the system we can consider as an anti ferromagnetic system, that means, they are coupled anti ferromagnetic ally. That we have seen in case of simple metal salt, what we can have in any chemistry laboratory, is the corresponding copper acetate salt, where 4 copper acetates are there, along with 2 water molecules which are binding towards this copper center in square pyramidal environment. So, the square base is forming from this acetate bridges. So, these are the corresponding acetate bridges and these are the 2 water molecules. So, we have typically one unpaired electron on this copper center, and the second unpaired electron on the other center.

So, in this particular situation, what we see that the 2 energy levels we can have, due to the corresponding exchange interactions between these 2 unpaired electrons, which we considered as the corresponding super exchange behavior for these 2 centers, and 1 unpaired electron is over here and another one is here; and this is the corresponding spin value for the first copper, and this is the corresponding spin value for the second copper. And if we consider that both the 2 electrons are occupying that one particular magnetic orbital; that means, the capital S value, the total spin value is equal to 0, or it is in this particular level where the total spin value is 1.

So, when these 2 are in opposite direction, and they are interacting in opposite way, we are basically giving a corresponding diamagnetic situation. So, depending upon these copper acetate molecules, whether these molecules are populating the ground acetate level, that the ground state energy level lower energy level, mostly, and if there is hundred percent occupancy of this particular level, we get a complete diamagnetic situation. Though the individual centers are paramagnetic, as we theoretically assume that 1 unpaired electron is present on this first copper center and the second one is on second copper, but if they are not interacting to each other, we get a paramagnetic situation.

But, when they are strongly interacting, and depending upon that interaction we can have a ground state level where this S is equal to 0; and we basically get the corresponding energy separation between these 2 levels, which we also can consider as the multiplied width; and these basically is related to the corresponding J value which is the corresponding interaction constant, not this J quantum number, but is the corresponding interaction parameter what can be detected with respect to that of the separation. So, we get some value which is close to sometime, close to this separation. And when this particular level is occupied, we get anti ferromagnetic interaction, and when the upper level we get, we get a corresponding ferromagnetic interactions.

So, in case of anti ferromagnetic interaction, and this particular temperature is very important, and we consider it as the nil point, or nil temperature, because this particular temperature is defined in such a fashion that above this temperature. So, we have a critical temperature. And above this critical temperature, the system is more or less behaving like the simple the paramagnetic system. So, if we are measuring the magnetic movement of 2 systems, where one is typically a paramagnetic system and another is ferromagnetic ally interacting system. So, at some high temperature, in this region or in this particular region, we are not able to identify the nature of these corresponding species; whether the compound is paramagnetic or anti ferromagnetic that we unable to identify, if we go for the corresponding magnetic measurements in this particular region, or in this particular region.

So, for that purpose, we have to cool down the system, and we have to go below this temperature, that means, below this nil temperature; what we see that our magnetic movement, our magnetic susceptibility is decreasing with the decrease in temperature, which is in opposite form. The behavior what we are seeing over here is, the susceptibility is decreasing with the increasing temperature, but below the nil temperature, the susceptibility is also decreasing with decrease in temperature.

And, by looking at the shape of this curve, because we can thought in some time also, the product of kai n T versus t also, because this particular thing can justify our concept that, at this temperature we have a sudden change in the corresponding alignment of this unpaired spins and the system is behaving as an anti ferromagnetic species, and we have a corresponding nil temperature. So, this abrupt lowering in magnetic moment with respect to the lowering in temperature is basically a clear indication for the anti-ferromagnetic nature of this species or these compounds.

Similarly, another temperature is also can be observed for some other system which is ferromagnetic in nature, where we get a curie temperature. And above this curie temperature, we see that the system is simply behaving like a paramagnetic system, because at this particular temperature, the measurement will not tell you, whether our species is a ferromagnetic one or a paramagnetic one. But below this Curie temperature what we see that, below this temperature, the paramagnetic system is changing in this particular way; that means, it is monotonous and it is also continuous.

But, for ferromagnetic system theory, there is abrupt change, and it is basically a continuously, not a parabolic one, but it is a continuous straight line curve for this, and it is increasing in a stiff fashion. So, stiffly, the rising in susceptibility value, as we decrease the temperature, is a characteristic feature for the all ferromagnetic materials. So, magnetic ordering or magnetic interactions are only observable at some lower temperature, that is why we are all interested to go for the magnetic measurements at lower temperatures. So, that is why we go down to liquid nitrogen temperature, or in some other cases, we can go to liquid helium temperature for these measurements.

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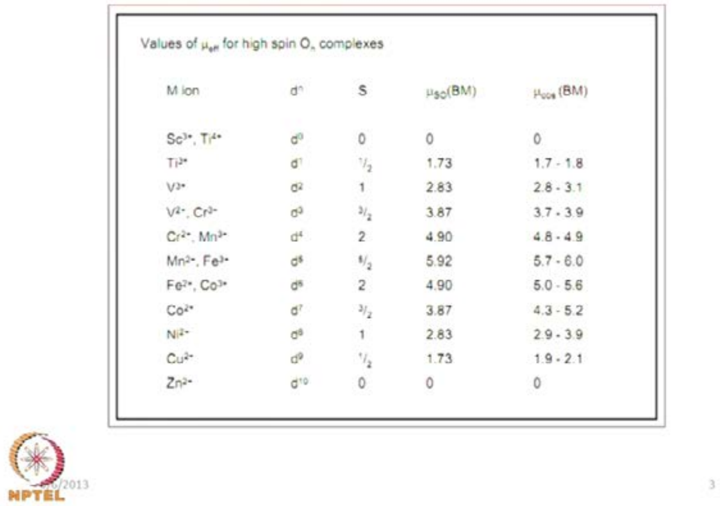

Values of μ_{eff} for high spin O_h complexes

M ion	d^n	S	μ_{SO}(BM)	μ_{obs} (BM)
Sc^{3+}, Ti^{4+}	d^0	0	0	0
Ti^{3+}	d^1	$^1/_2$	1.73	1.7 - 1.8
V^{3+}	d^2	1	2.83	2.8 - 3.1
V^{2+}, Cr^{3+}	d^3	$^3/_2$	3.87	3.7 - 3.9
Cr^{2+}, Mn^{3+}	d^4	2	4.90	4.8 - 4.9
Mn^{2+}, Fe^{3+}	d^5	$^5/_2$	5.92	5.7 - 6.0
Fe^{2+}, Co^{3+}	d^6	2	4.90	5.0 - 5.6
Co^{2+}	d^7	$^3/_2$	3.87	4.3 - 5.2
Ni^{2+}	d^8	1	2.83	2.9 - 3.9
Cu^{2+}	d^9	$^1/_2$	1.73	1.9 - 2.1
Zn^{2+}	d^{10}	0	0	0

So, what we see that, for all these systems, and if we just elaborate it up to copper, for a d 9 system to d 1 system, for the entire range from trivalent titanium to bivalent copper, we now know that we have the typical occupancy of these electrons. So, after d 5, what we have seen, for manganese 2 plus or Fe 3 plus, the number of unpaired electron is decreasing, as we go for the corresponding pairing in the system for the T 2 g levels. So, in the octahedral geometry, this is for only one particular geometry, because this can also we can calculate it out for other typical geometries of different symmetry, such as square planer, square pyramidal, trigonal bipyramidal, etcetera.

So, depending upon these number of unpaired electrons present in all these systems, we have the spin only values in mu B or bohr magnetron, and we can compare these values with that of the observed values which we can determine experimentally. So, experimentally determined quantities are sometimes very much different, what we see from this particular plot, at this particular table that, when we see that in case of Mn 2 plus or Fe 3 plus, the experimental magnetic movement is slightly higher than the theoretically predicted magnetic movement value based on the mu S equation; mu S equation is that S is a good quantum number. We are not bothering with that of the other 2 quantum number, that means, the L values or the J values.

But, when we move to a d 7 system or a d 8 system or in some places also the d 9 system, we see that the mu spin only values are always less than that of the range what can be predicted for the experimentally determined magnitude of these values for the different metal complexes. So, for different metal complexes, for simple mono nuclear one, we find that cobalt mono nuclear compound can register a magnetic movement value of, say, 5.2. But the spin value is predicting us for 3 unpaired electrons is equal to 3.87 and n is equal to 2. So, the magnitude, what we can calculate is root over 3 into 3 plus 2. So, is basically 15, root 15 is equal to 3.87; but it is going up to 5.2. So, there is some other thing which is contributing or which is increasing the magnetic movement values from 3.87 to 5.2.

Similarly, for nickel 2 plus, it is happening that the spin only value is 2.83, and we are going up to 3.9. So, there is some other contribution which is adding to the corresponding spin only values, similarly for copper 2 plus, though the magnitude is less, but it can go from 1.73 to 2.1.

So, next what we can do, therefore, that we not taking to consideration of the L values. So, what are the L values for the corresponding ground state spectroscopic symbol, what we have calculated in our previous class up to chromium 3 plus, that means, the d 3 system. So, today we will just find out what are the corresponding values for d 4 to d 9 system. And depending upon the spectroscopic symbol, we have the S value and the L value and the corresponding j values. And then we can calculate out the corresponding mu j values and mu L plus s.

So, those basically can tell us that this mu S is not operating for explaining the corresponding mu experimental values or mu observed values, but mu L plus L can identify the corresponding increase in the magnetic movement values beyond the spin only values.

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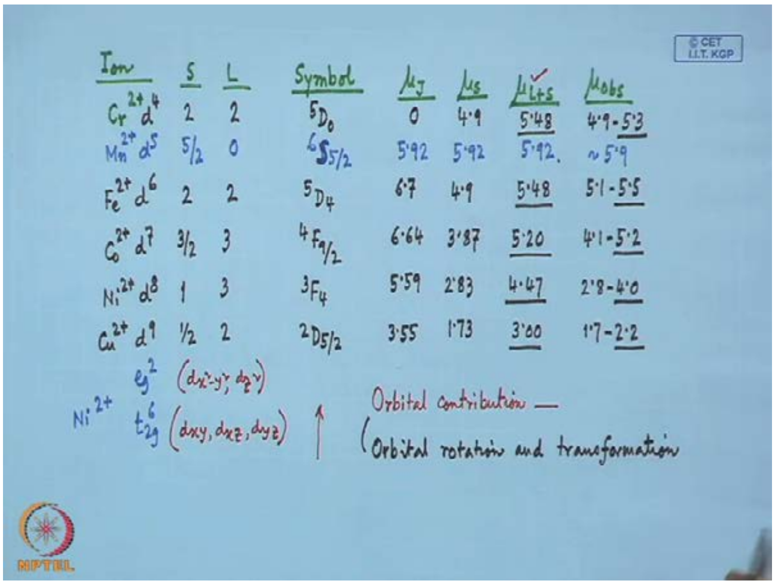

Ion	S	L	Symbol	μ_J	μ_S	μ_{L+S} ✓	μ_{obs}
Cr^{2+} d^4	2	2	$^5D_0$	0	4·9	5·48	4·9-5·3
Mn^{2+} d^5	5/2	0	$^6S_{5/2}$	5·92	5·92	5·92.	~5·9
Fe^{2+} d^6	2	2	$^5D_4$	6·7	4·9	5·48	5·1-5·5
Co^{2+} d^7	3/2	3	$^4F_{9/2}$	6·64	3·87	5·20	4·1-5·2
Ni^{2+} d^8	1	3	$^3F_4$	5·59	2·83	4·47	2·8-4·0
Cu^{2+} d^9	1/2	2	$^2D_{5/2}$	3·55	1·73	3·00	1·7-2·2

Ni^{2+} e_g^2 $(d_{x^2-y^2}, d_{z^2})$

t_{2g}^6 (d_{xy}, d_{xz}, d_{yz}) $\uparrow$

Orbital contribution —

(Orbital rotation and transformation

So, that we can see for the different values for, say, chromium 2 plus. So, if the metal ion is chromium 2 plus, which is our ion; and the corresponding ground state quantum numbers, that means, the S values and the L values we can have; then we can the symbol, the spectroscopic symbol; and then we can calculate the corresponding mu J value; mu S values what we are seen in the table now; then mu L plus S values; and the mu observed or mu obs values, the experimental values for this systems.

So, when we have chromium 2 plus which is a 3 d 4 system. So, is a 3 d 4 ion. And the corresponding ground state quantum number for capital S is 2 with respect to the 4 unpaired electron, and L value is equal to 2 for the electrons in the d level, and this corresponding spectroscopic symbol which we can find out from here is 5 D 0, and we are considering this J value as equal to corresponding L minus S, values not L plus S. So, mu J will therefore be 0, since this particular value of J is equal to 0.

But, mu S is equal to 4.9 which is related to the number of unpaired electron equal to 4; and this 4 number of unpaired electron, that means, the n value equal to 2; that means, it has the corresponding magnitude of root over 4 into 4 plus 2, that means, root 24. So, root 24 is 4.9. Now, we see that what is the corresponding value for the experimental one, we have seen just now, that it can range from 5.9 to 5.3.

So, what would be the mu L plus S? So, considering both L value and S value this can be 5.48, which basically justifying the upper limit or the magnetic movement what we can get, as an experimental magnetic movement. So, if there is sufficient amount of orbital contribution, our mu S equation is not sufficient to explain the correspondingly observed magnetic movement value, but mu L plus S can be used to determine the corresponding magnetic movement what we experimentally determine for this metal ion system.

Similarly, the next one which is manganese 2 plus, which is a d 5 system; and we have 5 unpaired electron, so S value is 5 half, and L value is equal to 0. So, the ground state on is 6 S 5 by 2, and mu spin only value is for 5 unpaired electron, and the observed values are close to 5.9, and this is also very much useful, depending upon the corresponding spectroscopic term, this is S not D, this is S. So, corresponding to the spectroscopic term which is S; that means, we do not have when we have the S ground state term, we do not have the corresponding orbital contribution. So, for mu j it is also 5.92 this is also 5.92. So, this is for d 5 system.

Then, iron 2 plus, which is the d 6 system. S value equal to 2, and L value equal to 2, then the time is 5 D 4, and mu j is 6.7, this is 4.9, and this is 5.48, and this value is ranging from 5.1 to 5.5. So, again it is close to the corresponding mu L plus S value, like in the case of chromium 2 plus which is closely related.

Then, we have the cobalt 2 plus, which is d 7 system. S value 3 by 2, L value 3, which is 4 F 9 by 2 is the term symbol, and this mu spin only is 3.87 for 3 unpaired electron, but the experimentally magnitude is ranging from 5.1 to 5.2. So, if we calculate the mu J equation it will be 6.64 which is quite high compared to the experimentally determined value, but the mu L plus S is quite close to that value which is 5.20.

So, we see that more or more we are deviating from the mu S equation, and we are slowly getting some equation where the mu L plus S values are matching with that of the experimentally determined quantities. So, this typical example, because most of the cases we encounter with several cobalt 2 compounds, in either tetrahedral or octahedral geometries which are having, registering some magnetic movement which is higher than the spin only values. So, we have the typical orbital contributions.

So, we have the next one as nickel 2 plus which is 3 d 8 system having 2 unpaired electrons in the e g level, which is t 2 g 6 e g 2, and L value equal to 3, so the ground term is 3 F 4, and the spin only value is 2.83, and the range is also from 2.8 to 4.0, and mu J equation is now quite high, because after this half field level, that is a after d 5, what we are getting, that continuously we are getting a highest level of this corresponding mu J values compared to mu L plus S; because in this particular case, these two values are same, but in this case, it is higher than the mu L plus S, in this case it is higher than the mu L plus S, and similarly in this particular case also it is higher than the mu L plus S, here it is 4.47. So, again it is justifying the corresponding higher magnitude of the observed magnetic value, in terms of the corresponding mu L plus S equation.

So, for the next one is the copper 2 plus which is 3 d 9 system, having 1 unpaired electron, L value equal to 2, and the term value is again returning back to the d term, so 2 D 5 by 2, with 1 unpaired electron the spin only calculation gives us 1.73 bohr magneton, but the experimental value is changing from 1.7 to 2.2, and J is equal to 3.55, and the mu L plus S is quite high compared to the experimental determined value of 2.2, but still that some contribution we can have, which can basically justify the higher level of this corresponding magnetic movement compared to the corresponding value what we can get from this spin only values.

So, we have something, that means, a corresponding thing what we are getting, that if we have a particular system, that means, these electrons, say, for nickel 2 plus what we can have, we have the t 2 g 6 and e g 2 electrons. So, what we will be seeing there that, we have several of these levels; the d 2 g levels we all know, that d x y, d x z and d y z, and these are d x square minus y square, and d z square. So, electrons are there, and these electrons are basically moving from one level to the other.

And, if the corresponding movement of the electron from one particular level to the other level is allowed; that means, we see that we can find, that we can rotate these electron from one particular shape to the other shape, because this particular orbital is a d x y, these d x z and d y z are inter comfortable in terms of the rotation along some specified axis. So, if the electrons are there in these particular levels, and we can move those electrons from one level to the other, so we can have the corresponding orbital contribution.

And, these orbital contributions are due to orbital rotation; why we are getting these corresponding L values in the magnetic movement compared to the only mu S values, because of these orbital contributions to the magnetic movement values, and these orbital contribution is due to the corresponding orbital rotation and the transformation. So, we have therefore, orbital rotation and transformation.

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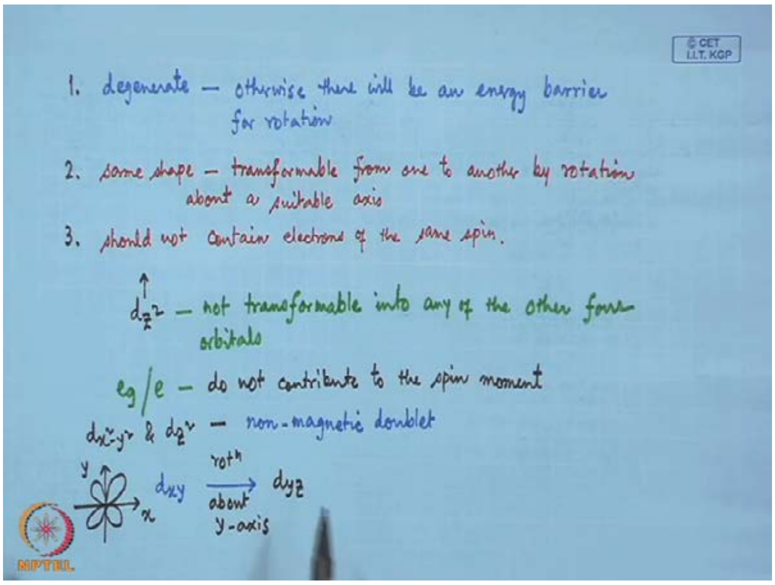

1. degenerate – otherwise there will be an energy barrier for rotation
2. same shape – transformable from one to another by rotation about a suitable axis
3. should not contain electrons of the same spin.

d_{z^2} – not transformable into any of the other four orbitals

e_g/e – do not contribute to the spin moment

$d_{x^2-y^2}$ & d_{z^2} – non-magnetic doublet

$d_{xy} \xrightarrow[\text{about } y\text{-axis}]{\text{rot}^n} d_{yz}$

So, what we see that, for the occupancy of this different levels, so 3 rules we must follow for these orbital contributions. The first one is that orbital must be degenerate, that means, if we have degenerate orbitals, like t 2 g set or the e g set, and there will be an energy barrier for rotation. So, if they are degenerate, then we can have the movement from one level to the other, otherwise there will be an energy barrier for rotation. So, whether these orbitals are degenerate or not, that will dictate whether it can contribute the corresponding orbital movement to the spin movement.

Then, orbitals must be of same shape. What we are talking about this d x y and d x z orbitals, then they must be transformable from one to another by rotation. So, they are transformable from one to another by rotation about a suitable axis. So, we should that also consider; and when this rotation we are allowing, the orbitals which we are talking about for the movement of the electron to the other, so they should not contain any electron. So, these orbitals should not contain electrons of the same spin. So, these are the 3 basic rules what we can follow for this orbital rotation model and the transformation model.

So, this how we can apply? We just see that. If we have the d z square orbital, and we have seen the d 2 g level of orbitals and the d x square minus y square orbital. So, whenever we have an electron, say, in this d z square orbital; that means, the electronic configuration is d z square 1, then we see that whether this can be transformable from one to other by rotation or not, but this d z square is not transformable, transformable into any of these 4 orbitals, into any of the other 4 orbitals, that means, d x square minus y square and the t 2 g set.

So, if we have electrons in e g level or e level, so when the electrons are present in e g or the e level, they cannot make any orbital contribution to the spin movement. So, do not contribute to the spin movement. So, we will have some situation where these electrons are there, but they will not definitely contribute to the corresponding spin movement. So, these two, therefore, the d x square minus y square and d z square, which are the e g set or the e set, so these two we cannot interconvert, and therefore, this two will not contribute any magnetic movement contribution with respect to the mu L values. So, they constitute basically m non magnetic doublet. So, these two levels we can consider as non magnetic doublet. So, they are non magnetic in terms of the corresponding orbital contribution, but if the electrons are there, the spin movements are always available, but the orbital movement we cannot.

So, the next one the d 2 g set level, that means, if we have the d x y. So, this d x y orbital we all know that is, this is x and this is y, shape of this d x y orbital is like this, and if we rotate about y axis, so about y axis we rotate this orbital. So, it can go from this, it is not moving from this x plane, so it will be going for y and this perpendicular z plane, so which is basically giving rise to the d y z orbital. So, if we can go for this d x y at the rotation and the y axis is 2 d y z. So, electron from this level can go to this level, and can contribute in terms of this orbital rotation. So, orbital rotation model predicts us that if we have an electron in the d x y or d x z level, that will basically contribute the magnetic movement in terms of these orbital contributions.

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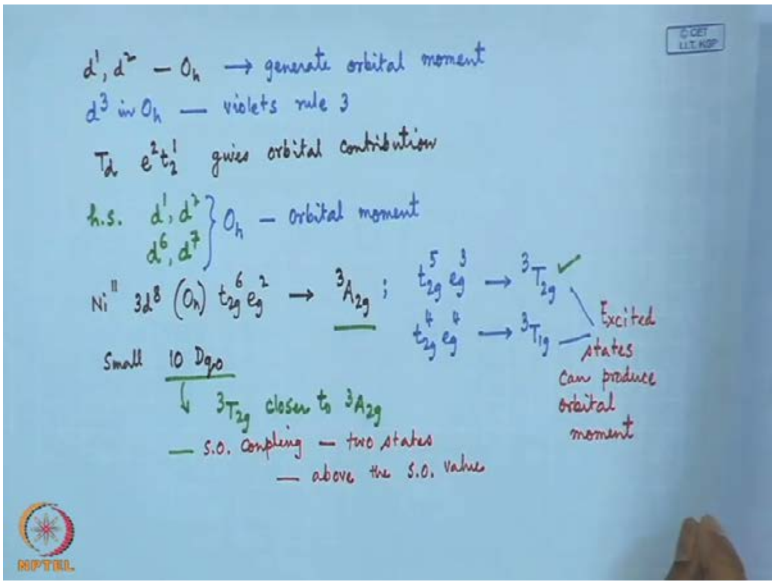

$d^1, d^2 - O_h \rightarrow$ generate orbital moment

d^3 in O_h — violets rule 3

T_d $e^2t_2^1$ gives orbital contribution

h.s. $\left.\begin{matrix} d^1, d^2 \\ d^6, d^7 \end{matrix}\right\} O_h$ — orbital moment

Ni^{II} $3d^8$ (O_h) $t_{2g}^6 e_g^2 \rightarrow {}^3A_{2g}$; $t_{2g}^5 e_g^3 \rightarrow {}^3T_{2g}$ ✓

$t_{2g}^4 e_g^4 \rightarrow {}^3T_{1g}$ — Excited states can produce orbital moment

Small $10\,Dq_o$

↓ ${}^3T_{2g}$ closer to ${}^3A_{2g}$

— S.O. coupling — two states

— above the S.O. value

So, if we have the d 1, d 2 in octahedral geometry, then what we do expect; that we have the, either the d x y 1 or d y z 1 and d x y 1, that means, 2 electrons in this 2, t 2 g level in octahedral geometry. So, they basically generate orbital movement, so would be able to generate orbital movement. But d 3 in the same octahedral geometry, is violets the rule what we have predicted earlier, the rule 3; that means the orbitals would not contain the electrons of the same spin. So, already we have these electrons in this spin. So, this will not contribute that particular rule. So, it will not have in octahedral field, say, d 3 will not have these orbital contributions. So, it violets rule 3.

But the same situation is completely reversed, if we go for the other geometry, the most common geometry what we are talking all the time, is the tetrahedral geometry with a d 3 electronic configuration, we have e 2 and t 2 1 electron configuration; since, like this d 1 system, we now have t 2 1 system. So, it will have then the corresponding orbital contributions. So, this electronic configuration for d 3 which is not giving any orbital contribution in octahedral geometry, but can give rise to the corresponding orbital contribution in tetrahedral geometry. So, it therefore, gives orbital contribution. So, we find these are very important and very interesting in terms of these corresponding orbital contributions.

So, we have in terms of the corresponding term symbols, that if we have the high spin system for d 1, d 2, 2 unpaired electrons in the t 2 g level, similarly the situation is same when we cross the half field configuration, that means, after d 5, we have d 6 and d 7. So, like wise, what we see for this d 1 d 2 case in octahedral geometry, similarly the d 6 and d 7 also can have in octahedral geometry this orbital contribution. So, we can have orbital magnetic movement, can have orbital movement.

So, in terms of these corresponding term symbols what we see that, in case of nickel 2 which is 3 d 8 in octahedral geometry we have t 2 g 6 and e g 2 configuration, and the corresponding ground state term after crystal field splitting of the 3 F term is 2 A g. And this 3 A g term is due to the corresponding configuration of t 2 g 6 e g 2, and this can go for the other 2 configurations, like the excited levels which T 2 g 5 e g 3 for the excited level term which is 3 T 2 g, and t 2 g 4 e g 4 which is for 3 T 1 g term. So, these are the 2 excited levels.

Since the ground level is A term, that means, when we have the electron field in the e g level, and e g level is the non magnetic tablet level. So, we do not have any contribution, any orbital contribution from the ground state electron configuration, but from the table what we have seen that, in case of nickel 2 plus, we have the magnetic movement which is in excess of the spin only value which is 2.84. But experimentally the amount of magnetic movement what we get by determining the magnetic movement experimentally is sometime close to 3.2 or 3.3.

That means, there is definitely the corresponding orbital contribution, but that orbital contribution is not coming from the corresponding ground state term, but it is coming from the excited state terms, and these excited state terms we have this unpaired electrons, basically in the e g level as well as in the t 2 g level, because the t 2 g level is not filled as t 2 g 6, but it is t 2 g 5 which is similar to t 2 g 1, that means, like this system or this system. So, they have orbital contribution or orbital movement.

So, these two configurations, the 3 T 2 g and 3 T 1 g configurations, these are the two excited states; and these excited state, these two excited states can produce orbital movement. That means, these two levels will contribute the magnetic movement for this nickel 2 system, where we have magnetic movement higher than the spin only value. So, if we just consider these 2 levels, and we all know that these are basically related to the crystal field spitting parameter, the 10 D q values, if it is in octahedral geometry it is 10 D q o value.

So, if have a small value of this 10 D q o, we basically get for that this excited level; that means, 3 T 2 g, the first one, this one, 3 T 2 g level would be closer to 3 A 2 g level, that means, the ground state level. So, what happens therefore, therefore, we can have this corresponding spin orbit coupling. So, this particular thing, the mixing of the excited state we call it as a spin orbit coupling, and which is mixing the 2 states, that means, 3 T 2 g is mixed up with the 3 A 2 g; and as a result, we have above the spin only value, we have the corresponding magnetic movement.

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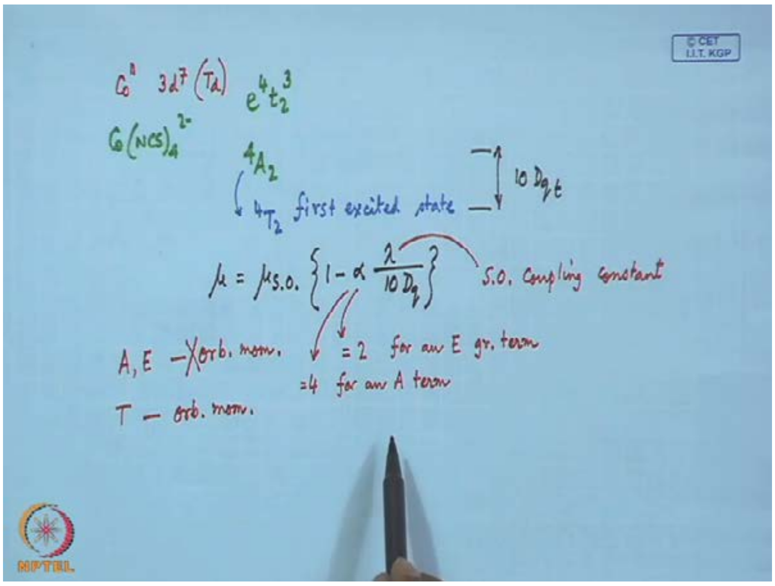

Co^{II} $3d^7$ (T_d) $e^4t_2^3$

$Co(NCS)_4^{2-}$

$^4A_2$

$^4T_2$ first excited state

10 Dq_t

$$\mu = \mu_{s.o.}\left\{1 - \alpha\frac{\lambda}{10\,Dq}\right\}$$

S.O. Coupling constant

= 2 for an E gr. term

= 4 for an A term

A, E – ✗ orb. mom.

T – orb. mom.

So, similar thing also happens when we get the corresponding cobalt system, which is 3 d 7. And in case of this, the cobalt we all know, that cobalt is very useful in giving the corresponding compounds in the tetrahedral geometries, such as cobalt NCS whole 4 2 minus. So, in this particular compound in tetrahedral geometry, we have the corresponding electron configuration is e 4 t 2 3.

So, we have in this particular situation, the ground state is 4 A 2, which is also not contributing any orbital movement to the system, but this particular 4 A 2 term will have a 4 T 2 term related to movement of the electron from one particular electron from here to here. So, this particular one will be e 4 t 2 4. So, for an electron configuration of e 4 t 2 4 we have an excited state, which is the first excited state. And these 2 levels, that means, the first excited state and the ground level, they are again separated by the corresponding crystal field term, that means which 10 D q t.

So, if they are separated by 10 D q t, and again due to the mixing what we get that, the corresponding magnetic movement, but we are getting and we are justifying these magnetic movement in terms of the corresponding L plus S values, is that mu spin only values, multiplied by 1 minus alpha into lambda divided by 10 D q; it can be the corresponding D q o, that means, D q octahedral or D q t for the tetrahedral geometry.

And, in this particular equation, where alpha is a constant, and it has different magnitudes for different terms, will be equal to 2 for an E ground term, and it can be equal to 4 for an A term, or A 2 term like this. So, these are therefore, so this A term and E term will not contribute any magnetic movement in terms of this orbital contribution to the spin only value, but T term can contribute. This T terms are arising as the corresponding excited state values, and therefore, we can find out from here the corresponding lambda value which is nothing but the spin only coupling constant.

So, the coupling, the mixing of all these things will therefore tell us, that these terms, the A and E terms, will not give any magnetic movement in terms of these corresponding orbital movement values. So, for these 1, the orbital movement values are not available, but for T term, as the corresponding orbital movement. So, whenever we have the corresponding T term, we get any orbital contribution from this particular system. So, this particular thing will tell us that, why we are getting some amount of magnetic movement which is in excess of the spin only values.

Thank you very much.