

Concepts of Chemistry for Engineering
Indian Institute of Technology, Bombay
Professor Debabrata Maiti
Lecture 37
Spectroscopic Term Symbol

(Refer Slide Time: 00:22)

Magnetism				
Ion	Config	OAM?	μ_{so}	μ_{obs}
Ti(III)	d1	yes	1.73	1.6-1.7
V(IV)	d1	yes	1.73	1.7-1.8
V(III)	d2	yes	2.83	2.7-2.9
Cr(IV)	d2	yes	2.83	2.8
V(II)	d3	no	3.88	3.8-3.9
Cr(III)	d3	no	3.88	3.7-3.9
Mn(IV)	d3	no	3.88	3.8-4.0
Cr(II)	d4 h.s	no	4.90	4.7-4.9
Cr(II)	d4 l.s	yes	2.83	3.2-3.3
Mn(III)	d4 h.s	no	4.90	4.9-5.0
Mn(III)	d4 l.s	yes	2.83	3.2
Mn(II)	d5 h.s	no	5.92	5.6-6.1
Mn(II)	d5 l.s	yes	1.73	1.8-2.1
Fe(III)	d5 h.s	no	5.92	5.7-6.0
Fe(III)	d5 l.s	yes	1.73	2.0-2.5
Fe(II)	d6 h.s	yes	4.90	5.1-5.7
Co(II)	d7 h.s	yes	3.88	4.3-5.2
Co(II)	d7 l.s	no	1.73	1.8
Ni(III)	d7 l.s	no	1.73	1.8-2.0
Ni(II)	d8	no	2.83	2.9-3.3
Cu(II)	d9	no	1.73	1.7-2.2

Now, once you know how the electronic configurations are and then you have to ask whether it is going to have any orbital angular momentum or not. Those questions obviously, when you read you will have you can verify it by this table, you do not have to verify right now, you can sit down I hope the table is not wrong, none of the data is wrong. So, you should be able to justify the data by itself this is like a self-check whether you have understood orbital angular momentum and t_{2g} e_g electronic configuration or not.

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Magnetism				
Orbital Contributions in tetrahedral Complexes				
Ion	Config	OAM ?	μ_{so}	μ_{obs}
Cr(V)	d1	no	1.73	1.7-1.8
Mn(VI)	d1	no	1.73	1.7-1.8
Cr(IV)	d2	no	2.83	2.8
Mn(V)	d2	no	2.83	2.6-2.8
Fe(V)	d3	yes	3.88	3.6-3.7
-	d4	yes	4.90	-
Mn(II)	d5	no	5.92	5.9-6.2
Fe(II)	d6	no	4.90	5.3-5.5
Co(II)	d7	no	3.88	4.2-4.8
Ni(II)	d8	yes	2.83	3.7-4.0
Cu(II)	d9	yes	1.73	

Magnetism				
Orbital Contributions in Octahedral Complexes				
Ion	Config	OAM ?	μ_{so}	μ_{obs}
Ti(III)	d1	yes	1.73	1.6-1.7
V(IV)	d1	yes	1.73	1.7-1.8
V(III)	d2	yes	2.83	2.7-2.9
Cr(IV)	d2	yes	2.83	2.8
V(II)	d3	no	3.88	3.8-3.9
Cr(III)	d3	no	3.88	3.7-3.9
Mn(IV)	d3	no	3.88	3.8-4.0
Cr(II)	d4 h.s	no	4.90	4.7-4.9
Cr(II)	d4 l.s	yes	2.83	3.2-3.3
Mn(III)	d4 h.s	no	4.90	4.9-5.0
Mn(III)	d4 l.s	yes	2.83	3.2
Mn(II)	d5 h.s	no	5.92	5.6-6.1
Mn(II)	d5 l.s	yes	1.73	1.8-2.1
Fe(III)	d5 h.s	no	5.92	5.7-6.0
Fe(III)	d5 l.s	yes	1.73	2.0-2.5
Fe(II)	d6 h.s	yes	4.90	5.1-5.7
Co(II)	d7 h.s	yes	3.88	4.3-5.2
Co(II)	d7 l.s	no	1.73	1.8
Ni(III)	d7 l.s	no	1.73	1.8-2.0
Ni(II)	d8	no	2.83	2.9-3.3
Cu(II)	d9	no	1.73	1.7-2.2

Same is true in here for tetrahedral complex once again, it is the same thing e and t2 right e and t2. So, the e configuration usually will not give you any unsymmetrical filling and e is not going to give you orbital angular momentum, but t2 can right. So, based on that because e is the dx², y² and dz², right. So, for example d1, d1 for octahedron is t2g1 right. That means orbital angular momentum is possible. d1 for tetrahedron is e1 right, it is splitting between e and t2. Is that clear? Any of you did not understand that I will be happy to discuss again. Yeah. No, this is that spin only value, one unpaired electron 1.73.

Yes, usually see, usually what also happens is simply the splitting in the tetrahedron. See, you cannot directly compare octahedral versus tetrahedral you have to also understand the trend in the sense the splitting between e and t2 is less in tetrahedron. This is octahedral. Yes, this

is the observed value and this is the calculated value that is the maximum you get. Okay. Yes, expected is you should get a little bit higher than that but it does not because some quenching is there it is, see we are not going to trick you that observe is less than the calculated that can happen sometime we will see more there could be some other contribution quenching. Quenching by spin extends which I will be discussing.

Okay. What I am mainly trying to say is spin-only valued should be good enough, but when you see the value is more than the spin-only value then orbital angular moment perhaps is there. How to calculate it? Simply by figuring out whether you are having orbital angular moment or not. If you experimentally see the value is little less or exactly similar or very close that means that some other way of quenching would be there which will be one at least one instance we will be discussing today, okay. It is, you know this is like too simplified in terms of teaching okay.

In reality, you can have lots of other practical components which maybe we are not discussing, but once again for this class, we are saying that only thing you want to worry about is the spin-only value and after that, if you find that the value is a little bit more, sometime 0.1 more, 0.2 more those are originating because of orbital angular momentum, okay. Because the orbital angular momentum will always add up. It depends on the directionality, right.

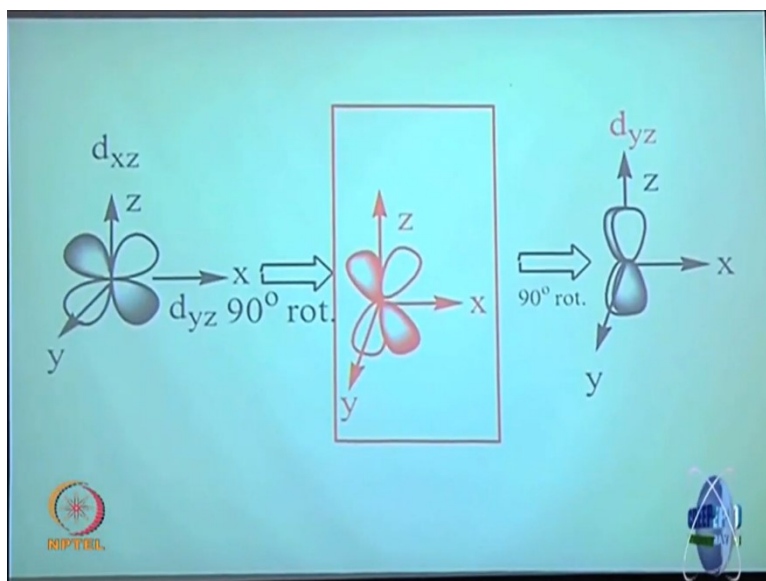
So, if you are imagining, let us say more of a spin-up and then it is another vector is there, two direction whatever this vector is having and I mean vector addition is usually you are going to take the modular value, the absolute value. And that is a good question again, we usually never actually $(\sqrt{L^2 + S^2})$ for the orbital angular momentum versus spin usually we deal separately and then take the pure value of it do the vector addition.

Now, if you want to do this, see it is orbital angular momentum actually does not depends on the spin, it is the motion around the orbital. So, spin-only value is dependent on the spin. So, therefore, up and down is coming. Orbital angular momentum, there is no spin component. Now that is the motion, simply the motion is we are discussing. Simple motion, it is not the up and down motion we are, up and down motion is the spin. I think that perhaps is the reason.

So, let us say some spinner up and some spinner down. So, orbital contribution for all those will be taken as just the orbital contribution like up spin and down spin of what is the orbital

contribution total we have seen, but we are not mixing up that with the spin value. Spin-only value is separate and orbital value is separate.

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Let us calculate. Sorry, where between the orbital and the spin? For spin-only values? n into n plus 2, μ 1 plus s . Okay the main equation, the first equation that is assumed that it is 90 degree. I think that is independent of the angle. Why we need an angle for that? Well, the spin I do not think spin and the orbit are up or spin orbit coupling can be there those both the coupling can be there, but if you are individually taking how one is affecting the other, if direction does not matter actually.

Sorry? Yeah, that is mainly so, that is when we have yeah, we usually say that when it is less than half fill that is l minus s we take when more than half-fill then we take l plus s values. I think it is independent of the direction right. Okay, I will try to find out if it is dependent, if the equation is dependent on the direction. Okay, let me proceed further.

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Octahedral complexes

However the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation as they are different shapes

Thus an electron in an e_g orbital can not contribute to orbital angular momentum

d_{z^2} $d_{x^2-y^2}$

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Orbital contribution to the magnetic moment

high spin octahedral d^n ions

think of possible t_{2g} electron arrangements

d^1

d_{z^2} d_{yz} d_{xy}

d_{xz} d_{yz} d_{xy}

d_{xz} d_{yz} d_{xy}

Possible t_{2g} arrangements = 3
Orbital contribution = YES d^1 e.g. $Ti(III)$

d^2

d_{z^2} d_{yz} d_{xy}

d_{xz} d_{yz} d_{xy}

d_{xz} d_{yz} d_{xy}

Possible t_{2g} arrangements = 3
Orbital contribution = yes d^2 e.g. $V(III)$

Magnetism

Orbital Contributions in Octahedral Complexes

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$Cr(IV)$	d^2	yes	2.83	2.8
$V(II)$	d^3	no	3.88	3.8-3.9
$Cr(III)$	d^3	no	3.88	3.7-3.9
$Mn(IV)$	d^3	no	3.88	3.8-4.0
$Cr(II)$	d^4 h.s.	no	4.90	4.7-4.9
$Cr(II)$	d^4 l.s.	yes	2.83	3.2-3.3
$Mn(III)$	d^4 h.s.	no	4.90	4.9-5.0
$Mn(III)$	d^4 l.s.	yes	2.83	3.2
$Mn(II)$	d^5 h.s.	no	5.92	5.6-6.1
$Mn(II)$	d^5 l.s.	yes	1.73	1.8-2.1
$Fe(III)$	d^5 h.s.	no	5.92	5.7-6.0
$Fe(III)$	d^5 l.s.	yes	1.73	2.0-2.5
$Fe(II)$	d^6 h.s.	yes	4.90	5.1-5.7
$Co(II)$	d^7 h.s.	yes	3.88	4.3-5.2
$Co(II)$	d^7 l.s.	no	1.73	1.8
$Ni(III)$	d^7 l.s.	no	1.73	1.8-2.0
$Ni(II)$	d^8	no	2.83	2.9-3.3
$Cu(II)$	d^9	no	1.73	1.7-2.2

Magnetism				
Orbital Contributions in tetrahedral Complexes				
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Ni(II)	d8	yes	2.83	3.7-4.0
Cu(II)	d9	yes	1.73	

Okay, we have d_{z^2} and $d_{x^2-y^2}$ which is not interconvertible. And we are started saying that for d^2 these are the value and then we are saying that these are the orbital contribution whether possible or not yes or no answer. Now, same way it is true for tetrahedral complexes, okay. You can find out whether it is there or not if there is any discrepancy then then just let me know. I think this should be this is from the book directly.

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Other Reasons for Orbital Contribution:

Although μ normally develops from GS, sometimes ES also may contribute, especially the GS-ES energy difference is very small.

Example:
 Take Ni^{2+} octahedral; d^8 ; GS: $t_{2g}^6 e_g^2$ no μ_l
 ES: $t_{2g}^5 e_g^3$ μ_l contributes

Similarly,
 Take Co^{2+} tetrahedral; d^7 GS: $e^4 t_2^3$ no μ_l
 ES: $e^3 t_2^4$ μ_l contributes

Therefore; $\mu_{obs} > \mu_s$ for both O_h Ni^{2+} and T_d Co^{2+}

GS = Ground electronic State;
 ES = Excited electronic State

Other reasons for orbital contribution. So, usually we are pretty much focused on the ground state electronic configuration. Sometime, whatever happens is let us say $t_{2g}^6 e_g^1$. $t_{2g}^6 e_g^1$ means there should not be any orbital contribution, but still if you can excite $t_{2g}^6 e_g^1$ to $t_{2g}^5 e_g^2$ one of the electron from t_{2g} level to e_g level up you can promote then you can promote or then you can induce orbital angular momentum.

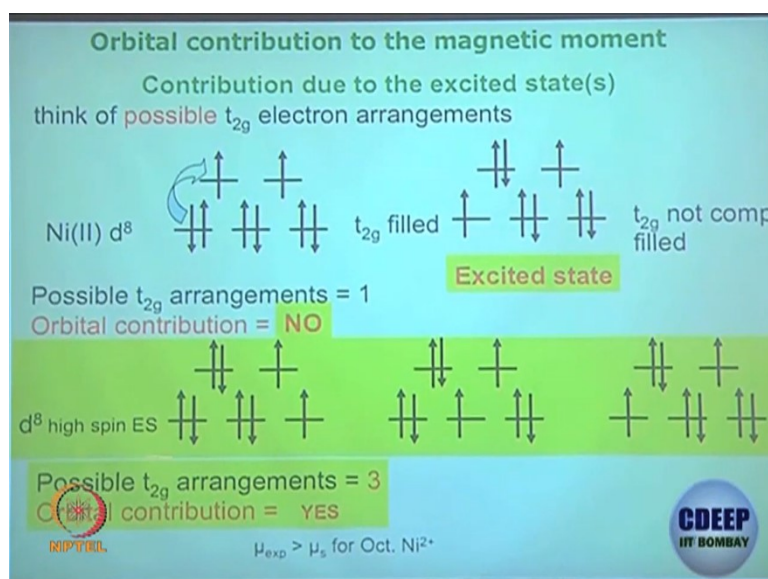
That is where we are talking that excited state can sometimes also contribute okay. These excited state contribution will not be as high as the ground state contribution. So, for example over here $t_{2g}^6 e_g^2$ no orbital, no orbital angular momentum should be there, but in excited state it should be $t_{2g}^5 e_g^3$, now, orbital angular momentum will be there of course, the absolute value will be less compared to if some other compound is giving from its ground state. So, the orbital angular momentum not necessarily coming just from the ground state, it can come from also excited state.

So, therefore, it this leaves an option or this gives a option to set a question saying that look the spin-only value should be this much or you calculate the spin only value which is let us say 1.73 or you know 2.0 or 4.99 whatever it is, but the observe wave 5.6. You do the electron distribution and see there is no way you can have orbital contribution, orbital angular momentum, but still the value is high then of course, you have to think perhaps ground state is not contributing there is a chance maybe in that excited state.

So, under the normal condition if you cannot explain what is going on then you are open to include that excited state. Same is over here $e^4 t^3$ should not have any orbital contribution orbital angular momentum now, in excited state $e^3 t^4$ you can have it. In all these cases, you see that μ_{observed} is greater than $\mu_{\text{spin-only}}$ for both octahedral nickel 2 plus and tetrahedral cobalt 2 plus because these are the electronic configuration for octahedron nickel 2 plus that is their tetrahedral cobalt 2 plus that is there.

So, at least these two terms should be very familiar octahedral nickel 2 plus tetrahedral cobalt 2 plus because these are the electronic configuration for octahedral nickel 2 plus that is there, octahedral cobalt 2 plus that is there. So, at least these two terms should be very familiar, octahedral nickel 2 plus and tetrahedral cobalt 2 plus these are one can give you excited state. Other than that, if any question is given in the exam, where you cannot once again cannot explain by normal understanding of orbital angular momentum like unsymmetrical filling in t_{2g} it is symmetrically filled still the value is high you can try to explain that by contribution from excited state. Is it clear? Okay you read it, it should be.

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Now, this is how it is show $t_{2g}^6 e_g^2$. Now one of the electron if you can convert, if you put let us say light if you put the energy or the distance between these two is not very high in excited state you can, excited state you can achieve therefore form $t_{2g}^6 e_g^2$ you can have $t_{2g}^5 e_g^3$. Now in this configuration you can have the orbital angular momentum. It is clear? Both ground state and excited state you need to consider.

Now this is another configuration. This is for $t_{2g}^5 e_g^3$ I guess this is the one of course in here you can have three different orientation that is what we are trying to say. So, not from ground state if you go to excited state, excited state can have three different configuration which is the origin for orbital angular momentum. No need to have this point just this is good enough, ground state there is no orbital angular momentum, excited state it should be there how it is coming, I think you have already learned because the relative positioning of the electron can vary.

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Therefore for O_h Ni(II) the magnetic moments are larger if the GS-ES gap is small.
BUT FOR Tetrahedral Ni(II) situation is entirely different

d^8 HS Tetrahedral

Possible t_2 arrangements = 3
Orbital contribution = YES

$M_{\text{calc}} O_h \text{ Ni(II)}$ is smaller than $M_{\text{calc}} T_d \text{ Ni(II)}$

Exp. NiCl_4^{2-} , Ni(HPMA)_4^{2+} (HPMA=hexamethyl phosphoramidate) have mag. moment larger than 4 BM.
(Larger the distortion smaller the mag.moment)

USEFUL IN DISCRIMINATING O_h vs T_d structures.

CDEEP
IIT BOMBAY

Orbital contribution to the magnetic moment

Contribution due to the excited state(s)
think of possible t_{2g} electron arrangements

Ni(II) d^8

t_{2g} filled t_{2g} not comp filled

Excited state

Possible t_{2g} arrangements = 1
Orbital contribution = NO

d^8 high spin ES

Possible t_{2g} arrangements = 3
Orbital contribution = YES

$\mu_{\text{exp}} > \mu_s$ for Oct. Ni^{2+}

CDEEP
IIT BOMBAY

Now, so, what we are trying to tell you hear it this is also a d^8 , this is also a d^8 configuration, nickel 2 plus is d^8 . Nickel 2 plus d^8 octahedral case, this is the scenario you have. Nickel 2 plus d^8 tetrahedral case. What is the electronic configuration? Nickel 2 plus octahedral and tetrahedral. Nickel 2 plus d^8 octahedral will be this is the electronic configuration. Octahedral with not so strong field again, strong field again should have given you the square planar geometry, this is nickel tetrachloride or nickel hex aqua or whatever.

Weak field again should give you the octahedral spaces. Whenever you see d^8 , be a little bit cautious, d^8 can have octahedral and tetrahedral sorry octahedral and square planar. Of course, if it is given clearly that is no worry, d^8 with, d^8 electronic configuration with strong field ligand like cyanide or carbon monoxide can give you square planar geometry sometimes

for these cases you do not have to worry, but in other cases you have to worry a little bit. Now, nickel 2 plus octahedral electronic configuration is given. Nickel 2 plus tetrahedral electronic configuration is $d^4 t_{2g}^4 e_g^0$ right.

So, $e_g^4 t_{2g}^0$ right. Now, the question simply is which one will have higher orbital or higher magnetic moment value? Both of them are having two unpaired electron. Here you have two unpaired electron here you have two unpaired electrons. Octahedral tetrahedral both of them are having two unpaired electron experimentally which one you think will give you higher magnetic moment value?

Tetrahedral, why is that? Simply because these contribution for octahedral these orbital angular momentum contribution coming from the excited state. In the ground state itself there is no orbital angular momentum. In the excited state there is but in tetrahedral case you can have orbital angular momentum due to the unsymmetrical filling of that t_{2g} orbital, that is and actually can go up to for two unpaired electron it can go up to four Bohr magneton. Okay, BM is that you need for magnetic moment. It is okay, it is given.

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Now, so far we have discussed about the d block elements. No, that also depends on the ligand, strong field, if the ligand in strong field usually then then only we will see. So, if it is a weak field ligand then you do not see too much of that. Okay, all right. Now, weak field means fluoride, chloride, water these are the weak field again. You have that you know (electrochemistry) spectro-electro chemicals or spectrochemical series right, not spectro-electro, spectrochemical series. Now, so far we tried to discuss the magnetism of d block

elements. We have simply learned, spin-only is good enough some few special cases, we have said that orbital angular momentum is essential and thereby values can increase.

If, once again, I think that is a valid point that if you see a little bit decreased do not worry about it because there may be other reasons, we are not worried about less value or lesser value of an experimentally observed magnetic moment, we are mainly worried about the higher value lesser value can come from some or a lot of other factors. Now, we are now trying to discuss the magnetic behaviour of lanthanides or actinides will not get into actinides, just simply lanthanides. So simply speaking, lanthanides are of little bit different class of compounds. Okay, it has f orbital, you know that f orbital is buried inside.

It is not the real outside electrons or the S, even, you know wherever if you see lanthanide cerium, Praseodymium yeah, whatever EM or whatever that 14 are there CPR, EM, SM, Samarium, gadolinium, whatever it is there all of those cases, F electrons are buried inside, what essentially that tells you is ligand will have very little effect. Ligand cannot influence the magnetic moment value because the F electrons are buried inside in ligand cannot affect the F electron too much or almost nothing.

So d orbitals are d block elements we were seeing that orbital angular momentum value are almost gone, that μ_l component is very little only when unsymmetrical filling is there then we are seeing, but over here you do not have to worry about anything, you have to do both l and s component. Orbital and the spin component because orbital component cannot be restricted by the ligand. So, as if you are dealing with a free metal species although metal complexes are there, lanthanide complexes are there, lanthanide ion is in the middle, ligands are surrounded but ligands cannot affect the magnetic moment value.

But you have seen that for octahedral complex or tetrahedral complex or d block elements ligand can influence. There is a splitting in that d orbital. F orbital we do not see such splitting or you can take it almost that there is no splitting in the F orbital because ligand and F orbital cannot interact too much that is fine, therefore, you have to bring back your previous equation which has magnetic moment values by considering both orbital and the angular component.

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Magnetism

Magnetic properties of lanthanides

FACT: The f electrons in lanthanides are buried in the (n-2) shell

- ∴ Thus 4f normally unaffected by surrounding ligands
- Hence, the magnetic moments of Ln^{3+} ions are generally well-described from the coupling of spin and orbital angular momenta ~ Russell-Saunders Coupling to give J vector
- spin orbit coupling constants are large (ca. 1000 cm^{-1})
- ligand field effects are very small (ca. 100 cm^{-1})
 - only ground J-state is populated
 - spin-orbit coupling $\gg$ ligand field splittings
- magnetism is essentially independent of environment




Magnetism

Magnetic moment of a J-state is expressed by:

$$\mu = g_J \sqrt{J(J+1)} \mu_B \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$$J = L+S, L+S-1, \dots, L-S$$

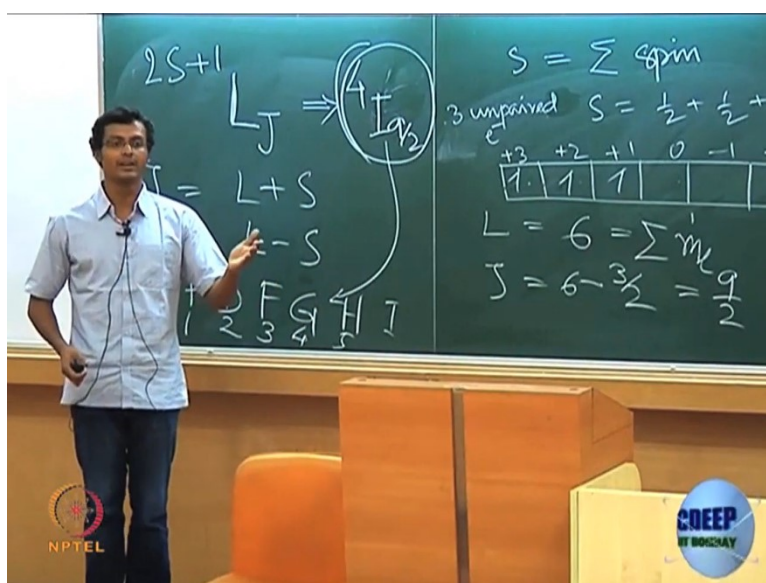
For the calculation of g value, we use
 minimum value of J for the configurations up to half-filled;
 i.e. $J = L-S$ for f^0 - f^7 configurations
 maximum value of J for config. more than half-filled;
 i.e. $J = L+S$ for f^8 - f^{14} configurations

For f^0, f^7 , and f^{14} , $L = 0$, hence μ_J becomes μ_S




Now, the facts that is the fact that F electrons in lanthanides are buried in the n minus 2 cell show you are in for calculations. What is the calculations? Let me show you this is the calculation, this is something I guess you have to know if not remember, I think a lot of you know this already. Start learning. Now, the so the number of unpaired electrons, that is the can that component can give you that S, summation of number of spins of the unpaired electron that is S you know. L, this L you know from this ML values right.

(Refer Slide time: 22:30)



Let me, so term symbol you have heard of. So, I will discuss a little bit $2S$ plus 1 LJ , J equals L plus S or L minus S absolute value of these. Now, S equals number of summation of spin or whatever way that is written summation of spin let us say, number of unpaired electron. Let us say you have three unpaired electron that means spin will be S will be half plus half plus half.

Now, if you have three unpaired electrons so, this is your F orbitals $1, 2, 3, 4, 5, 6, 7$. So, M_L values are plus 3 , plus 2 , plus 1 , 0 , minus 1 , minus 2 , minus 3 right three unpaired electrons simply means that. M_L maximum 3 plus 2 plus 1 . So, L equals 6 , 3 , 2 , 1 . Now, therefore, for that case three unpaired electron case you have six this L value at 6 . 6 I will come back to that you know S P term symbol. S , P , D , F , G , H , I and so on.

So, S L if L value is zero, then that S . If you have not studied before, you will just go for these Russell-Saunders term S P is 1 , D is 2 , F is 3 , 4 , 5 and so on $1, 2, 3, 4, 5$. Now, this capital S you have learned 3 by 2 , 3 by 2 , right? 3 by 2 , it is going to be 4 . So, $4, 6$ is going to be I okay, I will come back and explain in a moment and J is L minus S for the less than half field configuration.

So, J in this case will be 6 minus 3 by 2 , that is going to be how much? 9 by 2 . So, this is going to be your term symbol. Although you do not need to really know this one, like this J term for the class, but I think some of you at least 30 percent of you know, or 40 percent of you know, I do not know, okay.

So, what we are trying to tell you is, this is the Russell Saunders terms symbol, you know, kind of derivation. What it tells you the total spin, let us say you have the f^3 electron, 3 f electrons, f^3 configuration. Okay. CPR yes so, what is that 3 plus will be CPR EM, EM is what is the einsteinium no, EM is einsteinium maybe. Anyways, Plasmodium is 2 plus is going to be f^2 . I think EM is going to be 3 plus, I am sorry 3 unpaired electron anyway, 3 unpaired electron if you have that 3 unpaired electron will give you spin value S capital S is going to be 3 by 2, you have to calculate that L value. L value L equals summation of ML 3, 2, 1. So, that is going to be 6. S you know, L you know, J equals L plus S or L minus S. L plus S when it is more than half filled more than f^7 okay.

And L minus S when it is less than half filled. In this case three unpaired electron less than 7, f^7 so L minus S, L minus S that is becoming 9 by 2. Okay, now, you left up with just this one, $2S + 1 L_J$. $2S + 1$, S equals 3 by 2, you plug that in, so, that is becoming 4. Okay, L is your 6, that means that 6 means if L equals zero that is S, if L equals 1 that is P, if L equals 2, capital L equals 2 then D, F, G, H, I and so on. So, from there you get I and then J in this case we have calculated L minus S. Some of you who have who knows this, that is fine. No problem for you. those who those of you who did not hear it before just google it. You will be able to get it cleared.

(Refer Slide time: 28:17)

Magnetism

Sample Landé Calculation for a Ln^{3+} ion

e.g Pr^{3+} $[\text{Xe}]4f^3$; find Ground State from Hund's Rules

- $S = 1/2 + 1/2 = 1$
- $L = 3 + 2 = 5$
- $J = 6, 5, 4$; $J = 4$ is chosen for f^3
- $g = (3/2) + [1(1+1) - 5(5+1)/2(4)(4+1)] = 0.8$

$\mu_J = 3.577 \text{ B.M.}$ Experiment = 3.4 - 3.6 B.M

- Landé formula fits well with observed magnetic moments for all but Sm^{III} and Eu^{III} ions.
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NPTEL CDEEP IIT BOMBAY

I will show you one over here with Praseodymium 3 plus. Sorry, L plus S and yes, because less than half filled, f^7 . Yeah. Okay. Now, let us look at here. Whoever knows can you please calculate by yourself? Praseodymium 3 plus I am saying that electronic configuration is $4f^3$, f^2 . Okay. f^2 can you calculate whoever knows it? Calculate whoever does not hear

this before stay with me. I will explain okay. Now, f2 that means two unpaired electrons, two unpaired electrons spin equals half plus half total S equals 1.

Are you following me? Okay fine, if you get it right, the answer is given here definitely. Now, L equals so two unpaired electron it should be plus 3 and plus 2. L should be the maximum also. It is not like you will put at zero and minus 1 or anything so that is L equals summation of ML. ML is what? Plus 3, plus 2, plus 1, 0, minus 1, minus 2 minus 3. Seven of the seven, seven orbitals of F. For d it was plus 2, plus 1, 0, minus 1, minus 2, if it is d degenerate okay. And sure for p it will be plus 1, 0, minus 1 if it is d degenerate anyway. So, this is the L value summation of ML, two unpaired electron 3 and 2, 5. Now J will be in this case since it is (un) half filled, less than half filled less than seven electrons f14, f can have 14 electron, two is less than half, less than seven so L minus S, 5 minus 1, 4.

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Magnetism						
	config	g.s.	No. e-	color	calcd.	obsd
La	4f ⁰	¹ S ₀	0	Colorless	0	0
Ce	4f ¹	² F _{5/2}	1	Colorless	2.54	2.3 - 2.5
Pr	4f ²	³ H ₄	2	Green	3.58	3.4 - 3.6
Nd	4f ³	⁴ I _{9/2}	3	Lilac	3.62	3.5 - 3.6
Pm	4f ⁴	⁵ I ₄	4	Pink	2.68	-
Sm	4f ⁵	⁶ H _{5/2}	5	Yellow	0.85	1.4 - 1.7
Eu	4f ⁶	⁷ F ₀	6	Pale pink	0	3.3 - 3.5
Gd	4f ⁷	⁸ S _{7/2}	7	Colorless	7.94	7.9 - 8.0
Tb	4f ⁸	⁷ F ₆	6	Pale pink	9.72	9.5 - 9.8
Dy	4f ⁹	⁶ H _{15/2}	5	Yellow	10.65	10.4 - 10.6
Ho	4f ¹⁰	⁵ I ₈	4	Yellow	10.6	10.4 - 10.7
Er	4f ¹¹	⁴ I _{15/2}	3	Rose-pink	9.58	9.4 - 9.6
Tm	4f ¹²	³ H ₆	2	pale green	7.56	7.1 - 7.6
Yb	4f ¹³	² F _{7/2}	1	Colorless	4.54	4.3 - 4.9
Lu	4f ¹⁴	¹ S ₀	0	Colorless	0	0

Magnetism

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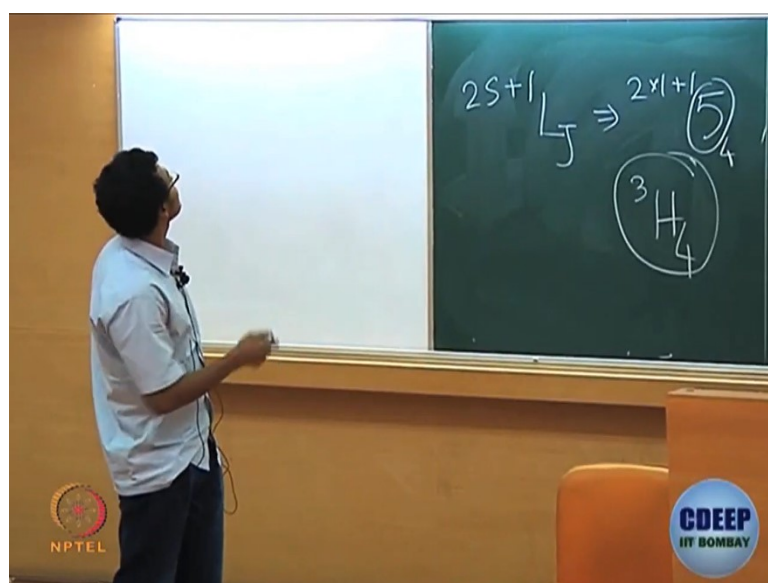
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Now, if you have that here Praseodymium 3 plus, 2 plus sorry 3 plus is $3H_4$ I think you have calculated right $3H_4$. How? Now you plug it in this equation $2S$ plus $1LJ$. $2S$ plus 1 means 2 plus 1 , $3L$, L is going to be 5 that is going to be H . So, $3H$ is it getting clear? Okay, let me just some of you may not be seeing it okay.

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It is going to be $2S$ plus one LJ . So, 2 minutes break you can take you can go for whatever. 2 plus $2S$ plus 1 , S equals 1 plus 1 , L equals 5 and J equals 4 . So, this 5 is going to be 3 and zero S, P, D, F, G, H good and $3H_4$, 4 is $2J$ plus 1 sorry L minus S . Is it correct? Okay break. Let me let me start, I think this math part is way too simple for you guys.

(Refer Slide time: 32:14)

Magnetism

Magnetic moment of a J-state is expressed by:

$$\mu = g_J \sqrt{J(J+1)} \mu_B \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$J = L+S, L+S-1, \dots, L-S$

For the calculation of g value, we use
 minimum value of J for the configurations up to half-filled;
 i.e. $J = L-S$ for f^0 - f^7 configurations
 maximum value of J for config. more than half-filled;
 i.e. $J = L+S$ for f^8 - f^{14} configurations

f^0, f^7 , and f^{14} , $L = 0$, hence μ_J becomes μ_S




Magnetism

	config	g.s.	No. e-	color	calcd	obsd
La	$4f^0$	$1S_0$	0	Colorless	0	0
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Eu	$4f^6$	$7F_0$	6	Pale pink	0	3.3 - 3.5
Gd	$4f^7$	$8S_{7/2}$	7	Colorless	7.94	7.9 - 8.0
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Ho	$4f^{10}$	$5I_8$	4	Yellow	10.6	10.4 - 10.7
Er	$4f^{11}$	$4I_{15/2}$	3	Rose-pink	9.58	9.4 - 9.6
Tm	$4f^{12}$	$3H_6$	2	pale green	7.56	7.1 - 7.6
Yb	$4f^{13}$	$2F_{7/2}$	1	Colorless	4.54	4.3 - 4.9
Lu	$4f^{14}$	$1S_0$	0	Colorless	0	0




Magnetism

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It is a, these two equations are there you calculate GJ first, GJ with S and L value and J value and then plug this into this equation that is all. For your verification that is the table, you should be able to calculate two three of them by yourself to get confidence nothing else. the values are given equations are given unpaired electrons are given L, S, J value you should be calculating by yourself then mu value calculated value, do not worry about the extra observed value too much just calculate the values.

You should be able to get exactly same values unless anything is given by mistake any wrong data are given I do not think any got wrong data is given. So, once again we are talking about the lanthanides f orbitals are not perturbed by ligand. therefore, both L and S component orbital and spin component of them magnetic moment you have to consider. Simply you have to know these two equations What are those two equations? These are the two equation. What is S? What is L? What is J? That you know, once you have that you have GJ calculated you put that GJ value and the J value you have already calculated from there, you put all these mu value you should be able to get, those mu values are calculated and shown in here for given electronic configurations.

For different electronic configuration it is given. So, you sorry, that is mistake, delete that newbie, okay? Its the calculation is shown for Praseodymium, PR 3 plus you can see from for just clarity, one of the example is shown here, Praseodymium 3 plus which is f2 electronic configuration, you can calculate this one first to yourself, and then go on to calculate any of these. Okay, this is you do not really have to worry about this bottom term, you can just calculate the just 1S, 2F, 3H and so on for the class purpose. But as you know, this is very simple 2S plus 1 LJ, this J you do not really have to worry. J equals L plus S or L minus S.

But still, I would say you should do it for the class purpose, you may not need to worry. Less than half filled electronic configuration L minus S. What is the half-filled? Half-filled 7. L plus S will be for the more than half-filled and from there you can get this term symbol Russel Saunders term symbol it is called.

Now, let me move on. So, this is the experimentally calculated value sorry, theoretically calculated value, this is the experimentally observed value. It is quite close, that is good enough okay here you do not have to worry about any orbital angular momentum because you are already taking care of it. You are calculating based on that, okay.