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Lecture – 15 Spectroscopic Term Symbol

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.

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	Ion	Config	0.771.5	$\mu_{\rm us}$	µ _{nim}
	TOID	41	10.	1.71	16-17
	VHVE	J1	100	1.73	1:2-1 X
0.11	Villi	32	10	2 X3	2 7/2/4
Orbital	Cit(IV)	32	100	2.83	2.8
Contributions in	V(II)	U.S.	2903	1 88	13-1 A
Contributions in	Cottin	TJ.	(NO.	3 58	12.10
Octahedral	MicIVI.	41	190	3 88	1.922 ii
Camplana	Culti	54 h s	50	4.901	4.7-4.9
Complexes	Citti	341 %	100	2.83	3233
	Maritti	J4 h v	TAT	4.90	4.965.0
	Mm(III).	Jily	10	2.83	12
	Medii	dShis	00	5.92	1000
	MixIII	dSTs.	363	1.73	1801
	ExcD1)	45 b v	no .	5.92	5.7561E
	twith.	4514	101	1.23	20/25
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	(11363)	37.h/s	10	1.5X	43-82
	C5(H)	47.15	(%)	171	I A:
(※)	Nillia	42.1%	(0.)	1373	DE COE
MPTEL	Netti	Lix	100	2.831	2 9/3 3 III BOM

Those question 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 2 g is electronic configuration or not.

(Refer Slide Time: 00:55)

Orbital C	Contribution	ns in tetrah	edral (Complexe
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	ves	1.73	

Same is true in here. For tetrahedral complex once again it is the same thing e and t 2 right e and t 2. So, e configuration usually will not give you any unsymmetrical filling in e is not going to give you orbital angular momentum, but t 2 can right. So, based on that because e is d x 2 y 2 and d z 2 right. So, for example, d 1; d 1 for octahedral is t 2 g 1 right; that means, orbital angular momentum is possible; d 1 for tetrahedron is e 1 right it is splitting between e and t 2. Is that clear any of you did not understand that I will be happy to discuss again.

Student: Sir, (Refer Time: 01:47) processing the first example.

Yeah.

Student: We calculated (Refer Time: 01:55) moment as under root s 4 s plus 1 plus (Refer

Time: 02:01). So, if the.

No this is the spin only value, one unpaired electron 1.73.

Student: No sir. Previous slide first one. (Refer Time: 02:09). So, if (Refer Time: 02:13) then

magnetic moment (Refer Time: 02:21) according to (Refer Time: 02:21).

Yes. Usually see usually what also happens is simply the splitting in the tetrahedral see you

cannot directly compare octahedral versus tetrahedral, you have to also understand the trend

in the sense the splitting between e and t 2 is less in tetrahedral.

Student: This is octahedral right.

This is octahedral. Yes this is the observed value and this is the calculated value that is the

maximum you get ok. Yes expected is you should get little bit higher than that, but it does not

because some quenching is there it is more. 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 exchange which I will be discussing ok.

What I am mainly trying to say is spin only values 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 excrementally 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 instant will be

discussing today ok. It is you know this is like too simplified in terms of teaching ok. In

reality you can have lot of other practical component 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. After that if you find that the value is little bit more sometime 0.1 more 0.2 more

those are originating because of orbital angular momentum ok.

Student: Why is that orbital angular momentum component always adds up to this quench angular momentum.

Because, no orbital angular momentum will always add up, it is all it is 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 to direction, whatever this vector is having and I mean vector addition is usually you are going to take the modular value the absolute value.

Student: Sir, (Refer Time: 04:58) spin has component of, if a spin angular momentum has one components which is pointing upwards because why is that orbital angular momentum also has a component in upward direction why not in downward direction? (Refer Time: 05:17) This.

That is a good question even. We usually never actually worried for the orbital angular momentum versus spin, usually we deal separately and then take the pure value of it do the vector addition ok. Now if you want to do thus see it is orbital angular moment that actually does not depends on the spin right, it is the motion around the orbital right. 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, simple the motion is we are discussing right simple motion, it is not the up and down motion where, up and down motion is the spin I think that perhaps is the reason.

Student: If that it means that it does not matter say like if we consider the electron to give (Refer Time: 06:19). Sir, we might be calculating.

No. So, the yeah. So, let us say some spin are up and some spin are down ok. So, orbital contribution for all those will be taken as just the orbital contribution right, up spin and down

spin what is the orbital contribution total we are we have seen, but we are not mixing up that with the spin values. Spin only value is separate and orbital value is separate. Let us calculate.

Student: But in formula we have assumed it for 90 degree.

Sorry.

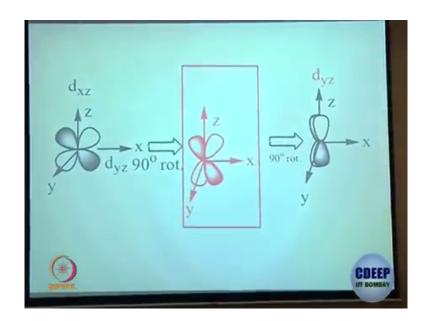
Student: In formula we have assumed it for 90 degree because it is.

Where between the orbital and the spin?

Student: (Refer Time: 06:56) 4 s s plus 1 that is that will come if you consider 90 degree.

For that spin only values?

(Refer Slide Time: 07:07)



n into n plus 2.

Student: (Refer Time: 07:08) mu i plus s.

mu l plus s, the main equation the first equation that is assume that it is 90 degree.

Student: Yes, (Refer Time: 07:22) mattered as you know.

I think that is independent of the angle, why we need an angle for that well.

Student: (Refer Time: 07:32).

Well the spin I do not think spin and the orbit are of course, 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.

Student: Direction is not.

Direction does not matter actually.

Student: No, that is the (Refer Time: 07:58).

Sorry.

Student: Direction is not really fixed that is why we get the range (Refer Time: 08:05) mu s

plus minus mu.

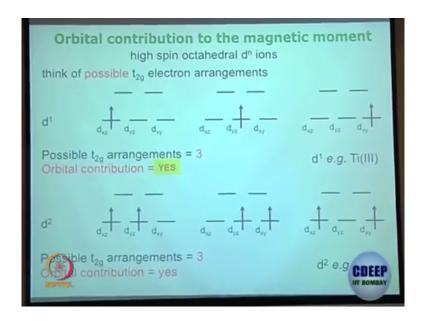
Yeah, that is mainly. So, that is when we have yeah we usually say that when it is less than

half fill that is I minus s we take, when more than half fill then we take I plus s values. I think

it is independent of the direction right. I will try to find out if it is dependent if the equation is

dependent on the direction, let me proceed further ok.

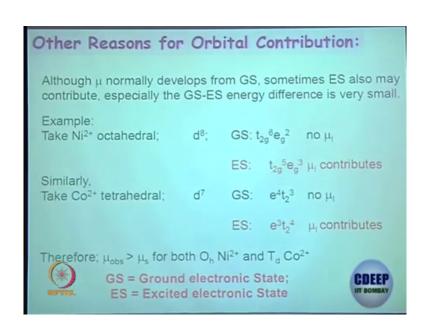
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We have d z 2 and d x 2 y 2 which is not interconvertible and we has started saying that for d 2 these are the value and then we are saying that these are the orbital contribution whether possible or not yes and no answer.

Now, same way it is true for tetrahedral complexes. You can find out whether it is there or not. If there is any discrepancy then just let me know. I think this should be this is from the book directly. Other reasons for orbital contribution.

(Refer Slide Time: 09:04)



So, usually we are pretty much focused on the ground state electronic configuration. Sometime what happens is let us say t 2 g 6 e g 1, t 2 g 6 e g 1 means there should not be any orbital contribution.

But still if you can excite t 2 g 6 e g 1 to t 2 g 5 e g 2 one of the electron from t 2 g level to e g level 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 sometime also contribute ok. This excited state contribution will not be as high as the ground state contribution ok.

So, for example, over here t 2 g 6 e g 2 no orbital angular momentum should be there, but in excited state it should be t 2 g 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 ok. So, the orbital angular momentum not necessarily coming just from the ground state, it can come from also excited state.

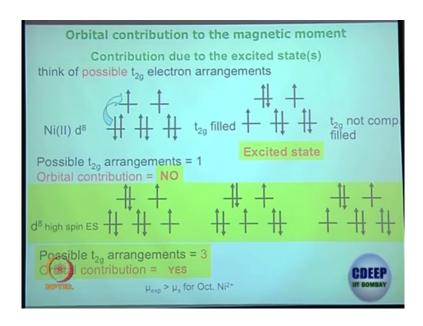
So, therefore, it this believes a (Refer Time: 10:45) or this gives a (Refer Time: 10:48) to set a question saying that, look the spin only value should be this much or you calculate the spin only value which is let us say 1.73 or you know 2 point or 4.99 or whatever it is, but the observe is 5.6, you 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 the excited state ok.

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 2 3 should not have any orbital contribution orbital angular momentum, now in excited state e 3 t 2 4 you can have it ok. In all these cases you see that mu observed is greater than mu spin only for both octahedral nickel 2 plus and tetrahedral cobalt 2 plus because these are the electronic configuration for octahedral nickel 2 plus that is there 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 these are the 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 2 g, it is symmetrically filled still the value is high, you can try to explain that by contribution from excited state, is it clear?

You read it should be now this is how it is.

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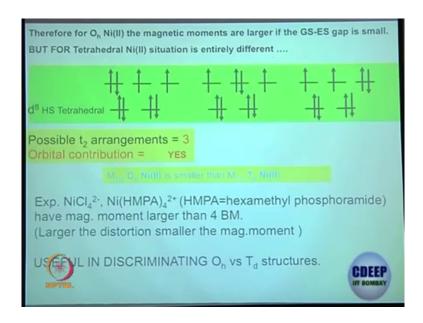


So, t 2 g 6 e g 2, now one of the electron if you can convert if you put let us a light if you put energy or the distance between these two is not very high, in excited state you can excited state you can achieve there from t 2 g 6 e g 2 you can have t 2 g 5 e g 3. Now in this configuration you can have 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 2 g 5 e g 3, I guess this is the one of course, in here you can have three different orientations 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 right, which is the origin for orbital angular momentum ok. 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 ok.

(Refer Slide Time: 14:10)



Now,. So, what we are trying to tell you here is, 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 ok.

Octahedral with not so, strong field ligand. Strong field ligand should have given you the square planar geometry, this is nickel tetra chlora or nickel hexa aqua or whatever weak field ligand should give you the octahedral species ok. Whenever you see d 8 be little bit causes, 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.

Sometime for these cases you do not have to worry, but in other cases you have to worry little

bit. Now nickel 2 plus octahedron electronic configuration is given, nickel 2 plus tetrahedral

electronic configuration is?

Student: d 4 t 2 4.

d 4 t 2 4, e 4 t 2 4 right. So, e 4 t 2 4 right. Now the question simply is which one will have

higher orbital or higher magnetic moment value? Both of them are having 2 unpaired electron

here you have 2 unpaired electron, here you have 2 unpaired electrons right. Octahedral

tetrahedral both of them are having 2 unpaired electron experimentally which one you think

will give you higher magnetic moment value?

Student: Tetrahedral.

Tetrahedral why is that? Simply because this contribution for octahedral this 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 2 g orbital right that is

the reason and actually it can go up to for 2 unpaired electron it can go up to 4 Bohr magneton

ok. BM is the unique formatting moment it is given, now so, far we have discussed about the

d block elements.

Student: Sir, doubt. Last class (Refer Time: 17:28).

No that also depends on the ligand strong field if the ligand is strong field, usually then only

you will see ok. So, if it is a weak field ligand then you do not see too much of that all right.

Now weak field means fluoride, chloride, water are these are the weak field ligand you have

that you know electrochemical spectra electro chemicals are spectra chemical series its right it is not spectra electro spectra chemical 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 little bit decrease do not worry about it because there may be other reason 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 a lot of other factor.

Now we are now trying to discuss the magnetism or magnetic behavior of lanthanides or actinides will not get into actinides just simply lanthanides. So, simply speaking lanthanides are of little bit different class of compounds ok. It has f orbital you know that f orbital is buried inside, it is not the real outside electrons are the s even you know wherever if you see lanthanide cerium, presidium yeah whatever Em or whatever that the 14 are there; CPR, Em, Sm, Samarium, Gadolinium whatever it is there, all of those cases f electrons are buried inside

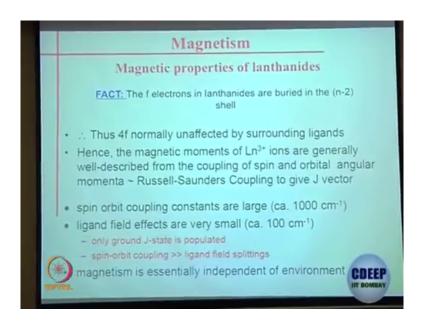
What essentially that tells you is ligand will have very little effect, ligand cannot influence the magnetic moment value. Because the f electrons are buried inside in it ligand cannot affect that f electron too much or almost nothing. So, d orbitals or d block elements we were seeing that orbital angular momentum value are almost gone right that mu l component is very little only when unsymmetrical feeling is there then we are seeing.

But over here you do not have to worry about anything, you have to do both 1 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 their either splitting in the d orbital.

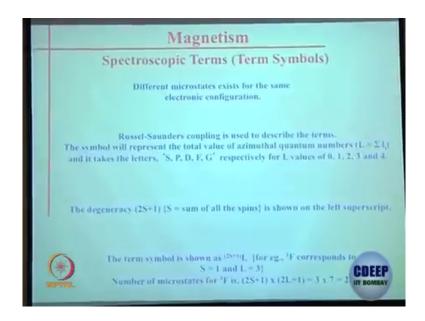
F orbital we do not see such splitting or you can you can take it almost that there is no splitting in that f orbital because ligand and f orbital cannot interact too much that is fine. Therefore, you have to bring back your previous equation which has magnetic moment values by considering both orbital and the angular component ok.

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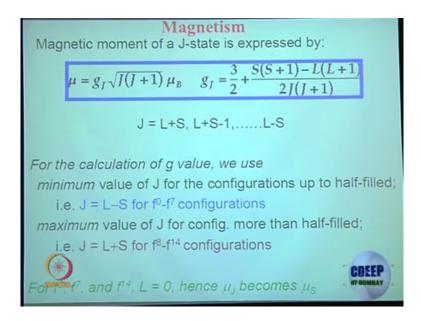
Now the facts that is the fact that f electrons in lanthanides are buried in the n minus 2 shell.

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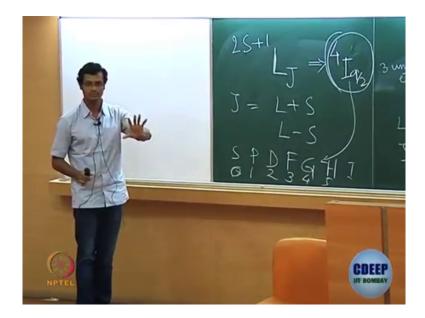
So, you are in for calculations what is the calculations?

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Let me show you this is the calculation ok. 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, number of unpaired electrons, number of unpaired electrons that is the can that component can give you the s summation of number of spin of the unpaired electron that is s you know; I this I you know from this ml values right let me. So, tom symbol you have heard of.

(Refer Slide Time: 22:38)



So, I will discuss little bit 2 S plus 1 L J equals L plus S or L minus S absolute value of these.

(Refer Slide Time: 22:52)



Now S equals number of summation of spin right or whatever way they that is written summation of spin let us say, number of unpaired electron. Let us say you have 3 unpaired electron 3 unpaired electron; that means, spin will be S will be half plus half plus half right. Now if you have 3 unpaired electrons, so, this is your f orbitals 1, 2, 3, 4, 5, 6, 7. So, ml values are plus 3 plus 2 plus 1 0 minus 1, minus 2, minus 3 right 3 unpaired electron simply means that right ml maximum 3 plus 2 plus 1.

So, L equals 6, 3, 2, 1. Now, therefore, for that case 3 unpaired electron case you have 6 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 0 then that is S if you have not studied before you just go for these Russells 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, I will come back and explain in a moment and J, 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?

Student: 9 by 2.

9 by 2. So, this is going to be your term symbol ok. 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 ok.

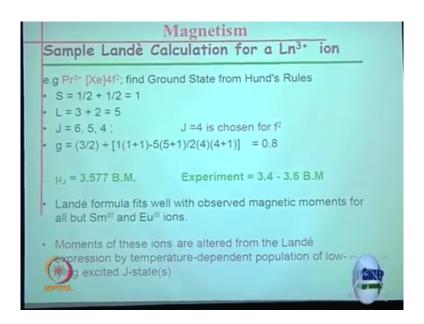
So, what we are trying to tell you is this is the Russells Saunders term symbol you know kind of derivation. What it tells you? The total spin let us say you have the f 3 electron, 3 f electrons f 3 configuration, cpr m. So, what is that 3 plus will be? cpr Em; Em is a what is the Einsteinium? No Em? Em is einsteinium maybe.

Anyways Praseodymium is 2 plus is going to be f 2 I think Em is going to be 3 plus; 3 sorry 3 unpaired electron anyway 3 unpaired electron if you have that 3unpaired electron will give you spin value S capital S is going to be 3 by 2. You have to calculate the 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? J equals L plus S or L minus S. L plus S when it is more than half filled more than f 7 and L minus S when it is less than half filled in this case 3 unpaired electron less than 7 f 7. So, L minus S, L minus x that is becoming 9 by 2 ok. Now you left up with just this one 2 S plus 1 L J; 2 S plus 1 S equals 3 by 2 you plug that in. So, that is becoming 4 ok. L is your 6; that means, that 6 means if L equals 0 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 I will show you one over here with Praseodymium 3 plus.

(Refer Slide Time: 28:23)



Student: Sir what is this; sir (Refer Time: 28:22).

Sorry?

Student: (Refer Time: 28:25).

Sorry, L plus S.

Student: L plus S we calculated L minus S.

Yes, because less than half filled.

Student: Less than.

F 7 yeah.

Student: Thank you.

Now let us look at here whoever knows can you please calculate by yourself. Praseodymium 3 plus I am saying that electronic configuration is 4 f 2 f 2, f 2 can you calculate whoever knows it calculate, whoever does not hear this before stay with me I will explain ok. Now f 2; that means, 2 unpaired electrons right 2 unpaired electrons means spin equals half plus half

total S equals 1, are you following me?

Student: (Refer Time: 29:16).

Ok fine, if you get it right the answer is given here definitely.

Now, L, L equals. So, 2 unpaired electron, it should be plus 3 and plus 2; L should be the maximum also right, it is not like you will put at 0 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, 7 of them 7 orbitals of f; for d it was plus 2 plus 1 0 minus 1 minus 2 if it is degenerate and so on.

For P it will be plus 1 0 minus 1 if it is degenerate anyway. So, this is the L value summation of ML 2 unpaired electron 3 and 2; 5. Now J will be in this case since its half fill less than half filled less than 7 electrons, f 14 f can have 14 electron, 2 is less than half less than 7; so, L minus S

Student: (Refer Time: 30:25).

L minus S 5 minus 1; 4 ok.

(Refer Slide Time: 30:35)

	config	g.s.	No. e-	color	calcd	obsd	
La	4f°	1S ₀	0	Colorless	0	0	
Ce	4f1	2F _{5/2}	1	Colorless	2.54	2.3 - 2.5	
Pr	452	3H.	2	Green	3.58	3.4 - 3.6	
Nd	453	419/2	3	Lilac	3.62	3.5 - 3.6	
Pm	4f4	51,	4	Pink	2.68		
Sm	4f5	6H _{5/2}	5	Yellow	0.85	1.4 - 1.7	
Eu	4f8	7Fo	6	Pale pink	0	3.3 - 3.5	
Gd	4f7	8S7/2	7	Colorless	7.94	7.9 - 8.0	
Tb	4f8	7F6	6	Pale pink	9.72	9.5 - 9.8	
Dy	4f9	6H _{15/2}	5	Yellow	10.65	10.4 - 10.6	
Но	4f10	518	4	Yellow	10.6	10.4 - 10.7	
Er	4f11	4115/2	3	Rose-pink	9.58	9.4 - 9.6	
Tm	4f12	3H6	2	pale green	7.56	7.1 - 7.6	
VOS	4f13	2F _{7/2}	1	Colorless	4.54	4.3 - 4.9	
1-1	4f14	150	0	Colorless	0	O CO	FF

Now if you have that here, Praseodymium 3 plus 2 plus sorry 3 plus its 3 H 4 I think you have calculated right 3 H 4.

How? Now you plug it in this equation 2 S plus 1 L J; 2 S plus L means 2 plus 1 3 L, L is going to be 5 that is going to be H. So, 3 H, is it getting clear?

Student: Yes.

Ok let me just some of you may not be seeing it ok.

(Refer Slide Time: 31:10)



It is going to be 2 S plus 1 L J. So, 2 minutes break you can take, you can go for whatever 2 plus 2 S plus 1; S equals 1 plus 1 L equals L equals 5 and J equals 4.

So, this 5 is going to be 3 and 0 S P D F S P D F G H, good and 3 H 4, 4 is 2 J plus 1 sorry L minus S, is it correct.

Student: Yes. Break.

Break.

Student: Yes sir. It is break time.

Let me start. I think this math part is way too simple for you guys, it is a these 2 equations are there, you calculate g J first, g J with S and L value and J value and then plug this into this

equation that is all.

The for your verification that is the table you should be able to calculate 2-3 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 observed value too much just calculate the values, you should

be able to get exactly same value unless anything is given by mistake any wrong data are

given I do not think any wrong data is given ok.

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 the magnetic moment you

have to consider. Simply you have to know these 2 equations, what are those 2 equation?

These are the 2 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.

Student: Previous slide mu is equal to (Refer Time: 34:09) mu b.

That is mistake delete that mu b ok. It is 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 f 2 electronic configuration you can calculate this one first yourself and then go on to

calculate any of these ok. 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?

Student: 7.

7. L plus S will be for the more than half filled and from there you can get this term symbol Russell 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 ok. 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 ok.