Symmetry and Group Theory
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Lecture - 62
Transition Metal Complexes: CFT and LFT

Last day we had a pretty heavy class. We discussed anthracene and not, naphthalene sorry, naphthalene. You can work out anthracene by yourself. It is doable. It is just one more ring and it is symmetric. Naphthalene right. And we did it in a good amount detail. So today, we are going to discuss transition metal complexes as you see on the projection. But we are not really going to work out everything.

By now you know very well how to construct the reducible representations, how to break them down, how to generate SALCs using projection operators. So there is no point in going through every step anymore. But my request to you is that after you go back from the class please work out every step by yourself, okay. Just watching a cricket match you might think it is very easy. But when you try to play yourself that might be a quite a different ball game.

So please do not give up the habit of working out these examples. And my suggestion is work out as many solved examples at least from Cotton's book as possible. Not only here but also in organic chemistry. This year we are not discussing the pericyclic reactions. We did it last year but then I think that is one thing that we could do without. We have done many other topics that we did not discuss last year. So pericyclic reactions is out of syllabus this year.

But for organic molecules as well as inorganic complexes please work them out as many of them as possible by yourself, okay? Right.

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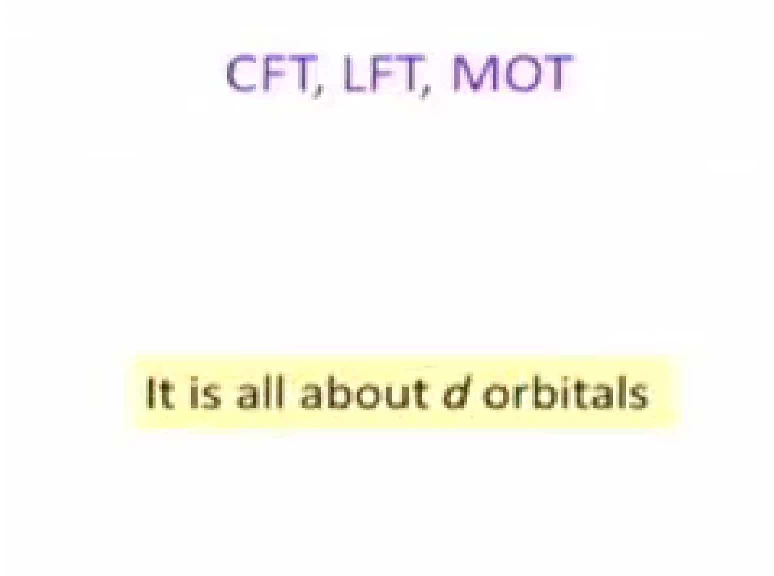

CFT, LFT, MOT

It is all about *d* orbitals

Now everybody has studied about transition metal complexes at different stages and you know that there are different kinds of theories, right to describe these complexes. Who discovered transition metal complexes? Werner right. that (()) (02:19) chloride and so on and so forth. So that was a long time ago. I think it was about 120 years ago that transition metal complexes are first prepared and then to understand what is going on there, several theories have been proposed.

The simplest theory as everybody knows is about dative bonds or coordinate bonds. That is why they are called coordination complexes in the first place. But there are other theories like crystal field theory, ligand field theory and molecular orbital theory that work equally well by and large to describe the transition metal complexes. We are not going to discuss valence bond theory and valence bond theory can be used to some extent.

We would not have time for ligand field theory but today what we will do is we will discuss crystal field theory a little bit and then see whether we can go on to molecular orbital theory. We will restrict ourselves to the octahedral complex today and I will ask you to work out tetrahedral complexes by yourself. Next day let us see what we do. Because we have two things to discuss, one is hybrid orbitals. The other is molecules like complexes like ferrozine, okay?

Let us see what we do next day, I have not made up my mind yet. But the point is no matter whether we are talking about crystal field theory or ligand field theory or molecular orbital theory I believe everybody have to understand that the discussion is centered mainly on d orbitals of the transition metal ions, right? The reason why you get such unique compounds of transition metal ions is the d orbitals. So this entire topic is about d orbitals.

So maybe you know what we are going to say next but it does not harm since d orbitals are so important for us in this discussion to revisit d orbitals and understand d orbitals thoroughly before we proceed to the metal complexes themselves. I am grateful to Professor Shashidhar. He has been careful to put in his name in the slide also. For the next few slides these are I think 15-year old slides.

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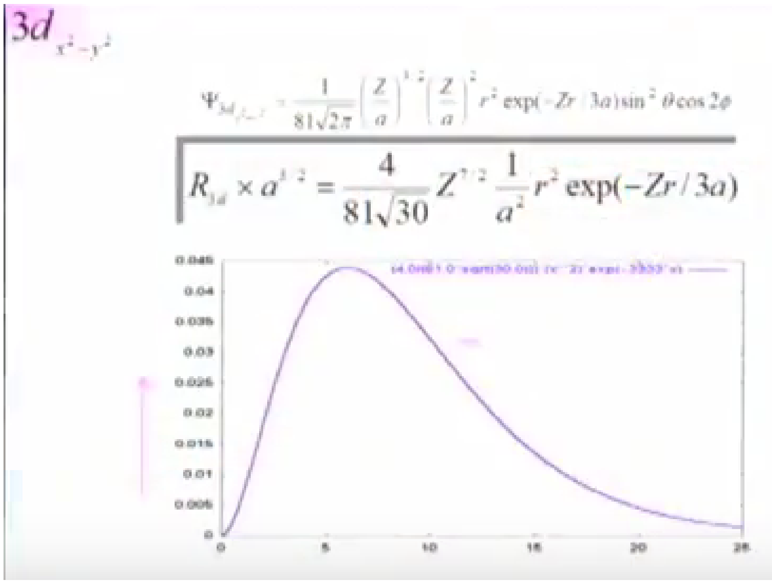

$3d_{x^2-y^2}$

$$\Psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z}{a}\right)^{2} r^2 \exp(-Zr/3a)\sin^2\theta\cos 2\phi$$

$$R_{3d} \times a^{3/2} = \frac{4}{81\sqrt{30}} Z^{7/2}\frac{1}{a^2} r^2 \exp(-Zr/3a)$$

He did a fantastic job of making a presentation on shapes of orbital, hydrogen atom in general. Apparently, he has more. But this is something that I have used I do not know how many times. It is a really nice slides. So I am proud to lift them from Professor Shashidhar's kitty, okay. So these are the d orbitals, right? Everybody knows the names in any case. So 3d x square - y square.

So 3d x square - y square is given by 1 by 81 root over 2 pi Z by a to the power 3 by 2, Z by a square r square e to the power - Zr by 3a sin square theta cos 2 phi. Please do not memorize this.

I got to know later that last year a student of mine memorized some character tables, kindly do not do such things. I get extremely scared when I hear this. Do not remember the form of d x square - y square orbital.

But what do we want to learn today is that why is it that the x square - y square orbital is called the d x square - y square orbital. So I think in this expression for the x square - y square, d x square - y square orbital you can make out which is the radial part and which is the angular part, right? Which is the radial part? r square e to the power - Zr by 3a. So it is no surprise that this is what the radial part looks like. r square increases with increase in r and e to the power - Zr by 3 decreases in r.

So the product of course goes through a maximum and you can work out whether maximum is l not going to that, right? Let us focus on the angular part. Can anybody translate this angular part for me? Sin square theta cos 2 phi. I want it translated to Cartesian coordinates. Can you do that? So what is cos 2 phi? Hope you have not forgotten the relationship between r theta phi and x, y, z. I will tell you the most difficult one, z = r + theta. Now you tell me what is x equal to?

R sin theta cos phi. And what is y equal to? So by using that, can you translate this sin square theta cos 2 phi into something in x and y and z? it is not necessary that x, y, z everything will be there. R square will get cancelled with the r square that is there, right.

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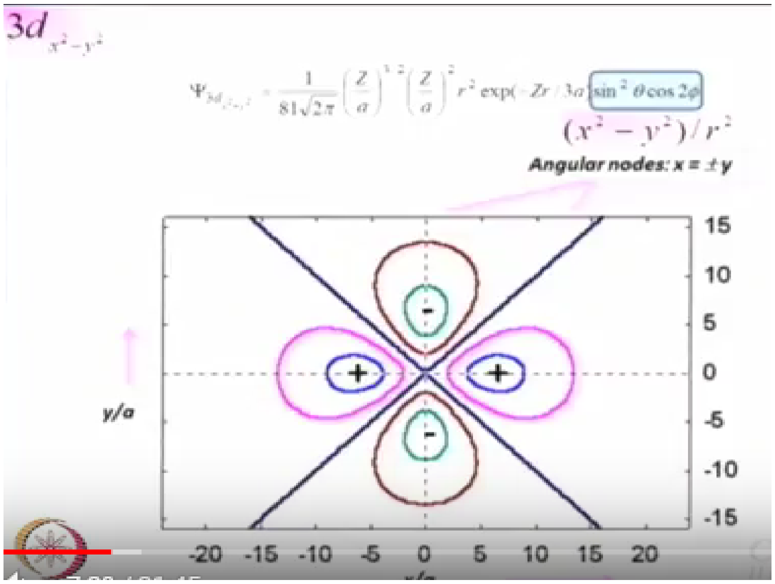

So x square - y square. So where do the nodes appear? Okay those who are still working, believe us. It is x square - y square. You can work it out later. Otherwise, you will miss out on the next discussion. Where do the notes appear? Right. What kind of nodes are they? Radial nodes or angular nodes? Angular nodes, right? You are equating the angular part to 0, nodes you get there from are angular nodes.

So x square - y square = 0 or x square = y square or x = plus minus y, right? That is the equation of the angular nodes. Now x equal to plus minus y represents what kind of a surface? In 3 dimensions? Planes? X equal to plus minus y? If you are working in the x y plane then they are 2 lines. If you are working in x, y, z space then they have planes. Where are the planes? Here are the planes, these 2 lines are sections of the planes, right?

Let us say like this, okay. So that is why 3d x square - y square or rather d x square - y square orbital is called the d x square - y square orbital because there is an expression of x square - y square. There is a term of x square - y square in the expression of the orbital and when that is equated to 0 x square - y square = 0 is the equation of the nodes, okay? So this is why it is called x square - y square.

What is a node? A node is a point or line or plane whatever with respect to which the wave function changes sign. Please remember wave function has to change sign, okay? Wave function would become 0 at infinity also. E to the power - 0 by a 0 at r equal to infinity the wave function would become 0. But r equal to infinity is not a node because wave function becomes 0. It does not change sign. At a node the wave function has to change sign, alright?

So if these are nodes, then what will happen? You start with plus, you go across the node you should get a minus, when you go across you get plus again, you go across you get a minus and just a check if you go across this plane now you go from minus to plus. What is this plus and minus? Electron is negatively charged when it is here. Electron is positively charged when it is here. No? Then what? Phase. Phase of what? Wave function, right? Phase of the wave function.

Whether the wave function is positive or negative, alright, got it, right? So you understand what it is. Now I want to make a point. If I want to talk about symmetry transformation of this d x square - y square orbital, will you agree with me that it is enough for me to consider the transformation of these planes and forget about what the orbital looks like. Those planes are, the cross-section of the plane is a straight line. It is easier for me to deal with.

I will work with the transformation of the planes. Will that not mirror or rather will that not map the transformation of the orbital itself? Example. Let us say there is C 4 axis perpendicular okay? C 4 is not good. Let us say there is a C 8 axis. C 8 means how many degrees? 345 degrees. Then. So do speak up, I am a little deaf, I cannot hear if you whisper. 45 degrees. So I turn it by 45 degrees, where will this line go? It will become the y axis. Where will this line go?

It will become the x axis. What will happen to the lobes? They will also turn but this lobe will still be between this line and that line, is it not? So what I am saying is instead of working with the lobes, I might as well work with the planes. There is no difference. Anchal do you agree with me? If you do not, please express yourself. Makes sense because when you move the planes the lobes are defined with respect to the planes is it not? So they will also transform accordingly.

No, I just took a C 4 axis. Whether we have a C 4 symmetry or not depends on what point group it is. I just used an arbitrary example. **“Professor - student conversation starts”** If you take a C 4 axis, let us assume there is C 4 axis. Okay. So the planes will be symmetric with the C 4 axis.

Yes. That is right. But that does not matter. The lobes will still transform that way. Is it not? Whether it is a symmetry operation or not that comes later. All I am saying is that transformation of the planes is going to define the transformation of the lobes also okay? That makes sense. Yes. What do you mean by planes when we are saying that (()) (13:07). **"Professor - student conversation ends".**

Do remember what the Werner's wave function looks like. This is lecture 22, slide one. 1s wave function what does it look like? Help him. So what will the radial part look like? Of course 1 s is all radial part, is it not?

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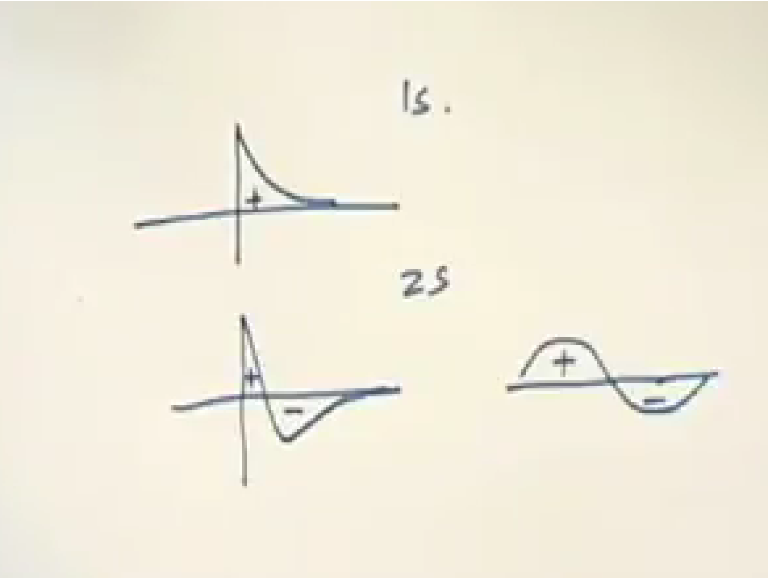

So if I plot it like this it is an exponential decay is it not? 1s. So is the wave function negative anywhere? No. it is positive everywhere, right? So that is the phase of the wave function. What about 2s? You remember what 2s looks like. If you start with positive it goes, there is a node right? And then it is like this. So this is plus phase, this is minus phase, the sign of the wave function and that is relative. I might as well write this as negative this as positive.

So if this is a wave, this is positive phase, this is negative phase? So this is also kind of a wave right? It is a wave function. It is the same thing. Plus or minus? **"Professor - student conversation starts"** When we talk about waves, we talk about sin waves. So we talk about that theta that is there and theta + phi. That is right but whatever you do it is plus here and minus here. It is just a sign is it not? So sin theta varies from say +1 to -1 as long as it is between 0 1 and 0, phase is positive. When it is from 0 -1 0 phase is negative. Same thing. It is a sin. **"Professor - student conversation ends".**

Mehak, question? For what? Basically, when you said that the mirroring of the plane is same as the mirror like. No transformation of the plane what should I say is the same as the transformation of the orbitals. That is what I am saying. Fine. So you understood 3d x square minus y square, okay? Next one is xy. Okay, xy and yz and zx are more or less similar. We will discuss only one. If you look at xy now what is the angular part? Sin square theta sin 2 phi.

So what is sin 2 phi? So will you agree with me that that is xy/r square. So where are the angular nodes? xy = 0. xy = 0 means x = 0, y = 0. What is x = 0? No, 3d. yz plane. And what is y = 0? Xz plane. So yz and zx planes are the nodal planes here and then again you go plus minus, minus plus, plus minus, minus plus as you cross the nodes, okay? So that is why this d xy orbital is called d xy orbital, got it?

I might as well write xy by r squared here understand? So the orbital also will transform in the same way as xy will transform. So that is another way of thinking. You can think that the orbital will transform in the same way as the nodal planes will transform or you can say that the orbitals will transform in the same way as xy will transform because you have xy there, right in the expression of the orbital, right? Is it not? And everything else is totally symmetric.

What I am saying is one way of thinking is that you transform the planes, okay and the orbital will follow. That is one way of thinking. The other way of thinking, perhaps the simpler way of thinking is that just look at the expression of the orbital. The expression itself contains xy right and everything else is totally symmetric right? So the orbital will transform in the same way as xy transforms.

So whichever symmetry species xy belong to will be the symmetry species of this d xy orbital. That is perhaps a little easier to think rather than thinking of how it transforms. Fine.

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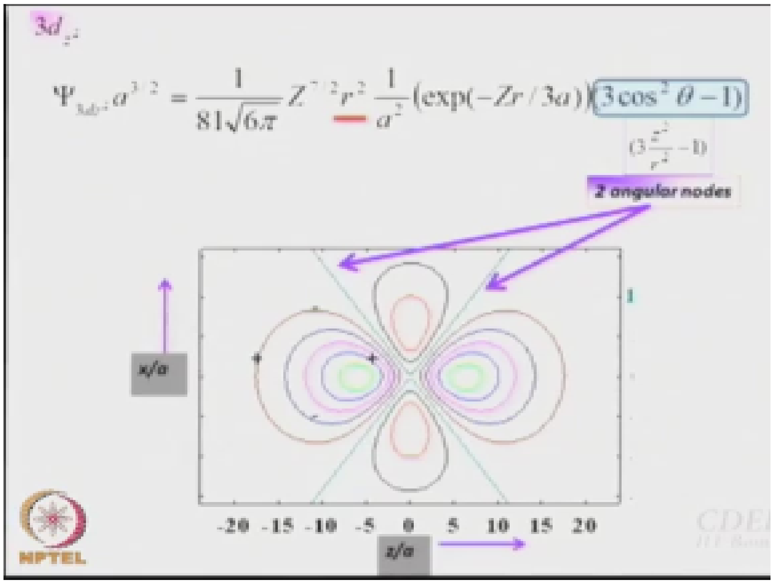

$3d_{z^2}$

$$\Psi_{3d_{z^2}} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} \underline{r^2} \frac{1}{a^2} (\exp(-Zr/3a)) \boxed{(3\cos^2\theta - 1)}$$

$$(3\frac{z^2}{r^2} - 1)$$

2 angular nodes

This is the orbital I like most. 3d z square and 3d z square you see it has 3 cos square theta - 1. Everybody knows that cos square theta would be z square by r square. So 3 z square by r square - 1. Since you have z square there you call it 3d z square, right? Simple? Now, there is something more to it. We will come back to that. But before that, where will the angular node be? Z equal to plus minus r? Now z equal to plus minus r that 3 is also there.

3z square = r square right. So that 1 by root 3 factor will come, okay. Now the point is this is a little different from the earlier one because r is also there. Is it not? So when you draw a section, we just draw 2 lines, okay? But if you think actually in 3D, you are familiar with this kind of a picture, 3d z square?

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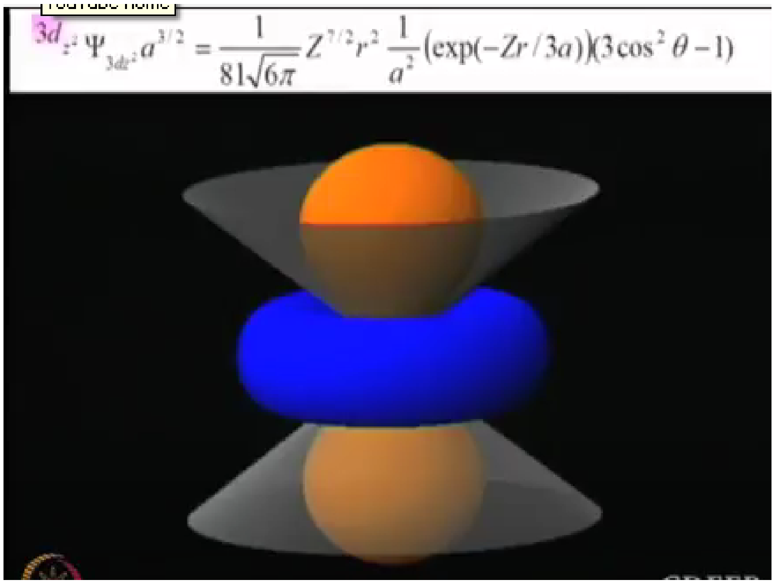

$$3d_{z^2}\ \Psi_{3dz^2}a^{3/2} = \frac{1}{81\sqrt{6\pi}}Z^{7/2}r^2\frac{1}{a^2}(\exp(-Zr/3a))(3\cos^2\theta - 1)$$

What is the shape of the node? Is it really 2 planes, no. It is like 2 funnels. Is it not? So this is a nodal surface. Actually it is only 1 surface, not 2. Or you can say this is one and that is one, right? Fine. Now let us come back to 3d z square from a different angle. I told you why the name is 3d z square is it not? Right. But in India, in other countries also, we often have more than one names, right? One is the proper name, the official name, the other is nickname is it not? Right.

So Elizabeth is Beth or Liz. Now I know you were not expecting that example. But, right? so that kind of thing. So the issue is this 3d z square is actually only a nickname. It is not really a full name, okay? It is only a nickname. Why do I say it is only a nickname because do not forget that this r is actually a spherical polar coordinate is it not? It is not Cartesian coordinate. Can you represent r in terms of Cartesian coordinates? What is it? What is r square?

R square there is no root. R square is x square + y square + z square. So if I write that then what does it become? 3 z square/x square + y square + z square - 1 = 0, right? Now simplify that expression and tell me what do you get in the (()) (21:06). What is it? 2z square - x square - y square = 0 is it not? So I represented completely in Cartesian coordinates then the full level should be 3d 2z square - x square - y square, alright?

And I have no option but to use this because z square does not even appear in the character table of octahedral point group. What appears is 2z square - x square - y square. So I have no option in this case but to use the full level. The full level is 2z square - xy - y square. Alright, understood?

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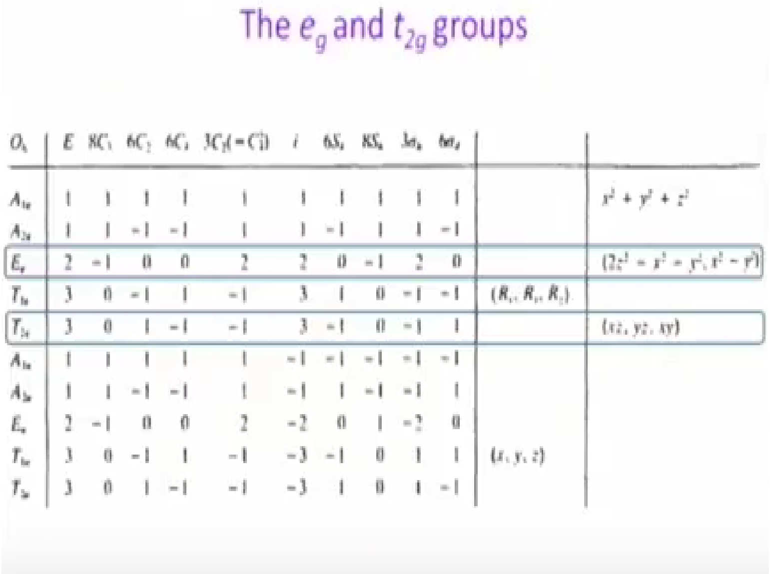

The e_g and t_{2g} groups

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Now, I want to know where they belong in the character table for OH because we are going to talk about octahedral point group today. As I have discussed earlier, when you have a bare metal atom, bare metal ion; what is the point group of bare metal ion? What shape is a bare metal ion? It is a sphere, the perfect shape, right? How many C 2 axis are there? And how many C 298 axis are there? Infinite, right? So it has infinite number of axis of different kinds.

It has infinite number of planes of different kinds and it has one number of yes point of inversion. Do not think it has infinite points of inversion. It does not. There is only one, okay? So that is called the R3 group, the spherical group. Now in that R3 group what happens is all the d orbitals are degenerate. All the d orbitals belong to the same group and they are degenerate. Not so in OH point group.

So in OH point group you see you have A 1g, A 2g, E g, T 1g, T 2g, A 1u, A 2u, E you, T 1u, T 2u. What is the highest dimensionality of any symmetry species? 3. There is no 5-dimensional symmetry species. So is it not obvious that in an octahedral complex where point group is OH it is impossible that all the 5 d orbitals would have the same energy. Is it not? They have to belong to different symmetry species, okay? Which symmetry species?

That can come directly if you look at the character table? What we are looking for? We are looking for 2z square - x square - y square. We are looking for x square - y square. We are looking for xy yx zx and see that they are in the character table. This 2z square - xy - y square and xy - y square belong to E g point group, doubly degenerate. And xy yz zx belong to T 2g point group. What am I saying? T 2g symmetry species.

E g symmetry species and T 2g symmetry species, right. That is why they have to have different energies. This is E g. E g, T 2g alright? So this is why in an octahedral field you expect the d orbitals to split into 2 groups, one group of two E g group and the other group of three the T 2g group. Where does the name E g come from? Where does the name T 2g come from? Mullican nomenclature of the symmetry species to which the respective d orbitals belong.

So now after all these years of studying chemistry the origin of the name is known to you, alright? Fine.

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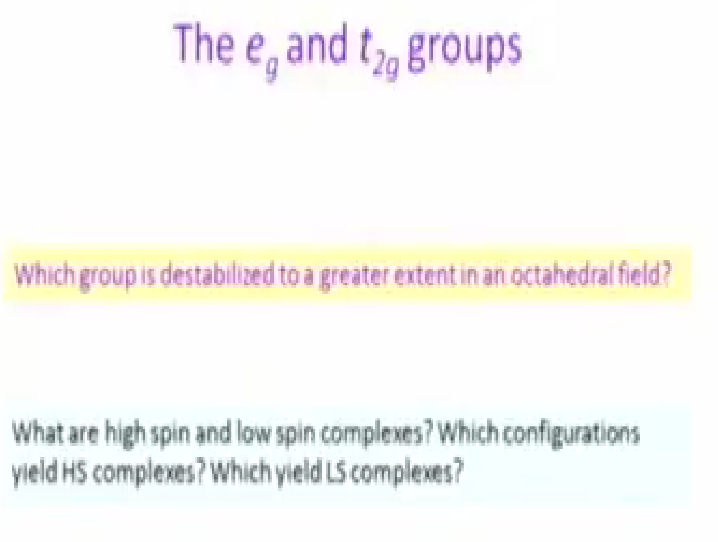

The e_g and t_{2g} groups

Which group is destabilized to a greater extent in an octahedral field?

What are high spin and low spin complexes? Which configurations yield HS complexes? Which yield LS complexes?

Okay now. This is not something I am going to discuss because you have studied this many times. You tell me which one is destabilized to a greater extent in octahedral field. You remember crystal field theory is it not? Remember crystal field theory? All orbitals are actually destabilized is it not? That is the consideration of crystal field theory. It is just that some are destabilized to a greater extent.

That is what gives rise to relative stabilization of one of the groups, relative destabilization of the other group, okay? So which one is destabilized to a greater extent? E g or T 2g? Why? They are along the axis and the approach of the ligands is also along the axis, okay? And so that is one question. Second question I have is what is a high spin complex, what is a low spin complex? You got to tell me.

So right now we will go with the simplistic view that inorganic chemists are comfortable and just say unpaired electron, no problem okay. So more unpaired electron is high spin and less unpaired electron is less spin, okay? Which configurations yield high spin complexes, which configurations yield low spin complexes? What are the configurations we are talking about? D1, d2, d3, d4, d5, d6, d7, d8, d9, d10.

Is it possible for you to get a high spin complex and a low spin complex for d1? No, right? What about d2? Can you get high spin complex, low spin complex. No, why not? Because they will be in the lower level. So what we are saying is this, okay.

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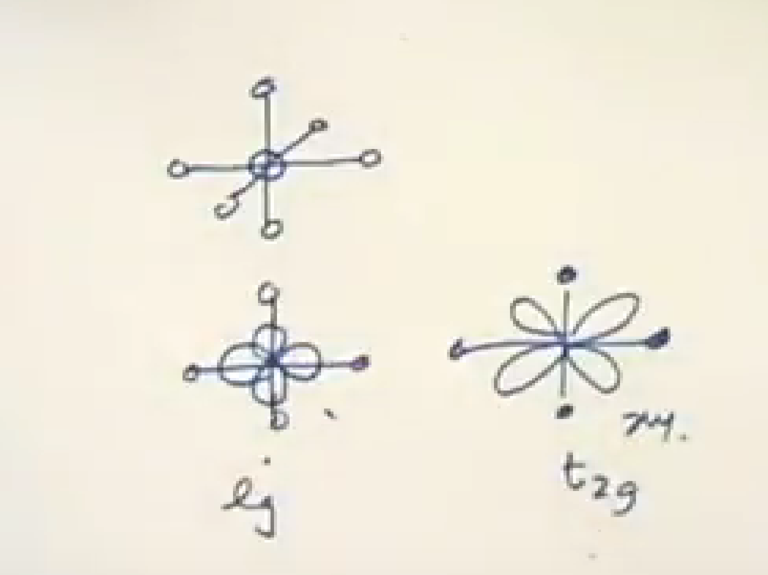

This is what an octahedral complex would look like. You have a central metal ion, okay? And you have these ligands approaching along the axis because it is octahedral, okay? Now see there are 2 kinds of d orbitals, right? One is like this. Which d orbital is this if these are x and y axis? So now dx square - y, you see ligand approach is directly onto xy –y. Now if I write like this, once again x and y. This is another kind of d orbital. What is it, xy right?

For xy the approach of the ligands is not head-on right? So this repulsion that you have here is less than what you have here understand. That is all we are saying. So which symmetry species is this, e g right? This belongs to e g symmetry species. It has e g symmetry. And this is t 2g. There are 3, xy, yz, zx and this you have z square and x square - y square, alright? D1, d2 oh, I see, fine. No, so you understand why e g is destabilized and t 2g is stabilized. e g is destabilized, right with respect to t 2g.

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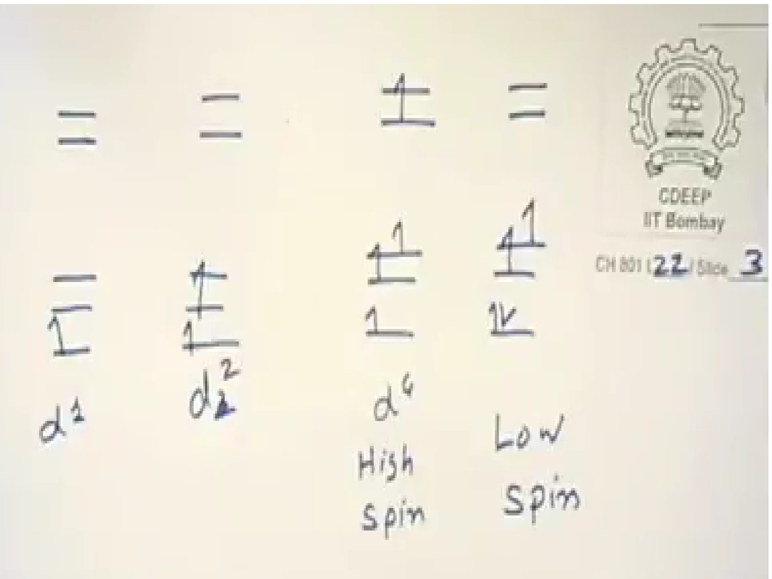

So e g is doubly degenerate, t 2 g is triply degenerate. So these are all same energy. I am just drawing them apart for the sake of convenience. So what I am saying is for d 1 configuration, you have one electron here right and it can only be either here or here or here is it not? So spin is only, what is a spin? +1/2 okay? If it is d 2 configuration, where will the second electron go? One here and one here. Is there any other possibility? D 3 third electron will go here, right?

Now d 4, when you go to d 4, there are two possibilities; 1, 2, 3, 4 this is one possibility. The other possibility is 1, 2; 3, 4 okay. How many unpaired spins do I have here? 4. How many unpaired spins do I have here? 2. So this is a high spin complex and this is a low spin complex, alright? When will high spin complexes form, when will low spin complexes form? It depends on the ligand but then it will further exactly. So energy gap between t 2 g and e g.

If the energy gap is very large, then the electron will rather pair up and stay here. If the energy gap is not very large, then the electron wants to stay by itself. Understood now what is high spin what is low spin complex. And we have already discussed which configurations yield high spin complexes and which configurations yield low spin complexes. So you can look up any inorganic chemistry book if you require, everything is discussed there.