Concepts of Chemistry for Engineering
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Lecture No. 32
Crystal Field Theory: Octahedral vs. Tetrahedral Complex

We have seen the octahedron complexes. We have seen the tetrahedral complexes. These are the two most important classes of compounds that are present over the, let us say, whatever chemistry known so far. There are other complexes. As you have seen, it could be penta-coordinated. The metal complex can be penta-coordinated. Two different types of geometry is possible for penta-coordination. Out of that trigonal bipyramidal is one of the preferred geometry. So, there are a lot of things that we can definitely go on and discuss about it.

But it is literally impossible to discuss each and every structure in detail, each and every metal complex kind of different geometry in detail and how their ligand field will affect the d orbital splitting. So, geometry changes, d orbital splitting pattern changes. I think just by learning octahedral and tetrahedral you have got that sense. Now, it has all to do with the way the ligand is approaching, sometimes ligand is approaching directly towards the atomic orbital of the, of each of those metal or d orbital of the metals. And thereby you can see the extent to which it gets stabilized or destabilized is differing.

So, if you take, technically speaking, if you take a trigonal bipyramidal perhaps you would be able to at least understand why their splitting is such that. In the syllabus, we for you guys we do not have any other geometry to discuss octahedral and tetrahedral. If possible you can look at little bit at trigonal bipyramidal, TBP.

Now, square pyramidal, square planar is something which we will come soon. Square planar is basically nothing but octahedral geometry you are having. You take out to z-axis. You have octahedral scenario. You take out to z-axis. That becomes square planar. So, we will discuss that.

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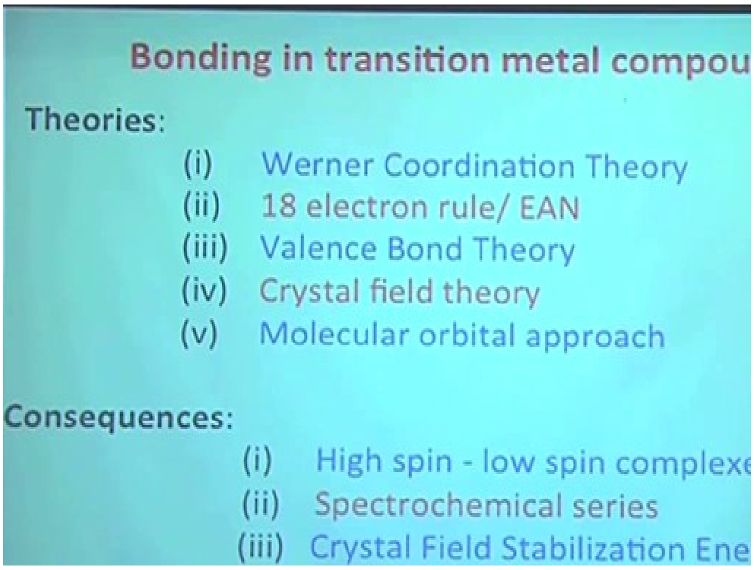

Bonding in transition metal compou

Theories:

- (i) Werner Coordination Theory
- (ii) 18 electron rule/ EAN
- (iii) Valence Bond Theory
- (iv) Crystal field theory
- (v) Molecular orbital approach

Consequences:

- (i) High spin - low spin complexe
- (ii) Spectrochemical series
- (iii) Crystal Field Stabilization Ene

So, in the last class, once again, we were discussing Werner coordination theory, 18 electron rule, valence bond theory and how good it is, and then how bad it is, and how good the crystal field theory is. Really, we will stop there, how good the crystal field theory is, and not too much we will get into the MO approach, molecular orbital approach. There are, I mean, no end to learning. I think for this course purpose, we will stop in there, not too much afterwards.

So, the major objective for this syllabus or for this chapter and the next chapter is definitely giving you an idea about these high spin, low spin complexes, the spectrochemical series, I hope you have come across this term in the last class, crystal field stabilization energy, Janh-Teller distortion and spinel. These are the last two topics we will discuss today. I will briefly give you an overview what we have discussed in the last class.

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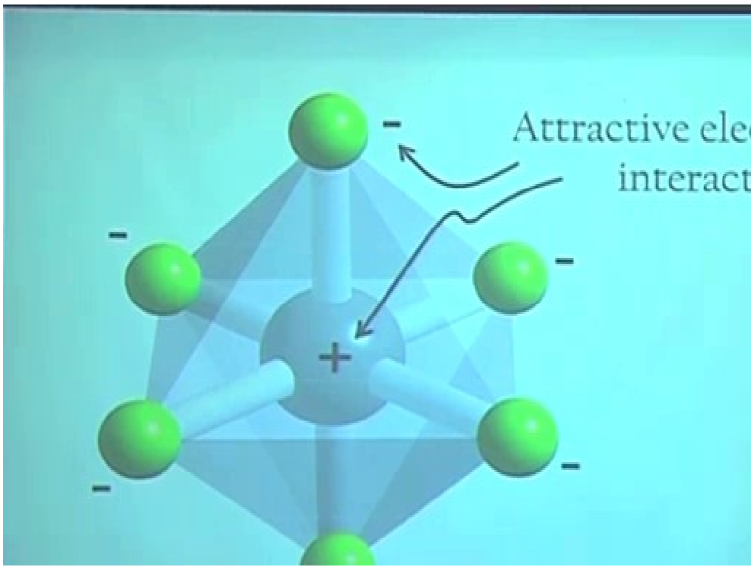

So, this is an octahedral complex. Metal center is there at the middle of it. So, that is at the center of the geometry. It is a metal center. Metal and ligand are almost having electrostatic interaction. It is a positive charge and negative charges are the ligand which are interacting with the metal center. Remember, in the valence bond theory, we were mainly assuming it is a coherent structure. As you see, this is axial position. That is also axial position. This is the direction where dz2 orbital is, dz square or dz2.

Now, these are the direction, these 4, 1, 2, 3, 4. These four are the ones where we have dx2dy2 orbital directly. It is not indirect. This is where is actually dx2y2. So, therefore, from this, you can understand why dz2 and dx2y2 orbital is most destabilize for octahedral geometry, because they are the one which facing the music basically. They are the one which is getting repelled most, because ligand electrons and d orbital electrons are repelling each other, very simple.

Now, all other orbitals dxy, dyz, dxz, they are not facing these ligands directly. They are in between, somewhere here, here, here, here, say in between. So, thereby, they are not going to get rippled too much. They are going to get rippled, but not too much. Relating to dx2y2 and dz2 they are going to stabilize.

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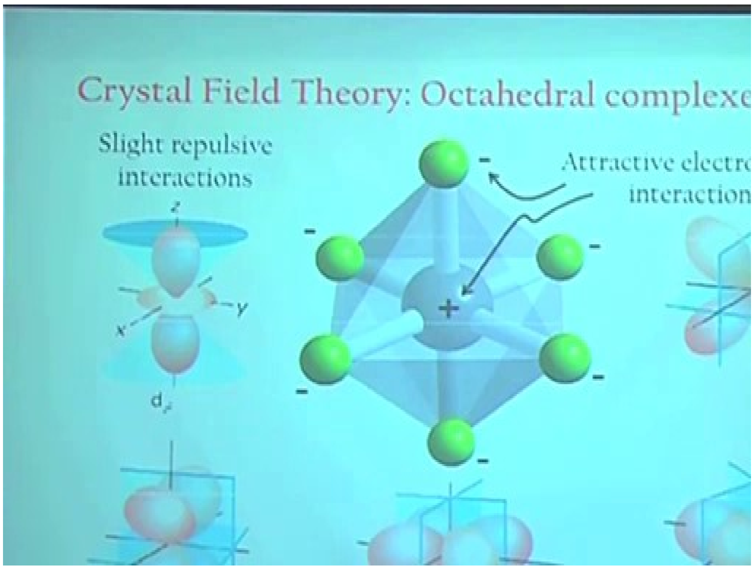
Crystal Field Theory: Octahedral complexe

Slight repulsive interactions

Attractive electr interaction

So, just a quick look at the orbitals what we have discussed in the last class, dz2 orbital, dx2y2 orbital. Now, these are the other orbitals. With respect to these three other orbitals, you can see where the ligands are. Therefore, you can understand the stabilization or the destabilization of these. That is a good question. Usually, that is where we will come to Jahn-Teller distortion. That I guess, that you will be able to clearly understand when we are discussing the Jahn-Teller distortion. That is the actually the origin of Jahn-Teller distortion and z elongation and z in. We will come back.

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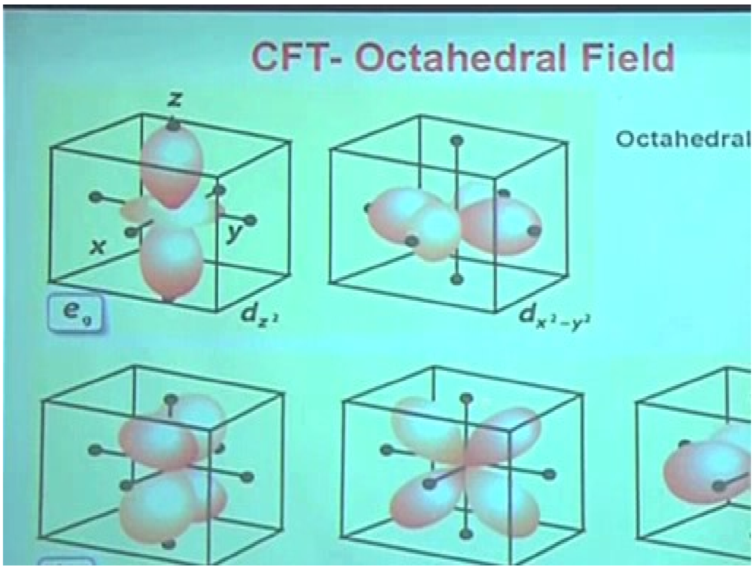
CFT- Octahedral Field

Octahedral

Now, this is the same thing in a different bottle. I think whatever fits you, you just look at it. It gives you a very clear idea. These are the ligands. The black balls are the ligands and the metal orbitals or d orbitals are shown in here clearly. No confusion right.

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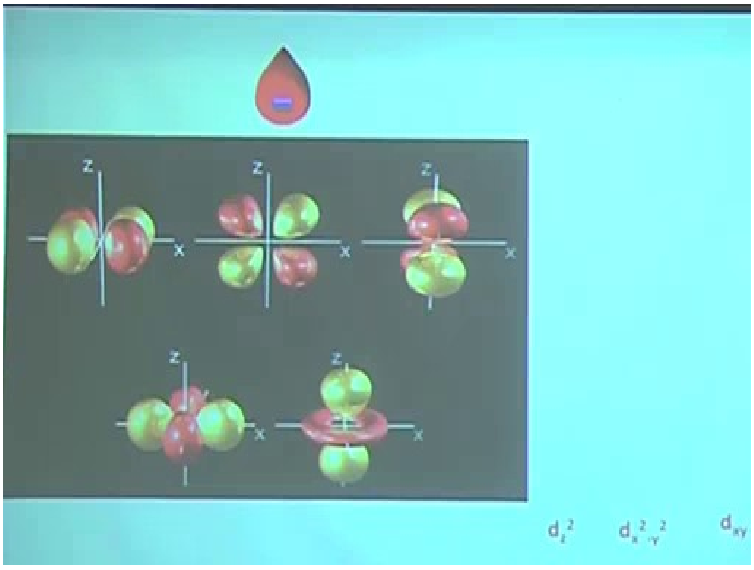

Now, as you were showing in the last class. So, these are d orbitals and this is, let us say, ligand electrons. Ligand electrons are coming for these orbitals to overlap.

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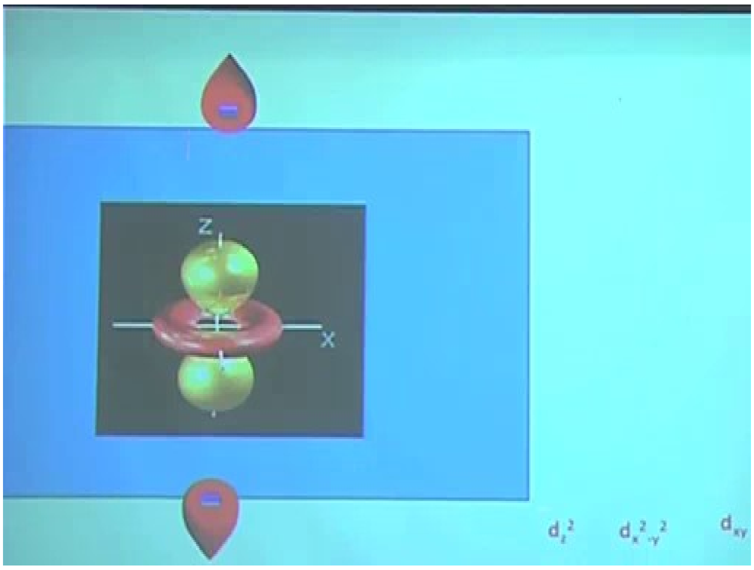

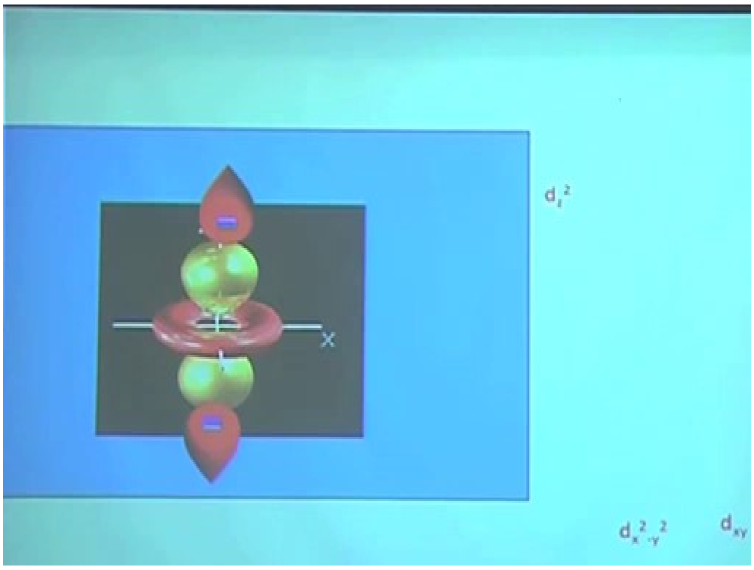

Now, first instance, we will discuss that dz2 interaction with the ligand. Ligand electrons comes. They will be repeating each other. Therefore, dz2 will be destabilized. Dz2 is facing the ligand once again directly.

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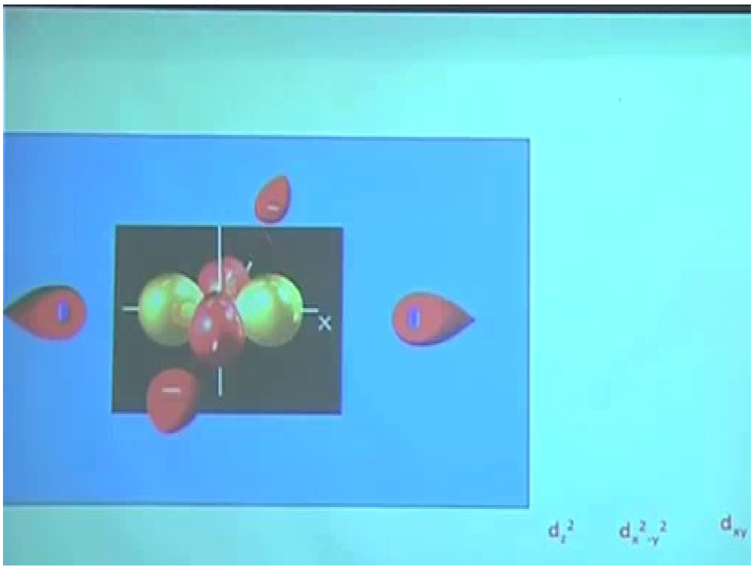

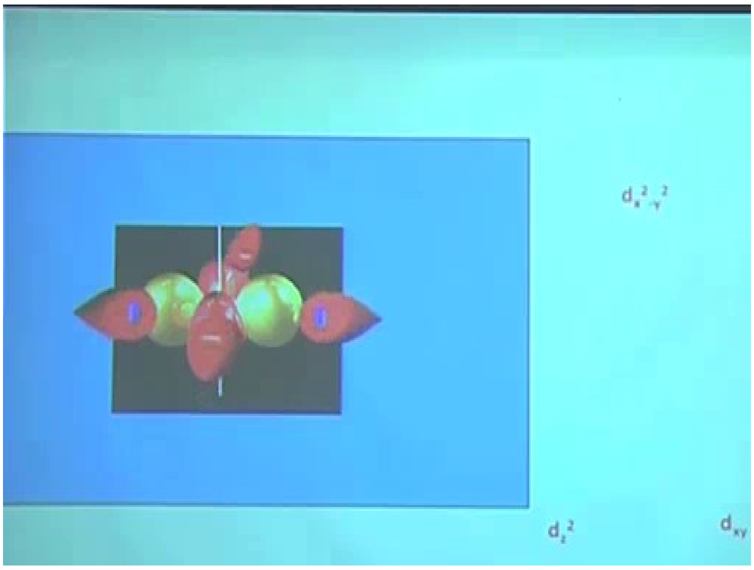

This is the dx2y2 one. Now, here you see that the four ligands are coming along all these axes. To answer to the previous question, one of the way you can see is these are four lobes, four lobes divided by 4 ligand and two lobes divided by two ligands kind of that is how perhaps it is, you do not have to worry usually.

But final details when it is unsymmetrically filled, dz2 and dx2 although they are of same energy, but if they are unsymmetrically filled, let us say, one is there in the eg orbital or three is there in the eg orbital then the problem comes. Now, so, you have seen how they are coming and thereby they are also getting, these orbitals are getting destabilized.

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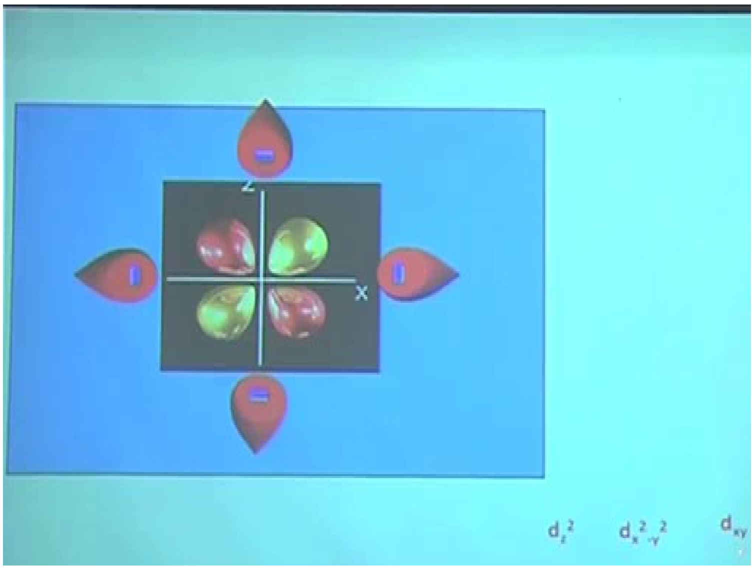

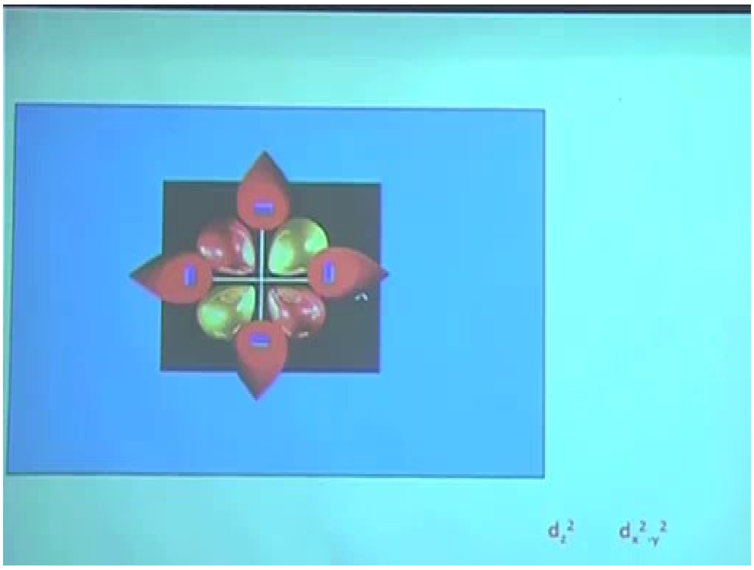

d_{z^2} $d_{x^2-y^2}$

All other d orbital like these three are like dxy, dxz and dyz, they are really not facing the orbitals directly. As you can see, they are sitting right in between and thereby you can see, so for example, over here we have shown dxz, same is true for dxy and dyz. Thereby, these orbitals are relatively, mind you relatively stabilized with respect to dz2 and dx2y2. If you compare the free metal ion, with respect to free metal ion everything is destabilized, because free metal ion has no ligand thereby no repulsion. The moment ligand comes repulsion starts. So, thus systems energy goes up.

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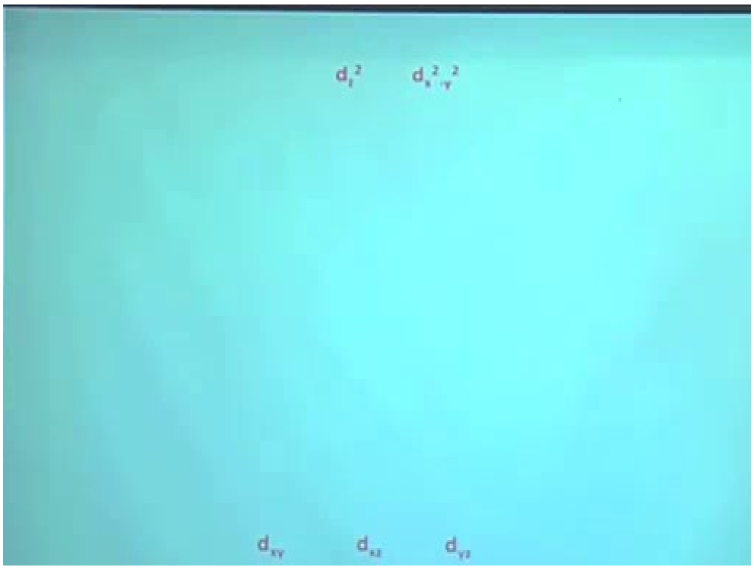

d_{z^2} $d_{x^2-y^2}$

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

Now, overall, therefore, you have two up, three down. But net stabilization with respect to the barycenter, the center in the middle, the net stabilization or destabilization for a completely filled d orbital, let us say d10 or d5 in a high spin situation which we have discussed should be the 0. Stabilization, if it is completely filled, total stabilization and total destabilization has to be the same.

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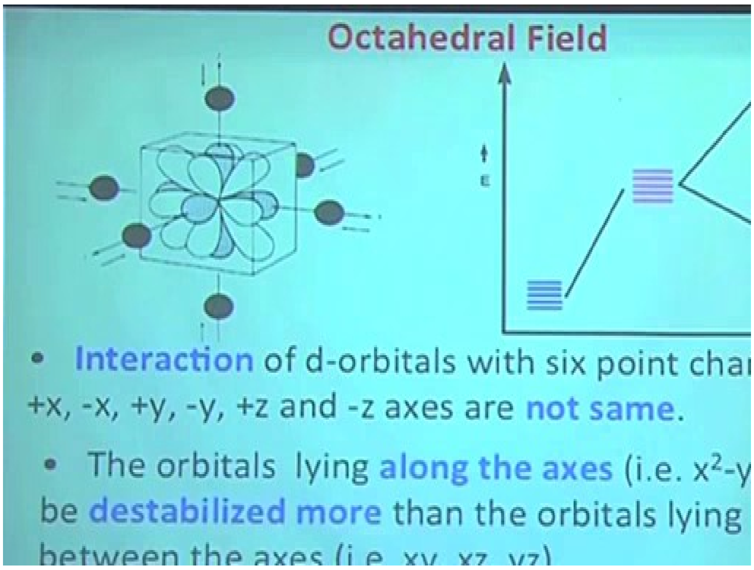

Octahedral Field

- **Interaction** of d-orbitals with six point cha
+x, -x, +y, -y, +z and -z axes are **not same**.
- The orbitals lying **along the axes** (i.e. x^2-y
be **destabilized more** than the orbitals lying
between the axes (i.e. xy, xz, yz)

Now, this is where, again once again this is kind of a clear picture. This is the octahedral field. We were showing 6 ligands coming at the box. So, if you are assuming this is your box 6 ligands are facing the way it is shown 1, 2, 3, 4, 5, 6. Now, this is the free metal ion. This is the metal complex. Three of the t2g got stabilized, two of the eg got destabilized. Now, this is eg not e, e will be for tetrahedral, t2g not t2. Now, of course, I think I have discussed this information already.

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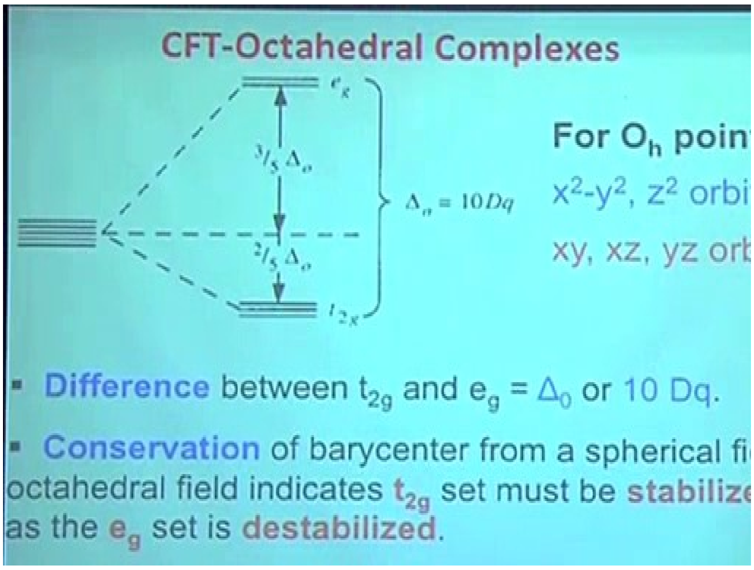

CFT-Octahedral Complexes

For O_h poin

x^2-y^2, z^2 orbi

xy, xz, yz orb

- **Difference** between t_{2g} and e_g = Δ_0 or 10 Dq.
- **Conservation** of barycenter from a spherical fi octahedral field indicates t_{2g} set must be **stabiliz** as the e_g set is **destabilized**.

Now, since this is three of them, this is two of them this distance between this barycenter and stabilization for t2g, ligand maybe different. Here we are thinking, say we have to ideal, deal with the idealistic one at the beginning ML6 ligands are same, ML6. We are not thinking like three of the chloride, three of the fluoride, that is a mixed situation. Of course, those situation comes, often comes, but this is if we do not understand, I mean, very simple situation, how can we go complex.

So, of course, let us say if you have three chloride and three cyanide, what will be the situation that is a special topic on this. How finer details you can get in the d orbital splitting. Initially, it may split and then they may further split. If you have all of them, let us say, weak field, like three fluoride and let us say three chloride. They may be having same.

But the moment you have one weak field, one strong field ligand, things will be a little bit complicated. So, overall, how much ligand, I think, overall, you have to see whether it is a strong field ligand or weak field ligand, whether it is a first point, whether it is a octahedral geometry or tetrahedral geometry, and thereby go for it.

For the exam purpose for this course, I do not think we will be tricking into anything which is mixed, little bit more complicated than that. For the exam purpose or for this course purpose, you have to just know octahedral field splitting and tetrahedral. And we will be discussing briefly about the square planar, because that is kind of comes automatically. Furthermore, if you want to learn maximum go to trigonal bipyramidal. We will give the splitting. But it is a more complex than we would like to think. We are just dealing idealistically. That is a good question.

So, over here, we see that destabilization should be 0.4, 2 by 5 delta 0, 0.4 delta 0 this destabilization would be 0.6 delta 0, we have discussed it, or 4Dq, 6Dq, if it is delta zero or 10Dq, we have discussed.

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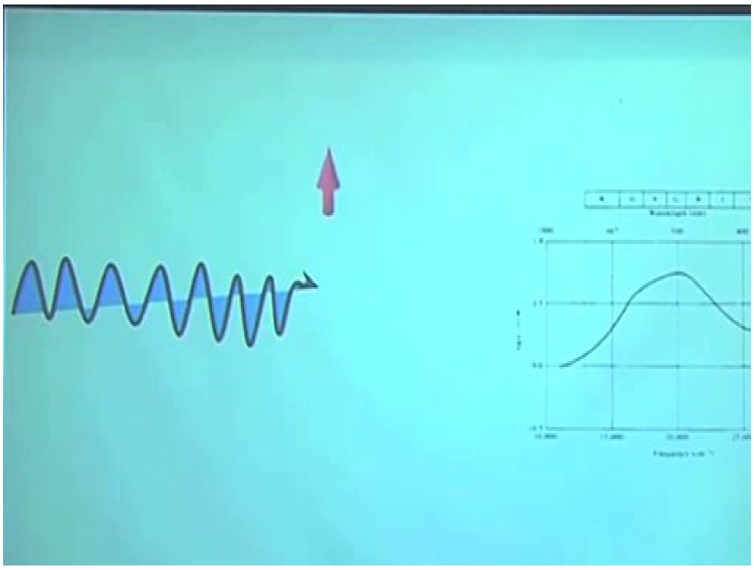

Now, the first advantage of this crystal field theory is you can explain the magnetic properties, you can expect to explain spectroscopic behavior, let us say, UV-vis study, why certain peaks are coming. So, this is where we were telling that if you have an unpaired electron, if you are moving from t2g to eg, the spectra you get will be something like this, absorption maximum.

Of course, we are not getting into finer details of the spectra, but this is the major origin where, from electrons are moving and where it is going. So, from t2g, this is a d1 electronic configuration. One electron is there. So, t2g1 that means over here, t2g1, one electron was over here, you all these three orbitals are degenerate, same energy, only way it can go is up to here.

Now, if you think if eg is splitted further, these two orbitals are dx2y2 and dz2, if it is splitted further so the electron can go to two different levels. Therefore, you can expect two different peaks. Whether intensity will be high or low that is, of course, then you have to think about the symmetry and lot of other things, which we will not be discussing, but you can sense where the spectra is coming from and where the electron is moving from, I mean, which orbital to where it is going. So, this is fine. So, you get the spectra.

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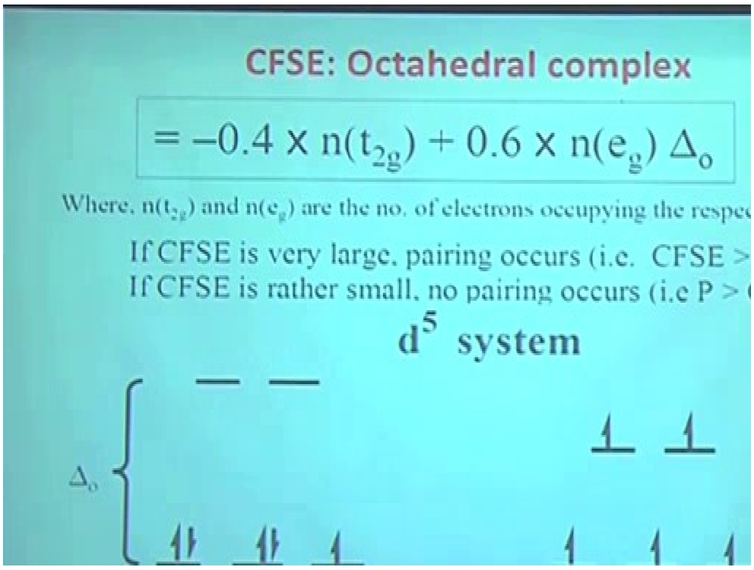

CFSE: Octahedral complex

$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\ \Delta_o$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respe

If CFSE is very large, pairing occurs (i.e. CFSE >

If CFSE is rather small, no pairing occurs (i.e P >

d^5 system

Now, we have also seen crystal field stabilization energy. So, you calculate, you are given. I think you have to really master this. You should be able to do it in your dream, d3 electronic configuration, what is the crystal field stabilization synergy if octahedral, d5 what is, if it is octahedral how many scenarios are there, two scenarios high spin and low spin right. So, what will be the crystal field stabilization energy?

Any question specially in exam if you see before even thinking too much I would say just imagine the scenarios. Only three scenarios you have octahedral two scenario high spin, low spin and tetrahedral only high spin scenario 99 percent case. We will discuss one case today which is otherwise, but that is it, octahedral two scenarios and tetrahedron one scenario, done.

So, once you have that, I think that answers should come out almost like why something is preferred or why something is not preferred. At least I would say out of 25 mark question 5 marks to 7 marks will be based on that indirectly. I mean, of course, it will not be given perhaps on a platter. Definitely you will be able to figure out that. So, please do familiarize. You should not be fearing about calculating and electronic configuration should be always correct. There should not be any mistake.

Now, so d5 system, for example, one case we were giving. So, this is the d5 high spin that means 3 stabilization, 2 destabilization, CFSE should be 0. That is what I was trying to say. So, net stabilization and destabilization should be 0 if it is symmetrically filled. So, this is 0. You do not have to even calculate. If it is d10, it is again 0. D10 means all of them are full. So, stabilization is equals to destabilization.

So, that is where, let us say, you are given d7 and this is the configuration 5, 6, 7. So, 5 take out 5, because 5, 3 plus 2 has stabilized, destabilized and cancel each other out. Now, you just deal with 2. 2 will be d7, two will be over here and here. So, that will be minus 8Dq or 0.8 delta 0 or delta octahedral. You should be able to do it really, really quick without calculating and going through the simple math.

Now, of course, d7 you can have also high spin and low spin configuration. For example, this one, what would be the CFSE, minus, so of course minus, that is out of question, its stabilization. Each of them are 0.4 so five of them 20 minus 20 or minus 2, minus 2 delta 0, that is it. Delta 0 means delta octahedral, delta 0, I mean, different people pronounce it different way. So, this is it. I mean, if you do it really simply I am sure 5 to 7 marks question will be there. I mean, invariably, whatever it is, the question is based on that. It is going to be based on that.

Now, of course, we have discussed it. Once again two scenarios high spin, because the spin is maximum high spin, low spin means spin is minimum. You see one unpaired spin. Now, if you look at the, I will come back to the magnet magnetic behavior. Magnetic behavior is nothing but due to the unpaired electron. So, the moment you have unpaired electrons, magnetic behavior comes because the parallel spin will cancel each other. You want to spin on that direction and I want to spin on this direction. So, it will be cancel out, cancelling.

So, this is the one will have low magnetic value, magnetic moment value, this is the one who will have high magnetic value. This is the origin for molecular magnet. A lot of molecules are magnet. And these are the ones you see the application almost everywhere, literally everywhere. You take any electronic gadgets, you take almost anything which is electronic in nature, which has some fancy application, it is the material which are having magnetic properties and that is why they are used, how expensive it is, based on that you will get your material. Of course, in lots of other cases you see the use of these things. I will show one or two case today.

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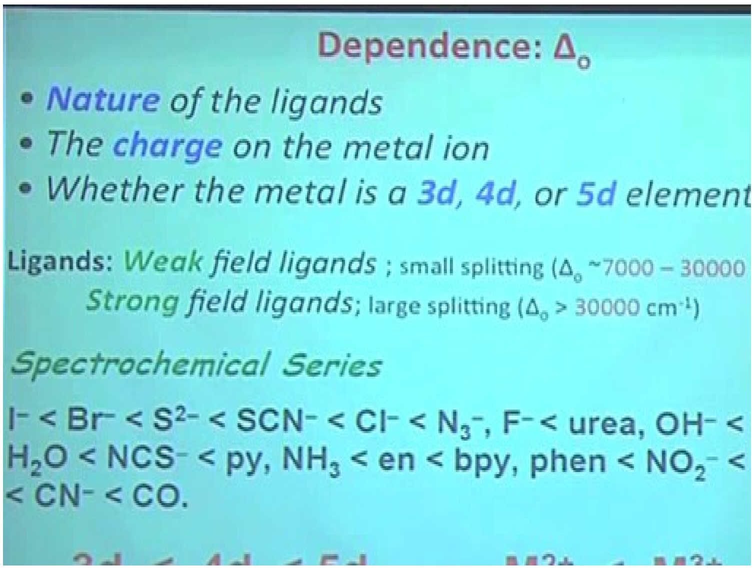

Dependence: Δ_o

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands: *Weak field ligands* ; small splitting (Δ_o ~7000 – 30000

Strong field ligands; large splitting ($\Delta_o > 30000\ cm^{-1}$)

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ urea, $OH^- < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < < CN^- < CO$.

So, dependence of delta 0 like how much splitting is going on that depends on the nature of the ligands as I was trying to tell you whether it is a weak field again or strong field ligand. Strong field means the splitting will be very high, weak field means the splitting between t2g and eg will be small. And therefore, for weak field ones we will always see high spin, means spin will not be pairing up. And the charge on the metal, of course, if it is a higher charge you will have higher separation, if it is 5d you will have higher separation compared to 3d.

So, this is the spectralelectrochemical series with respect to different ligands. These are the stronger one, stronger ligands. These will, these are the one which almost always will give you the low spin, high, which one, low spin complex, because the splitting will be high. Strong field ligand, splitting will be high, so the spin pairing will happen. It cannot go from t2g to eg. These are the one which are likely to give you low spin complexes.

Is it getting clear? If it is, you are getting, I mean, sometimes it is little bit confusing. It is either yes or no type of answer, question. I mean, the understanding is either yes or no, high spin or low spin. So, just get it clear.

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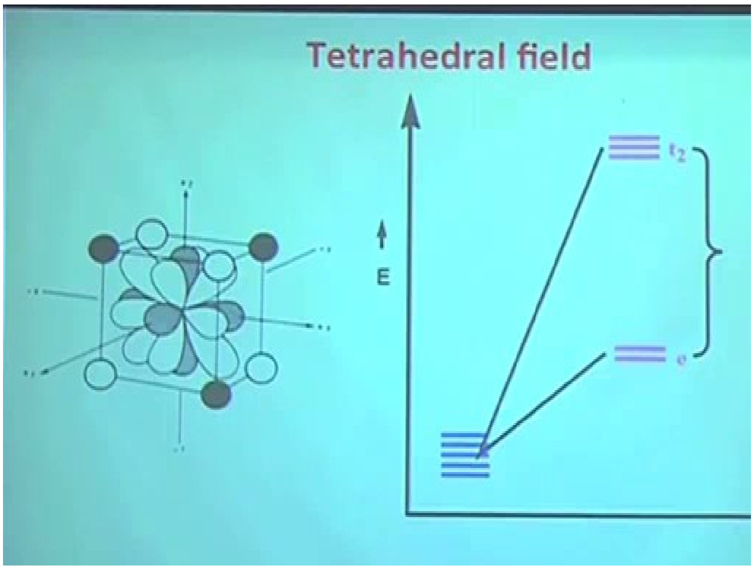

Tetrahedral field

Now, this is the trend we have shown. For tetrahedral case, we were dealing with a completely different scenario, which can be clearer from this picture. If you remember the previous picture for octahedral case, which was nothing but direct confrontation, here it is like more of a political approach, diplomatic approach. You do not go direct. You just talk with. So, they are talking and they are not directly confronting. Thereby, the scenarios are completely different. Since it is not interacting directly, overlapping directly with let us say those eg orbitals, previously we have seen for octahedral cases, dx2y2 and dz2.

Dz2 is over here actually and see the ligand where it is. Ligand is here, dz2 is here. Actually, those orbitals are now ones, those eg orbital for octahedral case are the ones which are farthest from the ligand, which are farthest, and thereby, they are the one which will get stabilized. The other three orbitals dxy, dyz, dxz, those are the ones which are nearer, not directly overlapping, but closer and thereby they are destabilized. Now, this difference is called delta t.

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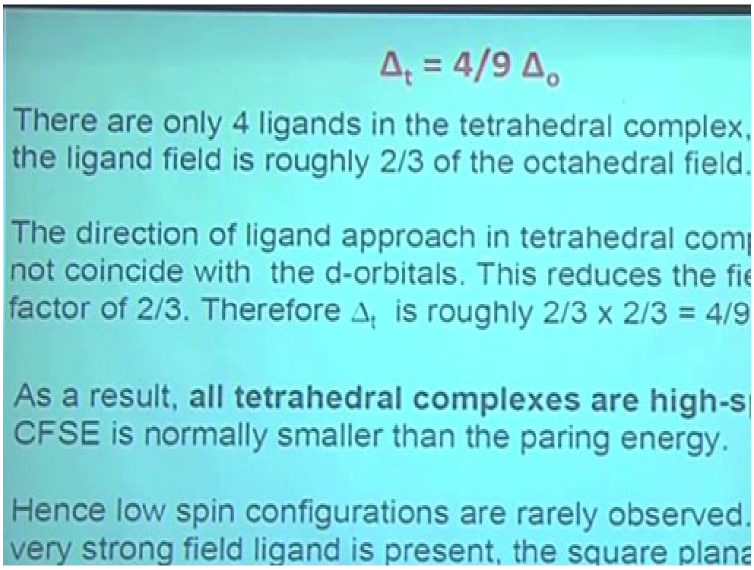

$\Delta_t = 4/9\ \Delta_o$

There are only 4 ligands in the tetrahedral complex,
the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral com
not coincide with the d-orbitals. This reduces the fi
factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9

As a result, **all tetrahedral complexes are high-s**
CFSE is normally smaller than the paring energy.

Hence low spin configurations are rarely observed.
very strong field ligand is present, the square plan

And this delta t is going to be four ninth of that delta 0 or delta 0, two-third coming from the number of ligands 6 to 4, octahedral to tetrahedral, another two-third coming from indirect approach not from direct approach. If it was directly approaching that is the case of octahedral case, but here is indirect approach. Basically you can calculate based on the angle, which angle it is coming.

So, roughly, these are like rough calculation. It is becoming two-third times two-third, 4, 9 of delta 0. So, delta t is always less. Therefore, you never see, almost never ever see low spin case for tetrahedral. Since the splitting is very less always you end up getting high spin case. So, never ever calculate tetrahedral for high spin, low spin.

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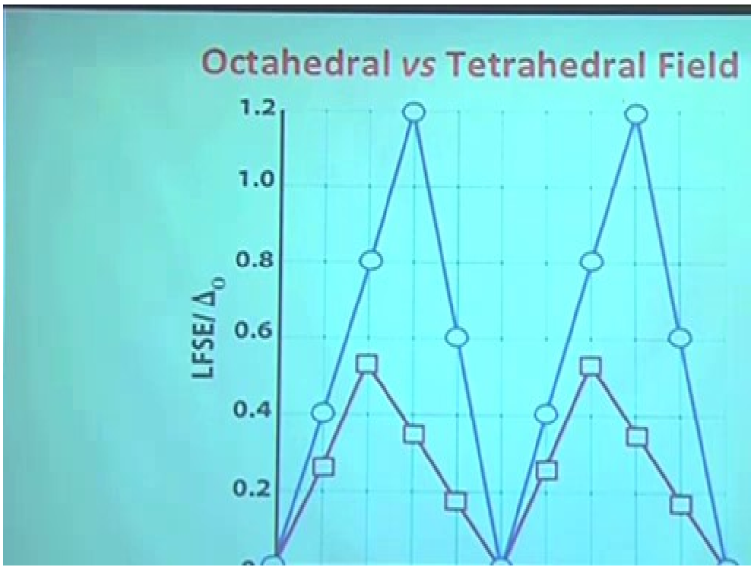

Now, this is the electronic configuration and their restrictive stability if you are comparing delta octahedral and delta tetrahedral directly. So, what happens, how much stability is there if it is d1 for octahedral case, d1 for tetrahedral case and we are comparing apple versus apple that means high spin versus high spin, high spin of octahedral and high spin of tetrahedral. Tetrahedral cannot have low spin. In tetrahedral case we have to normalize the value with the four nine of delta 0, these two. You do it, you will get this. Should be, you should be able to get it.