Basics in Inorganic Chemistry

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Lecture - 08
Crystal Field Theory: Octahedral Complex

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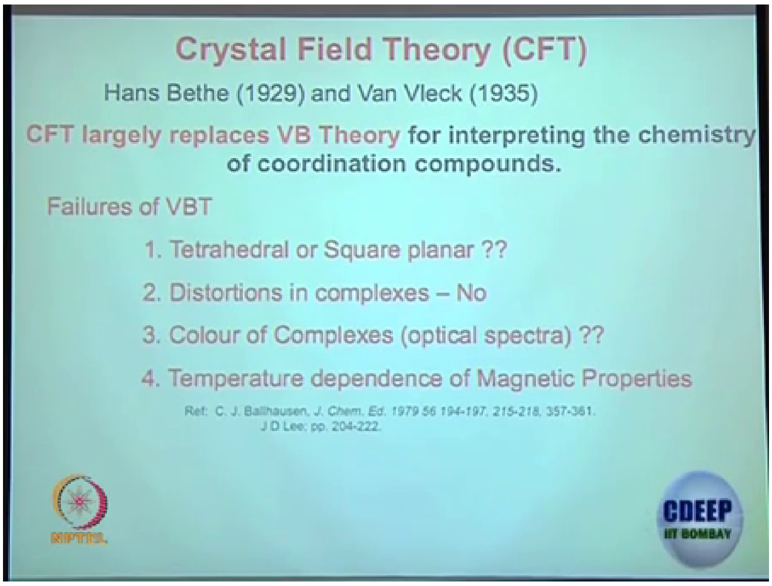

Crystal Field Theory (CFT)

Hans Bethe (1929) and Van Vleck (1935)

CFT largely replaces VB Theory for interpreting the chemistry of coordination compounds.

Failures of VBT

1. Tetrahedral or Square planar ??
2. Distortions in complexes – No
3. Colour of Complexes (optical spectra) ??
4. Temperature dependence of Magnetic Properties

Ref: C. J. Ballhausen, *J. Chem. Ed.* 1979 56 194-197, 215-218, 357-361.
J D Lee: pp. 204-222.

Lot of information you cannot get like why a specific compound is colored right, what happened to their magnetic properties; because these are the things we are really really interested in. So, this is where crystal field theory comes in. Of course, it is based on the failure of the valence bond theory or as that is how in the book you read. That where valence bond theory kind of fails, cannot explain further and crystal field theory basically picks up.

So, of course, we can just learn crystal field theory, but the problem is valence beam theory is so simple; I think nobody kind of; see you cannot forget the history of something and just take the present. I mean present is something different not crystal field, it is something different right, which we may not be or we will not be talking too much.

So, its you know present means temporarily present, hundred years down the line it would be explained in a completely different way or bit more better way. Of course, crystal field theory has tremendous limitation as well, but we may not be talking about those. So, as we progress or as the chemistry understanding progressed we will try to do. So, what we are saying that, valence bond theory really cannot explain tetrahedral and square planar ok. When it is, any distortion; what valence bond theory is discussing is an ideal situation kind of any anything bond, elongation, shortening these things cannot be explained by valence bond. In a moment you will see how the distortion is going on by crystal field theory.

Color of complexes of course, you cannot have any idea about the color; what color the complex should be, I say compound is this hybridization or this many ligands are there, this there, that there. Crystal field theory can explain how work; we did not explain it, but valence bond theory cannot explain those.

Temperature dependence, why magnetic properties are dependent on temperature; if you increase the temperature what happens with that magnetic susceptibility or the magnetic behavior goes up or goes down or how it goes down or how goes up those sort of thing we will be discussing ok.

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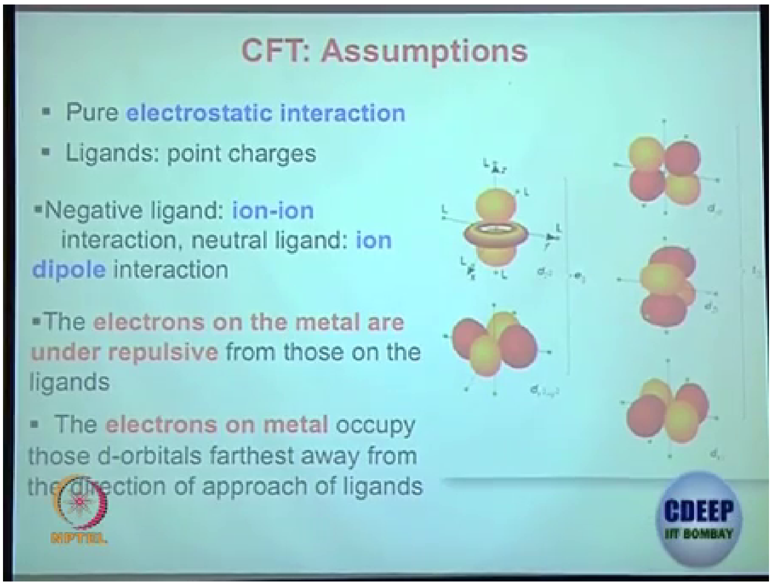

CFT: Assumptions

- Pure **electrostatic interaction**
- Ligands: point charges
- Negative ligand: **ion-ion** interaction, neutral ligand: **ion dipole** interaction
- The **electrons on the metal are under repulsive** from those on the ligands
- The **electrons on metal** occupy those d-orbitals farthest away from the direction of approach of ligands

Now crystal field theory; first we have to look at the orbital, this is something you have to kind of have it within your mind very clear, what we are talking about the atomic orbital these orbitals. Mainly the 5 d orbitals right, we have 5 d orbitals; how they are and along the axis, how they are, where they are.

Now, this is the z axis or g axis whatever you want to call ok. Now that DG 2 orbital is going to be like this; the electron density is going to be over here and over there along the z axis, so axis you can think along this one; let us say this is x axis, this is y axis, this is z axis ok. In 3 dimensional scenario, you can take this corner any corner; one axis, another axis by laser pointer failing; any corner you can pick up x, y, z of course, 90 degree angle, it is may not be always 2 here.

Now this is d z, 2 orbital show along the z axis, this is d x 2 y 2 along the x and y axis and this is let us say d y z; that means, in between y and z. So, if you look at here, if this is z axis, this is the electron density over here and the lobes are here and below this one there is lobe ok.

If it is x and y axis, then d x 2 y 2 will be along this x and y axis, along just right on top of those axis; right on top of the z axis is d z 2, right on top of x and y both plus and minus reaction is going to be your d x 2 y 2. In d x y will be in between; d x y where is d x y, d x y see this is let us say x axis or whatever y axis x and y as you see these are right on top of the axis, in between x and y axis is d x y. Similarly, in between y and z is going to be d y z.

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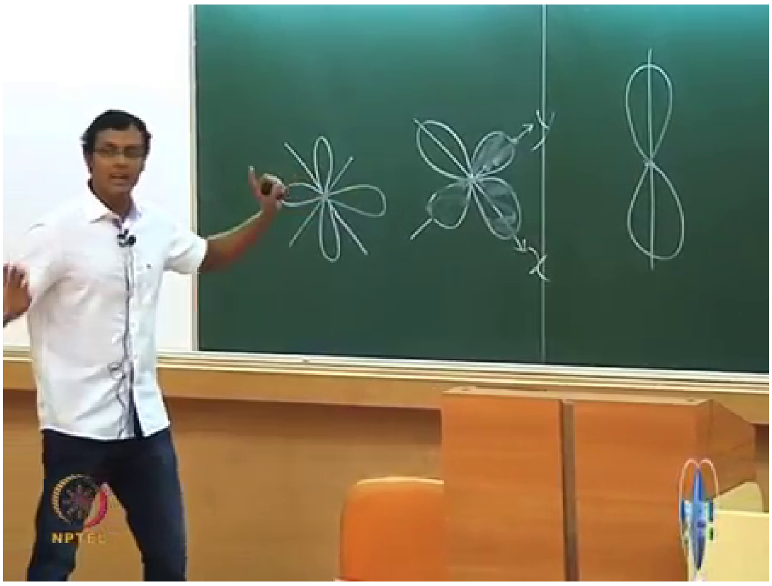

So, this is z axis center, the lobes are here; this is d z. Now, if you look and say that this is let us say x and this is y; d x 2 y 2 is going to be here, right. So and d x y is going to be, so this is y axis, this is x axis; right on top of y axis sorry, will come to that. So, it is going to be like that, ok. Now, you have to ensure, you have seen it before you have to be really really clear about the they are positioning. I think we will come to that, let me tell show you where they are over here, no will come back in a moment.

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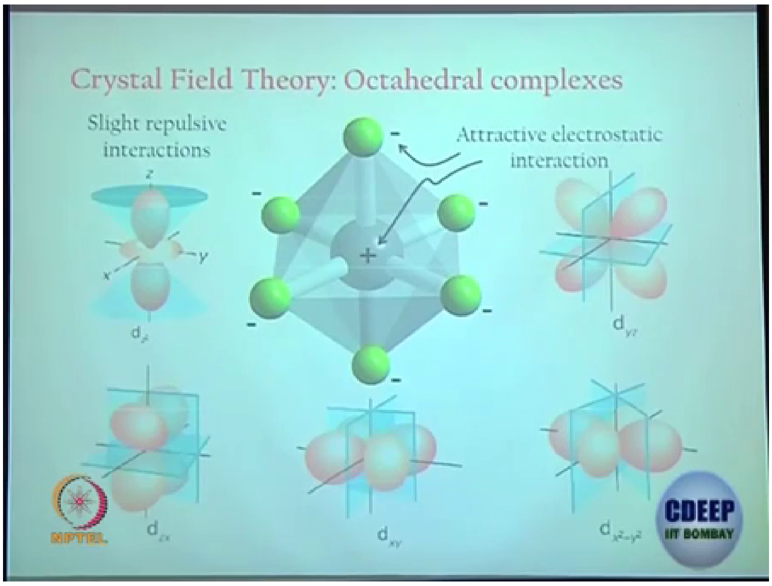

Crystal Field Theory: Octahedral complexes

Slight repulsive interactions

Attractive electrostatic interaction

Let me tell you. So, what crystal field theory assumptions are, is very simply these are electrostatic interaction; it is a metal center is a cation, ligand is an anion, most often so it is a cation-anion interaction or electrostatic interaction, ion-ion interaction or ion dipole interaction. Previously we are thinking just about the covalent interaction, right. Now if you are thinking should metal, about metal; metal has electrons if you are bringing ligand, ligand has electrons.

So, these ligand and electrons and metal electrons are going to repel each other; they are going to, they are electrons same charge, right. Although metal is positive, ligand is negative let us say or neutral or whatever it is; but if you bring them together, those electrons of the ligand and electrons of the metal they are going to repel each other; so, there by the energy of the total system going to be increased.

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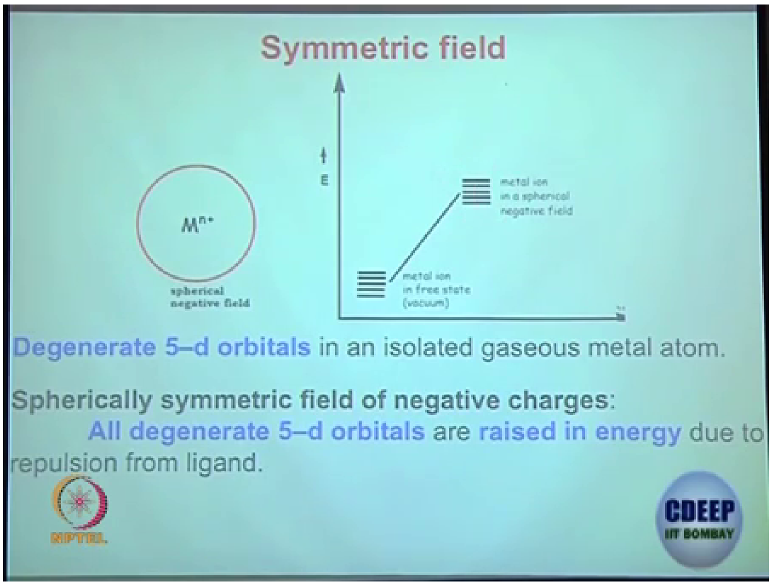

Symmetric field

Degenerate 5–d orbitals in an isolated gaseous metal atom.

Spherically symmetric field of negative charges:
All degenerate 5–d orbitals are **raised in energy** due to repulsion from ligand.

If d level energies are for example, over here; if you bring the ligand from the equal distance or from the all distance or all direction equally, then also the energy of the d orbitals will go up. It is a spherical, let us say cricket ball; you are going to put the pressure on cricket ball from all directions, cricket ball is going to be destabilized ball. In this case ligand approaching ligand is going to make cricket ball destabilized, ok.

Now this is under ideal situation, where is all the ligands let us say are coming from every distances or every directions, all the distance all the directions. Now in reality what you have seen is, ligands are not there from every directions, it is specific; ligand is here, here, here, here, here and here. Only few direction, this is the direction for z axis.

Let us say this is the z axis, this is the let us say whatever y axis, this is x axis, right. So, ligands are going to approach the metal center only from a specific direction, not from here; it is just along this direction not from here, not from here, not from there, it is a specific direction.

Now, these are the directions where the metal orbitals are there, there you have d z 2, there you have d x y; this is the one where you have d x y. So, eventually what you will see is I will show you, since ligands are coming from this direction directly those orbital d z 2 and d x 2 y 2 orbitals are going to be repelled very much; means there they are going to be unstable, they are going to be high in energy.

So, over here 5 d orbitals are there, since ligands are coming specifically from z or towards z axis, y and x axis any orbital that is facing those axis directly they are going to find the consequences; that means, they are going to have the energy increased, their energies will be increased. Any other orbital for example, d x y which is over here in the middle, they are going to be perturbed, but not too much.

In reality with respect to this one they are going to be stabilized; because this is the total stabilization,, with respect to that something is going to be destabilized something is going to be stabilized. Now let us look back, all the orbital if you look back one more time very carefully; this is the d z 2, anyone has anything to say please speak out.

Now, d z 2 orbital, d x 2 y 2 orbital and you can see all these orbital ok. Right now also if it is not clear you look back at the note I am sure it will be very very clear, the pictures are very clean.

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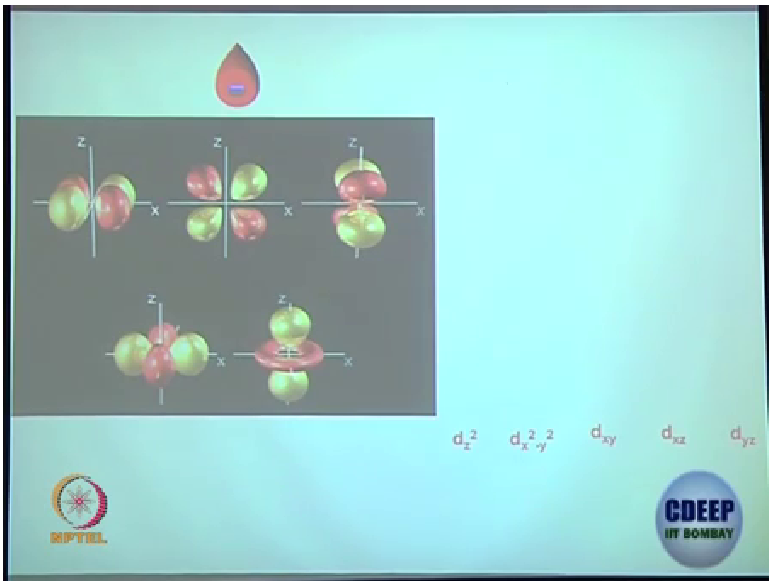

Now as we are saying, that plus and minus attracts an electrostatic attraction will be there. Now, two of these orbital which is d x 2 y 2 and d g 2 or d z 2 these are the orbital; let us say all these orbitals are there, these are the ones which will be facing the ligand directly like this.

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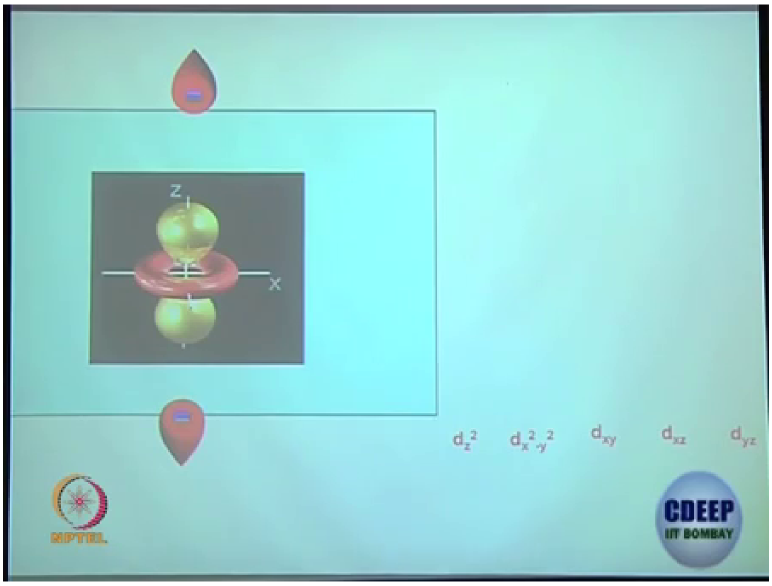

So, ligands will be coming directly from two different angle or from two different direction for d z 2. So, d z square orbital will be high in energy, right. It was previously it was all of them are same and are having same energy or so called degeneracy; 5 d orbital where degenerate that is so far you have mostly learned of course, you may have learned this one as well. But since you see that there is a discrimination, there is a preferential attack, you are going to get it destabilized; because they are going to interact directly.

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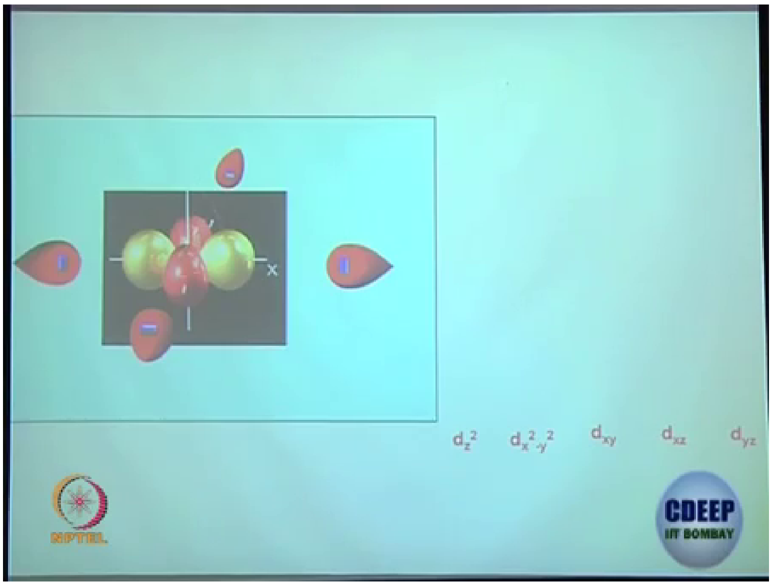

d_{z^2} $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}

Now if you look at the d x 2 y 2, this is the d x 2 y 2 orbital and four of the ligands are coming from this direction exactly; of course, this is going to be also destabilized.

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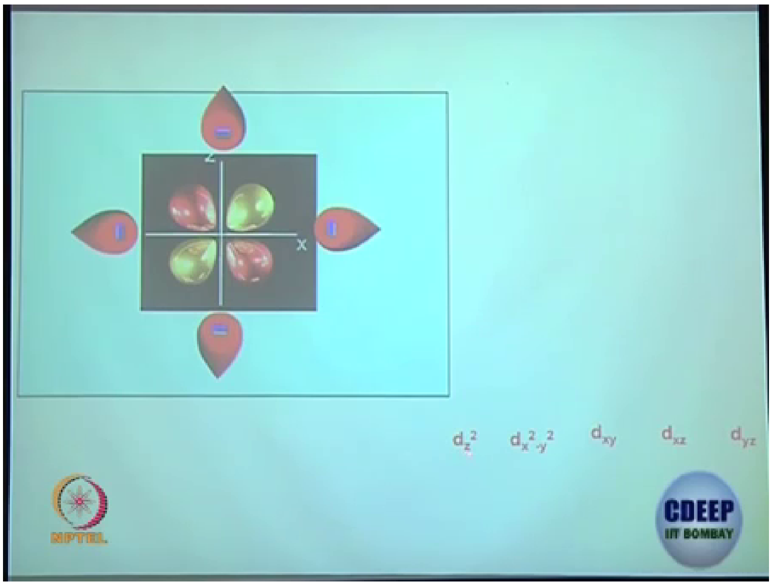

So, what do you have learned so far is d g d g 2 and d x 2 y 2 are going to be destabilized. But, if you are looking at let us say this is d x z orbital ok, x axis and z axis; d x z orbital and the ligands are approaching right actually from the middle, not directly towards these lobes.

So, their energy will not be overall destabilize, because we have already destabilized by bringing the ligand; comparatively they are going to be stabilized, that is how the ligands are coming right sorry that is how they are coming in. So, they are not fitting the bill right on top of each other, they are just you know squeezing in, not head on a collision. Now so, d x z will be stabilized; d x y, d y z is the same scenario, it is just different axis.

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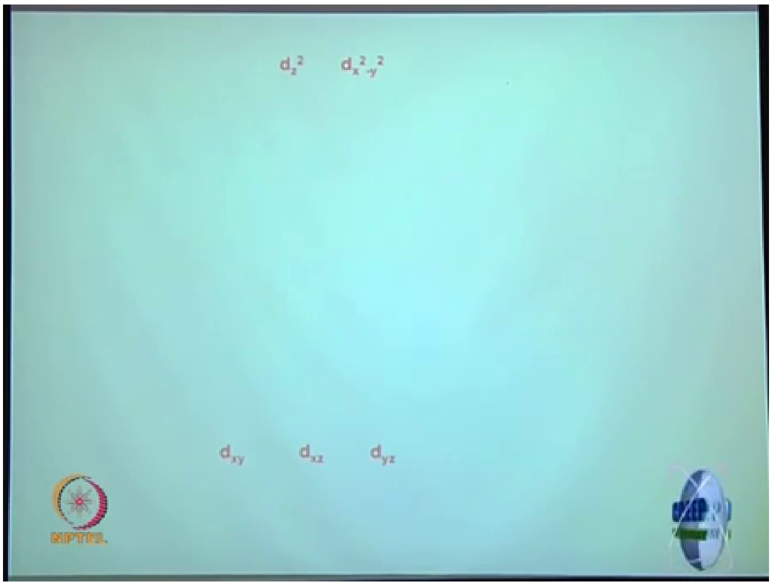

So, overall we see that it is split in to like this; two of them getting destabilized, three of them getting stabilized. Stabilized means stabilized with respect to where it started, not in the free ion over here. This is a free metal ion, with respect to free metal ion when you have a metal complex formation.

It is all the d orbitals are going to be net destabilization will be there, their energy is going to be high; with respect to these some of them will be destabilized, some of them will be stabilized, but the net destabilization is going to be this much. If you have a free metal ion it is stable; the moment you put ligand in it, it is going to be unstable or destabilized, with respect to that destabilization ok. So, that is how it is going to be.

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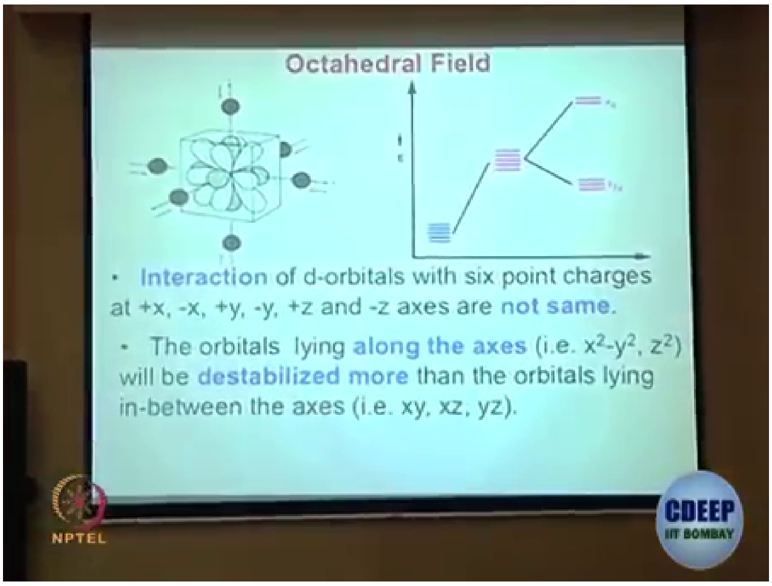

Octahedral Field

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

But with respect to free metal ion of course, they are destabilized. Now, this is what is octahedral field is all about, you see octahedral complex; 6 ligands are there, surrounding the metal center, 5 d orbitals getting destabilized and further splitted, this is no longer degenerate of the same energy, right.

Now, this is also another way to look at it; 2 ligands and these black balls are ligands and how they are coming. And all the d orbitals are superimposed over here you can see which are facing what. Now this is for octahedral field this is called e g orbital e g orbital and this is t 2 g orbital, three of them. So, e g is d x 2 y 2, d z 2 and t 2 g is d y z, d x z, d x y ok; so three of them and two of them.

Now the extent to which with respect, this is called barycenter where the 0 is ok; with respect to that the destabilization will be the same amount compared to the stabilization. Why it seems like unsymmetrical? Because there are three orbitals, so 6 electrons can be filled, 6 electron versus 4 electrons; so 4 time destabilization and 6 time stabilization. So, it is a there is a factor, this distance from the barycenter this distance is 0.6, this is 0.4; from the middle this is 0.6 and 0.4.

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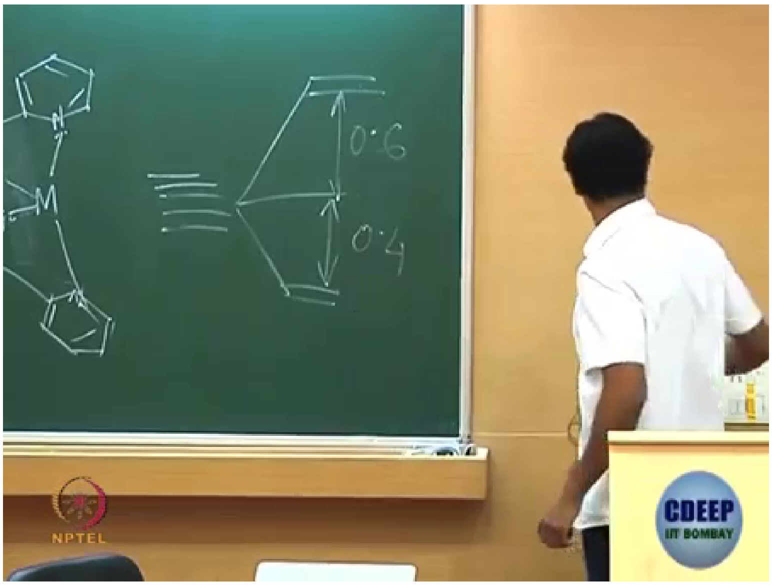

So, from here this is going to be 0.6, this is going to be 0.4 ok. I should have stabilized, I should have switch off this one; 0.6, 0.4 ok, we will come to that again.

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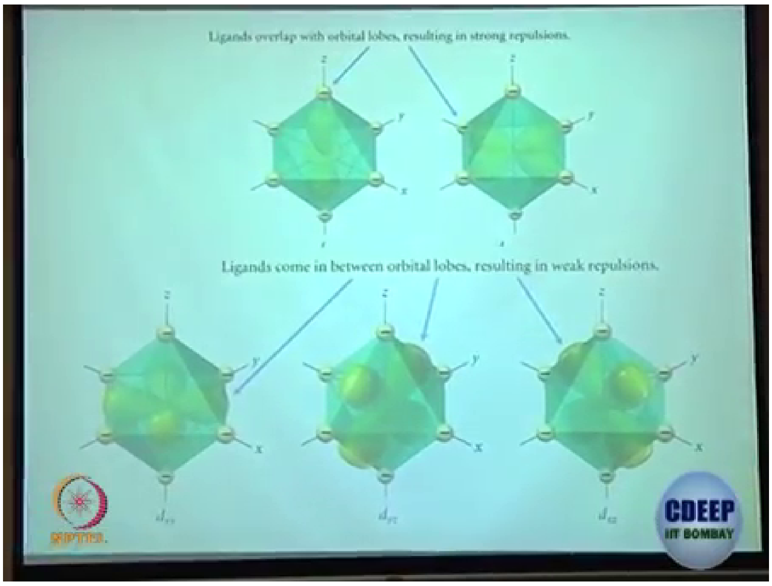

Ligands overlap with orbital lobes, resulting in strong repulsions.

Ligands come in between orbital lobes, resulting in weak repulsions.

Now, some more information's are given which you can read very clearly, I will not dwell too much on that; stabilized one, destabilized one. This is also another way of looking at this the same thing exactly same thing, you may not be able to see it clearly from here, but in slide it will be clear d z 2, d x 2 y 2 and the three two orbitals and three different orbitals in the compound form or in how they interact.

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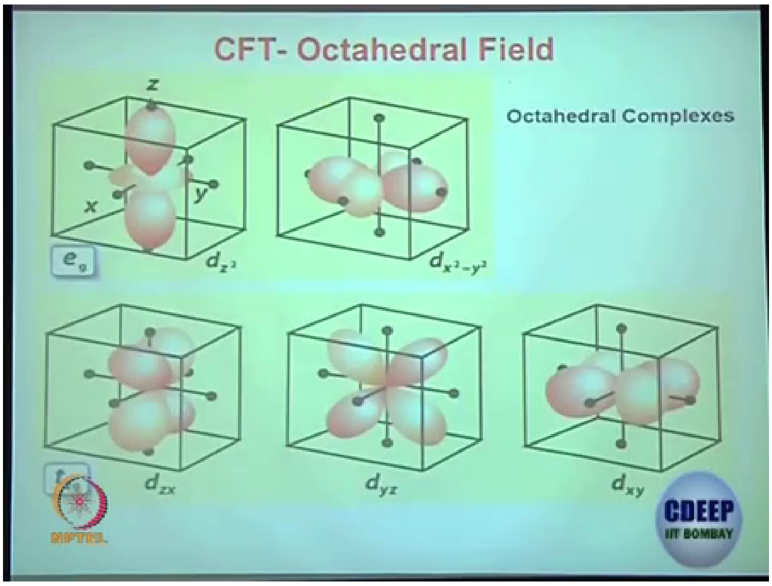
CFT- Octahedral Field

Octahedral Complexes

Further it is much better I think this is the last slide hopefully on that. You see z d z square and d x 2 y 2 d z x, d y z, d x y; same thing how the ligand is coming. See when you take the printout of these things, if you take the same printout I do not mind; but the information is not different. But once you are seeing in the computer for example, you will be able to see it clearly what exactly we try to say; that will give you a crystal clear picture hopefully, what is going on in here.

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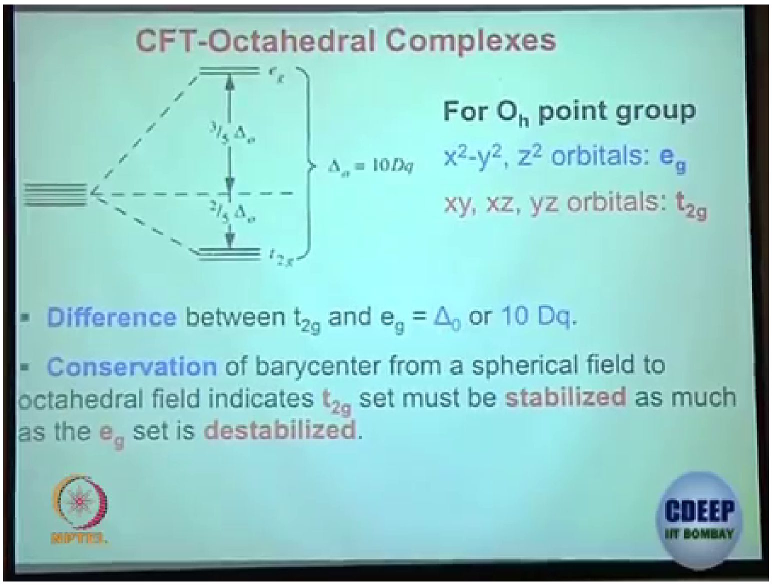

CFT-Octahedral Complexes

For O_h point group

x^2-y^2, z^2 orbitals: e_g

xy, xz, yz orbitals: t_{2g}

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

So, once again I will take the break in a moment, this is that 3 5 of the total distance is called delta 0 or 10 D q. This is going to be your 6 D q, this is 4 D q or so to speak 3 5 delta 0, 2 5 delta 0. This is something you need to remember, the total is called 10 D q, 4 D q and 6 D q; 0.4 and 0.6, 4 D q, 6 D q ok.

If it is delta 0 you are saying this is going to be 0.4 delta 0, this is going to be 0.6 delta 0 and these are the easy t 2 g we will be calling; the difference between them is delta 0 10 D q so on so forth. Anyway, so let us continue over here; what we see, this is the total 10 D q we are saying, what is D q it will be clear soon enough. Or this is the delta 0, the distance between this t 2 g and e g or the energy difference between these two; some of them are destabilized, some of them are stabilized.

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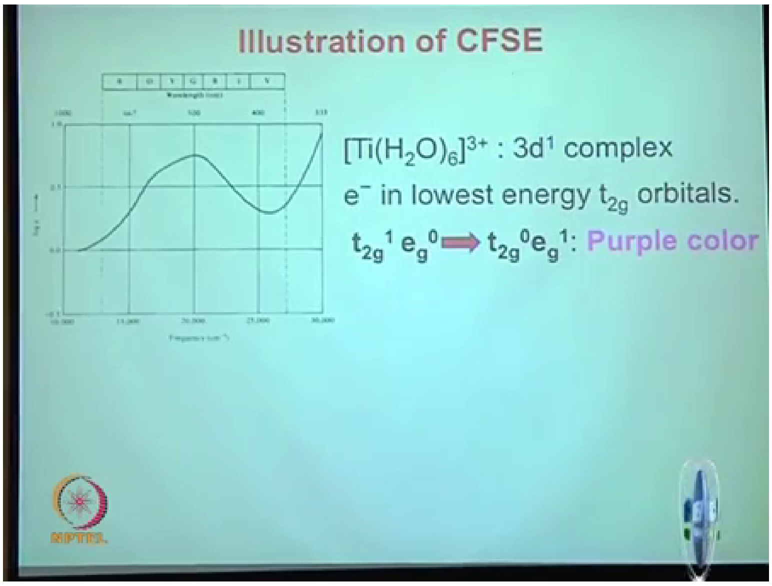

Illustration of CFSE

$[Ti(H_2O)_6]^{3+}$: $3d^1$ complex

e^- in lowest energy t_{2g} orbitals.

$t_{2g}^1 e_g^0 \Rightarrow t_{2g}^0 e_g^1$: Purple color

Let us say let us take some little more practical example; you have a titanium hexa aqua complex with 3 plus scandanium titanium scandium titanium, . It is d 2 x 2, it is going to be d 1 then after 3 plus. So, 3 d 1; so that means, no longer we will be saying it 3 d 1, we are going to say it t 2 g 1 e g 0.

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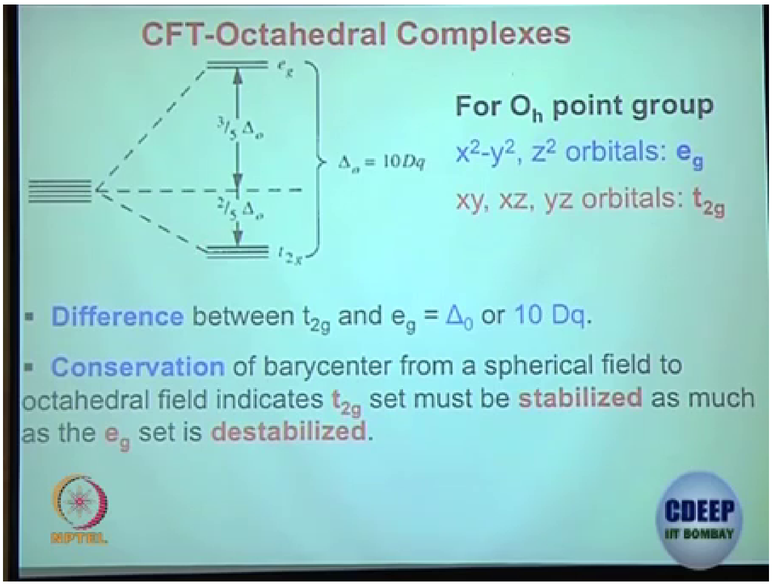

CFT-Octahedral Complexes

For O_h point group

x^2-y^2, z^2 orbitals: e_g

xy, xz, yz orbitals: t_{2g}

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

Because, if you see the filling up of the electron, now it is going to happen the one which is stabilized first and then either over here or back to here. So, the filling of electrons you are trying to see, no longer will be calling it d 1; it has to be defined as t 2 g what, e g what. Let us say t 2 g 5 e g 0, t 2 g 3 e g 2, t 2 g 4 e g 2 or t 2 g 6. So, how we are going to do that, this is what we are going to discuss.

So, in other words whether all the, let us say you have 6 electrons, 6 electrons if you are having, each of them are one orbital; therefore, technically you can have 6 of them over here or 3 of them over here, 2 of them over here and another over here, 4 plus 2, you can say 6 plus 0 or whatever other permutation combination you want to have. What order these d orbitals will be filled, that is what we are going to discuss.

The answer to that question is very simply, it will depend on that ligand; that is why it is also called ligand field stabilization energy. Ligand, if it is a strong ligand, what is a strong ligand let us say I will come back to that again; if it is a let us say cyanide, cyanide is a strong ligand, ok.

Aqua water, water let us say for example usually a weaker ligand or it is all relative again, there is a spectrochemical series will bring; that will tell what is strong ligand, what is weak ligand. Fluoride may be a weak ligand, so chloride may be weak ligand, C O may be a strong ligand so on.

So, depending on the difference this energy a is having, like how much difference is there between t 2 g and e g, it is this much or that much. If it is this much difference, then electrons will be occupied all t 2 g and e g; because you know that Hund's maximum principle that spin has to be maximum and shown. But if it is this one, that Hund's will may not be there applicable here; because you know it is very big the putting electron in this orbital, e g orbital is going to cost you too much of energy.

Of course another problem is the pairing, for if you want to pair up, pair up pairing energy is also there. If you want to pair up over here, some energy you have to give whether pairing energy is high or the distance or the energy difference between these t 2 g e g in is high; that you need to kind of know. You know, you do not need to memorize, we are going to tell you what is the scenario, ok.

So, we need to know what is the ligand, what usually is the pairing energy, what is the oxidation state of the metal that also varies; higher the oxidation state you will see the splitting will be high this t 2 g e g gap will be high, 3 d to 5 d gap will be increasing, 2 plus 2 5 plus gap will be increasing. Therefore, if the gap is increasing, pairing become easy; because you know it cannot go to much, if it is gap is too much. If gap is low, then pairing will not occur; it will be both in t 2 g and e g, if this is e g, this is t 2 g, that is what we are going to see now. I am kind of summarized over here.

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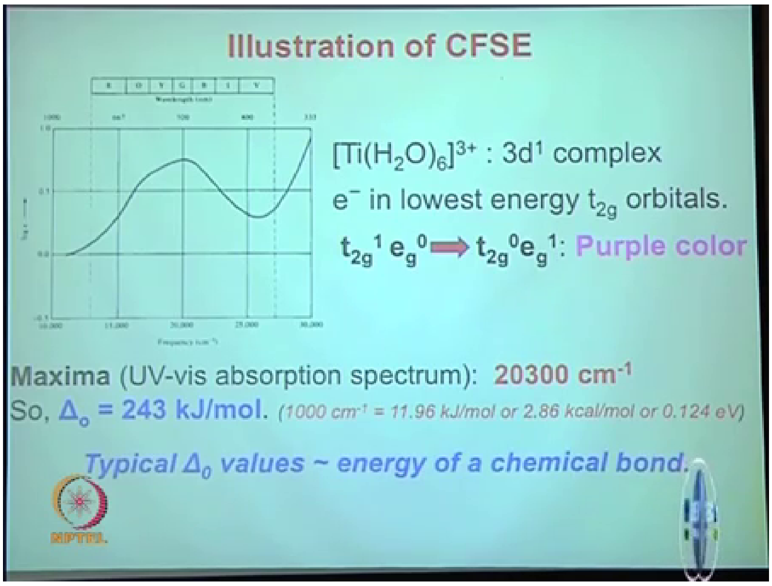

Illustration of CFSE

$[Ti(H_2O)_6]^{3+}$: $3d^1$ complex

e^- in lowest energy t_{2g} orbitals.

$t_{2g}{}^1 e_g{}^0 \Rightarrow t_{2g}{}^0 e_g{}^1$: Purple color

Maxima (UV-vis absorption spectrum): **20300 cm^{-1}**

So, **Δ_o = 243 kJ/mol.** *(1000 cm^{-1} = 11.96 kJ/mol or 2.86 kcal/mol or 0.124 eV)*

Typical Δ_0 values ~ energy of a chemical bond.

It is going to be t 2 g 1 e g 0, now everything you have to explain or you have to write in this format. Why we see purple color in this titanium hexa aqua complex, why do you see purple color; it is like this, the UV vis maximum, the absorption is going to be this 20300 or 20300 wave number. So, that is actually the gap between the t 2 g and e g we will show

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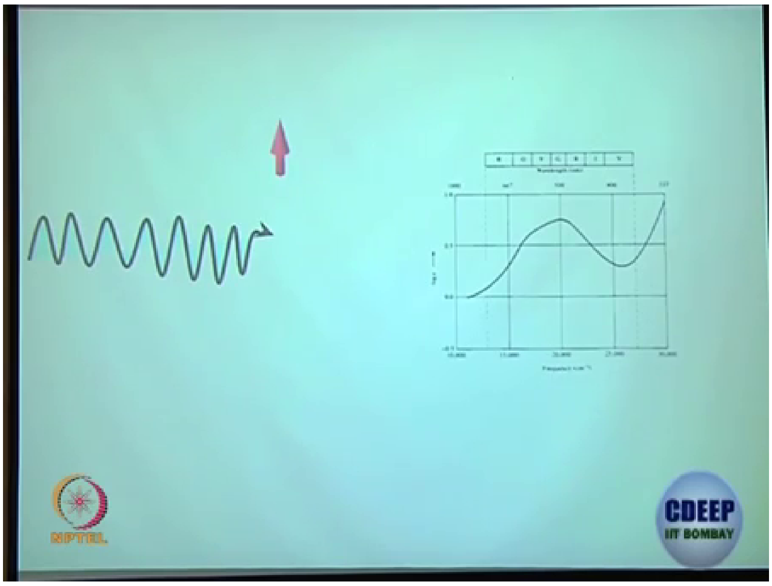

So, let us say this is your t 2 g electron and you put the energy, the light it is going to convert from t 2 g level to e g level and that is where you see the in terms it comes out that absorption energy, where it absorbs. That means, how much energy you have given to bring let us say t 2 g electron, one electron from here to here; that is what nothing but you see as absorption. The peak you see or you have a metal complex you shine light, you want to see the electronic transition from one level to other.

It could be let us say some time t 2 g, t 2 g or it could be usually the for one to see you have to have t 2 g to e g the conversion. From t 2 g orbital any of them because they are degenerate to over here; that is the energy you need and that is going to be your absorption energy. And depending on that how much energy you absorb, as we say why the color different color comes, how much energy is required based on that or what wave number is required based on that you will be able to see the color. So, you give them quite light simple light, we end up seeing some color based on what is being absorbed and what is being emitted or indirectly what is being emitted.

So, for t 2 g this titanium hexa aqua complex, we see that this is the UV-vis absorption, this is nothing but this transition from t 2 g to e g level and that is how the speak is coming ok; that is the absorption, that is happening from for transferring t 2 g electron to e g electron. Of course, there could be multiple transition, there could be multiple if it is a simple electron system, one electron system.

If you have 2 electron systems, 3 electron, 4 electron, 5 electron and so on and based on the electronic configuration you can have multiple transition; therefore, your peak could be like 3, 4 peaks or I mean your spectrum could be having 3, 4 peaks or different region, different things can happen. So, simply speaking some sort of transition has to occur. In d orbital itself 5 of them are degenerate, you are not going to explain; that is why you cannot explain color by crystal by valence bond theory.

But crystal field theory you an idea of where the origin of the color is, this is nothing but transition of one sub level to another one, right. So, this is where crystal field theory becomes superior compared to your valence bond theory. Valence bond theory what you have done, d 2 s p 3 or s p 3 d 2 whatever s p 3 and so on, there you cannot explain where the color is coming from, enough.

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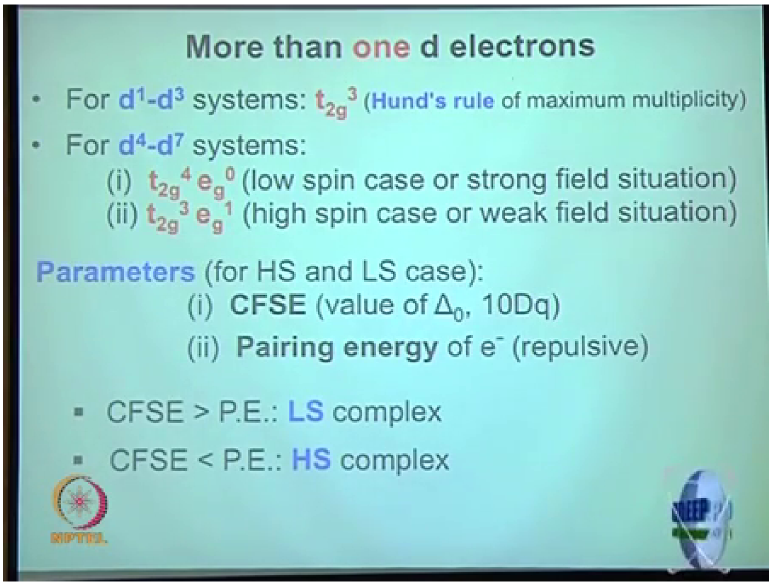

More than one d electrons

- For d^1-d^3 systems: t_{2g}^3 (**Hund's rule** of maximum multiplicity)
- For d^4-d^7 systems:
  - (i) $t_{2g}^4\ e_g^0$ (low spin case or strong field situation)
  - (ii) $t_{2g}^3\ e_g^1$ (high spin case or weak field situation)

Parameters (for HS and LS case):

(i) **CFSE** (value of Δ_0, 10Dq)

(ii) **Pairing energy** of e^- (repulsive)

- CFSE > P.E.: **LS** complex
- CFSE < P.E.: **HS** complex

Now, of course, as I said there are scenario where you can have more than one electrons, right. So, d 1 to d 3, so of course, Hund's rule will be promoted now for 4 electrons; you can have t 2 g 4 e g 0, t 2 g can have total up to 6 electron or you can have t 2 g 3 e g 1, three of them are going to be filled out, after filling out the fourth one will be the e g 1 e g, right. Now, I will come to come with that with more pictorial diagram, I think I will skip that.

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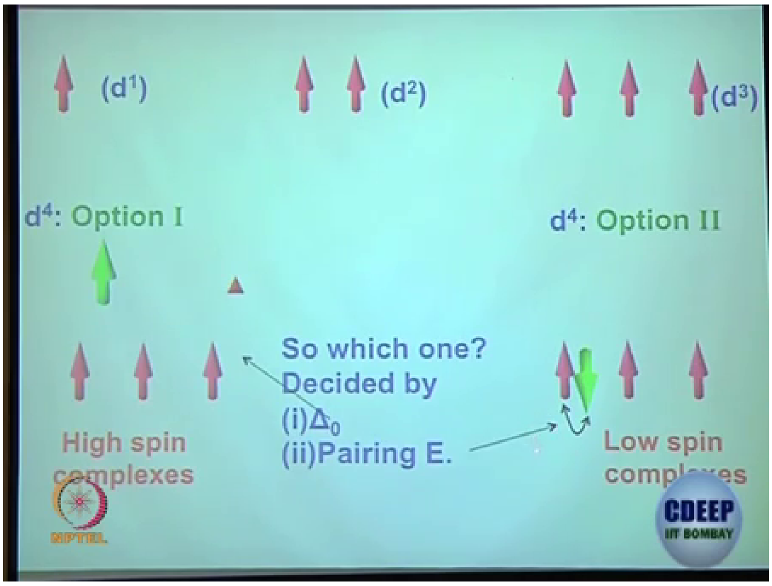

(d^1) (d^2) (d^3)

d^4: Option I

d^4: Option II

So which one?
Decided by
(i)Δ_0
(ii)Pairing E.

High spin complexes

Low spin complexes

Now, this is what it is. So, t 2 g orbital 1 electron, t 2 g orbital 2 electrons, t 2 g orbital 3 electron; there is no story of e g, because e g is high in energy, why it will go to high in energy. After d 3 then you have dilemma, then you have problem; whether you send it to e g or you pair it up with t 2 g. So, there are two scenarios; high spin complex we will have t 2 g 3 e g 1 d 4 option I; option II will be t 2 g 4 e g 0.

This is t 2 g, this is e g, e g over here nothing in there. So, you have low spin complex, this is high spin complex because 4 unpaired spins are there here, you have 2 unpaired spin. So, up to d 1, d 2, d 3 you do not have to worry at all; you just put t 2 g 1, t 2 g 2, t 2 g 3. After that whether it is t 2 g 4 e g 0, t 2 g 4 e g 0 or t 2 g 3 e g 1 which one is going to be predominant or which was going to be happening; that will be determined by ligand metal, which metal it is for d orbital they are having what is their oxidation state.

All this factor will put together will determine whether it is going to be a high spin complex or low spin complex. It is not complicated at all just go through simply I will try to explain when, what you can expect; you do not have to remember again, you do not have to remember what will be the delta 0 and what then what will happen that is that sort of memorization is not required, ok.

So, in the other word, if delta 0 or the 10 D q value we were talking, difference between t 2 g and e g if this is small, then you will see t 2 g 3 e g; if that difference is small, the spin will try to be maximum or you know electronic spin will be maximum. So, t 2 g 3 e g 1 will be happening if delta 0 is small; for this to happen, t 2 g 4 to happen you have to pair these two electrons, right. That means, you are dealing with pairing energy; if pairing energy is favored, if pairing energy is less compared to this delta 0, then you are going to have this low spin configuration, ok.

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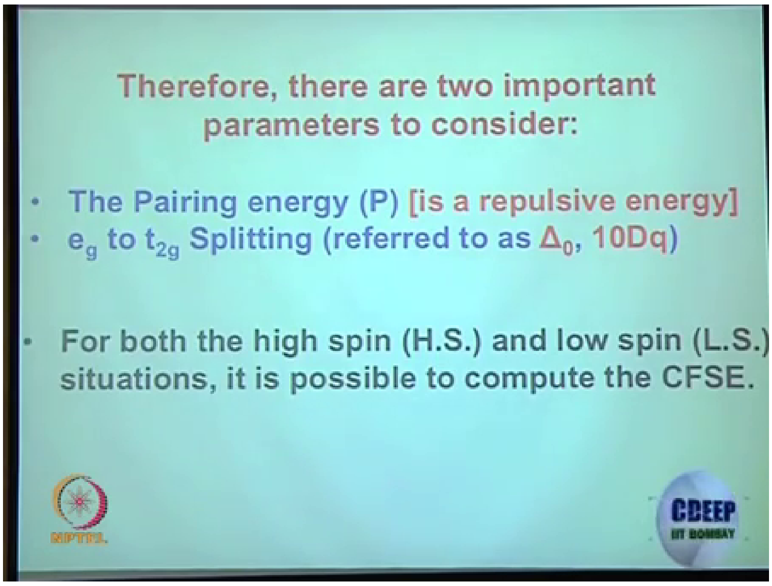

Therefore, there are two important parameters to consider:

- The Pairing energy (P) [is a repulsive energy]
- e_g to t_{2g} Splitting (referred to as Δ_0, 10Dq)

- For both the high spin (H.S.) and low spin (L.S.) situations, it is possible to compute the CFSE.

Now of course, lot of things I have given written the same thing again and again written; but essentially once it is clear to you, you do not have to read this slide too much ok, I think we have explained already.

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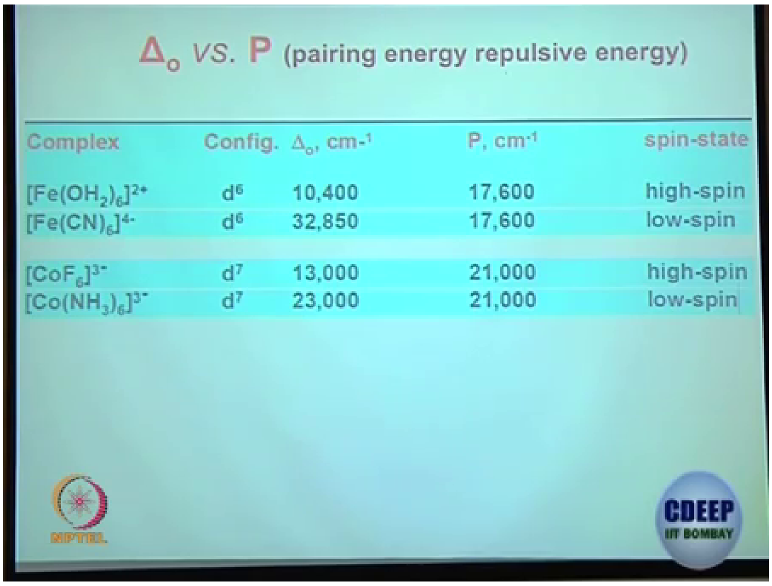

Δ_o vs. P (pairing energy repulsive energy)

Complex	Config.	Δ_o, cm^{-1}	P, cm^{-1}	spin-state
$[Fe(OH_2)_6]^{2+}$	d^6	10,400	17,600	high-spin
$[Fe(CN)_6]^{4-}$	d^6	32,850	17,600	low-spin
$[CoF_6]^{3-}$	d^7	13,000	21,000	high-spin
$[Co(NH_3)_6]^{3-}$	d^7	23,000	21,000	low-spin

Now I will just give you a phenomenon. So, what we again what we have said, up to d 3 you do not have to worry it is going to be t 2 g 1 t 2 g 2 t 2 g 3. After d 4 you have to decide, that again let us say at d 8 you do not have to worry it is going to be t 2 g 6 e g 2; 1 2 3 4 5 6 7 8 whatever way you want to fill out, d 8 d 9 d 10 you do not have to worry. It is going to be only one configuration possible, because your goal is to minimize the energy without compromising the spin.

Of course, Hund's rule says the spins should be maximum, right. You try to do that, but while you are trying to do that you have to also mind the gap, distance between t 2 g e g; whether it is going to be unpaired spin or paired spin. After filling t 2 g you have to from 4 5 6 really the one cases where at 7 as well; 4 5 6 7 you have to worry about whether it is going to be high spin or low spin, up to 3 it is going to be always high spin, there is no low spin scenario almost, right

And after 8 8 9 10 it is always one configuration, 4 5 6 7 it is going to be high spin and low spin that is what you are going to use; high spin means spin is maximum, low spin is spin it is minimized with the given situation. ok. Now something like these complexes, if you see some easy complex like very soothing for the eyes those are going to be high spin; like iron aqua very easy complex looks like water molecule iron is there, 3 2 plus 2 plus mind you easy complex, the difficult complex could be 3 plus means which is more higher charge.

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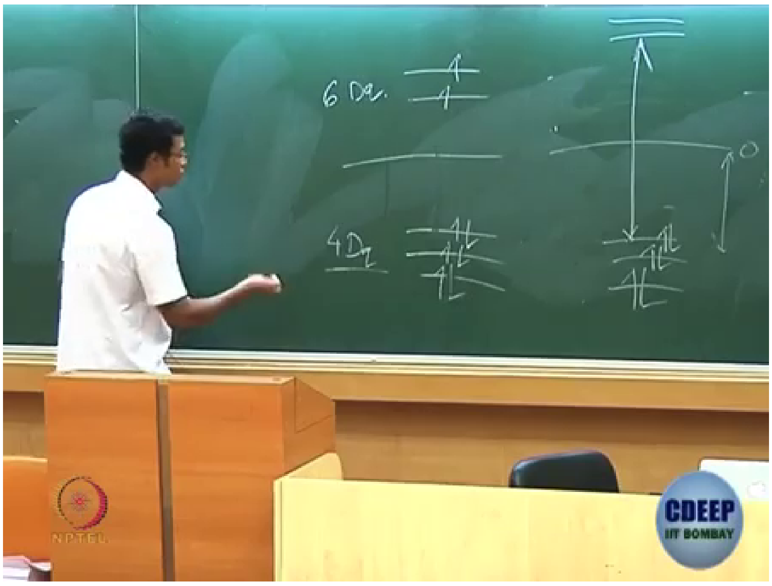

Now this is going to be high spin over here, because the delta 0 you see is this much, pairing energy is high; pairing energy high means you are not going to get it paired, you are going to have the unpaired spin, right. Now iron hexa cyanide, we are all talking about the octahedral complex do not forget that; 6 ligands are there, we did not talk about tetrahedral as of yet. So, 6 of them this is going to be a strong ligand, cyanide is a strong ligand; that means, the gap between t 2 g and e g is very very high ok, this will be d 6 right. So, those 6 will electrons will be t 2 g 6 not t 2 g 4 e g 2, I think some of them are some of you are having a little bit dizziness let us see try to explain in the board.

What we are having let us say d 6, this is t 2 g 3 3 of t 2 g and 2 of e g; you can have this as one scenario right, other scenario is nothing here all paired up, right. So, this is t 2 g 4 e g 2, this is a high spin situation that is what is happening in iron hexa aqua complex 2 plus. Now, iron cyanide 6 F e C N 6 hexa cyanide ok, 4 minus; now you have d 6 total electron, right.

Now of course, how it is it is iron 2 plus, this is also iron 2 plus both of them are iron 2 plus; iron 2 plus that is why it is 2 plus, iron 2 plus 6 minus that is why it is 4 minus outside right. Or both of them are d 6 electronic configuration only thing that is differing is the ligand; metal is in the same oxidation state, hexa coordinated, ligands are different. What you are seeing here is the distribution of electrons are different; the first one will have this electronic distribution, second one is going to have this electronic distribution.

Because let us say, so to speak the difference between these two guy is high, distance this difference is very large. If you look at, this delta 0 or 10 D q is this much pairing energy is less. So, thereby it will pair up very easily, it will electron cannot go and jump over there. In this case the pairing energy is high, but delta 0 is small, so it is going to be, it is going to follow your Hund's rule ok. Or I mean of course, it is always following Hund's rule, sometimes there is no option when there is no option you are going to end up getting that configuration.

This is usually speaking, most of the cases I think high spin will be preferred; of course, most of the cases is a wrong statement, but it is a ligand dependent, metal dependent. But lot of things that we see in the you know in the regular books usual books, those are going to be high spin species; unless it is high oxidation state of the metal and strong ligand it is not going to be low spin. If it is high oxidation state let us say iron 4 plus or you know some high oxidation state and ligand is strong ligand, then you are going to see low spin; because this t 2 g and e g splitting is going to be high, ok.

Now, next one cobalt F 6, cobalt is here 3 plus 6 of the fluoride 3 minus total d 7 configuration cobalt is d 7 s 2, iron cobalt yeah. And then if it is iron cobalt nickel d 7 s 2 it is 3 plus, right; I think something is wrong there, is it not.

It should be d 6, right

Student: Yes.

Let us assume that this is d 7, but discharged are wrong ok; cobalt is d 7 h 2, so 9 electrons if 3 are taken. So, 2 are taken then it is, let us say this is going to be your 4 minus ok; the charge is down here, I do not know how come. So, anyway it is a d 7 system both of them are d 7 system ignore the charge, just take my order, ignore the charge d 7 system d 7 system; one is high spin another is low spin. It is also to tell you sometime you see that ammonia complex is going to be low spin sometime it is high spin; again that depends on the metal center, I will give you a summary ok.

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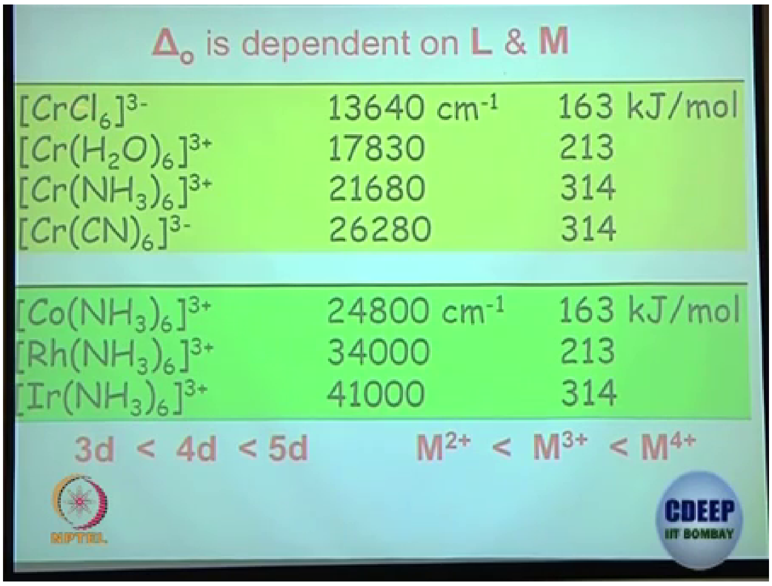

Δ_o is dependent on **L** & **M**

$[CrCl_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[Cr(H_2O)_6]^{3+}$	17830	213
$[Cr(NH_3)_6]^{3+}$	21680	314
$[Cr(CN)_6]^{3-}$	26280	314
$[Co(NH_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[Rh(NH_3)_6]^{3+}$	34000	213
$[Ir(NH_3)_6]^{3+}$	41000	314

3d < 4d < 5d $M^{2+} < M^{3+} < M^{4+}$

Let me give you the summary, the delta 0 will be increasing in this order 3 d, 4 d, 5 d; 5 d will be highest. Higher oxidation state will give you the higher delta 0. Now over here you see with the chromium, chloride aqua ammonium cyanide the energy between t 2 g and e g how they are differing.

So, you can say that this is a weaker ligand, this is little bit stronger, this is more stronger, this is the strongest in this series. So, the difference between t 2 g and e g can tell you what is the strength of these ligands are ok. Depending, keeping the metal constant oxidation state constant you are changing ligand and you are saying that the splitting you are varying, so that will indirectly measure the strength of the ligand, ok.

Now over here you are keeping ligand constant, oxidation state constant, everything constant, but you are changing the metal center; cobalt rhodium idiom in the periodic table look at, now you see how they are increasing. So, the overall trend is 3 d splitting with the least then 4 d then 5 d, metal oxidation state will also vary that is also over here.

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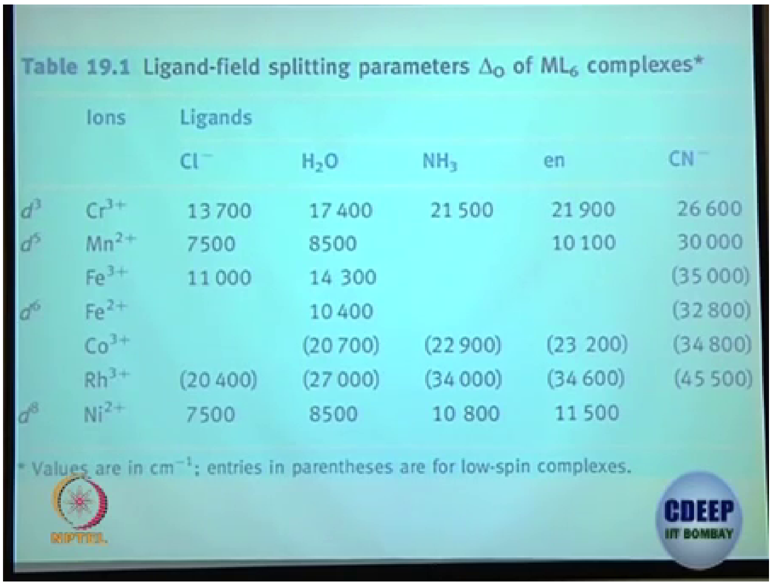

Table 19.1 Ligand-field splitting parameters Δ_O of ML_6 complexes*

	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13 700	17 400	21 500	21 900	26 600
d^5	Mn^{2+}	7500	8500		10 100	30 000
	Fe^{3+}	11 000	14 300			(35 000)
d^6	Fe^{2+}		10 400			(32 800)
	Co^{3+}		(20 700)	(22 900)	(23 200)	(34 800)
	Rh^{3+}	(20 400)	(27 000)	(34 000)	(34 600)	(45 500)
d^8	Ni^{2+}	7500	8500	10 800	11 500	

* Values are in cm^{-1}; entries in parentheses are for low-spin complexes.

All these things summarized together I will tell you what is summarized to, this is what it summarized to. You can take a series of compound, just vary one thing; either ligand you vary or metal you vary, you keep on doing, you come to a conclusion that 5 d will have higher splitting then 4 d and 3 d and higher oxidation state will have higher splitting.

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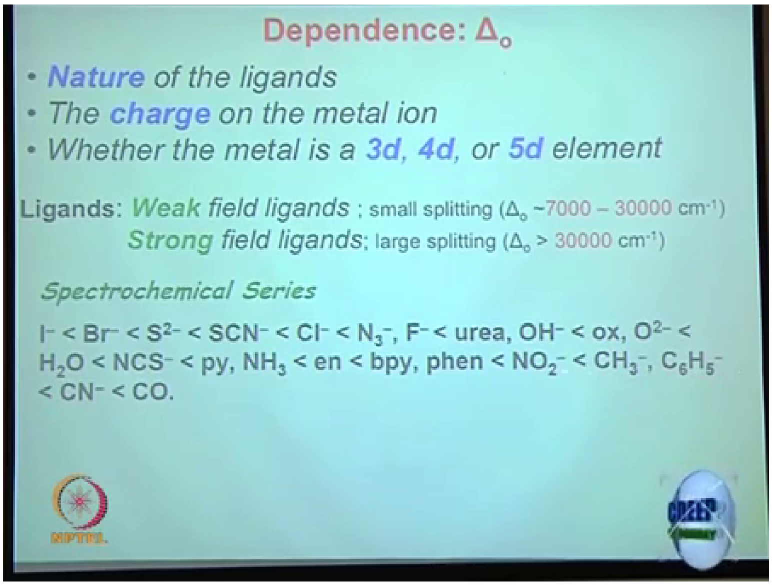

Dependence: Δ_o

- *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 cm^{-1})
Strong field ligands; large splitting (Δ_o > 30000 cm^{-1})

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO$.

Now, there is something called electrochemical series, this is what is electrochemical series; this is the strongest ligand then this one, then that, that, that. So, the idea here is, if you have a high oxidation state and strong ligand you are definitely going to get a low spin complex. High oxidation state splitting will be high, strong ligand splitting will be high, so low spin complex; means it is the splitting which is going to be high, so then electron cannot jump to the e g. So, it is going to be low spin; spin will be minimize, it will stay in t 2 g.

Now, you can think about the different permutation combination that is why it is not that very easy to say what is going to happen, unless you give the exact combination. So, the strong field ligand they will tend to give you high delta g or delta 0 right; t 2 g e g separation will be high therefore, it will give you a lower spin complex. Strong field ligand will tend give you a low spin complex; but that does not mean that any metal you take you will always get low spin with let us say cyanode or you know these any of the alkyl or nitrite.

You have to of course, you have to you also have learned that 5 d will have more splitting than 4 d and 3 d; higher oxidation state will have more splitting than lower oxidation state. So, it is a combination of all these three factors, where the ligand is in terms of spectro electrochemical spectrochemical series not spectral, spectrochemical series. When the ligand is whether it is strong field; this is the strong field, these are the weak field, where it is and then what is the oxidation state of the metal and what orbital metal is having ok.

If everything strong, strong, strong, then you are going to get high splitting, low spin. If it is very small you are invariably going to get high spin ok. You just read through little bit first the slide, look at the slide and then go through the books I hope it will be clear. Now, it is summarized in here once again and this is the summarize for this ligand.

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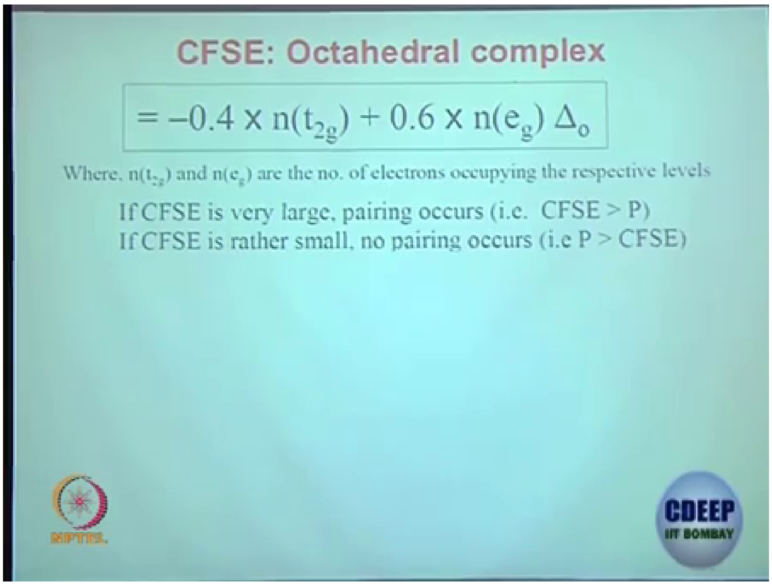

CFSE: Octahedral complex

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

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

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

So, overall after having these you should be able to calculate the crystal field stabilization energy; how much with respect to that 0, how much stabilize or destabilize it is. So, over here each of the electron over here I said it is 4 D q right, 4 D q and this is 6 D q. So, you can see that three of them, let us say if you have three of them 4 this is 4 D q, 4 times 3 will be 12 and 2 times 6 will be this is 6 D q this is also 12. So, 3 over here, 2 over here net stabilization net destabilization will be 0; nothing is left 3 over here 2 over here symmetrically filled 4 times 3, 2 times 6.

Now, the moment you put it here one electron, the stabilization energy crystal field stabilization energy, that is what called crystal field stabilization energy; 3 and 2 is 0 in this case it will be 4 D q. Of course, D q has a value different for different compound as we have seen in that D q is changing; but we do not you know memorize those data, just say that it is 4

D q. 4 D q could be 500 wave number, 4 D q could be 2000 wave number, but this is 4 D q; that D q depends on what is the extend of splitting how much, how far it is splitted.

Now this is having 4 D q stabilization this configuration, 3 and 2 cancels out just 4 D q left. If you have one more electron over here, 3 2 cancel out 8 D q right; one more 12 D q, 3 you see.

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So, you can calculate also 4 times 6 is going to be 24 and 2 time 6 this is stabilization this is destabilization 12. So, it is also 12 D q, right; 4 other way to say it 2 and 3 is canceling completely 0 1 2 3, 4 times 3 12.

So, this is 4 D q, this is 6 D q; over here it is each of them are 4 nothing is over there 4 times 6 minus 24 D q, stability stabilization means usually we put minus, that much it is stabilized. So, you can there these are number that is called crystal field stabilization energy.

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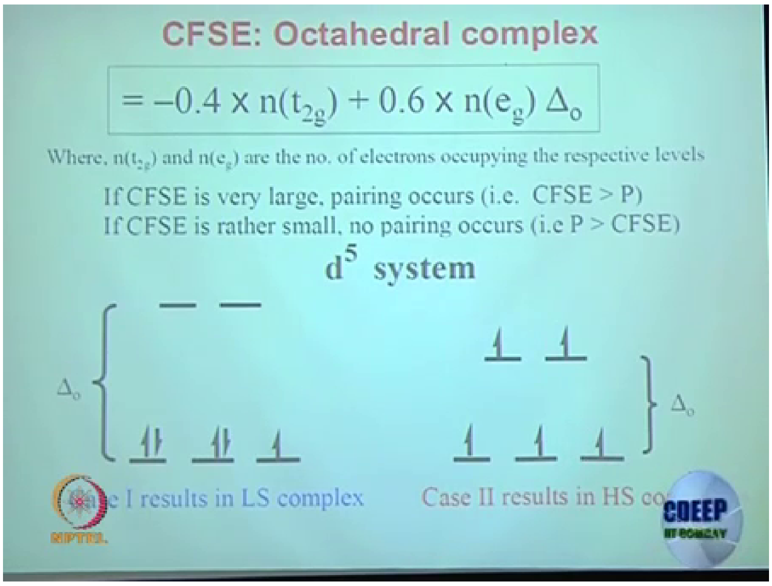

CFSE: Octahedral complex

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

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

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

d^5 system

e I results in LS complex

Case II results in HS co

So, you can of course, this you know calculate based on this; it is 4 or 0.4.

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I mean if you are saying delta 0, then it is 0.4 and 0.6; if it is if you are calling 10 D q, this is 6 D q and 4 D q, right. It is very simple math you should be able to do. For example, over here case one you have low spin case; that means, the splitting is high. Low spin case, so the stabilization is going to be 5 times 4; 5 electrons 4 D q each or 0.4 delta 0 each. So, it is going to be 20 D q, over here it is going to be 0, right

So, this is again it is called crystal field stabilization energy. Due to this crystal field theory the splitting comes and thereby what is the stabilization energy. You look back to the valence bond theory you do not talk about any stabilization; you cannot talk, all the orbitals are degenerate means same energy d x y, d x z, d x you know whatever, but the same energy. Here you have splitted them; therefore, stability and instability are coming into the picture, that is what is crystal field theory for octahedral.