Concepts of Chemistry for Engineering
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Lecture No. 30
Crystal Field Theory: Octahedral Complex

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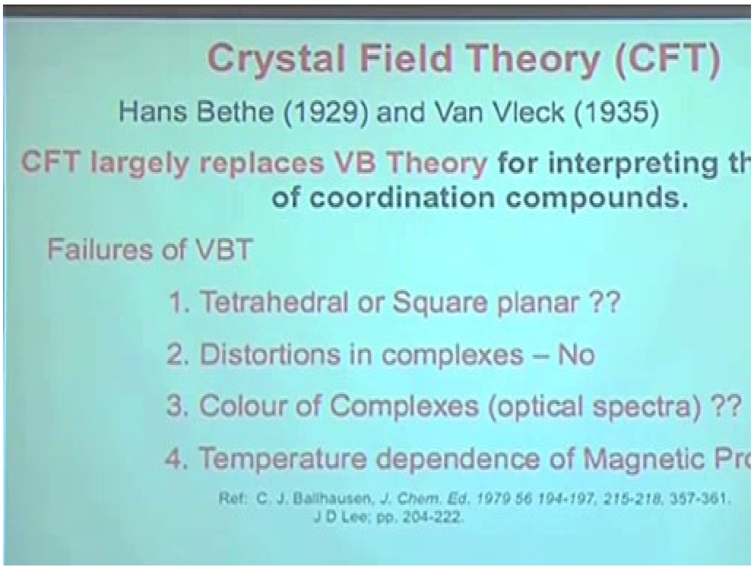

Crystal Field Theory (CFT)

Hans Bethe (1929) and Van Vleck (1935)

CFT largely replaces VB Theory for interpreting th
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 Pr

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

A lot of information you cannot get like why a specific compound is colored, 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 valance bond beam theory is so simple. I think nobody kind of, say you cannot forget the history of something and just take the present. I mean, present in something different, not crystal field. It is something different, which we may not be or we will not be talking too much.

So, it is, present means temporarily present. 100 years down the line, it would be explained in a completely different way or 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. When it is, any distortion. What valance bond theory is discussing is there an ideal situation kind of, anything bond elongation, shortening these things cannot be explained by valance 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 hybridizers and/or this many ligands are there, this there, that there, crystal field theory can explain, however, we did not explain yet, but valence bond theory cannot explain those.

Temperature dependence, why magnetic properties are dependent on temperature? If you increase the temperature, what happens, whether 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.

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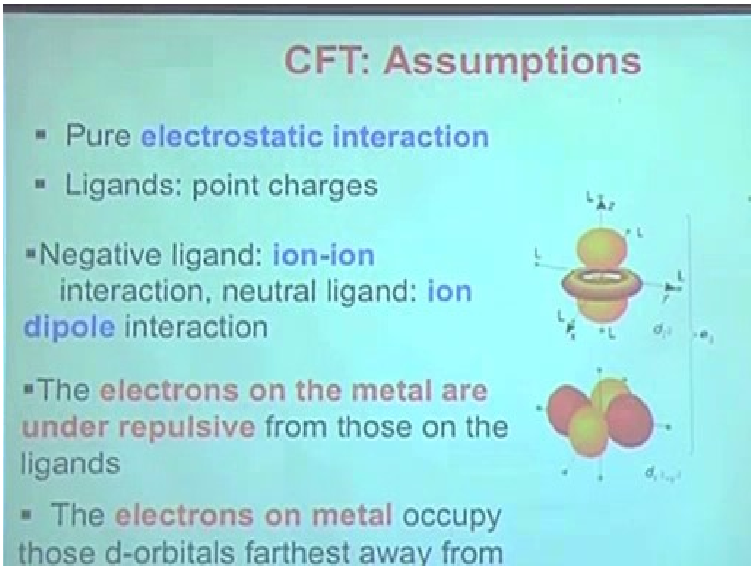
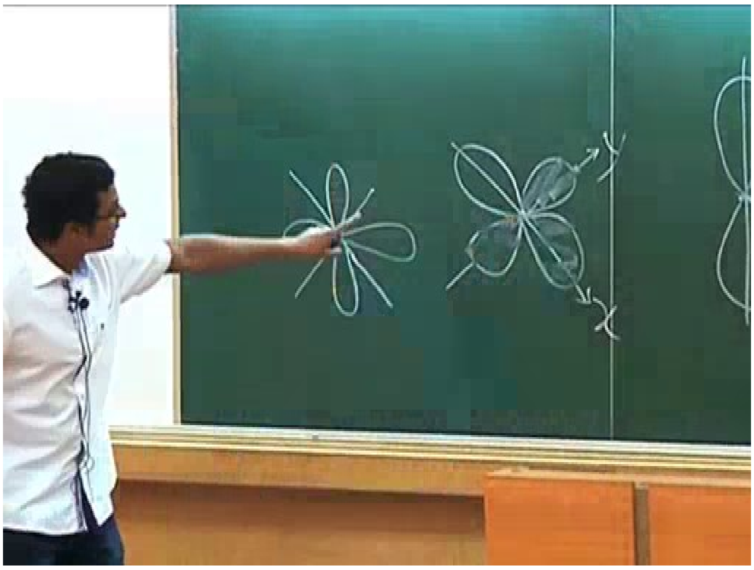


CFT: Assumptions

- 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



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 5d orbitals. We have 5d orbitals. How they are and along the axis how they are, where they are. Now, this is the z-axis or z-axis, whatever you want to call. Now, that dz2 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 in three dimensional scenario. You can take this corner, any corner, one axis, another axis, my laser pointer failing, any corner you can pick up, x, y, z, of course, 90 degree angle. It is may not be always true here. Now, this is dz2 orbital. So, along the z-axis this is dx2y2 along the x and y axis and this is let us say dyz 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.

If it is x and y-axis, then dx2y2 will be along these x and y-axis, along, just right on top of those axis. Right on top of the z-axis is dz2, right on top of x and y both plus and minus direction is going to be your dx2y2 and dxy will be in between. Dxy, where is dxy, 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 dxy.

Similarly, in between y and z is going to be dyz. So, this is z-axis center. The lobes are here. This is dz. Now, if you look and say that this is let us say x and this is y dx2y2 is going to be here and dxy is going to be. So, this is y-axis, this is x-axis. Right on top of y-axis, so we will come to that. So, it is going to be like that. Now, you have to ensure, you have seen it before, you have to be really, really clear about that their positioning. I think we will come to that. Let me tell show you where they are over here. No, we will come back in a moment. 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 and anion interaction or electrostatic interaction, ion, ion interaction or ion dipole interaction. Previously, we are thinking just about the covalent interaction.

Now, if you are thinking so 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 electron same charge. 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, thereby, the energy of the total system going to be increased.

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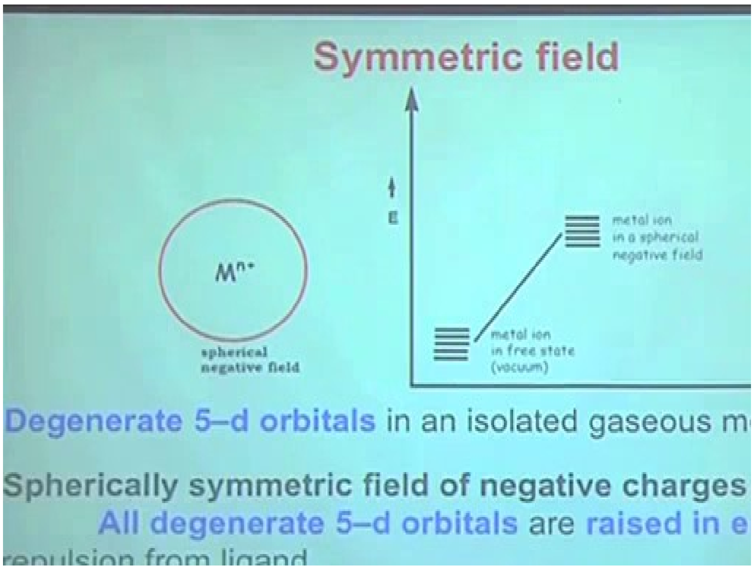

Symmetric field

Degenerate 5–d orbitals in an isolated gaseous m

Spherically symmetric field of negative charges
All degenerate 5–d orbitals are raised in e
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. Well, in this case, ligand, approaching ligand is going to make cricket ball destabilized. Now, this is under ideal situation, where all the ligands let us say are coming from every distances or every directions, all the distance, all the directions.

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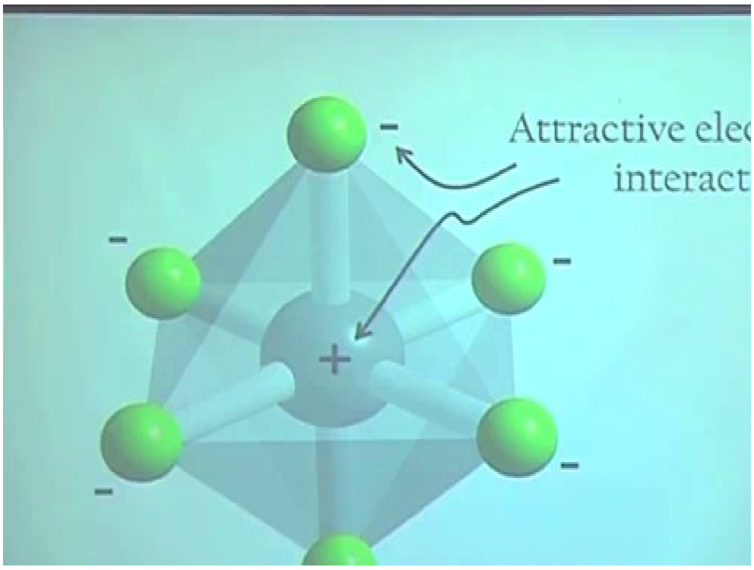

Now, in reality what you have seen is, ligands are not there from every directions. It is specific. Ligand is here, here, here, here, here and here, only few directions. This is the direction for z-axis. Let us say this is the z-axis. This is that, let us say, whatever, y-axis. This is x-axis. So, ligands 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 you have dz2, there you have dxy. This is the one where you have dxy. So, eventually, what you will see is, I will show you, since ligands are coming from this direction directly, those orbital dz2 and dx2y2 orbitals are going to be rippled very much means they are going to be unstable, they are going to be high in energy.

So, over here, 5d orbitals are there. Since ligands are coming specifically from z or towards z-axis, y and x axis, any orbital that is facing those axes directly they are going to find the consequences. That means they are going to have the energy increased. Their energy will be increased.

Any other orbital for example, dxy, 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.

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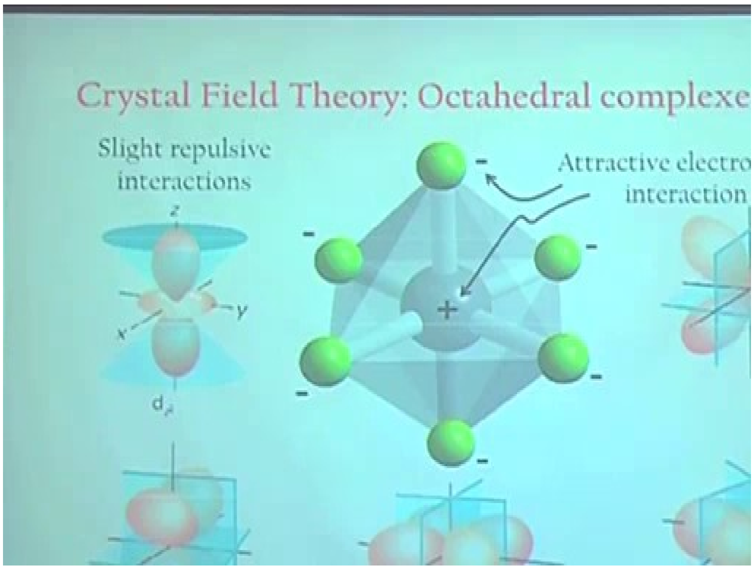

Crystal Field Theory: Octahedral complexe

Slight repulsive interactions

Attractive electro interaction

Now, let us look back. All the orbital if you look back one more time very carefully, this is the dz2, anyone has anything to say please speak out. Now, dz2 orbital, dx2y2 orbital and you can see all these orbital. 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. Now, as we are saying that plus and minus attraction, electrostatic attraction will be there.

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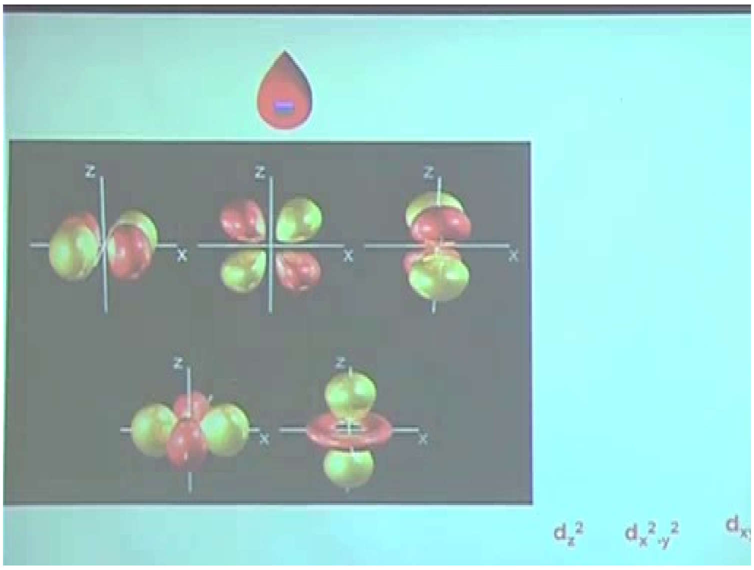

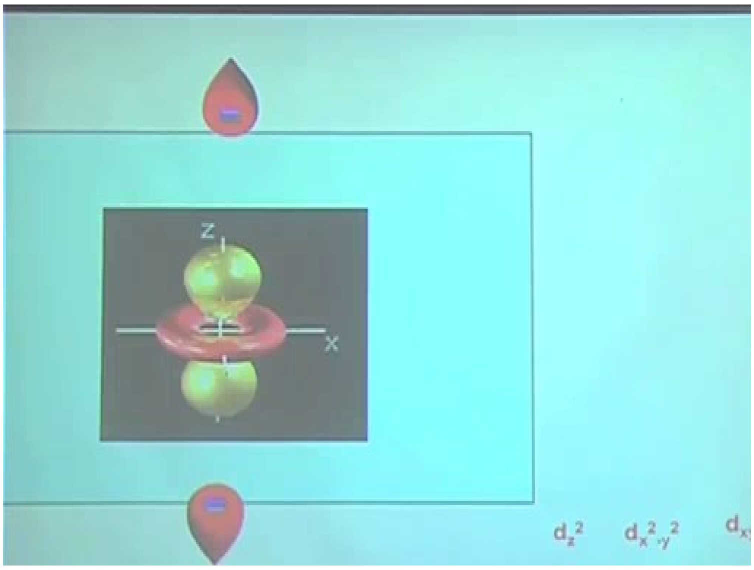

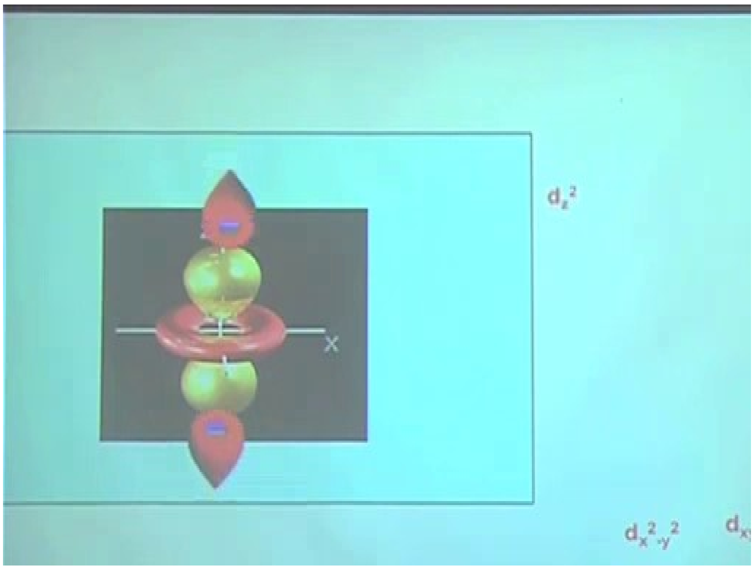

Now, two of these orbital which is dx2y2 and dz2 these are the orbital let us say all these orbitals are there, these are the ones which will be facing the ligand directly like this. So, ligands will be coming directly from two different angle or from two different direction for dz2. So, dz square orbital will be high in energy.

It was, previously it was all of them are same, having same energy or so called degeneracy, 5d orbital were 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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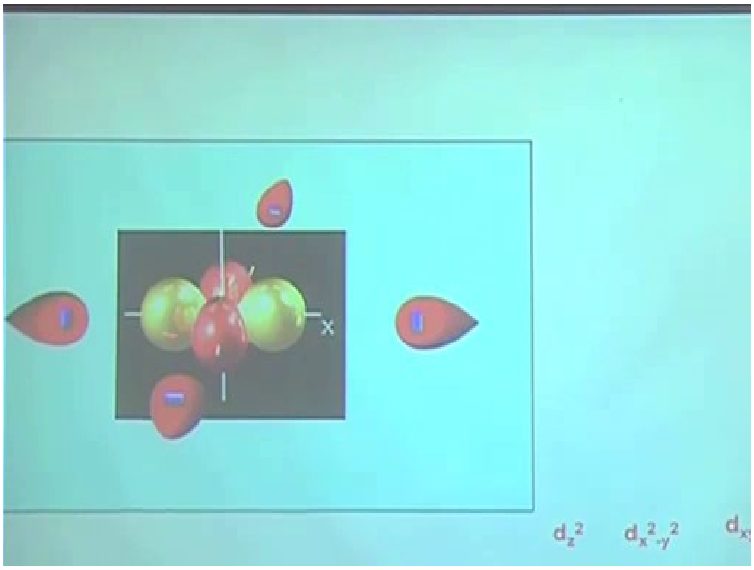

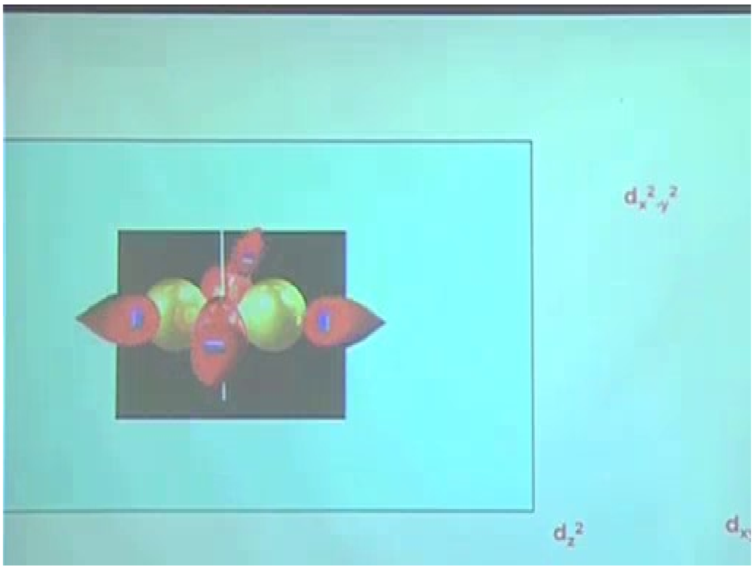

Now, if you look at the dx2y2, this is the dx2y2 orbital and four of the ligans are coming from this direction exactly. Of course, this is going to be also destabilized.

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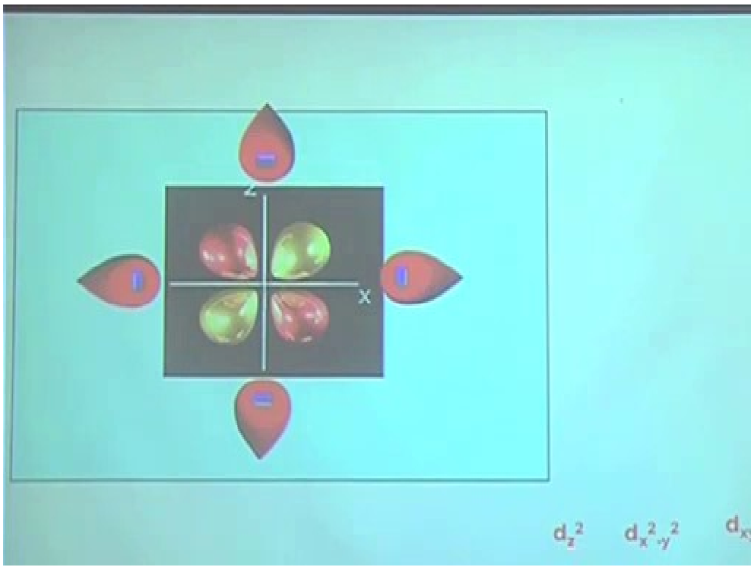

So, what you have learned so far is dz2 and dx2y2 are going to be destabilized. But if you are looking at, let us say, this is dxz orbital, x-axis and z-axis, dxz orbital and the ligands are approaching right actually from the middle not directly towards these lobes. So, their energy will not be overall destabilized, because we have already destabilized by bringing the ligand comparatively they are going to be stabilized that us how the ligands are coming.

That is how they are coming in. So, they are not fitting the bill right on top of each other. They are just squeezing in, not head on collision. Now, so dxz will be stabilized. Dxy, dyz is the same scenario. It is just different axis.

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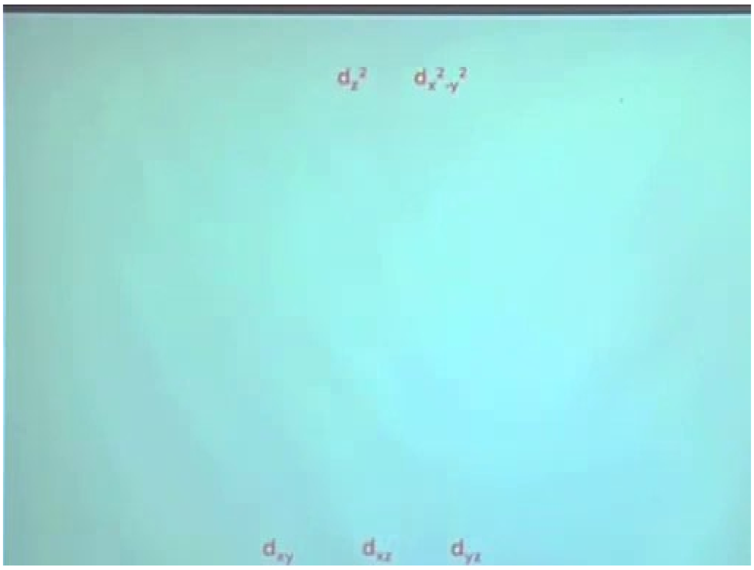

So, overall, we see that it is split into like this. Two of them getting destabilize, three of them getting stabilized. Stabilized means stabilized with respect to where it started, not in the free ion over here. This is a free metal ion. With respect to free metal ion when you have a metal complex formation, 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 this, 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. So, that is how it is going to be. But with respect to free metal ion, of course, they are destabilized.

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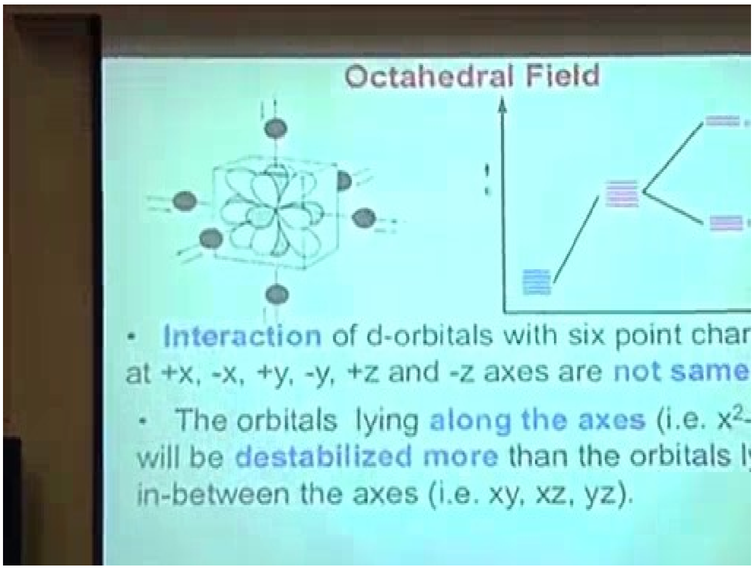
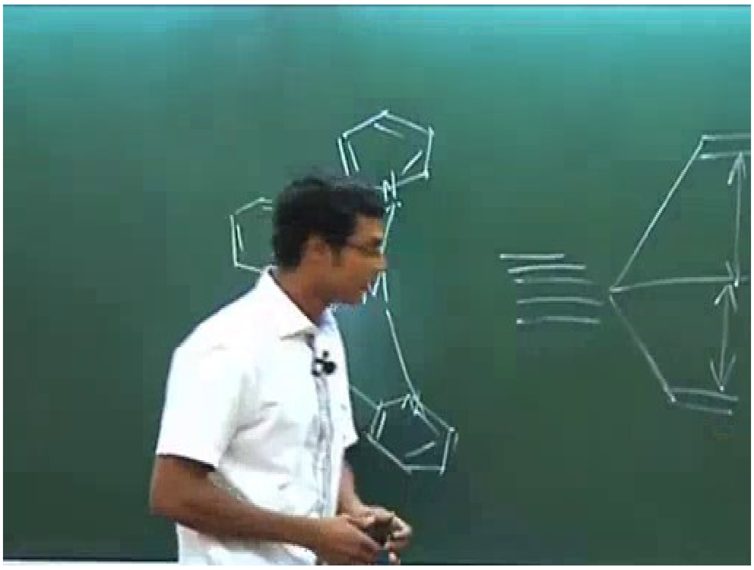


Octahedral Field

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



Now, this is what is octahedral field is all about. You see octahedral complex. 6 ligands are there surrounding the metal center, 5d orbitals getting destabilized and further splitted. This is no longer degenerate of the same energy. 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 eg orbital and this is t2g orbital, three of them. So, eg is dx2y2, dz2 and t2g is dyz, dxz, dxy, so three of them and two of them. Now, the extent to which, with respect, this is called barycenter, where the 0 is. 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 electrons versus 4 electrons. So, 4 time destabilizes and 6 times 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. So, from here, this is going to be 0.6, this is going to be 0.4. I should have stabilized, I should have switch off this one. 0.6, 0.4. We will come to that again. Now, some more informations are given which you can read very clearly. I will not dwell too much on that stabilize one, destabilized one.

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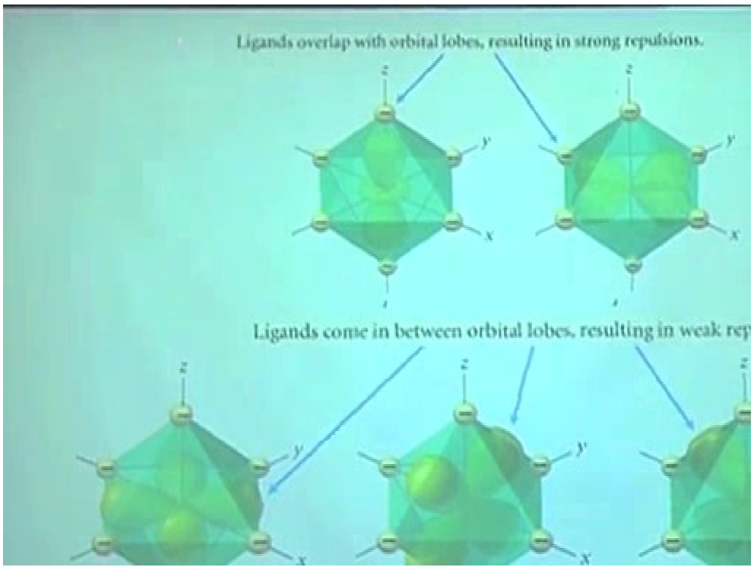

Ligands overlap with orbital lobes, resulting in strong repulsions.

Ligands come in between orbital lobes, resulting in weak rep

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, dz2, dx2y2 and the three, two orbitals and three different orbitals in the compound form or in, how they interact.

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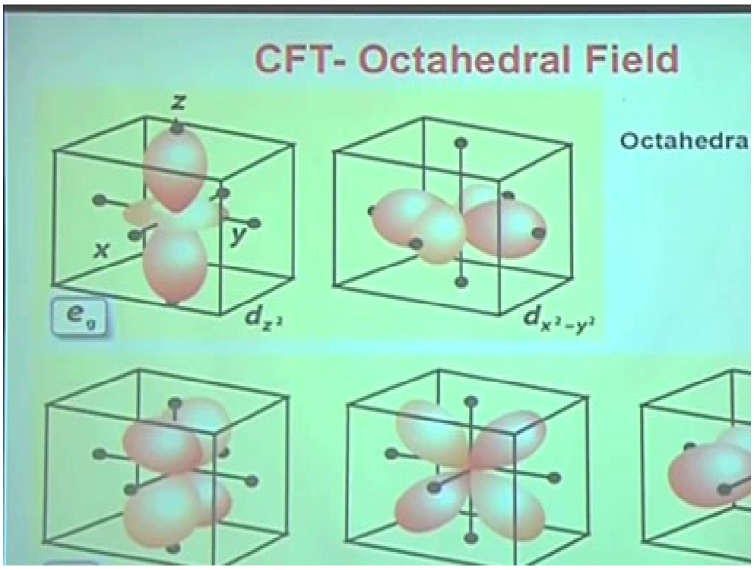

CFT- Octahedral Field

Octahedra

Further, it is much better. I think this is the last slide hopefully on that. You see dz square and dx2y2, dzx, dyz, dxy, 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 clearly what exactly we tried to say that will give you a crystal clear picture hopefully what is going on in here.

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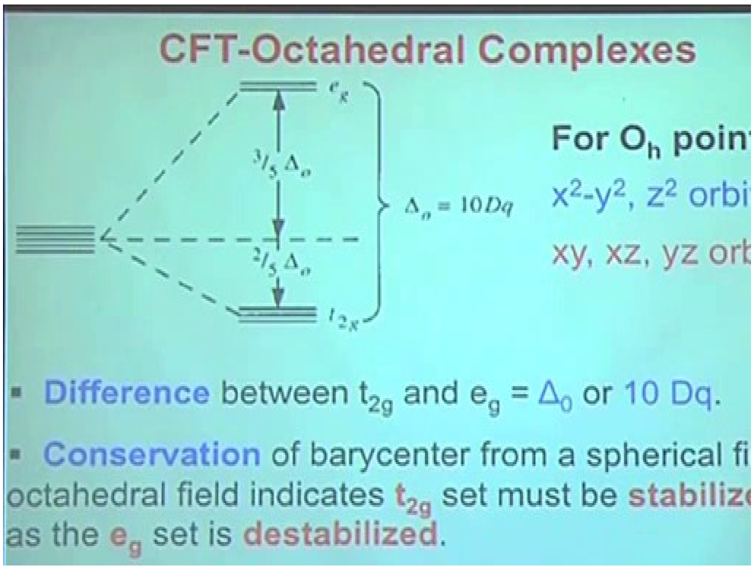

CFT-Octahedral Complexes

For O_h 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.

So, once again I will take the break in a moment. This is the 3, 5 of the total distance is called delta 0 or 10Dq. This is going to be your 6Dq, this is 4Dq or so to speak 3, 5 delta 0, 2, 5 delta 0.

This is something you need to remember. The total is called 10Dq, 4Dq and 6Dq, 0.4 and 0.6, 4Dq, 6Dq. 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 eg, t2g we will be calling, but difference between them is delta 0, 10Dq, so on and so forth.

Anyway, so let us continue over here. What we see, this is the total 10Dq we are saying. What is Dq it will be clear soon enough. Or this is the delta 0 the distance between these t2g and eg or the energy difference between these two. Some of them are destabilized, some of them are stabilized.

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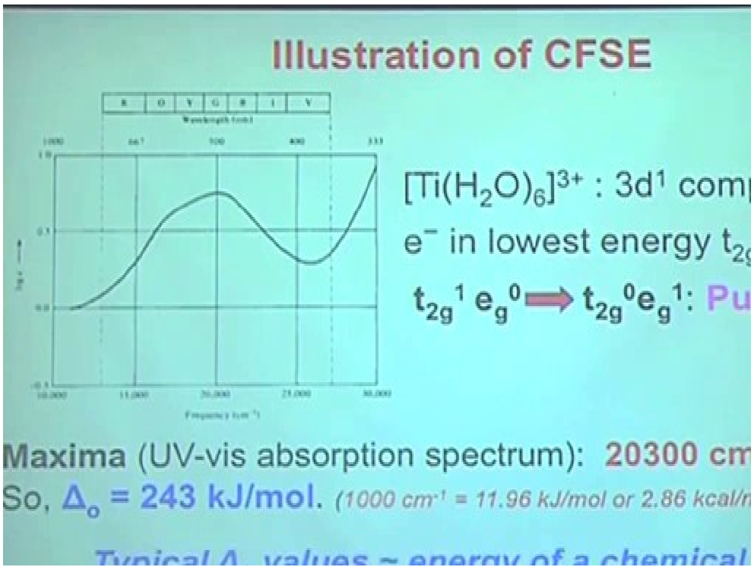

Illustration of CFSE

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

e^- in lowest energy t_{2g}

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

Maxima (UV-vis absorption spectrum): 20300 cm

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

Typical Δ_o values ~ energy of a chemical

Let us say, let us take some little bit more practical example. You have a titanium hexaaqua complex with 3 plus scandium titanium. It is d2s2, it is going to be d1 then after three plus, so 3d1. So, that means no longer we will be saying it 3d1, we are going to say it t2g1eg0, 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 we are trying to see no longer will be calling it d1. It has to be defined that as t2g what, eg what, let us say, t2g5eg0, t2g3eg2, t2g4eg2 or t2g6. 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 g6 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 your 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. Aqua, water, water let us say, for example, usually a weaker ligand or it is all relative again. There is a spectrochemical series we will bring that will tell what is strong ligand, what is weak ligand. Fluoride maybe a weak ligand, so chloride maybe weak ligand, CO maybe a strong ligan, so on.

So, depending on the difference this energy is having like how much difference is there between t2g and eg it is this much or that much. If it is this much difference then electrons will be occupied all t2g and eg, because you know that Hund's maximum principle that spin has to be maximum and so on, but if it is this one that Hund's rule may not be applicable here, because it is very big to putting electron in this orbital, eg 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 a 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 t2g, eg is high that you need to kind of know. You do not need to memorize. We are going to tell you what is the scenario.

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 valid. Higher the oxidation state you will see the splitting will be high. This t2g, eg gap will be high. 3d to 5d gap will be increasing. 2 plus to 5 plus gap will be increasing. Therefore, if the gap is increasing, pairing become easy because it cannot go too much if it is gap is too much. If gap is low, then pairing will not occur. It will be both in t2g and eg if this is eg, this is t2g. That is what we are going to see now.

I am kind of summarized over here. It is going to be t2g1, eg0. Now, everything you have to explain or you have to write in this format. Why we see purple color in this titanium hexaaqua complex? Why do we 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 t2g and eg will show.

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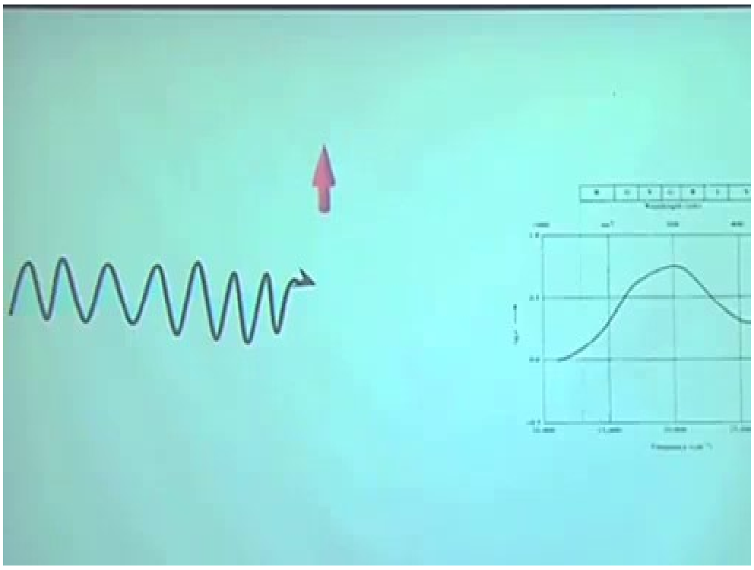

So, let us say this is your t2g electron and you put the energy, the light, it is going to convert from t2g level to eg level and that is what you see in terms it comes out that absorption energy where it absorbs that means how much energy you have given to bring, let us say, t2g electron, one electron from here to here, that is what nothing but you see as absorption the peak you see or you have a metal complex, you sign light, you want to see the electronic transition from one level to other.

It could be let us say sometime t2g to t2g or it could be usually the, for want to see you have to have t2g to eg conversion. From t2g 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 absorbed as you 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 white 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 t2, this titanium hexaaqua complex, we see that this is the UV-vis absorption, this is nothing but this transition from t2g to eg level and that is how does peak is coming. That is the absorption that is happening from, for transferring t2g electron to eg electron.

Of course, there could be multiple transition. There could be multiple, if, it is a simple electron system, 1 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, five 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 gives you an idea of where the origin of the color is. This is nothing but transition of one sub-level to another one. So, this is where crystal field theory becomes superior compared to your valance bond theory. Valance bond theory what you have done d2sp3 or sp3d2 whatever, sp3 and so on, there you cannot explain where the color is coming from.

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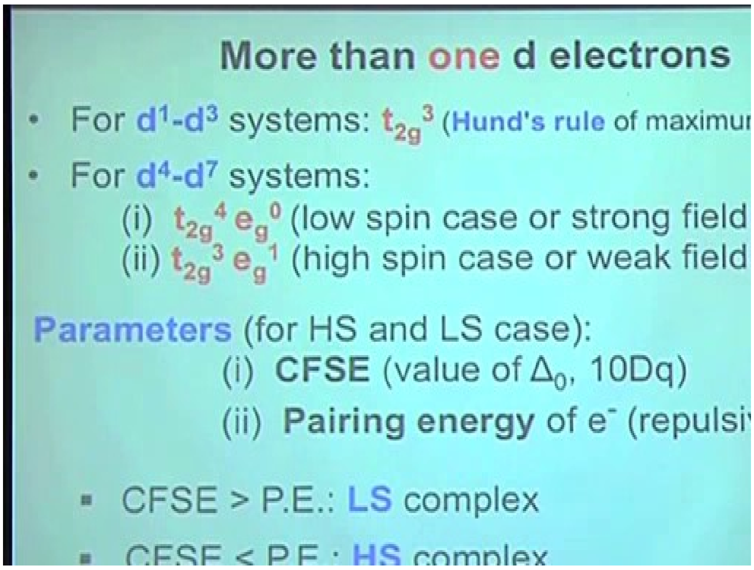

More than one d electrons

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

Parameters (for HS and LS case):
(i) **CFSE** (value of Δ_0, 10Dq)
(ii) **Pairing energy** of e^- (repulsi

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

Now, of course, as I said there are scenarios where you can have more than one electrons. So, d1 to d3, so of course, Hund's rule will be promoted. Now, for four electrons you can have t2g4eg0. T2g can have total up to six electron or you can have t2g3eg1. Three of them are going to be filled out. After filling out the fourth one will be the eg1, eg. Now, I will come to, come with that with more pictorial diagram. I think I will skip that.

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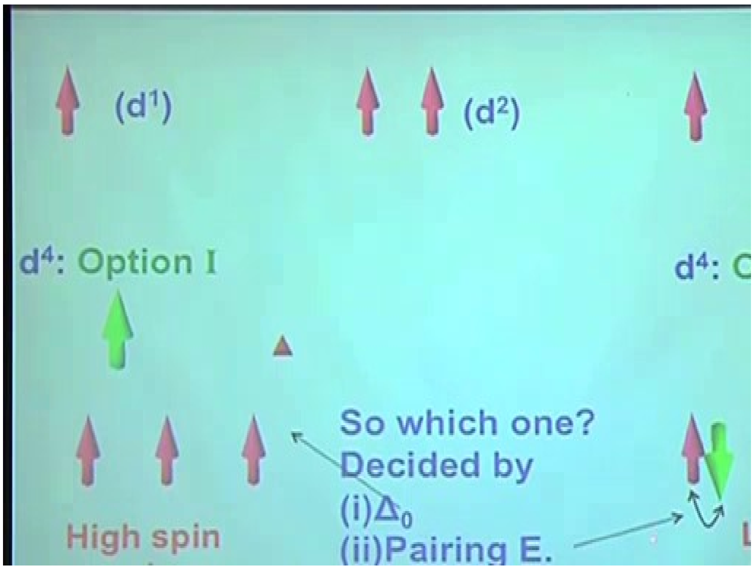

(d^1)

(d^2)

d^4: Option I

d^4: C

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

High spin

Now, this is what it is. So, t2g orbital one electron, t2g orbital two electrons, t2g orbital three electron. There is no story of eg, because eg is high in energy, while it will go to high in energy. After d3 then you have dilemma, then you have problem, whether you send it to eg or you pair it up with t2g. So, there are two scenarios. High spin complex will have t2g3eg1, d4 option I, option 2 will be t2g4eg0. This is t2g, this is eg. Eg over here, nothing in there. So, you have low spin complex. This is high spin complex, because four unpaired spins are there. Here you have two unpaired spins.

So, up to d1, d2, d3, you do not have to worry at all. You just put t2g1, t2g2, t2g3. After that whether it is t2g4eg0 or t2g3eg1 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, what d orbital they are having, what is their oxidation state, all these factors 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 g and then what will happen. That sort of memorization is not required. So, in other word, if delta 0 or that 10Dq value we were talking, difference between t2g and eg if this is small, then you will see t2g3eg. If the difference is small, the spin will try to be maximum or electronic spin will be maximum.

So, t2g3eg1 will be happening if delta 0 is small. For this to happen, t2g4 to happen you have to pair these two electrons. 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.

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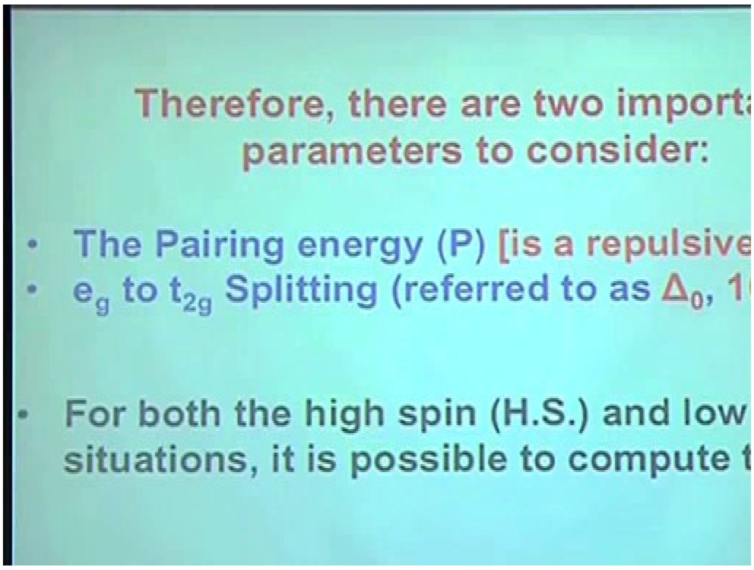

Therefore, there are two import
parameters to consider:

- The Pairing energy (P) [is a repulsive
- e_g to t_{2g} Splitting (referred to as Δ_0, 1

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

Now, of course, a 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. I think we have explained already.

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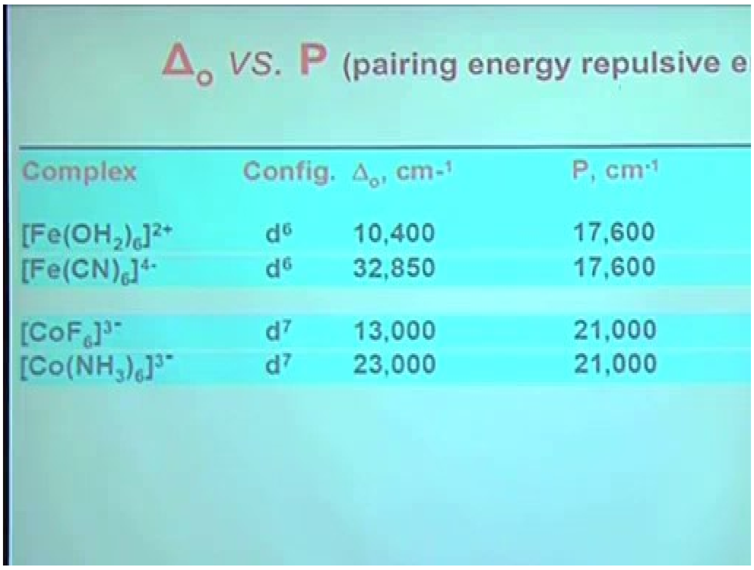

Δ_o *vs.* P (pairing energy repulsive e

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

Now, I will just give you a phenomenon. So, what we again what we have said up to d3 you do not have to worry. It is going to be t2g1, t2g2, t2g3. After d4 you have to decide. That again, let us say, at d8 you do not have to worry. It is going to be t2g6eg2. 1, 2, 3, 4, 5, 6, 7, 8, whatever way you want to fill out d8, d9, d10, 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. You try to do that. But while you are trying to do that you have to also mind the gap, distance between t2g, eg, whether it is going to be unpaired spin or paired spin. After filling t2g, you have to up from 4, 5, 6 really the one cases, where 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. And after 8, 9, 10, it is always one configuration. 4, 5, 6, 7 it is going to be high spin or low spin. That is what you are going to assume. High spin means spin is maximum, low spin is spin is minimized with the given situation.

Now, something like these complexes, if you see some easy complex like very shooting 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 three plus, means which is more higher charge. 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.

Now, iron hexacyanide, we are all talking about the octahedral complex. Do not forget that. Six ligands are there. We did not talk about tetrahedral as of yet. So, six of them, this is going to be a strong ligand. Cyanide is a strong ligand. That means the gap between t2g and eg is very, very high. This will be d6. So, those 6 electrons will be t2g6, not t2g4eg2. I think some of them are, some of you are having little bit dizziness. Let us see.

Try to explain in the board. What we are having, let us say, d6 this is t2g3, three of t2g and two of eg, you can have this as one scenario. Other scenario is nothing here all paired up. So, this is t2g4eg2. This is a high spin situation. That is what is happening in iron hexaaqua complex 2 plus. Now, iron cyanide 6, FeCN6, hexacyanide, 4 minus, now you have d6 total electron.

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. Both of them are d6 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 10Dq 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 in small. So, it is going to be, it is going to follow your Hund's rule 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 a lot of things that we see 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 some high oxidation state and ligand is strong ligand then you are going to see low spin, because this t2g and eg splitting is going to be high.

Now, next one cobalt F6, cobalt is here three plus, six on the fluoride, three minus total, d7 configuration. Cobalt is d7s2, iron cobalt. And then if it is, iron cobalt nickel, d7s2, it is 3 plus. I think something is wrong there. Is it not? It should be d6. Let us assume that this is d7, but this charge are wrong. Cobalt is d7s2, so nine electrons. If 3 are taken, so 2 are taken then it is, let us say, this is going to be your 4 minus. The charge is wrong here. I do not know how come.

So, anyway, it is a d7 system. Both of them are d7 system. Ignore the charge. Just take my word. Ignore the charge. D7 system, d7 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 that metal center. I will give you a summary.

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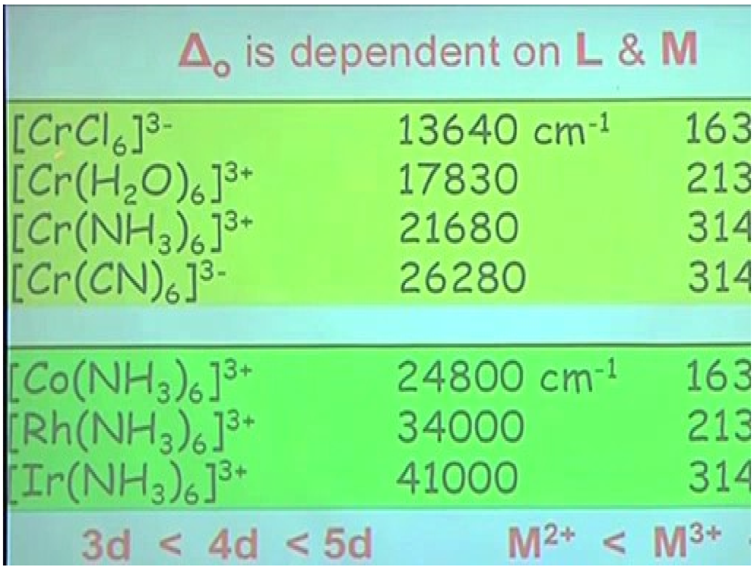

Δ_o is dependent on L & M

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

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

Let me give you the summary. The delta 0 will be increasing in this order 3d, 4d, 5d. 5d 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 t2g and eg how they are differing. So, you can say that this is a weaker ligand, this is a little bit stronger, this is more stronger, this is the strongest in this series. So, the difference between t2g and eg can tell you what is the strength of these ligands are.

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

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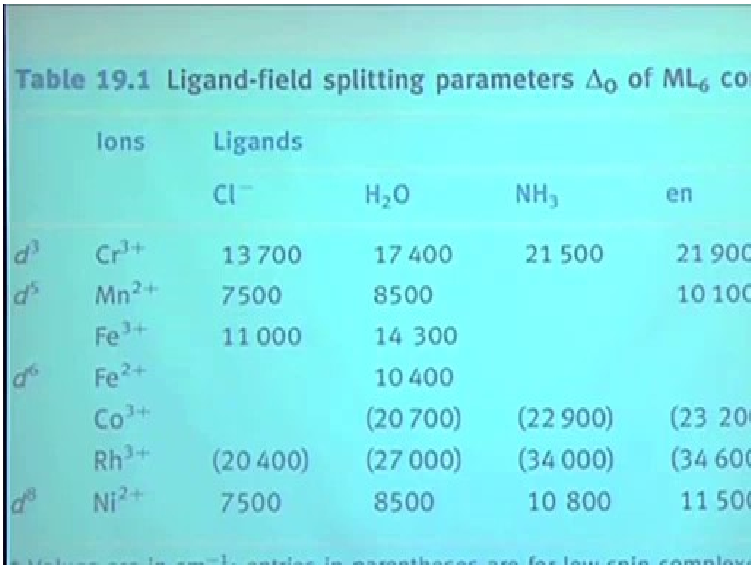

Table 19.1 Ligand-field splitting parameters Δ_O of ML_6 co

	Ions	Ligands			
		Cl^-	H_2O	NH_3	en
d^3	Cr^{3+}	13 700	17 400	21 500	21 90
d^5	Mn^{2+}	7500	8500		10 10
	Fe^{3+}	11 000	14 300		
d^6	Fe^{2+}		10 400		
	Co^{3+}		(20 700)	(22 900)	(23 20
	Rh^{3+}	(20 400)	(27 000)	(34 000)	(34 60
d^8	Ni^{2+}	7500	8500	10 800	11 50

That is also over here. All these things summarize together. I will tell you what is summarized to. This is what it is summarized to. You can take a series of compounds just vary one thing, either ligand you vary or metal you vary. You keep on doing. You come to a conclusion that 5d will have higher splitting than 4d and 3d and higher oxidation state will have higher splitting.

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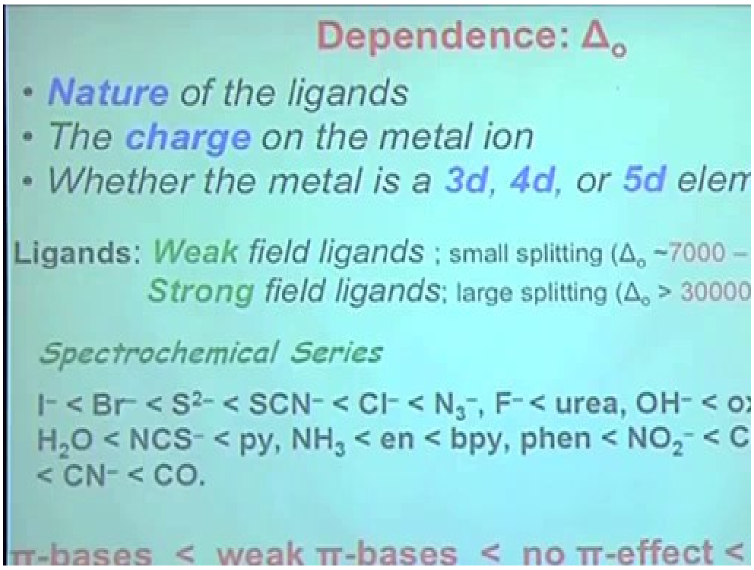

Dependence: Δ_o

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

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

Strong field ligands; large splitting (Δ_o > 30000

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-$, $F^- <$ urea, $OH^- <$ o

$H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- <$ C

$< CN^- < CO$.

π-bases < weak π-bases < no π-effect <

Now, there is something called electrochemical series. This is what is electrochemical series. This is the strongest ligand than this one than 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 the splitting which is going to be high, so the electron cannot jump to the eg. So, it is going to be low spin. Spin will be minimized. It will stay in t2g.

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 filled ligand they will tend to give you high delta g or delta 0, t2g, eg separation will be high. Therefore, it will give you a low spin complex. Strong field again will tend to 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 cyano or these any of the alkyl or nitrite.

You have to, of course, you have to, you also have learned that 5d will have more splitting than 4d and 3d. Higher oxidation state will have more splitting than lower oxidation state. So, it is a combination of all these three factors were the ligand is in terms of spectraelectrochemical, spectrochemical series, not specto, spectrochemical series, where 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.

If everything is 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. 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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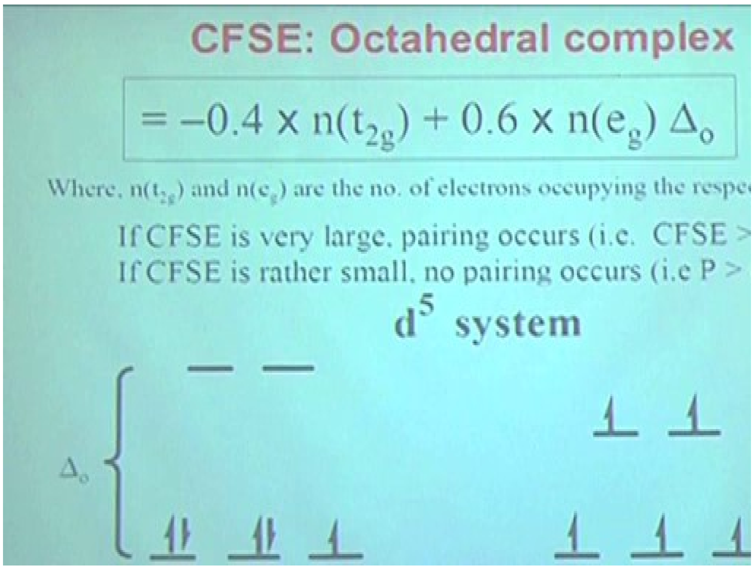


CFSE: Octahedral complex

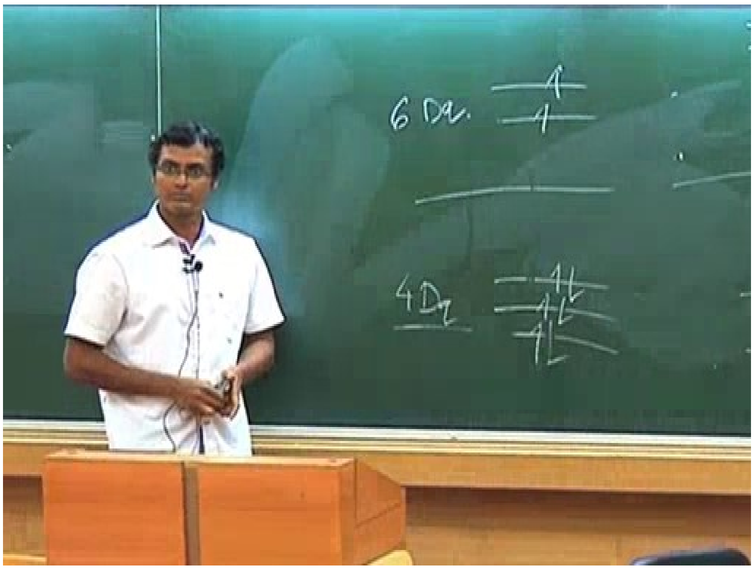
$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\ \Delta_o$

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



So, overall, after having these, you should be able to calculate the crystal field stabilization energy. How much, with respect to the 0, how much stabilize or destabilize it is. So, over here, each of the electron over here I said it is 4Dq and this is 6Dq. So, you can see that three of them, let us say, if you have three of them, this is 4Dq, 4 times 3 will be 12 and 2 times 6 will be, this is 6Dq, 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 4Dq. Of course, Dq has a value different for different compound as we have seen in that Dq is changing, but we do not memorize those data, just say that it is 4Dq. 4Dq could be 500 wave number, 4Dq could be 2000 wave number, but this is 4Dq. That Dq depends on what is the extend of splitting. How much, how far it is splitted.

Now, this is having 4Dq stabilization, this configuration. Three and two cancels out, just 4Dq left. If you have one more electron over here, 3 2 cancel out, 8Dq, one more, 12Dq, 3, 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 12Dq.

So, other way to say it, two and three is canceling, completely 0, 1, 2, 3, 4 times 3, 12. So, this is 4Dq, this is 6Dq. Over here, it is, each of them are four, nothing is over there, 4 times 6 minus 24 Dq. Stability, stabilization means usually we put minus. That much it is stabilized. So, you can, these are number that is called crystal field stabilization energy. So, you can of course calculate based on this. It is 4 or 0.4. I mean, if you are saying delta 0, then it is 0.4 and 0.6.

If we are calling 10Dq, this is 6Dq and 4Dq. It is very simple math. You should be able to do. For example, over here, case I, 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, 4Dq each or 0.4 delta 0 each. So, it is going to be 20Dq. Over here it is going to be 0.

So, this is again 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 valance bond theory. You do not talk about any stabilization. You cannot talk. All d orbitals are degenerate, means same energy, dxy, dxz, whatever, the same energy. Here you have splitted them. Therefore, stability and unstability are coming into the picture. That is what is crystal field theory for octahedral.