Advanced Transition Metal Chemistry – Crystal Field Theory

Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 15
Crystal Field Theory (CFT)

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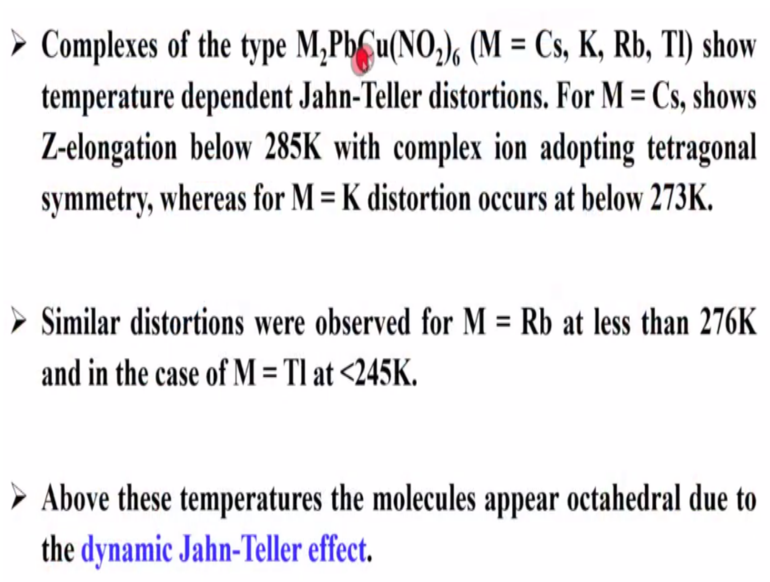

- Complexes of the type $M_2PbCu(NO_2)_6$ (M = Cs, K, Rb, Tl) show temperature dependent Jahn-Teller distortions. For M = Cs, shows Z-elongation below 285K with complex ion adopting tetragonal symmetry, whereas for M = K distortion occurs at below 273K.
- Similar distortions were observed for M = Rb at less than 276K and in the case of M = Tl at <245K.
- Above these temperatures the molecules appear octahedral due to the dynamic Jahn-Teller effect.

Hello everyone. I once again welcome you all to MSB lecture series on advanced transition metal chemistry. This is the 15th lecture in the series. In my previous lecture, I did discuss about Jahn-Teller distortion and I was telling you about complexes of this type. Here you can see clearly 6 anionic ligands are there and copper is in +2 state, to compensate 4 charges we have lead in +2 state and 2 alkali metals in the +1 oxidation state.

So, now it is a charge balanced complex and this complex shows temperature dependent Jahn-Teller distortion. The interesting thing is with variation in the alkali metal or cation it shows distortion at different temperatures. When M is caesium it shows tetragonal elongation below 285 Kelvin with complex ion adopting tetragonal symmetry, whereas for M = potassium, distortion occurs at below 273 Kelvin.

And once again, similar distortions were observed for M = rubidium, at less than 276 Kelvin and, when M is Thallium, it appeared at less than 245 Kelvin. And above these temperatures, the molecule appears octahedral due to dynamic Jahn-Teller effect. So, it is not only Jahn-Teller distortion come across, we can also see dynamic process with temperature.

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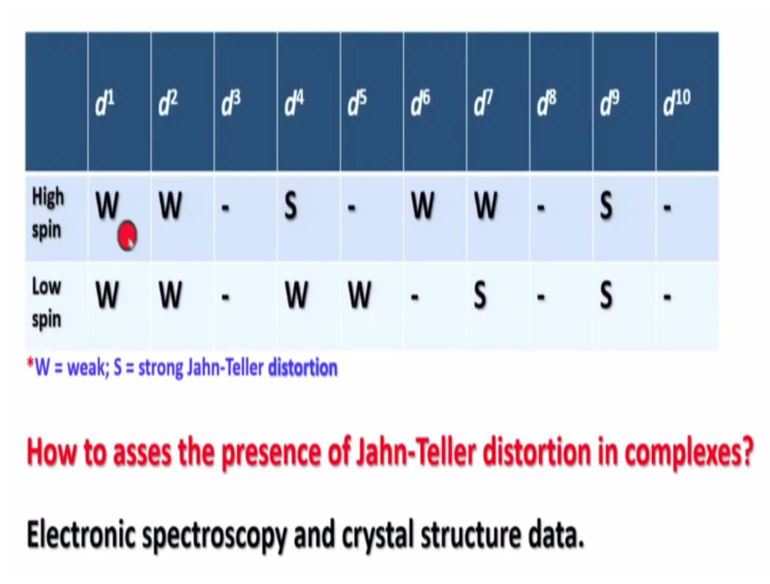

	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
High spin	W	W	-	S	-	W	W	-	S	-
Low spin	W	W	-	W	W	-	S	-	S	-

*W = weak; S = strong Jahn-Teller distortion

How to asses the presence of Jahn-Teller distortion in complexes?

Electronic spectroscopy and crystal structure data.

So, I have listed all electronic configuration d^1 to d^{10} to just assess what electronic configuration really shows Jahn-Teller distortion in complexes in case of both high spin and low spin. If you just see, when we have one electron in d orbital, irrespective of high spin or low spin, so they show weak Jahn-Teller distortion. And when we have d^4 electronic configuration, that means e_g has 1 electron and also in case of d^9 where we have 3 electrons, we come across very strong Jahn-Teller distortion.

That is what we saw in case of chromium 2+ and copper 2+ octahedral complexes. In case of d^5 and d^3, d^8 and d^{10}, we do not see at all. And in case of d^6 and d^7 we come across again weak Jahn-Teller effects. And in case of low spin, whether you take d^1, d^2, d^4, or d^5 in all these cases, we do come across weak Jahn-Teller distortion whereas in case of d^3, d^6, d^8 and d^{10} we do not see at all. Only in case of d^7 and d^9, we do come across Jahn-Teller distortion in case of low spin complexes.

Of course, in case of d^9 irrespective of their slow spin or high spin it is going to show strong Jahn-Teller distortions. Then fine, theoretically by just looking into the e_g electronic configuration, to an extent t_{2g} the electronic configuration, we can predict the possibility of a complex showing Jahn-Teller distortion, but how to assess the presence of Jahn-Teller distortion in complexes?

Two important aspects that comes to our mind to assess this Jahn-Teller distortion are electronic spectroscopy and crystal structure data. Of course, crystal structure data is quite straightforward. And the moment you determine X-ray structure, you will come across variations in the bond length that is bonding parameters that should tell you whether elongation is observed or compression is observed.

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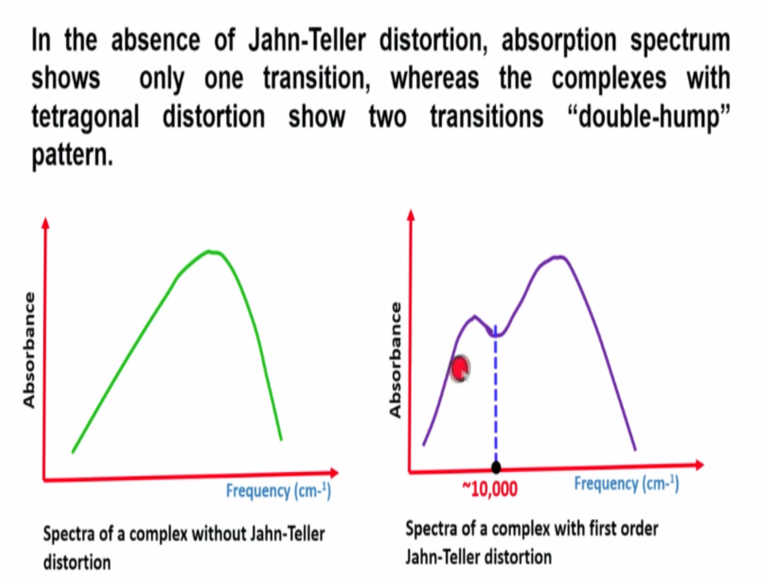
In the absence of Jahn-Teller distortion, absorption spectrum shows only one transition, whereas the complexes with tetragonal distortion show two transitions “double-hump” pattern.

Spectra of a complex without Jahn-Teller distortion

Spectra of a complex with first order Jahn-Teller distortion

How electronic spectra of these complexes vary? Let us look into this again. In the absence of Jahn-Teller distortion, absorption spectrum shows only one transition, whereas the complexes with tetragonal distortion usually show two transitions and we call it as double-hump pattern. How this double-hump pattern appears? This is the one without Jahn-Teller distortion, you can see simple one absorption here. And when we see Jahn-Teller distortion, we see two intensities here and of course one is weaker and one is stronger. Then how to visualize this one through electronic transitions?

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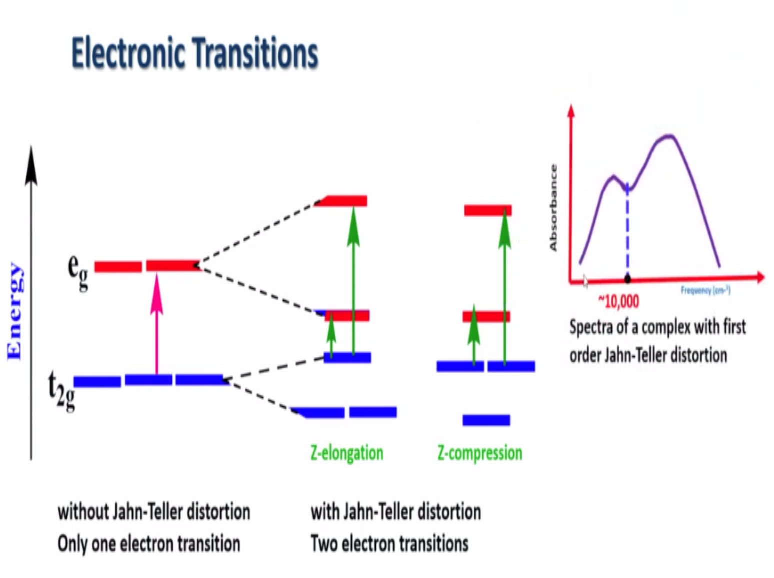

Electronic Transitions

Spectra of a complex with first order Jahn-Teller distortion

without Jahn-Teller distortion
Only one electron transition

with Jahn-Teller distortion
Two electron transitions

So, let us look into the electronic transitions that are responsible for showing this kind of absorption. Without Jahn-Teller distortion, you can always anticipate one transition from t_{2g} to e_g, but irrespective of whether we have z-elongation or z-compression with tetragonal distortion due to Jahn-Teller effect, they show two electronic transitions and this is the one and this is a one here in case of elongated complexes.

In case of compressed complexes also we see two electronic transitions. And this explains why we see double-hump pattern like this, in this pattern. So, that means there is a way to assess and understand whether Jahn-Teller distortion is there or not. If it is there to what extent it is effective, whether it is weaker or stronger can also be assessed simply by looking into the absorption spectrum of a particular complex.

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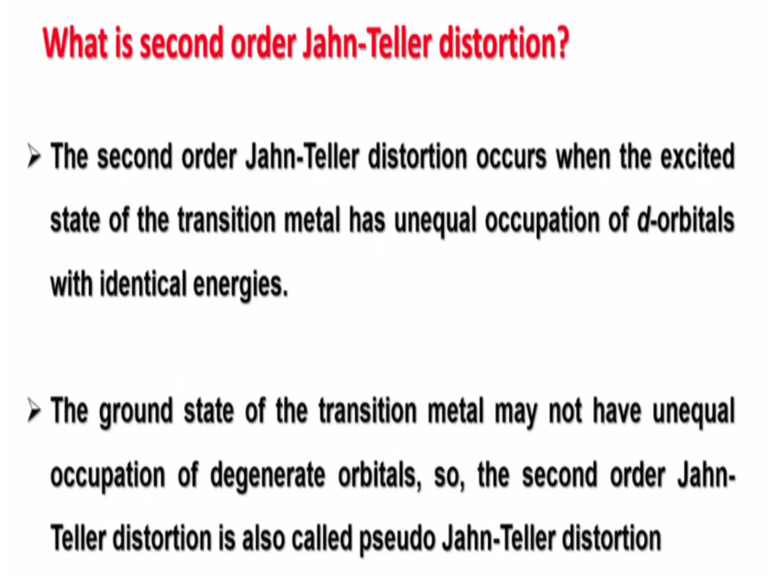

What is second order Jahn-Teller distortion?

- The second order Jahn-Teller distortion occurs when the excited state of the transition metal has unequal occupation of *d*-orbitals with identical energies.
- The ground state of the transition metal may not have unequal occupation of degenerate orbitals, so, the second order Jahn-Teller distortion is also called pseudo Jahn-Teller distortion

So, what is second order Jahn-Teller distortion? The second order Jahn-Teller distortion occurs when the excited state of the transition metal has unequal occupation of the d orbitals with identical energies. That means once when you excite an electron from the ground state to excited state and if the excited state has unequal occupation of the orbitals, very similar to d^4 and d^9, then we can anticipate second order Jahn-Teller distortion.

The ground state of the transition metal may not have an equal occupation of degenerate orbitals, so therefore the second order Jahn-Teller distortion is also called pseudo Jahn-Teller distortion.

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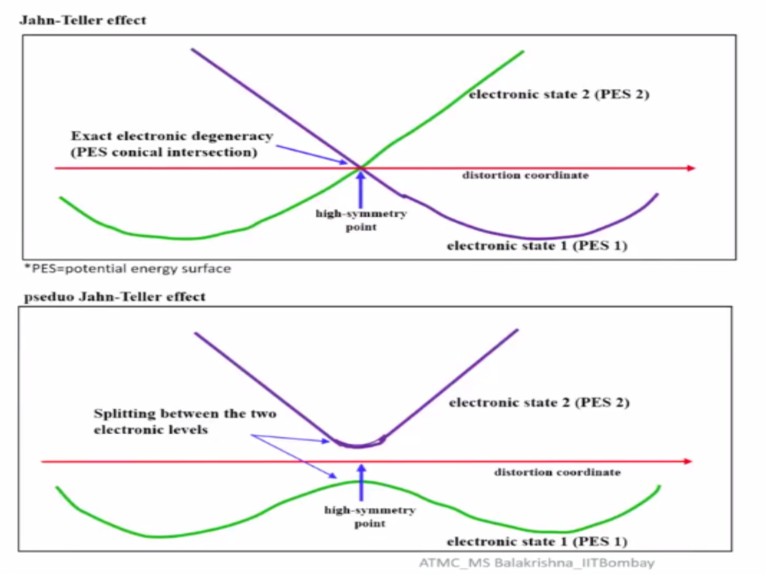

And if you just want to look into the potential energy surface, this is how it looks. And this is at high symmetry point where there is no effect and this is in case of Jahn-Teller effect, whereas in case of this one, it is pseudo Jahn-Teller effect. You can see here splitting between the two electronic levels and this is again high symmetry point and this electronic state 2 and electronic state 1, similarly electronics state 2 here and electronic state 1 is here.

So, you can also see pseudo Jahn-Teller distortion, regular Jahn-Teller distortion and also second order effects will also be there. This is because of the excited state in which uneven filling of electron or uneven electron occupation is observed.

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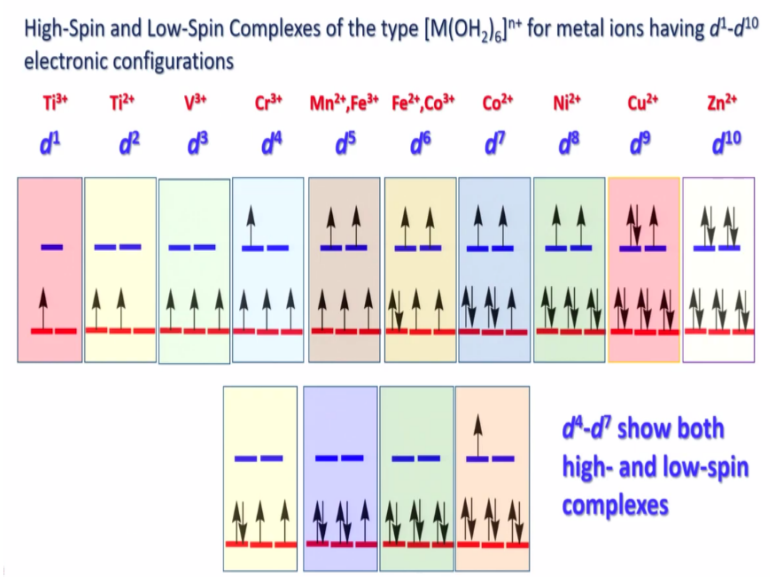
High-Spin and Low-Spin Complexes of the type $[M(OH_2)_6]^{n+}$ for metal ions having d^1-d^{10} electronic configurations

d^4-d^7 show both high- and low-spin complexes

Now, let us look into high spin and low spin complexes of the type hexaaqua M with a particular oxidation state for metals having d^1 to d^{10} electronic configuration. So, I have listed here for 3*d* series starting from d^1 to d^{10}. And the d^1 the most common one here if you consider it is titanium 3+ and one electron is there. And in case of titanium 2+ , d^2 system, we have 2 electrons are there. And vanadium 3+, 3 unpaired electrons are there.

And in case of d^4 chromium 3+ , we have 4 unpaired electrons and this entire series is due to high-spin complexes. And in case of d^5 we have two levels both are singly occupied, so maximum unpaired electrons can be seen, example Mn^{2+} so this is $3d^54s^2$. When you remove 4s electrons it will be d^5 system. Similarly, $3d^64s^2$, remove 3 electrons so that, Fe will be in +3 state, this is d^5. In case of d^6 again Fe2+ and cobalt 3+.

We have 4 unpaired electrons and in case of cobalt2+, d^7 system we have 3 unpaired electrons and nickel 2+ octahedral, we have 2 unpaired electrons. The d^9 system we have 1 unpaired electron and in case of d^{10} zinc, cadmium, mercury; so we do not have any unpaired electrons at all. And of course, only d^4, d^5, d^6, and d^7 show both high spin and low spin complexes and the electronic configuration I have given here. This series is for low spin complexes and this series is for high spin complexes.

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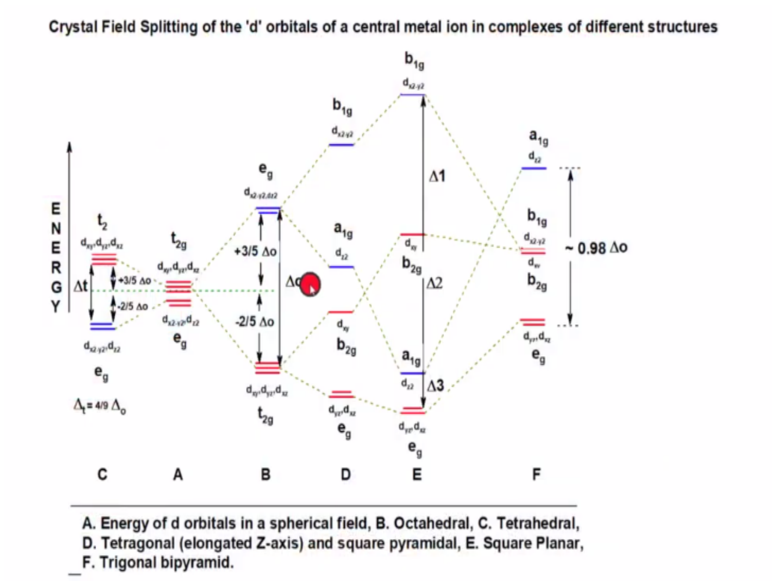
Crystal Field Splitting of the 'd' orbitals of a central metal ion in complexes of different structures

A. Energy of d orbitals in a spherical field, B. Octahedral, C. Tetrahedral, D. Tetragonal (elongated Z-axis) and square pyramidal, E. Square Planar, F. Trigonal bipyramid.

And this is a consolidated diagram that shows various crystal field splittings of the d orbitals under the influence of different ligand field. You can clearly see here, this is for tetrahedral and of course this is a degenerate system in the absence of ligand field. And when you have this octahedral ligand field, this is how the splitting is. And then if you go for D; A, B, C this one and if you go for D, I have listed here tetragonal elongation.

And when you have tetragonal elongation this t^{2g} as well e_g will be further split and this is what exactly looks like. And if you recall this is very similar to a square planar and of course when you have strong ligand field, d_z^2 comes below d_{xy} and d_{xy} goes little bit up. So, that means, elongation has something to do with square planar geometry, they show similarities. And then the E, square planar complex, you can see here, as I mentioned it comes a little down here and this is a typical square planar splitting.

And in case of F, this is for trigonal bipyramidal one. And also, you can see the relative CFSE crystal field stabilization energy and also relative separation between the HOMO and LUMO. In case of molecular orbital theory, we frequently use highest occupied molecular orbital and lowest unoccupied molecular orbitals, the gap between that one is called crystal field stabilization energy, same thing we use in ligand field theory also, so keep that in mind. And this is how one can show consolidated diagram for various ligand fields.

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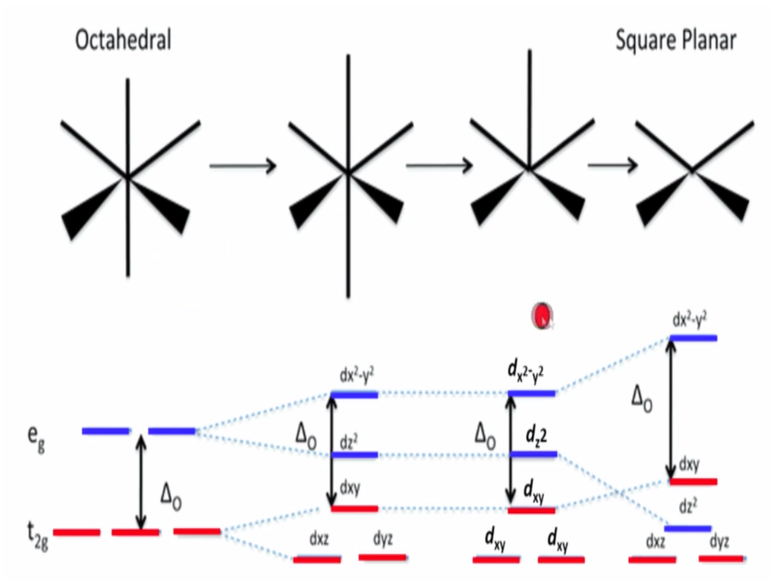

So, now let us look into the relationship between octahedral and square planar, which goes through tetragonal distortion and then losing one ligand to achieve square pyramidal and eventually when you take out this ligand and also in axial position, we will end up with square planar. So, that means, when you change from octahedral to distortion, tetragonal distortion, in particular tetragonal elongation and then get rid of one ligand to have square pyramidal geometry.

And then get rid of this one to end up with square planar geometry. Then, thus look into the relative positions of various d-orbitals when we try to do this transformation from octahedral to square planar. You can see here the relative energies and how they are going to transform can be clearly seen here. This is tetragonal elongation. Of course, tetragonal elongation remains more or less same, for square pyramidal, there is no change.

That means the crystal field splitting whatever we write for octahedral with tetragonal elongation, holds good for square pyramidal geometry as well. So, that means if you remember octahedral, remembering for tetragonal elongation by looking into what actually happens to these orbitals, and then that remains more or less the same for square pyramidal geometry.

And then here only the difference between square pyramidal and square planar is d_z^2 comes further down whereas d_{xy} energy slightly elevated, that is, it so that now remembering the crystal field splitting is rather much easier.

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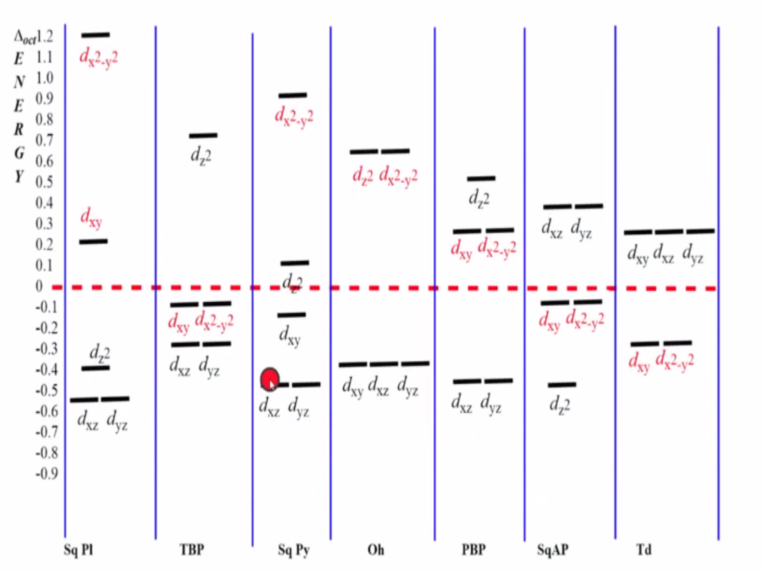

Again, I have listed here the relative energy of various d-orbitals with respect to the corresponding ligand field. I have shown here, this is what exactly I wrote in the previous one and this is written in a different format here. And here I have included square planar, trigonal bipyramidal, square pyramidal and octahedral and also here I have included pentagonal bipyramidal. And here square antiprism I have included and here this is tetrahedral.

So many textbooks give this kind of splitting diagram only for standard octahedral and tetragonal elongation and compression and square planar geometries, but not for many others that is the reason I thought I should include crystal field splitting for most of the geometries we come across in coordination chemistry with coordination number varying from 2 to 9.

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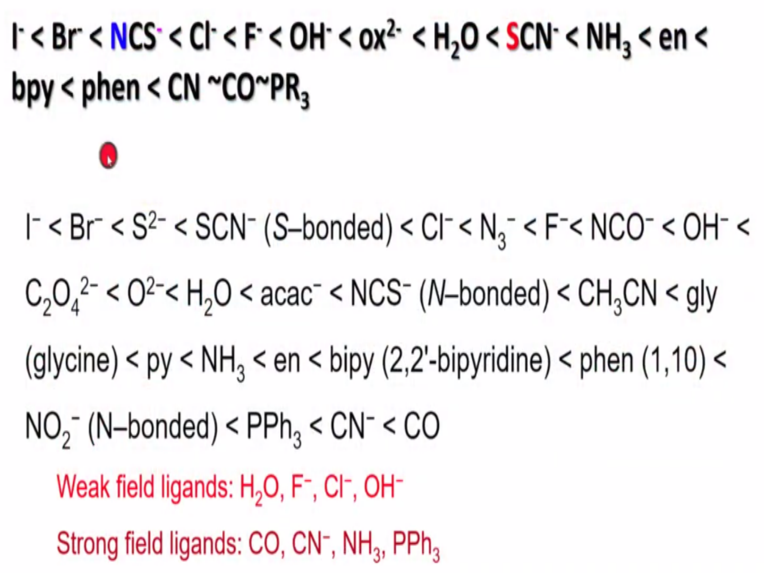

$I^- < Br^- < NCS^- < Cl^- < F^- < OH^- < ox^{2-} < H_2O < SCN^- < NH_3 < en <$ bpy < phen $< CN^- \sim CO \sim PR_3$

$I^- < Br^- < S^{2-} < SCN^-$ (S–bonded) $< Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O <$ acac$^-$ $< NCS^-$ (N–bonded) $< CH_3CN <$ gly (glycine) < py $< NH_3 <$ en < bipy (2,2'-bipyridine) < phen (1,10) $< NO_2^-$ (N–bonded) $< PPh_3 < CN^- < CO$

Weak field ligands: H_2O, F^-, Cl^-, OH^-

Strong field ligands: CO, CN^-, NH_3, PPh_3

So, now, I have listed here various ligands in the order of their ligand field strength and this we call it as spectrochemical series. And there is a background for spectrochemical series that is crystal field theory. So, crystal field theory through CFSE that can be measured using electron spectroscopy, later I shall elaborate more about electronic spectroscopy. So, using that one, you can look into the relative strengths of these ligands.

And you can put them at an appropriate place, give appropriate rank in the spectrochemical series. So, this is in the increasing order of ligand field strength and among them, I have listed here short one. Iodide is the weakest ligand, whereas cyanide, carbon monoxide and tertiary phosphines are the strongest ligands. And of course, when you look into crystal field theory through CFSE you can judge, whether a ligand is weak or strong with respect another ligand.

But why a particular ligand is weak ligand, why a particular ligand is strong ligand that information, really it does not come here. It can only show through experiments, what happens. But when we go to molecular orbital theory, I shall tell you how to classify these ligands and why a given ligand is a weak ligand or a strong ligand or of intermediate strength that I shall clarify when I go to molecular orbital theory.

So, I have given an extended spectrochemical series here. This includes most of the ligands we come across and also, I have listed some important weak field ligands, here for example, water, fluoride, chloride and hydroxo. And similarly, I have also listed important strong field ligands carbon monoxide, cyanide, ammonia, triphenylphosphine.

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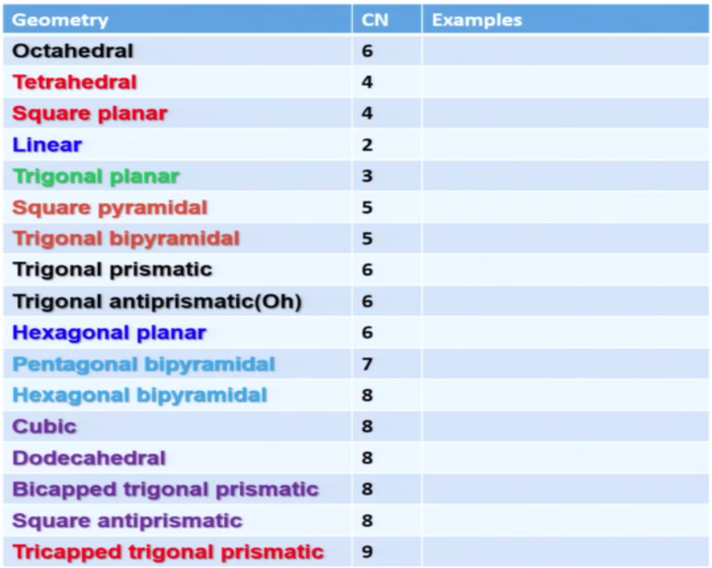

Geometry	CN	Examples
Octahedral	6	
Tetrahedral	4	
Square planar	4	
Linear	2	
Trigonal planar	3	
Square pyramidal	5	
Trigonal bipyramidal	5	
Trigonal prismatic	6	
Trigonal antiprismatic(Oh)	6	
Hexagonal planar	6	
Pentagonal bipyramidal	7	
Hexagonal bipyramidal	8	
Cubic	8	
Dodecahedral	8	
Bicapped trigonal prismatic	8	
Square antiprismatic	8	
Tricapped trigonal prismatic	9	

So, before I try to make it very clear about how to write crystal field splitting diagrams starting from octahedral, so let me list some of those geometries we come across among coordination compounds. The most common one is octahedral with coordination number 6, tetrahedral coordination number 4, and again square planar coordination number 4. Linear we have 2 and trigonal planar 3, square pyramidal 5, trigonal bipyramidal 5.

Again trigonal prismatic 6, trigonal antiprismatic or octahedral same 6, hexagonal planar 6, pentagonal bipyramidal 7, and hexagonal bipyramidal 8, and cubic 8. Dodecahedral 8, bicapped trigonal prismatic 8, square antiprismatic 8 and tricapped trigonal prismatic 9. We have plenty of examples for each case among coordination compounds. Now to make you familiar with writing crystal field diagrams for any given geometry, I will start with octahedral compounds.

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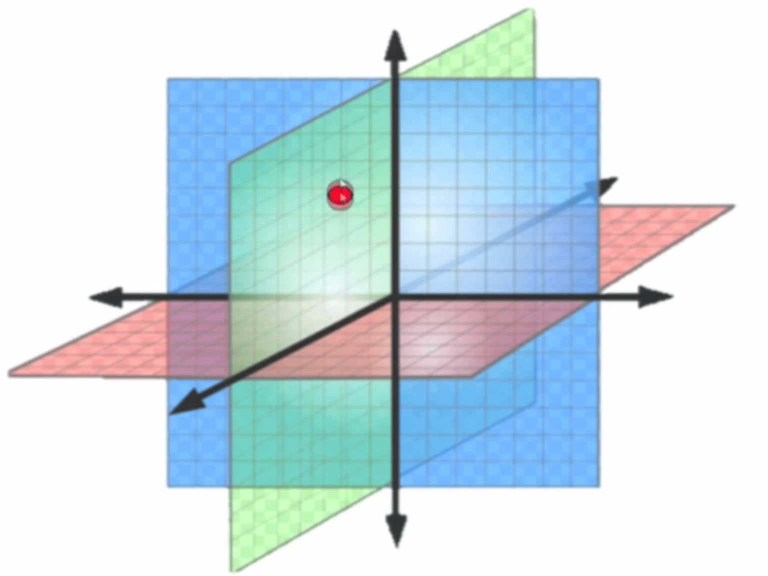

This is what is very important. You should be able to write Cartesian coordinates and then you should be able to identify different planes we come across. For example, if you assume this is z-axis and this is the x-axis and this is y-axis, you should be able to distinguish between the xy plane and xz plane and yz plane and then you should be able to assess the orientation of different orbitals with respect to Cartesian coordinates. And also, we can see their impact when the ligands are approaching the metal from different directions as per that, defined the geometry for that particular complex.

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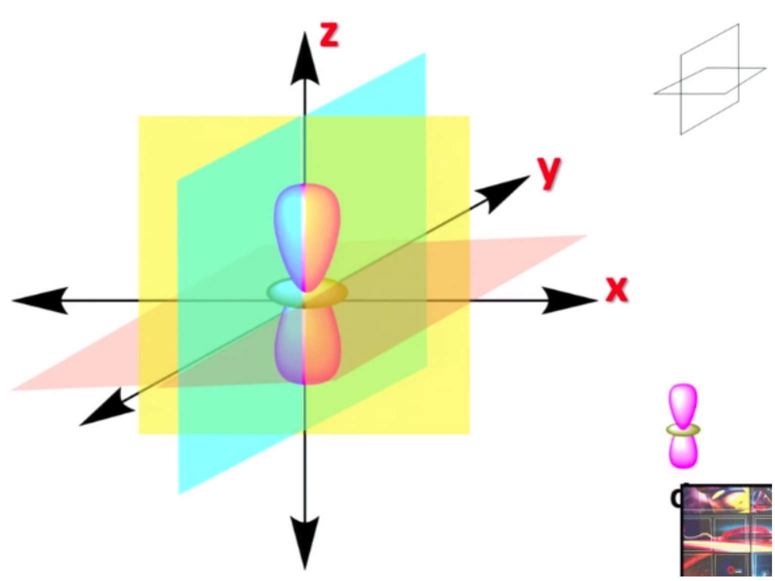

So, first what you should do is write Cartesian coordinates and here the origin is there. Try to place your metal at this 0 and then identify the plane and you can see clearly xy plane and this is xz plane and this is yz plane. Now you start putting d_{z}^{2}, d_{z}^{2} orientation is in this direction. Now, we know, if the ligands are approaching in this direction, what would happen to the energy of d_{z}^{2} in that particular ligand field, it can be clearly visualized here.

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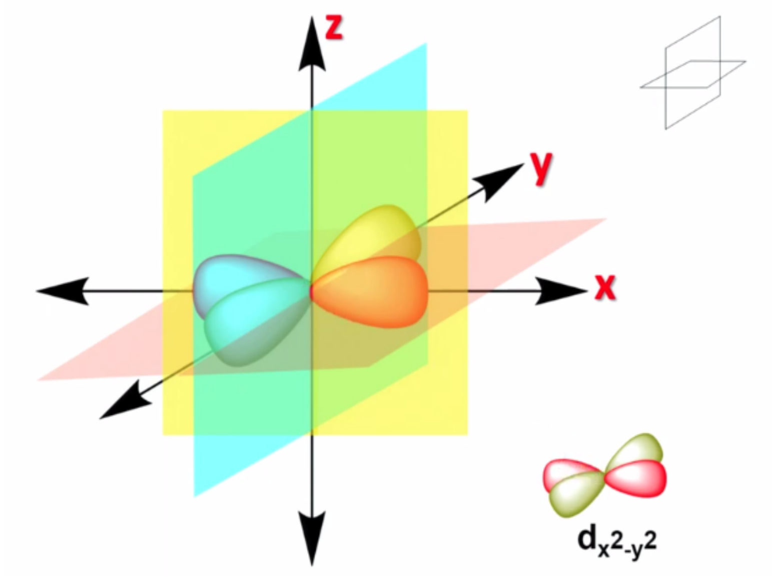

Similarly, I am going to put $d_{x}^{2}{}_{-y}^{2}$. This is along the x, – x and y, – y. So, whatever the ligands approaching in this direction would have impact if electrons are already present in this orbital.

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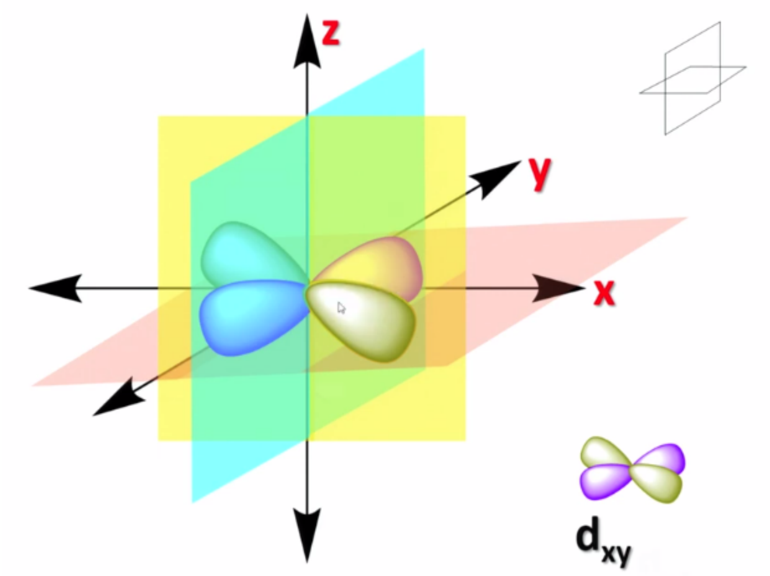

Now this is d_{xy}, d_{xy} is slightly spread between the x and y axis, take $d_{x^2-y^2}$ just rotate it by 45 degree that will change to d_{xy}. So, this is also in xy plane, but is between the planes.

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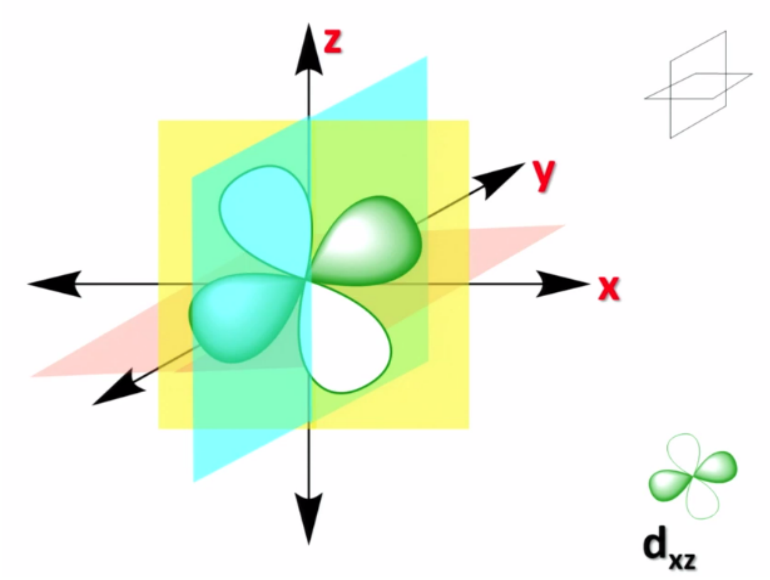

Now, XZ plane we have.

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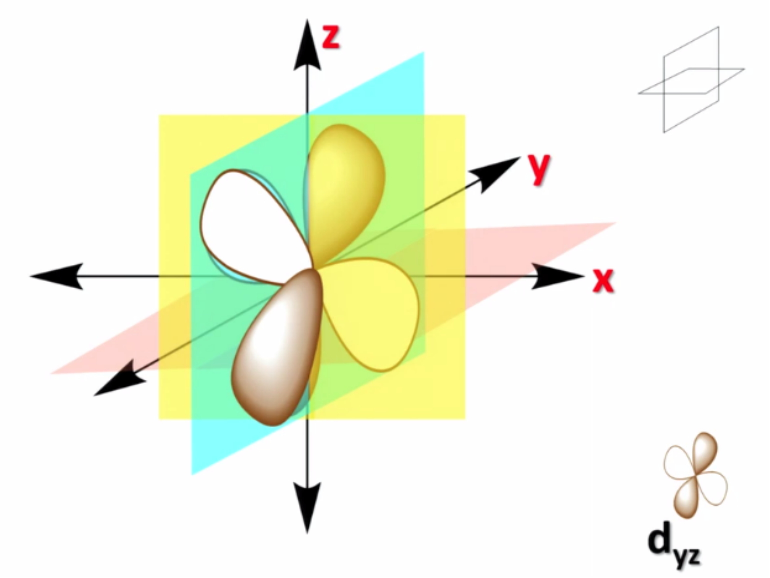

And then we have yz. So, this should be understood properly. Once you understand properly, so writing crystal field splitting diagram for anything can be very easy and it is not memory based. You should remember: it is not memory based, but you should have good analysis of impact on those things, so that you can write relative energy of d-orbitals with respect to any given crystal field or ligand field.

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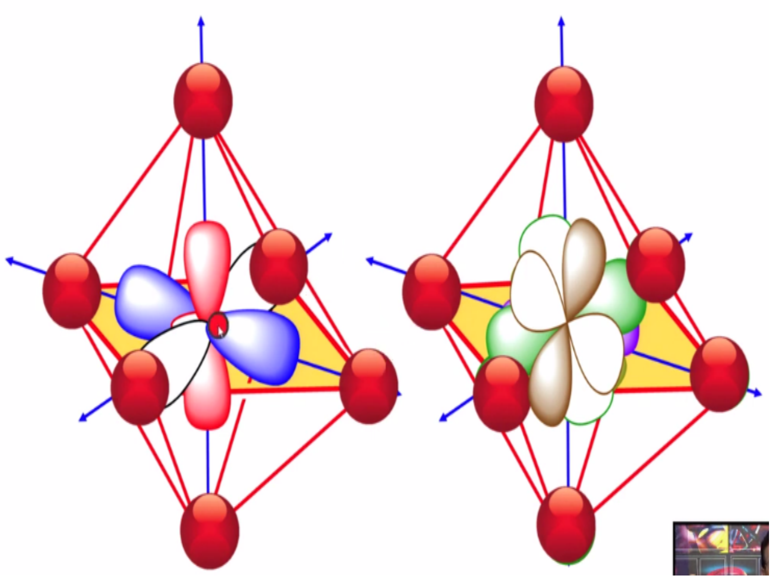

Now, I have written two octahedral molecules with the 6 ligands shown here and this is the place where metal is sitting. So, now I am putting here set of d_{z^2} and $d_{x^2-y^2}$. You can see here they are coming on their way directly that means the energy of these two should be elevated higher, increases. And on the other hand, if you see here d_{xy}, d_{xz} and d_{yz} and strictly speaking they are not coming on the way of ligands, but they are in between.

As a result, the impact of ligand field is less on them, their energy is lower. So now, without worrying too much you should be able to write crystal field splitting, doubly degenerate these two and triply degenerate these three.

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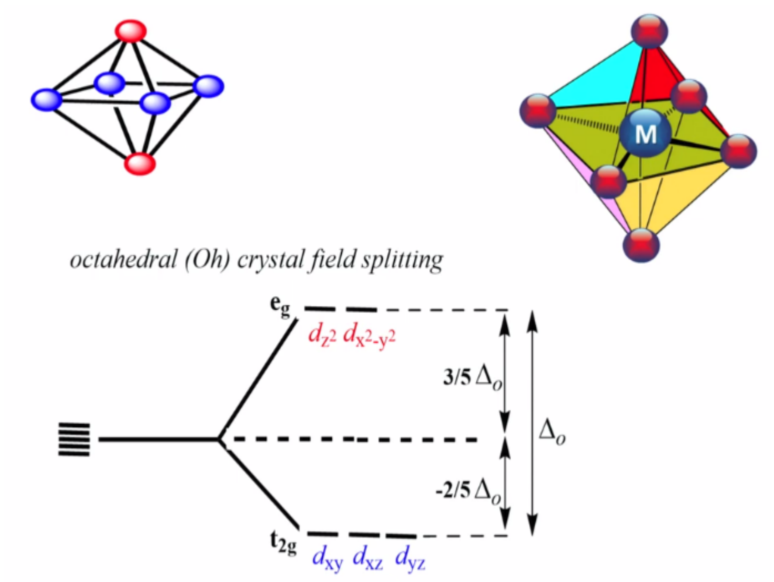
octahedral (Oh) crystal field splitting

And this is how we arrived at the octahedral crystal field splitting, here with respect to barycentre. It is very easy. So, remember this one, practice couple of times and you will not do any mistake in writing crystal field splitting diagram for other geometries.

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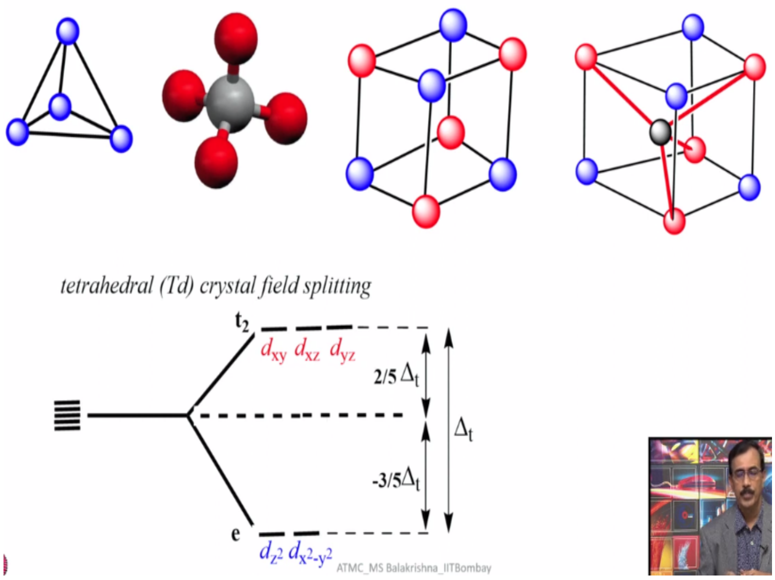
tetrahedral (Td) crystal field splitting

Now, let us look into a tetrahedral molecule. And of course, you can also write like this. And to understand ligand field influence, it is very ideal to imagine this tetrahedral molecule inside a cube, something like this. This is a cube here. With intention I have shown alternate corners with the different coloured spheres. This is the tetrahedral molecule I am visualizing here. This is the metal centre and these red ones are the 4 ligands present at alternate vertices of this symmetric cube.

Now, once if you make connections to central metal from these 4 ligands, then you will end up with a regular tetrahedral geometry. And now what you should do is the way I placed Cartesian coordinates, you place the Cartesian coordinates and then place all the 5d orbitals and you can see the influence of ligand field on this one. In this case, what happens: none of this d_{z^2} and $d_{x^2-y^2}$ will be coming on the way of direction of approach of ligand.

In contrast, d_{xy}, d_{yz} and d_{xz} would be having little larger overlap with the direction of approach of the ligand. As a result, reversal of octahedral splitting takes place in this one. Hence, we write in this fashion crystal field splitting for tetrahedral molecules here. So, energy is elevated here. And if you just write you can see, they have larger overlapping, whereas here less overlapping, so energy of e will be lower. Why we call e and t_2 because it is noncentral symmetric. So, t_2: d_{xy}, d_{xz} and d_{yz}.

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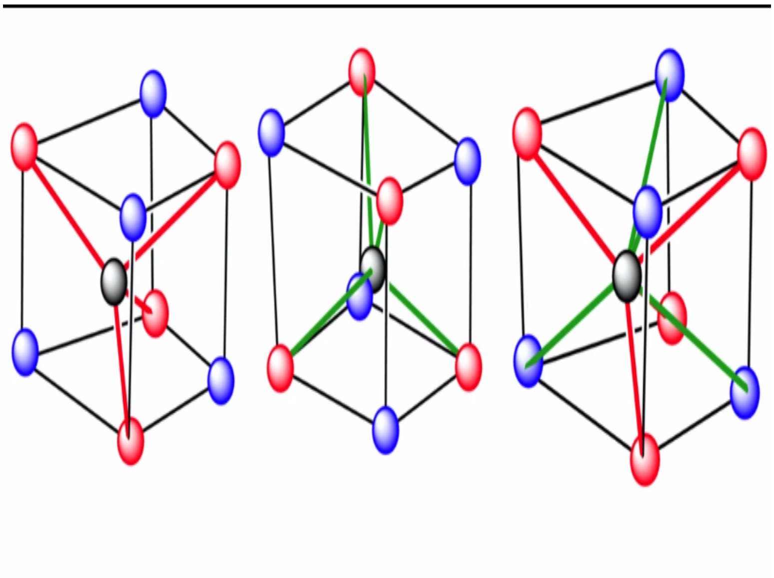

Now, let us look into one more. This is the tetrahedral molecule just I explained. So, here one system and I have another system here. That means here, I have used alternate corners in this fashion. Let me use other alternate corners to generate one more tetrahedral molecule. What would happen if I superimpose this one on this one, something like this. If I superimpose these two, it appears like the metal is common, but it is making bond with all eight corners having almost coordination number 8.

This is what I am referring to cubic splitting. So, that means when 8 ligands are approaching the metal to form a metal complex with composition ML_8 having cubic structure, this is how you can visualize. That means, if I make an attempt to write crystal field splitting for this one, it should be very similar to that of tetrahedral. That means two tetrahedral molecules you superimpose on another one in opposite direction, you end up with common metal and 8 ligands occupying eight corners of cube.

So, that means the crystal field splitting of cubic system is more or less is identical to that of tetrahedral. So, that means tetrahedral and cubic have the same crystal field splitting, okay further it is simplified. So, in my next class, I shall tell you more about several other geometries, until then have an excellent time reading and digesting crystal field theory and especially chemistry of transition elements.