

**Advanced Transition Metal Chemistry – Crystal Field Theory**  
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**Lecture – 13**  
**Background to Crystal Field Theory (CFT)**

Hello everyone. Once again welcome you all to MSB lecture series on advanced transition metal chemistry. In my 12<sup>th</sup> the lecture, I did mention about the interesting aspects of valence bond theory and how there are some exceptions or how there are some you know different type of hybridization we came across to explain totally different types of bonding especially in case of heavier *p*-block elements where we have multiple bonding.

Now, we shall move on to another very fascinating concept which appears almost complete in explaining all properties, reactivity and all applications and spectroscopic properties of transition metal complexes or coordination compounds, that is crystal field theory. Before I really start digging into crystal field theory, let me try to give you the background to this crystal field theory.

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The basic idea of the crystal field theory, that the metal ion in the complexes is subjected to an electric field originating from the ligands, is observed by **Becquerel** in 1929.

The same year, **Bethe** carried out work by correlating symmetry and crystal field strength influence on electronic levels of the gaseous metal ions and laid down foundation to Crystal Field theory.

The basic idea of the crystal field theory that the metal ions in the complexes is, subjected to an electric field originating from the ligands, was first observed by Becquerel in 1829, the same Becquerel who discovered radioactivity along with Marie Curie and Pierre Curie, Henri Becquerel. The same year Bethe who has contributed significantly in developing crystal field

theory, a physicist, carried out work by correlating symmetry and crystal field strength influence on electronic levels of the gaseous metal ions and the laid down an excellent foundation to crystal field theory. That means the Bethe's base contribution is quite remarkable in developing a complete concept of crystal field theory.

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During the same time Dutch physicist Kramers reported that the electronic levels in molecules containing an odd number of electrons must remain at least twofold degenerate (Kramers degeneracy) in the absence of any magnetic field; which is closely related to Bethe's double group theory.

The first application of the new theory was made by Van Vleck (1932). By realizing that the quenching of the orbital momentum would be a consequence of the crystalline field model, he succeeded in explaining why the paramagnetism of the complexes of the first transition series corresponds to a "spin-only" value. Also, the crystalline field model was able to predict in which cases there would be small deviations from this empirical rule.

During the same time Dutch physicist Kramers reported that the electronic levels in molecules containing an odd number of electrons must remain at least to two-fold degenerate. So, this is also called as Kramers degeneracy rule in the absence of any magnetic field, which is closely related to Bethe's double group theory. Double group theory means when he started explaining, he told that that degeneracy of gaseous metal ion will not remain intact when it enters to crystal field.

And it is destroyed and it forms a set of two groups that is what he mentioned, that is called Bethe's double group theory. And this is more or less similar to what Kramers observed and called it as "Kramers degeneracy rule" and that way, many physicists contributed significantly to our crystal field theory. In fact, the physicist who developed this theory, which appears almost perfect even today to explain literally everything about transition metal complexes. The first application of new theory was made by Van Vleck in 1932.

By realizing that the quenching of the orbital momentum would be a consequence of the crystalline field model, he succeeded in explaining, why the paramagnetism of the complexes of the first transition series corresponds to a spin-only value, spin-only values calculated using the equation. Also, the crystal field model was able to predict in which cases there will

be small deviations from this empirical rule. That means crystal field theory explains involving orbital momentum, the small variations that observed in the magnetic properties.

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Later calculations of Schlapp and Penney and of Jordahl, showed that both the anisotropy and the variation of the magnetic susceptibility with temperature could be exactly predicted and calculated. They also confirmed the basic idea in the Bethe-Van Vleck approach that the crystal field reduces the **degeneracy of the electronic levels of the gaseous metal atom.**

Also another Dutch experimental and theoretical physicist Gorter, showed in his paper that the crystal field of a regular tetrahedron will produce the same levels as those produced by a regular octahedron but with the level order inverted.

Later calculations of Schlapp and Penney and of Jordahl, all are physicists, showed that both the anisotropy and the variation of the magnetic susceptibility with temperature could be exactly predicted and calculated. So, that means, they showed that, yes, using crystal field theory one can use calculations and explain all these properties related to magnetic properties. They also confirmed that basic idea in the Bethe-Van Vleck approach that the crystal field reduces the degeneracy of the electronic levels of the gaseous metal atom.

That means, yes, they further confirmed that crystal field theory is correct and the degeneracy of the orbitals are destroyed or removed. Also, another Dutch experimental and theoretical physicist Gorter showed in his paper that the crystal field of a regular tetrahedron will produce the same level as those produced by regular octahedron, but with the level order inverted. Now, we know that how the splitting is, in octahedral field is reversal in case of tetrahedral field.

For example, in case of octahedral field, if you have  $e_g$  higher energy and  $t_{2g}$  lower energy, when you go to tetrahedral field opposite is true  $t_2$  becomes higher in energy and  $e$  becomes lower in energy. So, this was predicted through experimental and theoretical work by physicist Gorter.

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Later attention was given to understanding and calculating the magnetic behaviour of the complex ions. Eventually van Vleck's crystal field theory became a popular and a complete theory to explain almost all aspects of coordination compounds.

Later when ligand field theory and molecular orbital theory (MOT) were developed, CFT and VBT appeared to be special cases of MOT, as shown by van Vleck and British physicist Penney's treatment of the Mn(II) ion and other metal ions.

Concept of strong and weak ligand, work on  $K_3Fe(CN)_6$ , Mn(II) ion and magnetic behaviour of vanadium, titanium and chromium proved the efficacy of CFT.

So, later attention was given to understanding and calculating the magnetic behaviour of the complex ions. Eventually van Vleck's crystal field theory became a popular and a complete theory to explain almost all aspects of coordination compounds. So, later when ligand field theory and molecular theory were developed, there is a reason for modifying or refining crystal field theory to turn into ligand field theory and eventually come up with molecular theory, there is a reason, I shall tell you those things later.

Crystal field theory and valence bond theory almost appeared to be special cases of molecular orbital theory. So, that means it indicates molecular orbital theory has taken the best part of crystal field theory as well as valence band theory and also one can call this modified molecular orbital theory is more or less same as ligand field theory. And these things were shown by Van Vleck and also British physicist Penney. And Penney again worked in looking into the magnetic properties of manganese ion and several other metal ions.

The concept of strong and weak ligand, work on potassium ferricyanide, manganese 2 ion and also magnetic behaviour of vanadium, titanium and chromium proved the efficacy of crystal field theory. And unlike the coordination theory too many conflicts came from Blomstrand. So, here we did not see much of rivalry, but people started looking into it and critically evaluating and start appreciating, and also they used in their later work.

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With the input from CFT, Jahn and Teller had shown in 1937 *that no nonlinear molecule could be stable in a degenerate state and such a configuration must immediately distort*, via nuclear displacements in the molecule, in such a way that the degeneracy is removed. Van Vleck calculated the Jahn-Teller distortions for molecules of the form  $ML_6$  and showed how this configurational instability affected the magnetic moment of the molecules.

With the input from crystal field theory, Jahn and Teller, we call Jahn-Teller theorem or Jahn-Teller distortion, I am talking about the same two gentlemen here. With the input from crystal field theory Jahn and Teller had shown in 1937 that no nonlinear molecule could be stable in a degenerate state and such a configuration must immediately distort. That means when we have; this is more or less applicable for  $d_z^2$  and  $d_{x^2-y^2}$ .

Because they are always lying in the direction of approach of the ligands, especially in octahedral geometry and also this is probably more pronounced among octahedral complexes. That means when they have uneven filling or uneven or odd number of electrons, that is what it is referring, so that means no nonlinear molecule could be stable in a degenerative state and such a configuration must be immediately distorted.

So via nuclear displacements in the molecule in such a way that the degeneracy is removed. So that means such molecules will try to remove the degeneracy and go to lower symmetry. So, van Vleck calculated the Jahn-Teller distortions for molecules of the form  $ML_6$  that means octahedral molecules and showed how this configurational instability affected the magnetic moment of the molecules.

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**Crystal field theory** of Bethe and Van Vleck does not consider the role played by the ligands other than producing a steady crystalline field.

**Ligand field theory** indicates a hybridization of the pure crystal field theory with the molecular-orbital theory of Mulliken.

The ligand field theory incorporates the best features of both the pure **crystal field theory** and **the molecular-orbital theory** and is a superior route for understanding the metal complexes.

Nearly all the results of the crystal field theory are also valid in the ligand field theory.

Crystal field theory of Bethe and Van Vleck does not consider the role played by the ligands other than producing a steady crystalline field. That means the role of ligand ends there after generating an electric field to influence the metal ion and its electron, so that is what, crystal field theory is all about. But ligand field theory indicates a hybridization of the pure crystal field theory with molecular orbital theory of Mulliken.

So, what ligand field theory does is, it takes hybridization concept and also takes pure crystal field theory and also considers molecular orbital theory of Mulliken. So that is the reason it is a very perfect and refined theory to explain literally everything related to ligand field theory. There are few things that could not be explained with the crystal field theory that also can be explained without any ambiguity using ligand field theory.

So, the ligand field theory incorporates the best features of both the pure crystal field theory and the molecular orbital theory and is a superior route for understanding the metal complexes considering all aspects. So, nearly all the results of the crystal field theory are also valid for the ligand field theory. And now as precisely these people concluded crystal field theory looks like a subsidiary branch of ligand field theory, although crystal field theory contributed significantly to come up with ligand field theory.

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### References:

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So, these are some references that are pertinent to early work on crystal field theory before Bethe and Van Vleck proposed their wonderful crystal field theory. If you are interested, you can look into these books and also papers.

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- This is an electrostatic model and uses the ligand electrons to create an electric field around the metal centre.
- Attraction between the central metal atom and the ligands in a complex is purely electrostatic.
- Metal is a positive ion of charge equal to its oxidation state and is surrounded by negative or neutral ligands such as  $\text{NH}_3$ , the negative end of the dipole in the ligand is directed towards the metal ion.

So, now we know that crystal field theory is an electrostatic model and uses the ligand electrons to create an electric field around the metal centre. So, that means the electric field that is generated with the ligands that are approaching the metal, they have a greater influence on deciding what kind of geometry the metal should assume. This attraction between the central metal atom and the ligands in a complex is purely electrostatic.

That means according to crystal field theory concept, the attraction between the central metal atom and the ligand in a complex is purely electrostatic. That means if the metal is cationic in

nature and the ligands are anionic, then it is purely the ion-ion interaction. On the other hand, if the metal is cationic and the ligand is neutral and ligand will generate a dipole, so then it is called ion-dipolar interaction. How it generates dipole?

When you have a ligand such as ammonia or water because of the electronegativity difference N or oxygen would carry negative charge, and whereas peripheral hydrogen atoms carry positive charge, now this negatively charged N or O will be directed towards the metal that is the reason we call it as ion-dipolar interaction. Metal is a positive ion of charge equal to its oxidation state and is surrounded by negative or neutral ligands such as ammonia or cyanide. The negative end of the dipole in the ligand is directed towards the metal ion.

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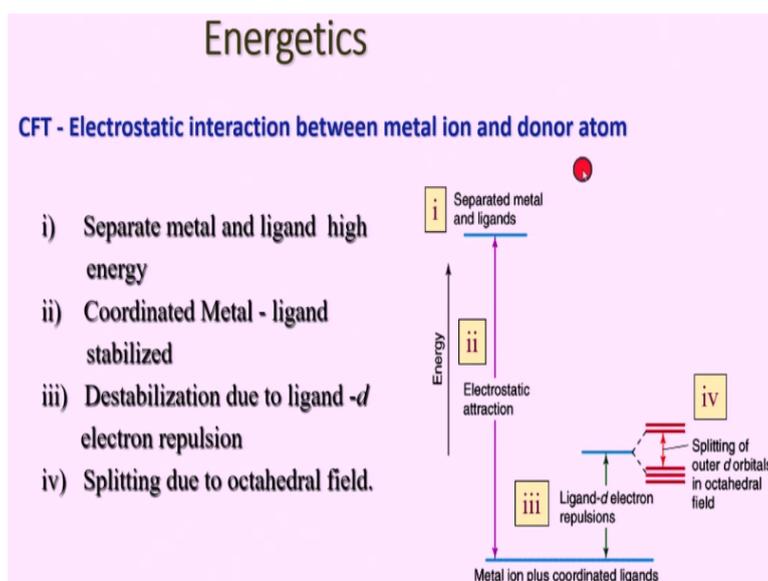
- The electrons on the metal centre are under repulsive forces from those on the ligands. Due to this the electrons occupy the “*d*” orbitals furthest away from the direction of approach of ligands.
- Ligands are point charges
- No metal orbital & ligand orbital interactions
- In the free metal all the *d* orbitals have the same energy and are degenerate
- Ligand field destroys the degeneracy of those orbitals and they possess different energies.

The electrons on the metal centre are under repulsive forces from those on the ligands. That means when the ligands are approaching the metal with a pair of electrons, and already electrons are present in *d*-orbitals, they would experience a repulsive force. As a result of this one, the electrons already present on them metal would occupy *d*-orbital farthest away from the direction of approach of ligands.

That means when the ligands are approaching the metal and electrons already present in the *d* orbitals will occupy positions farther away from the direction of approach of the ligand. And here ligands are the point charges. And crystal field theory gives emphasis and it states that no metal and ligand orbital interaction. That means according to crystal field theory, there is no orbital interaction in metal complexes.

In the free metal, all the  $d$  orbitals have the same energy and are degenerate. You take a metal ion, metal atom, you atomize it into metal gaseous, metal ions till all the  $d$  orbitals are degenerate. Once they enter into ligand field, the ligand field destroys the degeneracy of those orbitals and they possess different energies depending upon the type of ligand field we have in the vicinity of metal centre.

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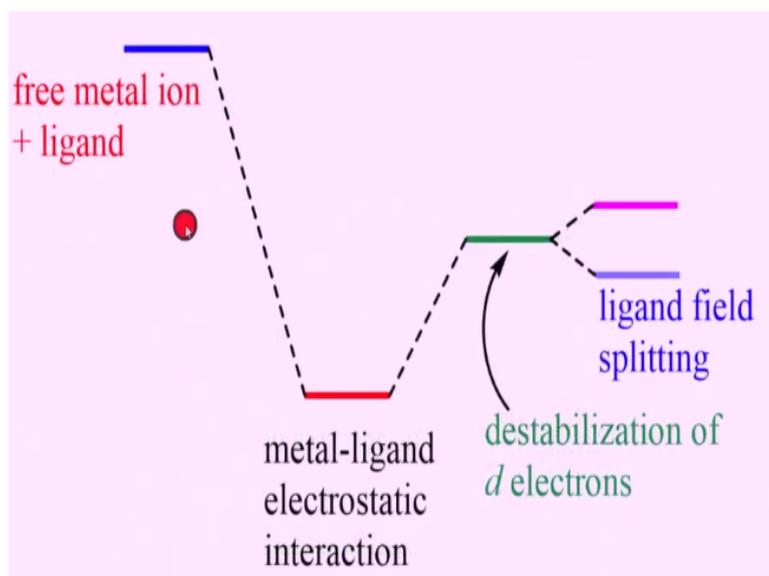


So, that is depicted in this diagram. Electrostatic interaction between metal ion and donor atom is what the crystal field theory says. For example, if we just look into it separated metal and ligands have high energy and coordinated metal and ligand stabilized 2 here. And then destabilization due to ligand  $d$  electron repulsion. Always when the metal to ligand bonds are established, the energy would tend to decrease.

But on the other hand, the electrons that are already present in the metal atom would experience repulsive forces, as a result, again energy is elevated, and further splitting due to octahedral field is shown here. So, that means, one should be able to write in this order, separated metal and ligands and this is electrostatic attraction and metal ion plus coordinated ligands will be low in energy.

And ligand  $d$  electron repulsion would increase it and then depending upon the direction of approach of the ligands and orbits in which electrons are there, the splitting takes place in this fashion. And this is a typical splitting pattern, I have shown for an octahedral complex where  $t_{2g}$  is triply degenerate and  $e_g$  is doubly degenerate,  $e_g$  is nothing but  $d_z^2$  and  $d_{x^2-y^2}$  and  $t_{2g}$  is nothing but  $d_{xz}$ ,  $d_{yz}$  and  $d_{xy}$  orbitals.

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To make it clear, I have shown here. So, free metal plus ligands would be having higher energy and then metal ligand electrostatic interaction establishes metal to ligand bond and as a result the energy drops considerably and then the repulsive forces increases and depending upon the type of ligands we have and their relative orientation with respect to their direction of approach of the ligand, they split and this splitting vary with various ligand fields.

The splitting would be different for different crystal fields, for example octahedral, square planar, tetrahedral, trigonal bipyramidal, all those things. Now one by one we shall start looking into those things.

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## Ligand Field Theory

- Ligand field theory is one of the very useful bonding theories to explain the electronic structure of complexes.
- It is originated from the crystal field theory of ionic crystals to metal complex systems.

So, what is ligand field theory? Ligand field theory is one of the very useful bonding theories to explain the electronic structure of complexes. It is originated from the crystal field theory of ionic crystals to metal complex system, and this theory was originally developed to understand solid state chemistry.

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➤ Consider a ligand field generated by six ligands coordinating octahedrally to a central metal.

➤ The electron pair of the ligands is called the ligand field. Negative charge of anionic ligands, or a negative end (lone pair) of neutral ligands, exert a repulsive force on the metal  $d$ -orbitals which is anisotropic depending on the direction of the orbitals.

➤ Consider the metal cation at the origin from which Cartesian coordinates are constructed.

➤ Then,  $d_{x^2-y^2}$  and  $d_z^2$  orbitals are oriented along the directions of the axes and the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals are directed between the axes.

So, consider a ligand field generated by six ligands coordinating octahedrally to a central metal atom. Of course, it is very appropriate to call crystal field theory as ligand field theory because the electric field is greatly influenced by the ligand field. So, the ligands that are approaching the metal ion. As a result, probably it is more appropriate to call this theory as ligand field theory rather than crystal field theory.

So, consider a ligand field generated by six ligands coordinating octahedrally to a central metal. The electron pair of the ligand is called the ligand field. Two electrons, pair of electrons, negative charge of ionic ligands or negative end of a neutral ligand exert a repulsive force on the metal  $d$  orbitals which is anisotropic depending on the direction of the orbitals. These are the fundamental aspects, one should remember.

Now, consider the metal cation at the origin from which Cartesian coordinates are considered. It is very simple, you write Cartesian coordinates the  $x$  axis,  $y$  axis and  $z$  axis and we extend it, so that the  $x$  axis,  $-x$ ,  $y$ ,  $-y$ ,  $z$  and  $-z$  are there. At the origin, place the metal atom and then also at the origin try to keep all five  $d$ -orbitals and you just analyse the relative orientation. So, the job is done.

So, now when you look into their relative orientation and the direction of approach of the ligands, for example, after putting the metal atom at the Cartesian coordinate origin, now bring six ligands in octahedral fashion. That means now if you try to write an octahedral geometry with metal at the origin of Cartesian coordinate, you can see the direction of approach of ligands towards the metal coincide with  $z$ ,  $-z$ ,  $x$ ,  $-x$ , and  $y$ ,  $-y$  directions.

So, now if you look into  $d_z^2$  and  $d_{x^2-y^2}$ , are oriented along the direction of the axis that means  $d_{x^2-y^2}$  is oriented along  $x$  and  $-x$  and  $y$  and  $-y$ . The  $d_z^2$  is along  $z$  axis. So, that means whatever the ligands that are approaching along these, would experience maximum repulsion as a result, energy is elevated. On the other hand, when the six ligands are approaching along the six directions.

And if you look into the orientation of other remaining d orbitals  $d_{xz}$ ,  $d_{yz}$  and  $d_{xy}$ , they are between these axes, they are between these planes. As a result, what happens? They experience less repulsive forces from the electrons coming from the ligands. As a result, what happens, their energy is lowered with respect to the *zero* energy or barycentre.

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- If ligands are placed on the axes, the repulsive interaction is larger for the  $e_g$  orbitals ( $d_{x^2-y^2}$ ,  $d_z^2$ ) than for the  $t_{2g}$  orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ), and the  $e_g$  orbitals are destabilized and the  $t_{2g}$  orbitals are stabilized to an equal extent.
- The energy difference between the  $t_{2g}$  and  $e_g$  orbitals is important and the average energy of these orbitals is taken as the zero energy.
- If the energy difference between the two  $e_g$  and three  $t_{2g}$  orbitals is set to  $\Delta_o$ , the energy level of the  $e_g$  orbitals is  $+3/5 \Delta_o$  (and that of the  $t_{2g}$  orbitals is  $-2/5 \Delta_o$ ).
- ( $\Delta_o$  may also be expressed as  $10 Dq$ . In this case, the energy level of the  $e_g$  orbitals is  $+6 Dq$  and that of the  $t_{2g}$  orbitals  $-4 Dq$ .)

If ligands are placed on the axes, the repulsive interaction is larger for  $e_g$  orbitals, that is what I mentioned, then for the  $t_{2g}$  orbitals and the  $e_g$  orbitals are destabilized and the  $t_{2g}$  orbitals are stabilized to an equal extent. The energy difference between the  $t_{2g}$  and  $e_g$  orbitals is important and average energy of these orbitals is taken as “zero energy” that is where we put barycentre.

If the energy difference between the two  $e_g$  and the three  $t_{2g}$  orbitals is set to  $\Delta_o$ , this is called crystal field stabilization energy for octahedral splitting, the energy level of the  $e_g$  orbitals is  $+3/5 \Delta_o$  and that of the  $t_{2g}$  orbital is  $-2/5 \Delta_o$ . So, if you put here four electrons, and you put here six electrons, then you will end up with zero electron at this barycentre. So,  $\Delta_o$  may also be expressed as  $10 \Delta q$  or  $10 Dq$ .

In this case, the energy level of the  $e_g$  orbital is plus  $+6 Dq$  and that of the  $t_{2g}$  orbital is  $-4 Dq$ . So, this is how crystal field stabilization energy is defined. I think I will stop here and I will give some time for you to read and understand. In my next lecture, I will proceed with explaining more geometries through simple methods so that you should be able to write crystal field splitting diagram literally for any geometry that comes to your mind. With this have an excellent time reading chemistry.