

**Title: Limitations of Crystal Field  
Theory**

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Crystal Field Theory is one of the most accepted theories proposed for explaining the bonding in coordination complexes. It was proposed by Hans Bethe. It treated the atoms as hard spheres and interaction between them is purely electrostatic. The central metal atom has a positive charge and the surrounding ligands have a negative charge. When this negatively charged ion approaches towards the positive metal ion, the electrostatic attraction causes changes in the energy levels of the metal ion and bonds to form in the end. Crystal Field Theory was successful in explaining the bonding in most of the complexes. But it had some limitations too. In this article, we will discuss the limitations of the Crystal field theory.

### **Limitations of CrystalField Theory**

Theories are always based upon assumptions. These assumptions may fit perfectly with experimental data. However, there are some limitations of CFT too; which are discussed below:

- This theory always took only d orbitals into consideration. Contribution of s and p block was never taken into consideration.
- It treated the atoms as hard spheres and interaction between them was considered totally electrostatic. But it cannot be true in reality.
- This theory did not give any importance to the orbitals of the ligands. It only talked about the central metal ion.
- This theory could not explain the behaviour of some complexes about why some orbitals show large splitting and some show less splitting.
- It cannot explain why  $\text{H}_2\text{O}$  is a stronger ligand while  $\text{OH}^-$  is weaker than water.
- One of the main drawbacks is that CFT does take care of covalent character between metal and ligands. It only took the ionic character into consideration.
- All the consequences and effects that are present due to the covalent character are not explained by Crystal Field Theory.

So, these are the limitations of crystal field theory. To overcome these limitations, Ligand Field Theory (LFT) was proposed later. LFT gave equal importance to the ligand orbitals.

The main drawback of the crystal field theory is that it does not consider the covalent character in metal-ligand bonding at all. It treats the metal-ligand interaction in a purely electrostatic framework which is pretty far from reality. All the effects which originate from covalence cannot be explained by this theory. Therefore, the main limitations of crystal field theory can be concluded only after knowing the causes and magnitude of the covalence in the metal-ligand bonds.

### ➤ *Evidences for the Covalent Character in Metal–Ligand Bond*

The crystal field theory considers the metal center as well as surrounding ligands as point charges and assumes that the interaction between them is 100% ionic. However, quite strong experimental evidences have proved that there is some covalent character too which cannot be ignored. Some of those experimental evidences are as follows:

**1. The nephelauxetic effect:** The electrons present in the partially filled *d*-orbitals of the metal center repel each other to produce a number of energy levels. The placement of these levels on the energy scale depends upon the arrangement of filled electrons. The energy of these levels can be given in terms of “Racah parameters” *B* and *C* (a measure of interelectronic repulsion). The energy difference between same multiplicity states is expressed in *B* and *Dq* while between different multiplicity states is given in term of *B*, *Dq* and *C*. It has been observed that the complexation of metal center always results in a decrease in interelectronic repulsion parameters which in turn also advocates a decrease in the repulsion between *d*-electron density. Now, as the magnitude of this interelectronic repulsion is dependent upon the distance between the areas of maximum charge density, the decrease in its value is expected only when the *d*-orbital lobes extend in space. This is called as the nephelauxetic effect and measured as the nephelauxetic parameter ( $\beta$ ).

This extension or nephelauxetic effect may be attributed to the larger orbital overlap between metal and ligand resulting in greater stabilization due to covalent bonding. Hence, the direct effect of covalent bonding between metal and ligand is to decrease the interelectronic repulsion parameters. In other words, greater the decrease in “Racah parameters”, larger is the extent of covalent bonding between metal and ligand. Different ligands have different capacity to extend their *d*-orbital and are arranged in ascending order, known as the nephelauxetic series as:



It has been observed that the nephelauxetic ratio always follows a certain trend with respect to the nature of the ligands present. However, there are many ligands that do not form complexes with a particular metal ion; the Racah parameter and for these complexes cannot be calculated empirical rather experimentally.