Symmetry and Group Theory

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Lecture -53
Crystal Field Theory Part- I

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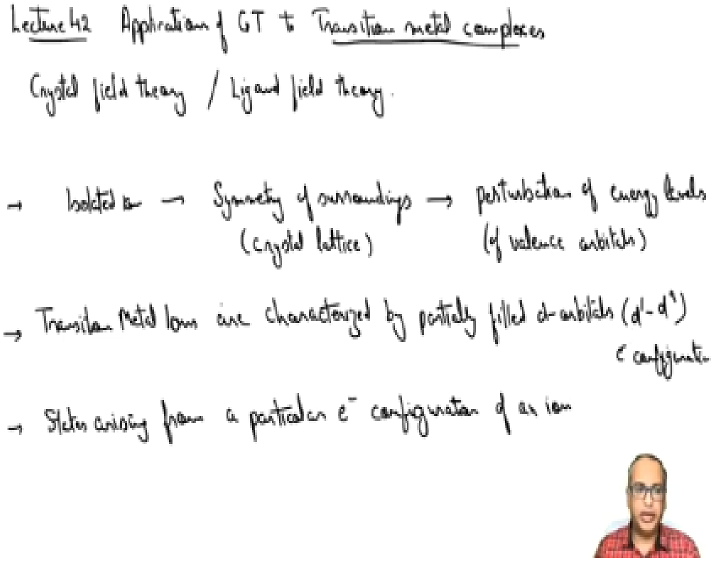

Lecture 42 Application of GT to Transition metal complexes

Crystal field theory / Ligand field theory.

→ Isolated ion → Symmetry of surroundings → perturbation of energy levels
(crystal lattice) (of valence orbitals)

→ Transition Metal Ions are characterized by partially filled d-orbitals (d^1-d^9)
e configuration

→ States arising from a particular e^- configuration of an ion

So, today we will be looking at some other applications of group theory, so let us start the today's lecture. So, we will be looking at application of group theory to understand the bonding in transition metal complexes. Now this is explained typically by crystal field theory or the updated version of that is ligand field theory where we will see what are the differences. So, how the discussion started with crystal field.

So, if you take an isolated ion and if symmetry of the surroundings are taken into consideration; so, symmetry of surroundings is created basically by the crystal lettuce in which that particular ion is sitting in. So, crystal lattice will define the symmetry of the surrounding. In what orientation different ligands are coming in, what is the what kind of field is generated by the crystal.

So, that will dictate the symmetry of the surrounding. And if you see that there is a perturbation of energy levels of, we can say, valence orbitals. This has been observed and to explain this phenomena crystal field theory was coined. So, what basically happens so here we are discussing transition metal complexes. So, transition metal complexes, how are they characterized? So, transition metal complexes or we can say transition metal ions.

Because we are talking about ions, let’s not form the complex yet. So, transition metal ions are characterized by we can say partially filled d orbitals. So, d orbitals would have a particular energy when they are in isolated ion and when isolated that particular ion is now put into a crystal lattice of some ligand. Then there would be perturbation of energy levels of those d orbitals.

So, we will see how that perturbation happens, whether they are destabilized, what d orbitals are stabilized? What are destabilized? And all that is explained can be explained by at least relative energies can be explained by group theory. So, partially filled d orbitals meaning that you have d1 to d9 configuration electronic configuration, which is also explained by the term symbols. So, if you remember crystal field theory studying in inorganic chemistry course.

So, you must have learned terms symbols which explains the d1 to d9. And those terms symbols are basically split into different degenerate, non-degenerate orbitals when they are put into a crystal lattice. So, we can say these are the different points of crystal field theory, so you can say states arising from a particular electronic configuration of an ion. So, it can be from d1 to d9 anywhere;

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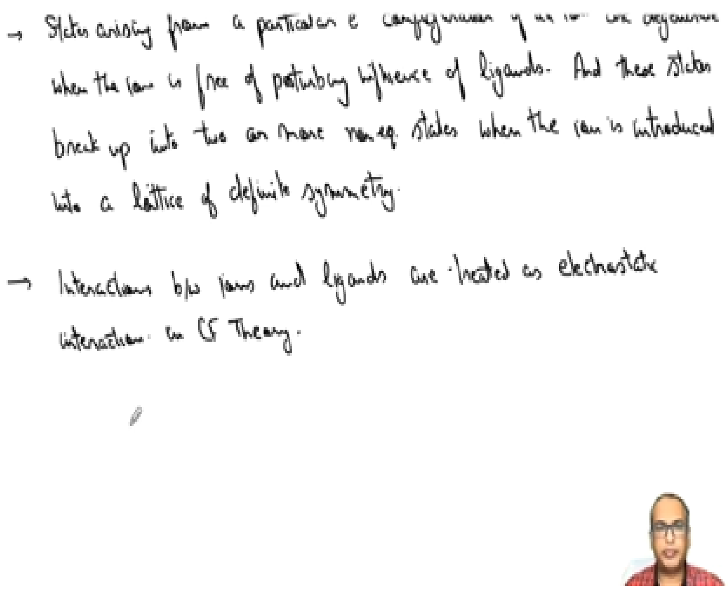

→ States arising from a particular e configuration of an ion are degenerate when the ion is free of perturbing influence of ligands. And these states break up into two or more non-eq. states when the ion is introduced into a lattice of definite symmetry.

→ Interactions b/w ions and ligands are treated as electrostatic interaction in CF Theory.

Any electronic configuration would have a particular state which is defined by the term symbol are degenerate when the ion is free of perturbing influence of ligands. So, when there is no perturbing influence of ligands, these d orbitals are the state arising from a particular electronic configuration would be degenerate. And then we can say and these states break up into two or more non-equivalent states when the ion is introduced into a lattice of definite symmetry.

So, they should also see that these interaction between ions and the incoming ligands are treated as electrostatic interactions, interactions between ions and ligands, in crystal field theory I mean, are treated as electrostatic interaction. We can apply in crystal field theory.

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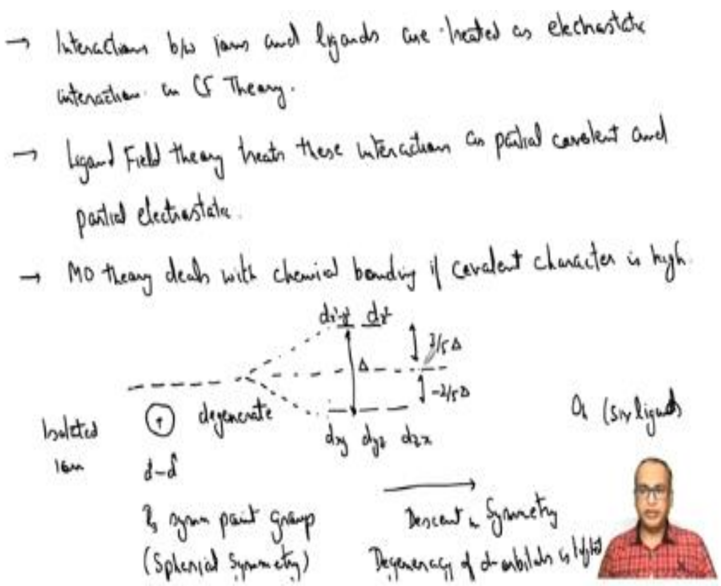

→ Interactions b/w ions and ligands are treated as electrostatic interaction in CF Theory.

→ Ligand Field theory treats these interactions as partial covalent and partial electrostatic.

→ MO theory deals with chemical bonding if covalent character is high.

Now but there is a possibility of having some partial covalent character and partial electrostatic. In that case, the theory is modified and it is called as ligand field theory. So, we can say ligand field theory treats these interactions as partial covalent and partial electrostatic. And of course, if it is purely electrostatic then we have already seen that MO theory explains the bonding. So, we will just write it for completeness that a MO theory deals with bonding if covalent character is high.

So, that makes sense so this is basically crystal field theory and what we see is that if there is an ion let us say it can be d1 to d9 anything, it has to be partially filled. So, if you see that the five d orbitals are all degenerated. So, this is a isolated ion case. Now if it is an isolated ion central metal atom transition metal ion will have five d orbitals, which are all equal in energies, so we will say degenerate.

And why this will be degenerate? Because this will belong to R3 symmetry which we have not discussed actually. R3 symmetry point group, which is also called as spherical symmetry. So, spherical symmetry basically you can think of any symmetry element, which you can think of will be present in this. So, that is why it is called as highly symmetric case and this will be a spherical symmetry, R3 symmetry point group.

Now when you go from here to let us say octahedral case where there are six ligands approaching. So, the outside symmetry or the external symmetry of this will be modified based on the ligand field now. So, the let us say if you dip this particular iron into a crystal lattice which is of octahedral symmetry or if this particular ion, in other words, if you can say that if this particular ion is surrounded by 6 ligands at equidistance.

And the ligands are also equidistant from each other to minimize the ligand-ligand repulsion, then this would be octahedral symmetry. So, now Oh point group is a subset of R3. So, basically what we are doing is, we are doing descent in symmetry. And we have learnt that when we go for descent in symmetry there is a possibility that degenerate set of orbitals may undergo splitting and then it may not remain as degenerate when you go for descent. So, what happens?

These d orbitals can either form something like this. So, this will be d xy, d yz, d zx and this will be d x square - y square and d z square, or let us say if you do the same thing in tetrahedral field, then the pattern will be reverse, we will see how it works out. So, you can say that the degeneracy is lifted here. So, degeneracy of d orbitals is lifted so now that the degeneracy is lifted there must be some sort of an energy gap, which is created.

This will be delta, complete of this will be delta and then we can say that if we divide this into two parts if this was my original ground set so then this particular thing is equal to minus 2 by 5 delta and this will be 3 by 5 delta. This is to basically balance the separation energy and this type of separation energy can be confirmed by looking at the dd transition spectra and so on. So, the matching the energies from the spectroscopy onto this.

So, basically due to crystal field, there is a change in symmetry so there is a descent in symmetry of isolated ion and then you see that there is degeneracy of d orbitals which was there in the R3 point group, which gets lifted when you go to Oh point group.

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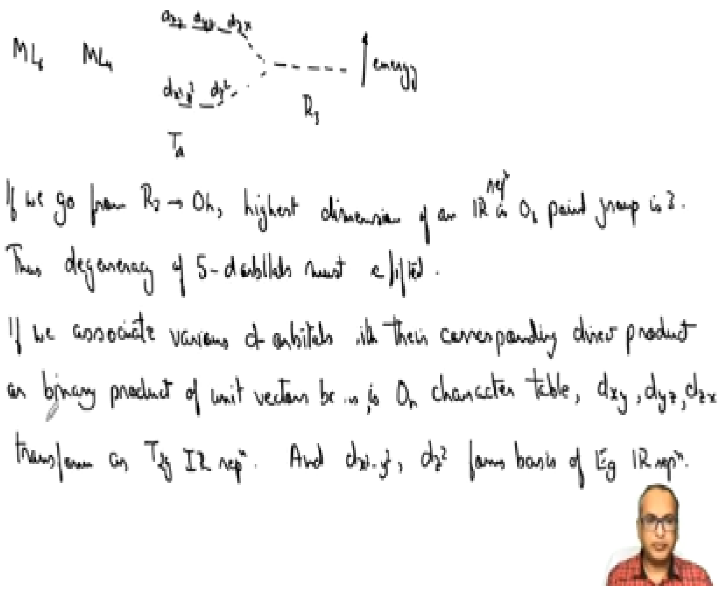

If we go from $R_3 \rightarrow O_h$, highest dimension of an IR rep^n in O_h point group is 3.

Thus degeneracy of 5-d orbitals must be lifted.

If we associate various d-orbitals with their corresponding direct product or binary product of unit vectors given in O_h character table, d_{xy}, d_{yz}, d_{zx} transform as T_{2g} IR rep^n. And $d_{x^2-y^2}$, d_{z^2} forms basis of E_g IR rep^n.

So, by the way this is the most common formation, most common coordination in transition metal complexes ML6. But as I said, we can also have ML4 type of tetrahedral complexes, in that case we will see that the degeneracy is lifted like this. So, if you had isolated ion with five d orbitals then in case of tetrahedral this is in Td and this is R3, the symmetry is lifted like this. And then you have dx square minus y square dz square here and d xy, yz, zx goes over there if this is my energy axis.

So, why this kind of splitting happens? Why there is split up of 3 is to 2 that, 3 orbitals are arranged in a particular with a particular energy and 2 orbitals are arrange with the particular energy, why that happens? So, group theory does explain that so let us see that if we go from R3 to Oh so highest order or highest dimension of an IR in Oh point group is 3. That we can see from Oh character table that highest dimension of an irreducible representation, IR representation is 3.

So, thus we can say degeneracy of five d orbitals must be lifted. So, that must happen now, because those five orbitals cannot form a basis for an IR representation, which has dimension as 5. So, maximum dimension is 3, so d orbitals can only make a basis for up to a dimension of 3 and that is how it gets broken up into 3 and 2. So, now let us see that why these set of orbitals d xy, d yz, d zx combined together and pair together.

And d x square minus y square and d z square pair together, so let us see that. So, that we have already seen that we can associate the basis functions or the direct product or the binary product of unit vector transformations to d orbitals, that we have seen. So, if we associate various d orbitals with their corresponding direct product or we can say binary product both are same things of unit vectors basis and we have to do this in Oh character table.

We will see that d xy, d yz, and d zx transform as T2g IR representation. And d x square minus, y square and d z square forms basis of Eg IR representation. So, because they do that, they will degenerate and these 3 will be degenerate. So, we can also verify it actually so let us verify that. So, let us go to next page.

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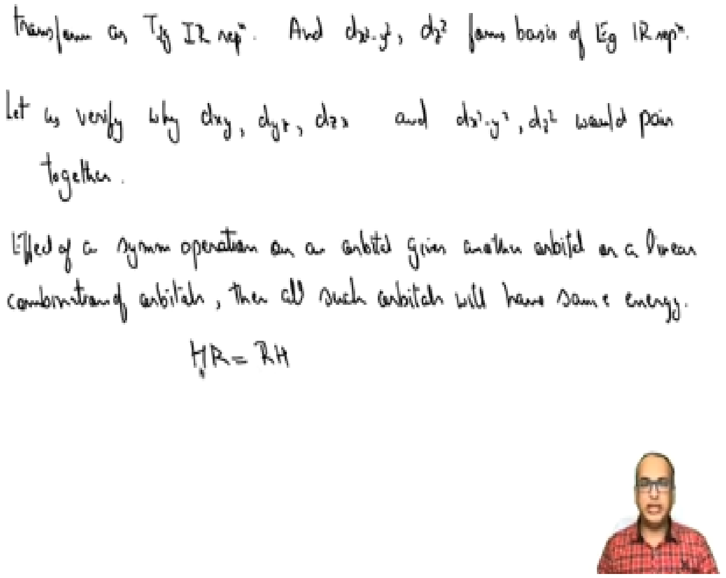

transform as T_{2g} IR rep^n. And $d_{x^2-y^2}$, d_{z^2} forms basis of E_g IR rep^n.

Let us verify why d_{xy}, d_{yz}, d_{zx} and $d_{x^2-y^2}$, d_{z^2} would pair together.

Effect of a symm operation on an orbital gives another orbital or a linear combination of orbitals, then all such orbitals will have same energy.

$$HR = RH$$

So, let us verify why d xy d yz d zx and dx square minus y square d z square would pair together, so this can be easily verified. So, suppose if you have any symmetry operation under Oh point if you take any particular symmetry operation and that symmetry operation is able to convert one of the orbitals into the other or into a linear combination of the other two, then it would mean that your merely changing the coordinates of that particular orbital and not the energy.

We have seen that the Hamiltonian and R commute with each other, so symmetry operation commutes with Hamiltonian. So, you do not change the energy of that orbital. So, that means if we apply let us say any symmetry operation under Oh which and it gets converted into d yz or it gets converted into d zx. Then we are sure that these three have same energy because they are inter-convertible by symmetry operation.

Similarly, if these two are inter convertible by symmetry operation of Oh point group then they will also have same energy. So, we can say that these will be degenerate so let us specify that. Let us write down that we have if effect of symmetry operation on an orbital gives another orbital or a linear combination of two orbitals then all such orbitals will have same energy. And this comes out of the fact that Hamiltonian commutes with symmetry operation.

So, this basically tells you if you first do a symmetry operation and then measure energy or if you first measure energy and then do symmetry operation it should be equal that would mean that effect of symmetry operation does not change the energy of that particular orbital. And if you are getting those orbitals, so we will let us see that actually. Let us look at that example.