Symmetry and Group Theory
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Lecture -54
Crystal Field Theory Part- II

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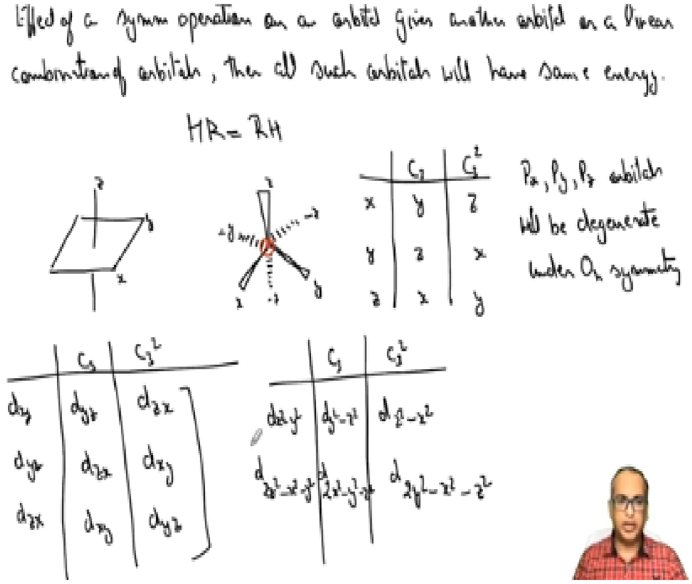

Effect of a symm operation on an orbital gives another orbital or a linear combination of orbitals, then all such orbitals will have same energy.

$HR = RH$

	C_3	C_3^2
x	y	z
y	z	x
z	x	y

P_x, P_y, P_z orbitals will be degenerate under O_h symmetry

	C_3	C_3^2
d_{xy}	d_{yz}	d_{zx}
d_{yz}	d_{zx}	d_{xy}
d_{zx}	d_{xy}	d_{yz}

	C_3	C_3^2
$d_{x^2-y^2}$	$d_{y^2-z^2}$	$d_{z^2-x^2}$
$d_{2z^2-x^2-y^2}$	$d_{2x^2-y^2-z^2}$	$d_{2y^2-x^2-z^2}$

So, let us look at octahedral case only, so let us say we have this and if we have this as x, y, and z we can also draw it like, so I am trying to draw it in a way so that it is easier to identify the C3 axis. So, this is my x, y, and z this is my - z, - x, - y and this is my C3 axis which is now equidistant from all three and going perpendicular to the plane of the board if I have drawn it like this.

So, now if I let us first do C3 operation on x, y, z. So, if we have let us say let us make a table do C3 operation and we will also do C3 square operation on x, y, and z. So if it is C3 onto x, x goes to y if we do C 3 square x goes to z, y goes to z and y goes to x, z goes to x, z goes to y. So, that means x any property which is oriented along x, y, z that is Px, Py, P z orbitals that will be degenerate. So, Px, Py, Pz orbitals will be degenerate under Oh symmetry.

Similarly, let us also look at d orbitals now. So, if we want to draw, so we have dxy, dyz, dzx and maybe here we will draw for the rest of the two, so d x square - y square and d z square, so by the way d z square is not the complete representation, so it is actually a short form, so the full functional form is 2 z square - x square - y square, this will be required C3, C3 square, C3, C3 square.

So, now what happens if you do C3 on d xy, how do you calculate that? So, you do not need to actually measure that you just need to see the effect of C3 onto x and effect of C3 onto y independently and you will get the correct answer, so x goes to y here, so I am reading from here and y goes to z, so I can say if C3 is applied on d xy I will get yz. Similarly, if C3 square is applied I will get zx.

Similarly, again C3 is applied on yz so y goes to z, z goes to x, so I will get d zx and d xy. Similarly, d xy and d yz, so now you can see that these three orbitals are interconvertible by doing one symmetry operation, one symmetry operation or two symmetry operations so this would mean that there is no change in energy between these orbitals. So, that means I can say that these three belong to same energy and these have same symmetry also T2g symmetry.

So, we label this set of orbitals as T2g. Now let us look at this one, so C3 if you do on x square - y square you will get y square - x square and z square - x square. Similarly, if you do C3 on this you will get 2 x square - y square - z square, of course d. And here we will get z goes to y so 2 y square - y goes to x, x square - z square. So, I hope this is clear so now it is not easy to see whether these two orbitals are same or getting interconverted or not.

So, but let us look at it more carefully that we have also said that it could also be a linear combination of each other. So, let us say if this particular orbital is a linear combination of these two or not.

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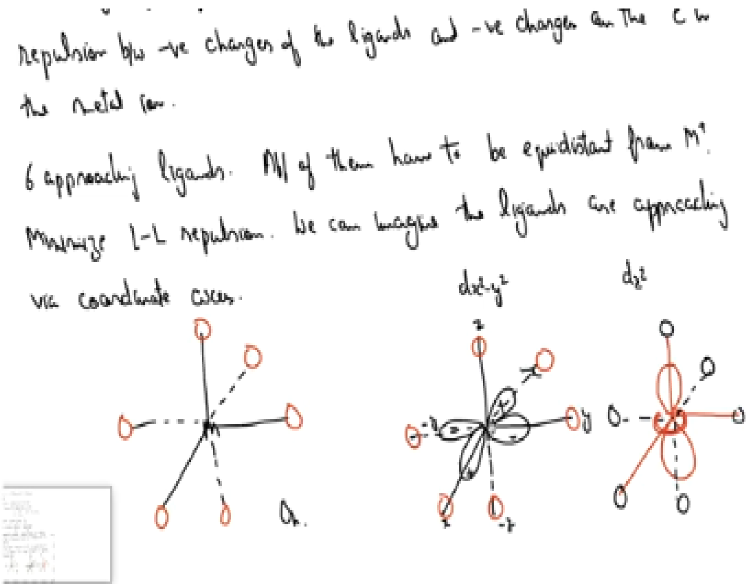

repulsion b/w -ve charges of the ligands and -ve charges on the e in the metal ion.

6 approaching ligands. All of them have to be equidistant from M⁺. Minimize L-L repulsion. We can imagine the ligands are approaching via coordinate axes.

So, let us look at this, so let us see one of the orbitals which is 2 x square - y square - z square which actually is obtained after we did C 3 operation onto d z square or 2 z square - x square - y square. So, if this can be can this be expressed as linear combination of the two d orbitals, so one is d 2z square - x square - y square + b times d x square - y square. And now we can just take the functions of this because we want to see if the linear combination is there in terms of functions.

So, we will just take the mathematical part y square - z square equal to a 2 z square - x square - y square + b x square - y square. Now comparing the coefficients of x y and z what do we get? So, we can say if we look at the coefficient of x it is - a if we look at coefficient of x here + b and on the left-hand side it is 2. Similarly let us look at the coefficient of y so we have - 1 and here we have - a and – b.

So, we have two variables two equations we can solve it, so this gives us a is equal to – half, b is equal to 3 by 2. So, now we can say that this d 2x square - y square - n square is equal to - half of d z square + 3 by 2 of d x square - y square. So, similarly other orbitals or other results of the symmetry operations can also be worked out and we will see that they will always form a linear combination of the two.

So, although it looks very different, but they are actually indeed linear combination of each other. So, that means that we can say that these two orbitals will always have same energy, I mean at least in octahedral field. So, now let us see why Eg set of orbitals so these are Eg set of orbitals these are Eg set and the other triplet is T2g set, so why E g set of orbitals increase and T2g set of orbital relatively decrease in energy?

So, let us say if we place a transition metal ion in spherical field, so to start with it was a isolated ion now we are putting it in a spherical field again so again R3 to R3, so initially symmetry of this metal ion is R3 now spherical field will also have R3 symmetry that is spherical symmetry so that means there is no change in relative energies of different d orbitals T2g and Eg set it will not break into T2g and Eg set;

Because R3 does not have any such IR representation called T2g or E3. So, all 5 d orbitals will continue to remain degenerate but there will be an increase in energy. So, why there would be an increase in energy? Because now imagine that there is an electronic field which is coming because of the ligands surrounding ligands and now there would be a repulsion in the valence electrons with the valence electron of the central or the transition metal ion;

And the spherical field which is created by ligands. So, that repulsion will increase the energy of those d orbitals, so we can say that the energies of all 5 d orbitals would rise together, this is if it is placed in a spherical field and this happens as a result of repulsion of negative charges of the ligands repulsion, we should say repulsion between negative charges of ligand and negative charges on the electrons in the metal ion.

So, now imagine that instead of spherical field now we have octahedral field, so how do we get octahedral fields? So, we have let us say we have six ligands six approaching ligands and all of them have to be equidistant from M + central metal atom, now if they all have to be equidistance and they all have to minimize ligand-ligand repulsion, then we can imagine that the, what we can imagine, we can imagine the ligands are approaching via coordinate axis.

So, of course this is true when you have this is only an assumption, so when you have metal atoms sitting at the origin let us say, and these are your coordinate axes, so ligands are now coming from these sides because that way it will be equidistant from metal atom and also equidistant between each other so the ligand-ligand repulsion would also be minimized and there is no preference of one ligand over the other because all of them have to form similar bonds.

So, this happens in octahedral case, now so why Eg set of orbitals would increase in energy and T2g set of orbitals will decrease in energy? So, let us see the case for that, so now if you think that let us first talk about Eg set of orbitals. So, Eg set of orbitals one is d x square - y square another is d z square. So, how do I draw d x square - y square? So, you have these are lying along the axes, this is my x, - x, y, - y, z, - z and these are my positive lobes;

These are my negative lobes. So, now if you see that the ligands are approaching from coordinate side, coordinate axis, six ligands and now there is a direct interaction between these orbitals and this the ligands incoming ligands. So, other than z, all of them are oriented direct head-to-head, and similarly, for dz square what happens, so you have so here also the ligand is now coming one from this side another from this side.

So, idea is that there is direct interaction between the orbitals and the ligands and because both of them are oriented along coordinate system. Of course, this is a imaginary thing that both of them are oriented along coordinate system but this is just for like you can take any other combination without having to imagine that this is actually oriented along coordinate system but you will still find the same answer.

So, this would mean that there is a there is more repulsion between Eg set of orbitals and the ligands, so that means there is relatively more increase in energy of Eg.

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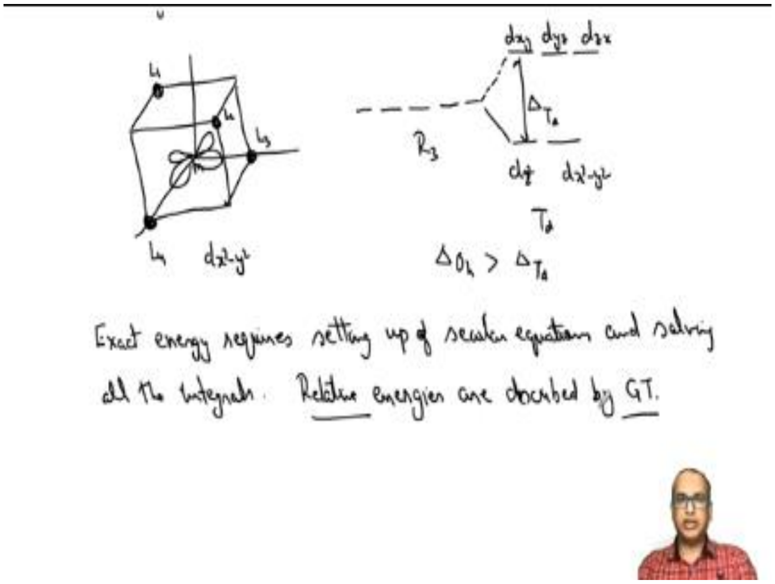

Exact energy requires setting up of secular equations and solving all the integrals. Relative energies are described by G.T.

So, now if I try to draw the same thing for let us say dxy orbital you should be able to appreciate that it is not oriented along the axis. So, it is oriented somewhere in between, this is my dxy let us say. Similarly, dyz and dzx will also be there but the ligands are still oriented along, so this would mean that my energy level diagram would look like this. So, I have R3 symmetry and I have these two orbitals are increasing in energy d x square - y square and d z square.

And three orbitals are decreasing in energy relative to this so you have d xy, d yz, d zx now this happens when it is octahedral. Now similarly you can also think of tetrahedral case where this order gets reversed so why this order gets reversed? So, if I try to draw tetrahedral field around my isolated central atom my metal is still sitting here at the origin and now if I try to draw how would I draw it, so I am drawing a cube around this thing.

So, that drawing a tetrahedral atom would be easier, so now my ligands are there are four ligands now which are approaching from these sides these are my ligands this is my metal and L 1, L 2, L 3, and L 4. Now if you see that the ligands are not approaching from the axis but they are approaching in between, so if I say that this is my let us say if I try to draw d x square - y square only two lobes will have direct interaction.

If I this is my d x square - y square whereas if I draw d xy all four lobes will have relatively more interaction with these ligands as compared to d x square - y square. So, I can say that in tetrahedral field, the order is reversed, so I have d xy, d yz, d zx and d z square d x square - y square. So, of course overall delta would also be different in Td tetrahedral point group versus octahedral point group.

So, which delta would be higher which delta would be lower, so if you see that here the interaction is stronger because there are more ligands which are oriented along coordinate axis. So, interaction between the orbitals and the ligands is much stronger than the interaction here, so that means the change in energy or the perturbation is also higher in Oh. So, this delta I will say delta Oh and this I will say delta Td.

So, relatively speaking, delta Oh will be higher than delta Td. Of course, the order will also be reversed but there would also be another difference that delta Oh will be higher than delta Td. So, of course if you have to calculate the exact energy, so we will just write down that so exact energy requires setting up of secular equation and solving all the integrals, whereas group theory will give you relative idea of which energy would be higher, which orbitals would be higher in which particular field and so on.

So, relative energies are described by group theory, so we can say relative energies only so we can only talk about relative and not the exact energies. So, I think this finishes first lecture on crystal field and we will see more that how do we explain yawn teller distortion under different fields in octahedral or in tetrahedral wherever it is there, so we will see all of this in next class. So, that is all for today.