Symmetry and Group Theory

Dr. Jeetender Chugh
Department of Chemistry and Biology
Indian Institute of Science Education and Research, Pune

Lecture -56
Jahn-Teller Distortion – Part II

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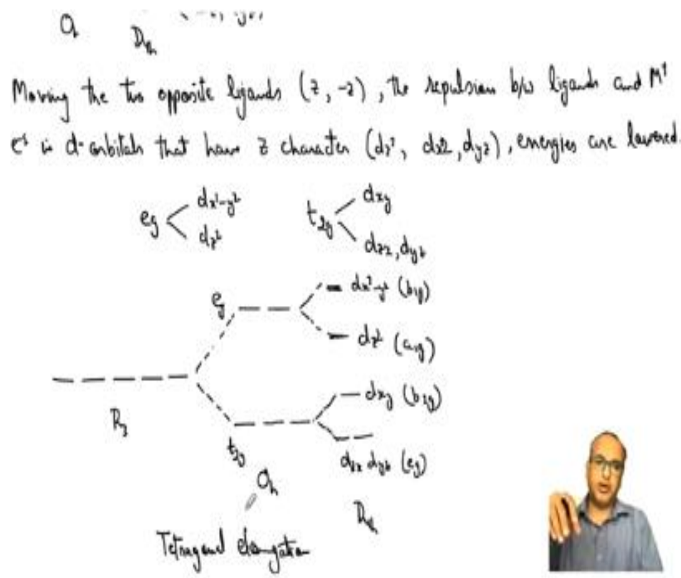

So when these two ligands in opposite z direction are moving, so let us write it down actually, so moving the two opposite ligands let us say one from z and one from minus z side, the repulsion we can say the repulsion between ligands and M + electrons in d orbitals that have z character that means d z square d xz, d yz, energies are lowered, so what do I mean? So, I mean that when you go from eg we have seen that you go into what was the two.

For eg it is a1g and d z square and d x square minus y square, so that means d z square will be lower in energy as compared to d x square minus y square and if you go from t2g, d xz, z x and d yz will be lower in energy as compared to d xy this is the result of the lower repulsion along z axis now. So, when the repulsion is lowered along z axis the orbital energy along z axis would also be reduced.

So why these orbitals would reduce energy because they have substantial z character in their orbitals, so whereas these ones have x and y characters so these are along transverse axes or transverse plane and these are along z axis. So, these orbitals would experience lower energy these orbitals would experience higher energy. So let us see explicitly how the molecular orbital diagram changes in these two cases.

So let us start from isolated atom isolated ion with R3 symmetry spherical symmetry, so from here we actually go to octahedral case, which can be written as like this, so this is my octahedral case and this is t2g set and this is eg set, now this eg set further breaks and I get this now this will be 1 orbital this will be my d x square minus y square and if I want to write the symmetry of this, this will be b1g and this is d z square the symmetry of this will be a1g.

And these two orbitals one will go up and two will go down this will be d xy this will be d zx and d yz the symmetry here is now e g symmetry here is b 2g. Now this was and this one is now D4h point group. So and what is this case this case is tetragonal elongation. Elongations because now the two z or ligands are actually taken apart and hence that lowers the repulsion between orbitals of containing z character and the ligand orbital.

So due to that decreased repulsion, the z orbitals are actually decreased in energy so reverse will happen if there is a tetragonal compression. So now if you are trying to compress the two or ligands along z axis or along the opposite axis the reverse will happen. So let us try to see how the MO diagram of that would look like.

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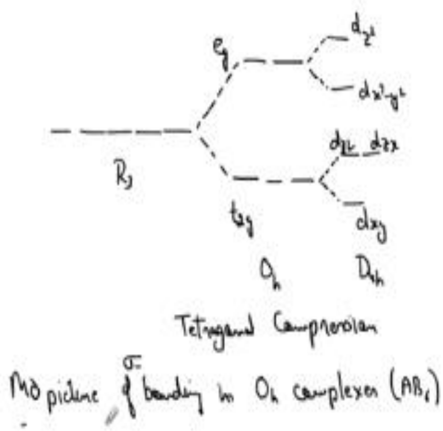

So in that case you will again start with R3 and t2g, eg under octahedral and now the reverse will happen. So, you will have d z square and d x square - y square and the corresponding symmetries will come here and you will have 2 here d xy will be lower d yz and d zx. So, this will be D4h only but this is the case of Tetragonal Compression. So, it is also we should also be able to see that if there is a tetragonal Compression and there is a stabilization of x y orbitals;

Then there is a corresponding destabilization of z orbitals, that means if on one side that is z versus a transverse side if on one side there is a compression of bonds then the other side there will be a compensatory elongation of bond to match the energy. So that is if there is a compression along z axis there is elongation along x y axis if there is compression along x y axis there is elongation along z axis so that is to stabilize or to balance the loss of energy and gain of energy.

So now that we have understood the Jahn-Teller Distortion and the symmetry aspects of it. So let us also try to understand the bonding in using MO theory again, so the bonding in a molecular orbital theory for sigma bonding picture in Oh complexes. So, this is our next topic, so molecular orbital picture of bonding in Oh complexes. So, this we already know I am just because we are on octahedral complexes so I think it is better to describe this sigma bonding picture, so that it is fresh in memory.

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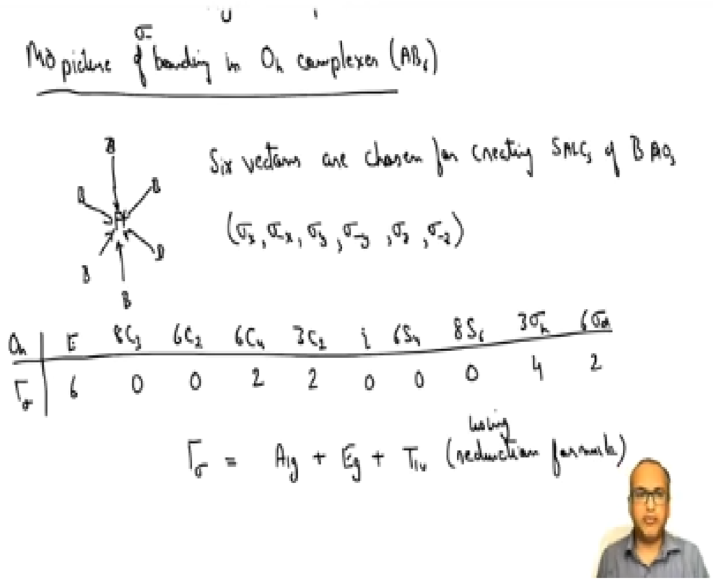

So, let us see, so what are the steps we have to take? So, if you remember we have to create SALCs using the sigma bonds like this, so 6 vectors are chosen for creating SALCs of B atomic orbitals. So, these will be called as so we can say that the bases are sigma x, sigma - x, sigma y, sigma - y, sigma z, sigma - z. So, this if you take all of this and create a reducible representation under Oh symmetry.

So you will have tau sigma which will be E, 8C 3, 6C 2, 6C 4 and we have 3C 2, i then we have 6S 4, 8S 6, 3sigma h, 6 sigma d, do we have 48. So this is what it all so now if you consider this 6 basis vectors and which vector moves which does not move and use that principle to see what will be the trace under this reducible representation so E will have 6 because this will be a 6 by 6 matrix.

C3 everything will move so 0, C2 everything will move to 0, C 4 two of them will not move opposite vectors will not move so 2, C2 this is the C2 which is where again two of them opposite ones will not move and i everything move S4 everything will move everything will move sigma h, 4 vectors will not move which are in plane so 4, sigma d 2 vectors will not move. So now upon reduction using reduction formulas. This is sigma tau sigma will give rise to A1g + Eg + T1u this comes from reduction formula, we can say using reduction formula.

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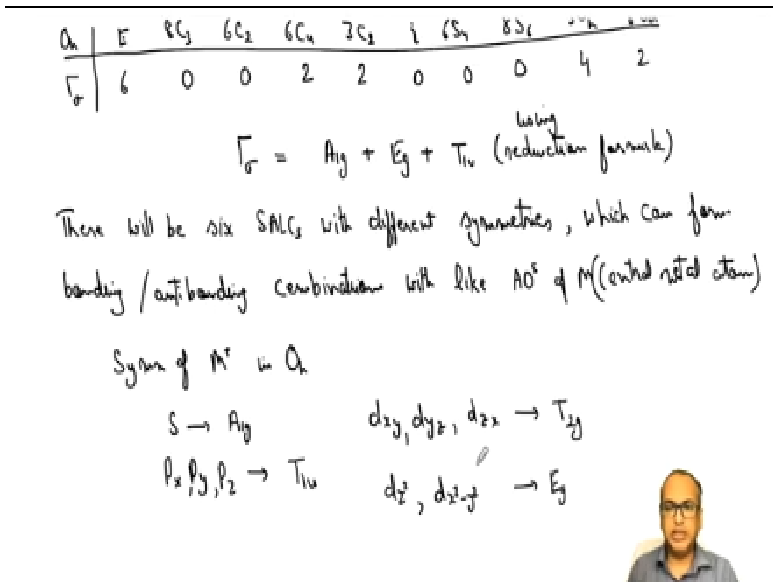

So that means 1, 2, 3, 4, 5, 6, so 6 dimensional representations of six dimensional IR representations are coming, so this would mean that there would be 6 SALCs with different symmetries which can form bonding, antibonding combinations with like atomic orbitals of M that is the central metal atom. So what are the central metal atom symmetries under Oh? So, we can write down symmetry of M plus in Oh, we can say that S transforms as A1g.

So, we have a matching over here, then P x, P y, P z they transform as T1u. So, we have another matching over here. So, this set of SALCs can match with P x, P y, P z and then d xy, d yz, d zx will match with T2g, there is no corresponding T2g. So these will remain non-bonding then d z square and d x square - y square will transform as Eg, so this will also form bonding and antibonding;

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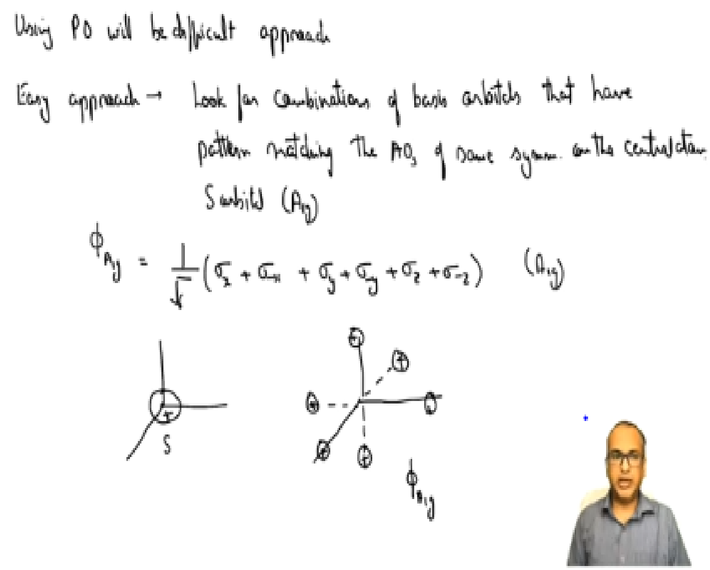

So let us go to next over here, so now using P O, using projection operator will be a difficult approach here because we are dealing with triply-degenerate representation. Already in case of doubly degenerate we have seen that how difficult it is to find out the other SALCs like the second or third SALCs is not really trivial. So, what we do is we will try to look for an easy approach I am just writing it down as easy approach.

So, what we do here is, look for combinations of basis orbitals that have pattern matching the atomic orbitals of same symmetry. See SALCs have to be combined with atomic orbitals now if we find out the SALCs pattern of SALCs combination that will match the symmetry of atomic orbitals we can actually build up those SALCs. The same symmetry on the central atom we will see how to do it.

That is why I wanted to take this up because this is a little different approach than regular projection operator approach. So for example if we want to find phi A1g we earlier what we used to do is we used to take a projection onto any of the basis orbitals using A1g symmetry and find out. But now what we want to do is we want to match the symmetry of phi A1g with the A1g symmetry atomic orbital of central metal atom.

So what is the central metal? Which orbital which has A1g symmetry that has S symmetry, S orbital. S orbital is A1g that means, so now the six SALCs should have same combination or same phase as S orbital, so we can say that this is I am directly writing after normalization. So 1 over root 6 I am writing so if I combine sigma x + sigma - x + sigma y so all of them have same phase + sigma - y + y x minus x are the directions;

But the phase of the orbitals are all same + sigma z + sigma -z. So, this will have A1g symmetry because all the possible signs are positive in nature, so I can pictorially also represent it something like this so if I have central metal atom as S orbital which will be positively phased and so my SALCs, phi A1g can be written as like this can be drawn as like this, so I have positive, positive, positive, positive, positive, positive;

So, all positives will match to give you the molecular orbital from this. So, S of metal atom will combine with phi A1g of SALCs of this B atom, so this can be labeled as phi A1g.

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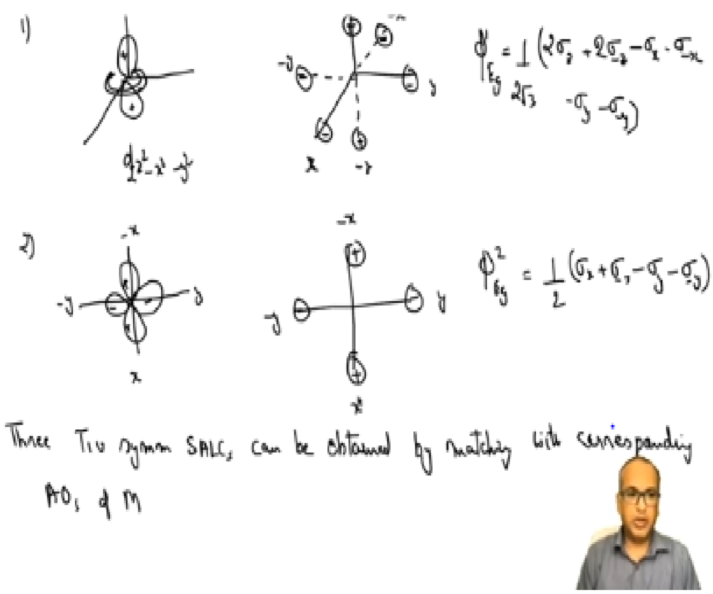

So this is a very simple approach so directly we have understood that what will be the combination of different orbitals based on the central metal atom orbital of same symmetry, so now let us move further with the next set of orbitals. So now the Eg there are two Eg SALCs can be obtained by matching symmetry with 2 Eg orbitals of M, M is a central metal. So let us see, the first one;

First one here is d z square this is positive, positive and negative over there and what will be the combination of different atomic orbitals here which will give rise to n SALCs? So z and z side we will keep them as positive to match positive, positive. And since x and y the whole belt is negative so I will put negative phase here. So, this is my x y, - x, - y this is z, - z. So, my phi Eg 1 can be written as again this will be so I can have 2 sigma z + 2 sigma – z.

So these two are positive so remember that this is 2 z square - x square - y square, so for two z square there will be two sigma z and two sigma - z and rest will be - sigma x, - sigma – x, - sigma y - sigma - y and the corresponding normalization coefficient will be 1 over 2 root 3. So, I hope this is clear so because there is positive lobes along z and - z so we are taking sigma z as positive and sigma - z is positive;

Because there is a negative belt around x and y transverse plane so we are taking all sigma's along x and y as negative and the factor of 2 comes because there is actually 2 z square - x square - y square so z square is 2 so that is why we are taking 2 and coefficient of z square is 2; So that means there is more wave function along z axis, as compared to transverse plane, so that is why we are taking to match this we are taking this.

So now the second Eg is dx square - y square, so the only we do not have to consider z axis here, so we have + + - - so the SALCs will also be like this. So, you have + x - x + minus minus. So this is y - y so I can say phi Eg second will be sigma x + sigma - x - sigma y - sigma - y. And this will be 1 by 2. So, you can also you should be able to test out whether these are orthogonal or not by multiplying the coefficients of it and taking summation over it.

So these all should be normalized and orthogonal. That condition we cannot skip. So now for T1u because the third symmetry was T1u, so three T1u symmetry SALCs can be obtained by matching with corresponding atomic orbitals of M.

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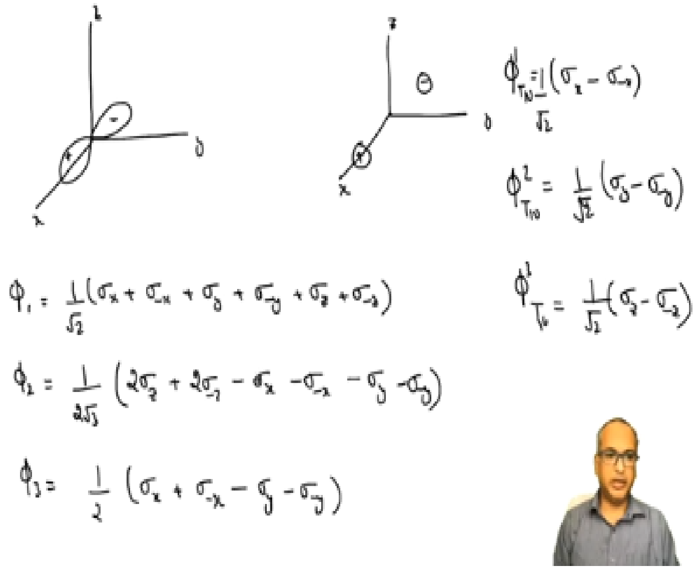

So now how do I do that so T 1u had atomic orbitals as p x, p y, p z, so if I am trying to compare p x, p y, p z so p x is like this, this is my x, y, z positive negative. So what kind of atomic orbital combinations would happen to make SALCs? So now I will have a positive here and a negative here, this is my x, y, z so my phi T1u, 1 will be equal to sigma x - sigma – x, so positive 1 sigma x i negative 1 sigma - x i and this will be 1 over root 2 for normalization.

Similarly, phi T1u, second will be 1 over root 2 sigma y - sigma - y and the third will be phi 3 T1u 1 over root 2 sigma z - sigma - z. So now we have all three SALCs all 6 SALCs. So let us list them down so phi 1 we have sigma x + sigma - x + sigma y + sigma - y + sigma z + sigma - z and this is 1 over root 6, phi 2 was 1 over 2 root 3 this is 2 sigma z + 2 sigma - z - sigma x - sigma - x - sigma y - sigma - y.

And third one was 1 over 2 sigma x + sigma these are two positives - x - sigma y - sigma - y and three are written here, so we have got six of them three with T1u symmetry two with Eg symmetry one with S A1g symmetry.

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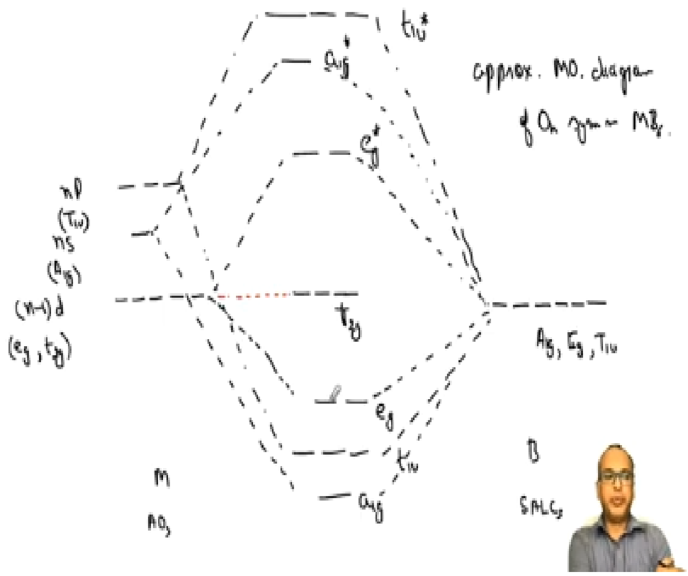

So now let us draw the MO diagram for this again, so MO diagram would be an approximate MO diagram actual energies would really depend on the extent of overlap between a particular metal ligand and what is the type of ligand whether it is a high-field ligand in strong-field ligand and all those things would matter, but I am just trying to give you an approximate MO diagram here. So, we will have five let us start with metal and the atomic orbitals SALCs.

So, you have six SALCs here and this is n - 1 d orbitals which will have Eg set and T2g set then you have S orbital ns let us say which will have A1g symmetry then you have 3p orbitals np which will have T1u symmetry. So, the orbitals are written with lower case whereas symmetry is written with the upper case. So, I have mixed both of these but if you are describing orbitals then you will write lowercase letters with e and t.

If you are describing the symmetry of that then you will write with uppercase and like I have written uppercase here. So, either way is fine but name of the orbitals go with lowercase name of the symmetry Mulliken symbol go with uppercase. So now if you have noticed that the symmetries here were A1g, Eg and T1u. So, T2g really does not match so that T2g will remain as non-bonding.

So this I will write is lowercase so T2g orbitals would not form bonding and they will just remain like this let me draw this, now Eg there are two Eg's here, so Eg will match with Eg and you will get two bondings and two nonbonding or two anti bondings I will write E g here and E g star over here also this S will combine with one of this, so you will get A1g and the second will go over A1g.

So again, these energies are not precise and even the relative energies of this will depend on the direction of the ligand approach, the repulsion, the extent of overlap all those will define whether Eg will be more stable or A1g will be more stable and so on so forth and this will be T1u, so T1u will come somewhere over here but again this might flip. So, you will have three T1u and you will have so star dictates describes anti-bonding this is bonding orbital;

And this will be non-bonding orbital, so this is an approximate I will say approximate MO diagram for Oh symmetry molecule let us say MB6. Now different books might have different diagrams where the symmetry of these three orbitals and these three orbitals might get flipped. Because again I am saying that this is we can only get an approximate picture from group theory and actual picture you will have to set up the secular equations and calculate the energy.

But it does give you approximate explanation of what is going on based on symmetry, so that finishes our discussion on bonding including now the crystal field theory. So, in the next class which is the last week, the application which will be discussing is the spectroscopy. So, we will be looking at different types of spectroscopy there. So please if you have not gone through any course of spectroscopy so please go back and read a little about so that spectroscopy. So that it is easier when we are discussing that, that is all for today, thank you.