Symmetry and Group Theory

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Lecture -55
Jahn-Teller Distortion – Part 01

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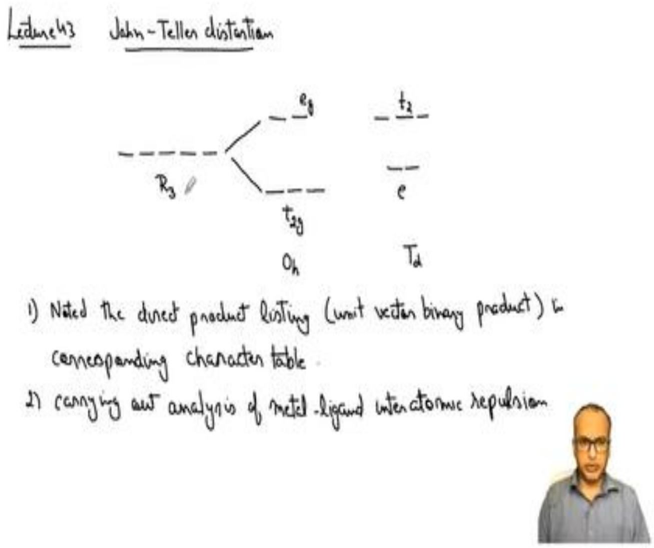

So, welcome back. Let us continue our discussion of application of group theory on to crystal field theory. So, today we will be discussing something called as Jahn-Teller distortion. So, far we have looked at the crystal fields splitting of d orbitals. So, initially if the d orbitals are in spherical symmetry for an isolated atom, we saw that under octahedral field, they undergo splitting which is pictorially depicted like this where t2g set of orbitals undergo stabilization and eg set of orbitals undergo destabilization under in octahedral field.

And if you undergo tetrahedral field then the reverse was seen, and how do we do that? This is done by t 2; e and t 2 in case of each, there is no g here, e and t2. So, here what we did? So, we noted so the steps which we followed were, we noted the direct product listing, we can also say unit vector binary product in corresponding character table. And the second step was we first noted down the direct product listing.

And then we carrying out the analysis of metal-ligand interatomic repulsion produced by the corresponding geometry. So, in case of Oh, we saw that the t2g is stabilized because of this interatomic repulsion between metal orbitals and the ligand orbitals and eg got stabilized. Similarly, in case of tetrahedral we saw due to this repulsion e is stabilized and t2 is destabilized, so this we saw.

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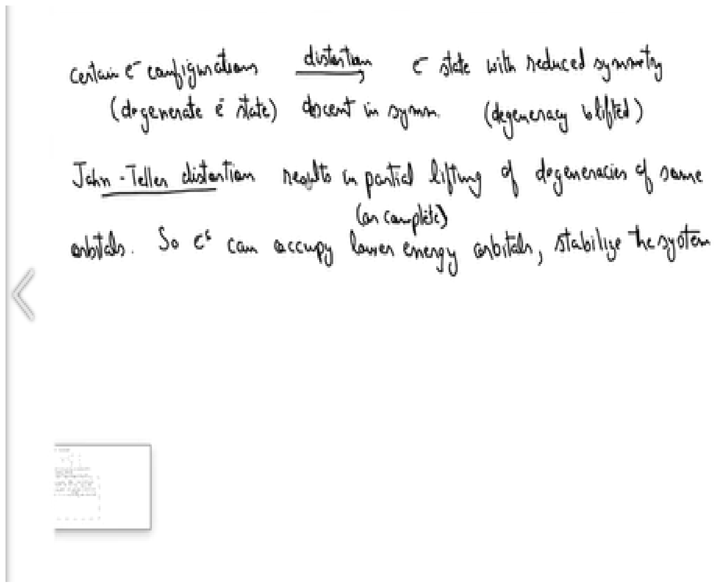

So, now the next step is, to further understand the distortion, what do you mean by the distortions? So, certain electronic configurations, so we can say certain electronic configurations which are degenerate in nature electronic state they can undergo distortion. What do you mean by distortion? Distortion means change in geometry or change in shape. So, if you undergo change in shape there would be some sort of reduction in symmetry.

So, you go to an electronic state or electronic configuration with reduced symmetry. You can also call it as descent in symmetry, which we have learned earlier. So, this is also called as the process is descent in symmetry. And whenever there is a descent in symmetry, we have seen that in some cases a degenerate state can undergo combination of non-degenerate. So, we can say other words, degeneracy is lifted.

So, one such distortion is called as Jahn-Teller distortion. You must have studied this in your earlier classes, but we will look at it in more detail and with respect to symmetry aspect. You can say this results in partial lifting of or complete also partial or complete, it depends on the metal ligand pair. So, partial or complete lifting of degeneracies of some orbitals. So, when this happens, so electrons can occupy lower energy orbitals and, in the process, what happens?

It is stabilized the system. So, overall energy of the system is decreased, so this you can also see this is not a Jahn-Teller distortion. But again, there is a descent in symmetry. So, earlier electrons were occupying this state and now they occupy t2g and eg. So, some of the electrons will occupy lower energy state, so the overall energy as compared to R3 will be lower in case of octahedral.

So, when you go descent in symmetry, you are actually lowering the energy of the system thereby stabilizing the system.

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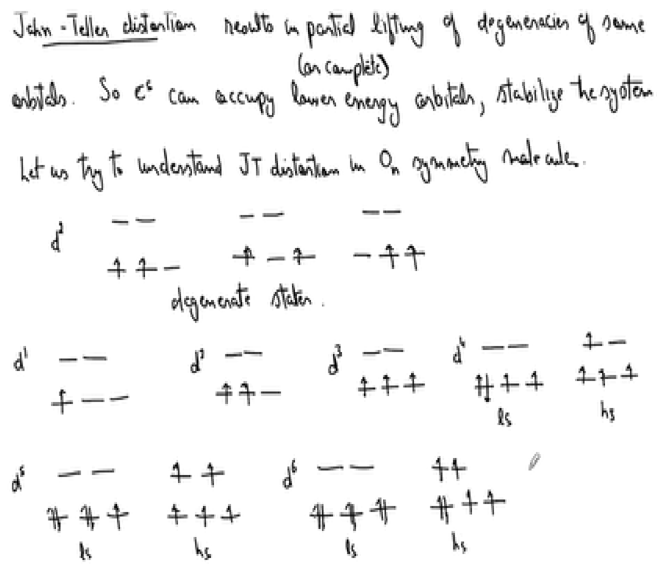

So, this is not true for all of them, but in certain electronic configuration only where distortion is possible it happens. So, we can say that the perfect geometry for those states does not exist as stable state. And if you want to stabilize yourself you have to descent in symmetry and you have to deform yourself and you go to lower symmetry. So, now let us try to understand this distortion Jahn-Teller distortion under octahedral system.

So, let us try to understand Jahn-Teller distortion in Oh symmetry molecules. So, Jahn-Teller distortion occurs only in those cases where there is degeneracy in electronic state. So, what do you mean by degeneracy? So, for example, if you are talking about d2 state, so d2 electronic configuration. So, we can say that this is in octahedral so I am going to draw eg and t2g separately.

So, then I mean that d2 electronic state can be written in following ways, it can be filled in following ways. So, I can say this and they are all equally energy. So, this can happen in d2, you cannot pair the electrons because that would be against Hund's rule of maximum multiplicity. So, these are the only three states possible but these are all degenerate states. So, because there is degeneracy in d2 electronic state, the d2 state can undergo Jahn-Teller distortion.

So, let us see now let us list all possible states which can undergo Jahn Teller distortion. So, for that let us first list down different states to see whether a particular state will have degeneracy or not. So, let us say d1 will have degeneracy, d2 we have already seen d2, but let me draw it here again, so d2 will also have degeneracy. Now d3, now if you see d3 all three orbitals of t2g are symmetrically filled, that means there is no degeneracy possible.

So, now let us look at d4. So, d4 there are two possibilities in d4, one is d 4 low-spin complex, another is d4 high-spin complex. So, the high-spin complex will have three t2g half-filled and one e g, this will be high-spin. So, this is also a symmetric, this is also a symmetric both of them have degenerate states possible, so both of them can undergo distortion. So, let us move to d5 so d 5 also can have low-spin and high-spin complex, so let us first draw low spin.

This is low spin so I will write less and this one is high spin, so this cannot undergo distortion whereas this can undergo because there are no degenerate states possible. So, d6 can also undergo low-spin high-spin, so you have let us first draw the low-spin so we have high-spin.

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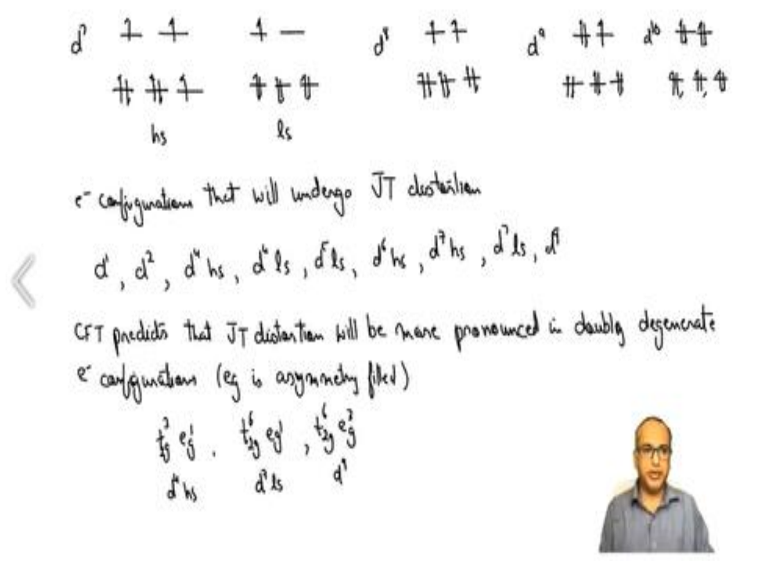

Now for d7, so d7 will have 5 plus 2; 7 and then there is another possibility for d 7, which will be low spin. I draw high-spin first here, this is low-spin. Now d8, so d8 is only one possibility there and no degeneracy, d9 will have also have one possible no low-spin high-spin and d10 will have all filled. So, now let us list down what all configurations will undergo Jahn-Teller distortions.

So, electronic configurations that will undergo Jahn-Teller distortion, which will be, you will have d1, d2, d4 high-spin. Then you have d4 low-spin will also undergo. Then d5 low-spin, d6 high-spin, d7 high-spin, and d7 low-spin will also undergo and I think d9. Others will not undergo Jahn-Teller distortion. Now CFT also predicts that distortion will be more pronounced if eg set is asymmetrically filled or we can say if it is doubly degenerate electronic configuration.

So, we will write it down so CFT predicts that Jahn-Teller distortion will be more pronounced in doubly-degenerate. We will see how we can explain this? But let us first write it down, doubly-degenerate electronic configurations. So, what do I mean when I say doubly-degenerate? That means eg is asymmetrically filled. Because if t2g is asymmetric fill, it will be triply-degenerate electronic configuration.

So, if eg is asymmetrically filled then you will end up getting doubly-degenerate and that will undergo more pronounced Jahn-Teller distortion. So, now what are the possibilities? For eg, so if you say t2g 3 and eg 1, that is d4 case, d4 high-spin case. Then similarly if you have t2g fully filled and eg half-filled and t2g fully filled and eg 3/4th filled. So, these will undergo doubly degenerate configurations and there the distortion will be higher in these cases.

So, this is the case of d9 and this is the case of d7, and this is d7 low-spin and this is t2g 3 and eg so this is eg 1, so this is d4 and this will be high-spin case, d4 high-spin case.

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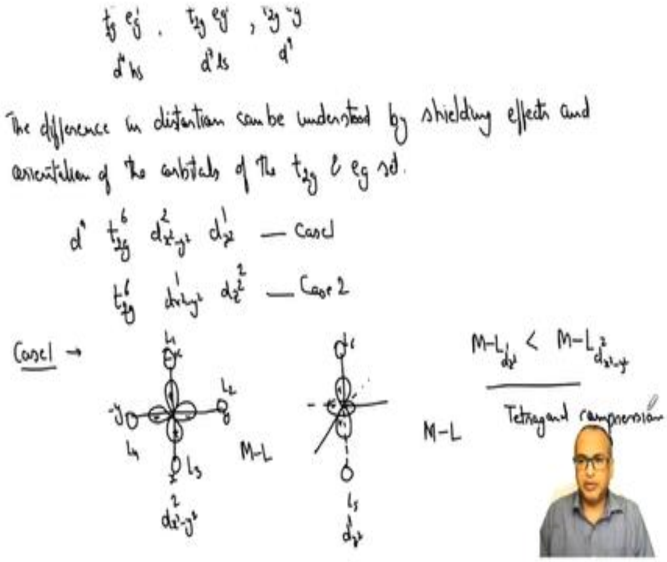

So, now let us consider one of the examples. So, let us consider d9, so before we go let us try to understand that why eg versus t2g undergo more versus less distortion. So, the difference in distortion can be understood by shielding effects and orientation of the orbitals of the t2g and eg cell. So, let us take example of d9 and see what are the different possibilities, what are the different degenerate possibilities.

So, for d9, we can say this will be t2g 6 and eg can be now further broken into x square minus y square 2 and d z square 1, this can be considered as case 1. And the other possibility is t2g 6 d x square minus y square 1 and d z square 2, now this will be case 2. So, now let us see what happens in case 1. So, if you carefully see that the electrons are filled there are more number of electrons in the x square minus y square as compared to d z square.

So, if I want to draw the picture, so let us say this is my d x square minus 1 square, x, y, minus x, minus y, these are positive these are negatives. Now my ligands are approaching from these sides at from the coordinate axis and then of course there are two up and two down. There is one up and one down also. So, in case of d z square plus there are two ligands coming from here, L5, L6 and these ones can be name is L1, L2, L3, L4.

So, if you have d x square minus y square fully filled and d z square partially filled, the electronic repulsion or electronic shielding between the electrons of ligands versus the metal atom, there would be more electronic shielding here. So, the attraction between ligands and the metal atom will be less as compared to this one. So, if you consider the metal ligand bond here versus metal ligand bond here this length will be, we can say that the metal ligand bond of d z square, there would be less shielding here.

So, more attraction more attraction means the length will be shortened. So, I can say this versus metal ligand bond where I have d x square minus y square completely filled. So, this particular case is called as tetragonal compression. So, tetragonal compression or any kind of tetragonal distortion will happen when there is a shortening or stretching of bonds along the z axis.

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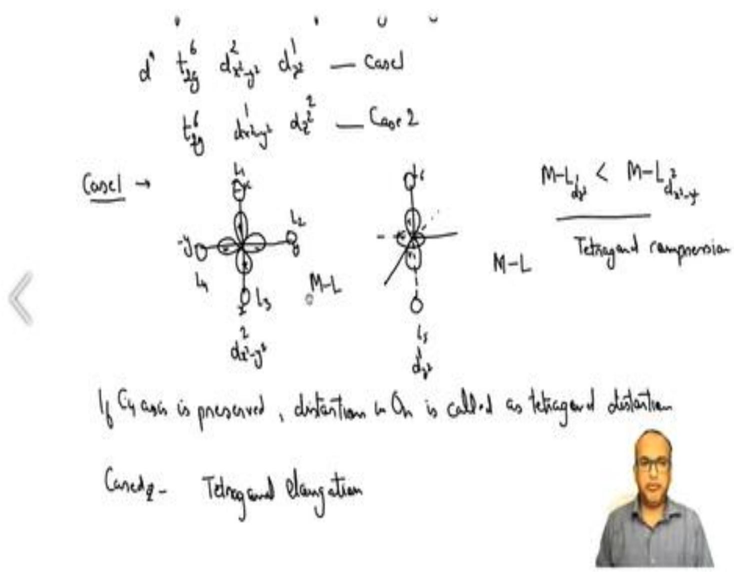

So, we can say if C4 axis is preserved, distortion in Oh is called as tetragonal distortion. Now it can be a compression or tetragonal elongation based on which orbital is more filled as compared to the other. Now if you consider the case 2 the reverse will happen here and you will call this as tetragonal elongation. This should be very clear now should not be problem, so it is moved to next page.

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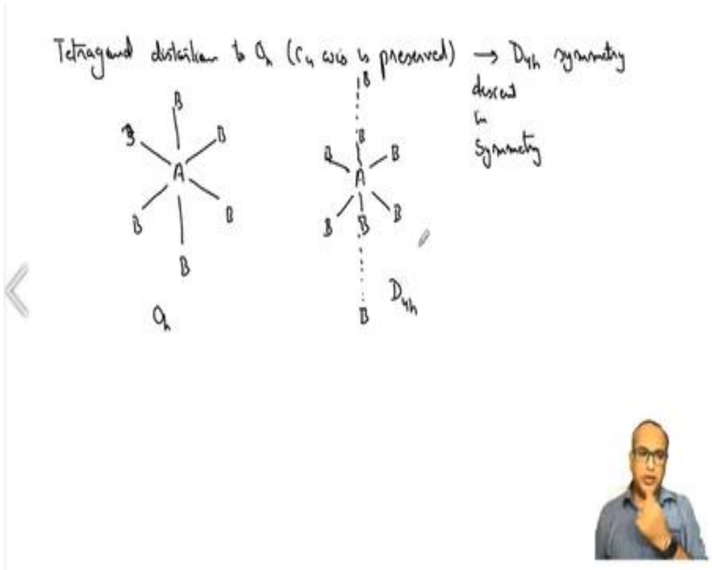

And let us discuss tetragonal distortion a little bit more. So, if there is a tetragonal distortion to octahedral, we know that the C4 axis is preserved. That means there is a descent in symmetry and it undergoes D4h symmetry. It under goes descent in symmetry and the final symmetry is from Oh you end up in D4h, descent in symmetry. So, let us see pictorially what do I mean, so if you have A let us say B, so in case of octahedral all 6 A-B bonds are equal.

But if you increase these bonds which are two opposite bonds or compress these bonds you will end up something like this. Either you will get something like this or you will get something like this. One case it will be called as compression another case, it will be called as elongation. But in both the cases the point group, you will get is D4h now, instead of Oh.

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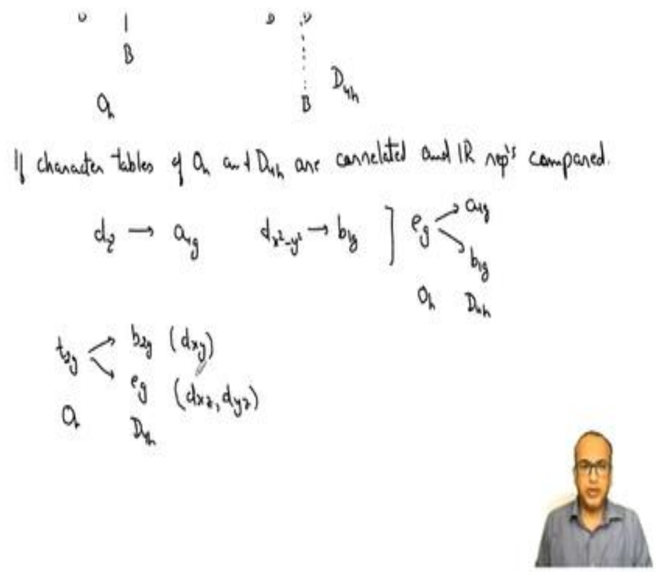

So, now if you try to see what happens to t2g and eg set, when you correlate the two-character tables. So, if character tables, we have seen this in descent of symmetry, how do you correlate, how do you draw the correlation diagram between two point groups. If character tables of Oh and D4h are correlated and IR representations compared. What do we get? So, we get d z square actually correlates with a1g and d x square minus y square correlates with b1g, that means this comes from the fact that my eg correlates to a1g and b1g.

So, when I go from octahedral to d4h, I go descent in symmetry and there is a lifting of degeneracy of eg orbitals into a1g and b1g. And hence if I try to match the symmetry d z square is now forming the basis for a1g representation and d x square minus y square forms the basis for b1g representation. So, similarly if we look at the t2g set of orbitals. So, t2g now correlates to b2g and eg.

That means two of the orbitals are still degenerate one has lost degeneracy. But all three are not degenerate from Oh to D4h. So, I have not drawn the complete correlation table because I expect that you know, how to draw all these correlation tables by now by looking at the descent in symmetry chapter. So, now let us so if I look at the basis for b2g it is actually d xy and for eg it is d xz and d yz.

So, this is how the symmetry will break when you go conduct a trigonal elongation or compression. So, let us say if we are progressively stretching this, it will eventually go to a ML4 kind of or AB4 kind of molecule which will be a completely pure D4h which you know, that it will be a D4h state. So, that will be the extreme case where now these two ligands will not take part in bond formation. Because they will not be part of the crystal field.