Symmetry and Group Theory
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Lecture - 63
Jahn-Teller Theorem, Tetragonal Distortion MOT: ML6, Sigma and Pi Bonds

Now, one more important thing is Jahn-Teller theorem, right? What is Jahn-Teller theorem? It is there in front of you.

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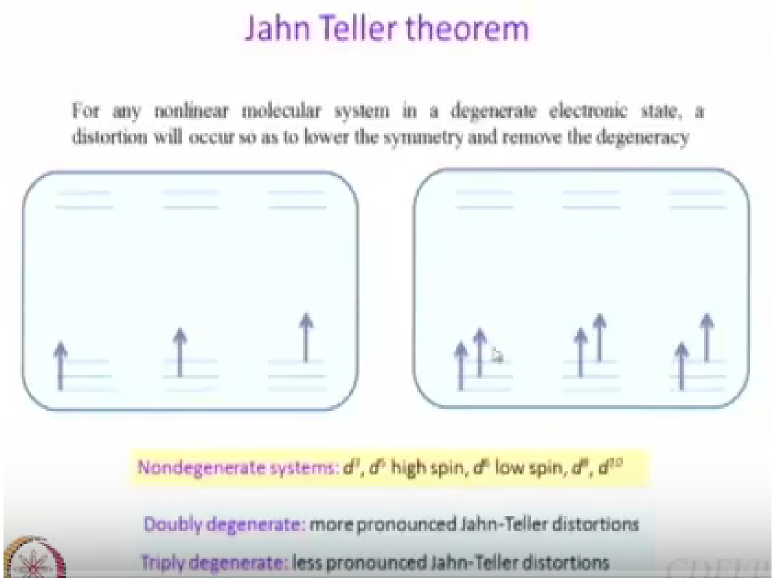

Jahn Teller theorem

For any nonlinear molecular system in a degenerate electronic state, a distortion will occur so as to lower the symmetry and remove the degeneracy

Nondegenerate systems: d^3, d^5 high spin, d^6 low spin, d^8, d^{10}

Doubly degenerate: more pronounced Jahn-Teller distortions

Triply degenerate: less pronounced Jahn-Teller distortions

For any nonlinear molecular system in a degenerate electronic state, a distortion will occur so as to lower the symmetry and remove the degeneracy. Does this remind you of anything? Anything we discussed in class in recent past? Okay, proceed. The what symmetry is there, the what degeneracy is there. Yeah, what is that?

"Professor - student conversation starts" An improved degenerate orbitals will always likely to interact with each other. What is that called? Configuration interaction also does the same thing, right. When you have 2 orbitals of same symmetry coming very close together in energy they interact and they make sure that degeneracy is removed. So that is what I am reminded of when I read Jahn-Teller theorem, okay, fine. **"Professor - student conversation ends".**

So think of this. Is this a degenerate electronic state or not? What about this? Degenerate? So the point is non-degenerate systems are these d 3, d 5, high spin d 6, low spin **etc**. etc. Doubly degenerate states show more pronounced Jahn-Teller distortions. Triply degenerate states produce less pronounced Jahn-Teller distortion okay. Why are we discussing all this is a class of symmetry? In d 3 you have 3 electrons in 3 orbitals, right?

So all 3 orbitals that are there are occupied, there is no other choice. Here you have a choice. You have for example d 2. You have the choice of having this or this or this unoccupied, okay? In d 3 there is no such choice, okay. Fine. Why are we discussing all this in a class of symmetry all of a sudden? Distortion, symmetry will change. Can you have a complete sentence as an answer. That will be nice. So first was a word, second attempt was a phrase.

Let us have a sentence now. You are right, tell me. Just tell me what the answer is. Point group will change their property. Exactly. Due to distortion what will happen is octahedral point group will not remain an octahedral point group anymore. What kind of distortion is brought about by Jahn-Teller effect? What is that called? Tetragonal distortion. It is called tetragonal distortion. Tetragonal distortion. So generally what happens is, is axial distortion.

It becomes longer or it becomes shorter, okay. So let us talk about that. So this is OH for you. This is t 2g, this is e g.

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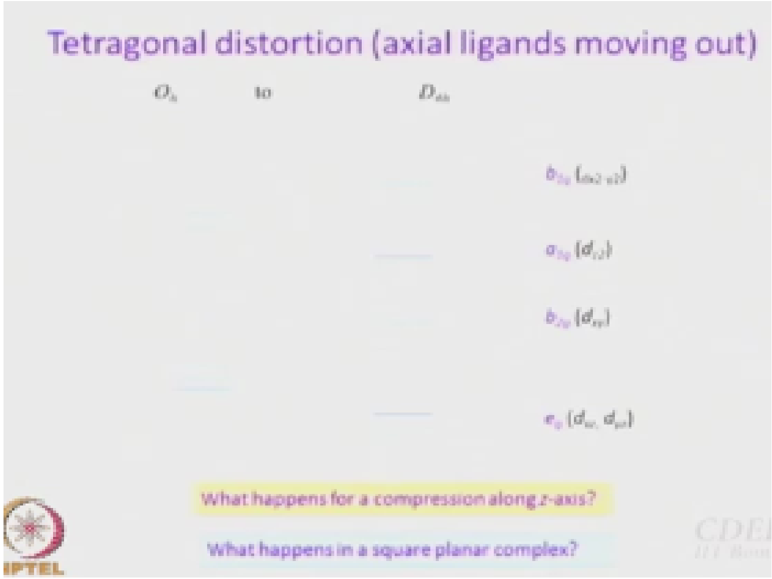

Tetragonal distortion (axial ligands moving out)

What happens for a compression along z-axis?

What happens in a square planar complex?

Which orbitals are there in t 2g? d xy, d yz, d zx. Which orbitals are there in the e g set? d x square - y square and d 2 z square - x square - y square orbital, okay? Now when I have a tetragonal distortion when actual ligands move out then from octahedral point group I go to d 4h point group, right? What will happen to these states? To answer that of course you will need the character table.

What you need to know is what will e g break up into and what will t 2g break up into if it does. D 4h. Does anybody have the character table? Can you do that correlation? What is the, you know what I am talking about right? I am talking about group subgroup relationship that we have talked about earlier, okay? I am talking about group subgroup relationship between the OH group and the d 4h group and I am asking you what is the fate of the e g group in d 4h.

Is there an e g point group in d 4h, no. How many, why am I saying point group again and again? E g symmetry species. Do we have e g in d 4h? We do? But does e g map to e g? Actually it does not. You work it out yourself please, so this is homework. Correlation diagram between OH and d 4h. Please work this out yourself. So if you use the character table it is not very difficult for you to show what I am going to show you now.

What happens is that e g splits into 2 sets, t 2g also splits into 2 sets and using the group subgroup relationship you can work out that the topmost level is b 1g and that is d x square - y square. Then you have a 1g dz square. Then you have b 2g d xy. Lowest energy is e g d xz d yz. So t 2g breaks up into b 2g and e g whereas e g breaks up into b 1g and a 1g, alright? So I think you have already studied Jahn-Teller effect, most of you.

So what we are showing here is that how this Jahn-Teller effect, how we can predict at least some things by using a character table. If you know that you are going from OH point group to d 4h point group then you can tell just looking at the character table and just by constructing the correlation diagram between OH and d 4h you can tell that the what is e g in OH has to break up into a 1g and b 1g and what is t 2g in OH has to break up into e g and b 2g.

The question is how will you say whether b 2g is higher in energy or e g is higher in energy? How will you say whether b 1g is higher in energy or a 1g is higher in energy. How will you do that? How will you do that? Can you do it using character table using symmetry. Can you do it? Can you say that it is necessary that a 1g has to have a lower energy than b 1g? No. So for that you have to go back to the diagram I was drawing right and you have to see that in d 4h now which are the orbitals that are affected more, which are the orbitals that are affected less, okay?

What is tetragonal distortion I said? Actual ligands are moving out, okay? So now you see in e g you have x square - y square and you have dz square. So what I am saying is the ligands are moving out along z direction. So which orbital will get relatively stabilized? Dz square or dx square - y square? Definitely dz square right? so the energy ordering comes from there but the fact that it is going to split that can be predicted from symmetry itself.

Using only symmetry you cannot say which one will be higher, okay? Similarly, if you look at the t 2g set, d xz and d yz have a z component. Whereas xy does not have any z component. So when the ligands move out along the z direction, these are the orbitals that will be relatively stabilized, okay? That comes from an energy discussion, fine. So I want you to figure out what happens when you compress along z axis. What happens tell me?

So will these two just interchange or not? Fine. And the other thing you work out yourself, square planar complex. Work out the energetics and symmetry of the orbitals in a square planar complex, okay.

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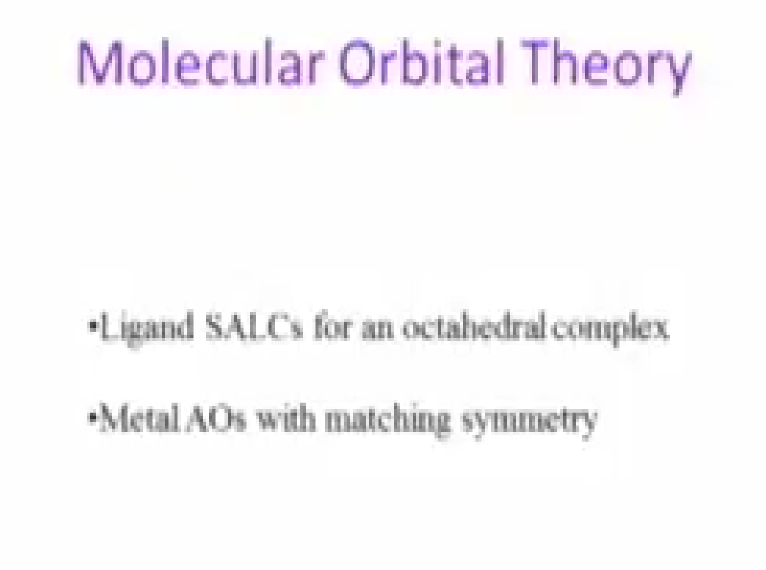

Molecular Orbital Theory

- Ligand SALCs for an octahedral complex
- Metal AOs with matching symmetry

Now we move on to molecular orbital theory. We do not want to spend too much time on crystal field theory. And in molecular orbital theory actually our job is already half done, okay? What did we say was our approach in molecular orbital theory? We said that we are going to work with by and large a system where you have central atom and you have pendant atoms. Using the orbitals of pendant atoms we are going to generate the SALCs.

And then we are going to look for atomic orbitals on central atom that have the right geometry, right symmetry to combine with the SALCs. Is that what we said? Step 1, focus on the pendant atoms, get hold of the atomic orbitals of the pendant atoms that will participate in the bonding, generate SALCs, we will write.

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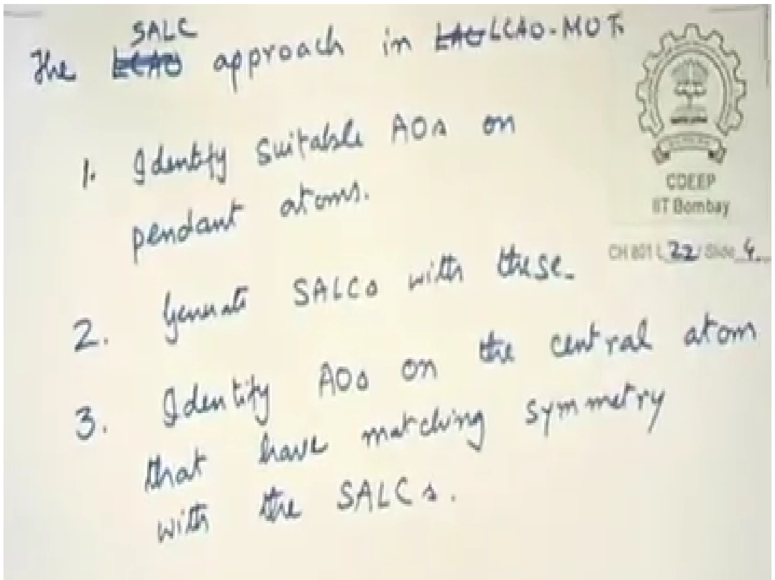

The ~~LCAO~~ SALC approach in ~~LAO~~ LCAO-MOT

1. Identify suitable AOs on pendant atoms.
2. Generate SALCs with these
3. Identify AOs on the central atom that have matching symmetry with the SALCs.

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No.1 is identify suitable atomic orbitals on pendant atoms. No. 2 Generate the SALCs with these atoms. No. 3 Identify AOs on the central atom that have matching symmetry with the SALCs. This is our approach, right? So that is what we have to do and if you remember for an octahedral complex we have already generated the SALCs have we not? The sigma SALCs we have already generated. Fine?

So all we have to do is we have to look at the metal atomic orbitals and find which one of them which ones of them have matching symmetry that is all. So we start with ML 6 octahedral complex.

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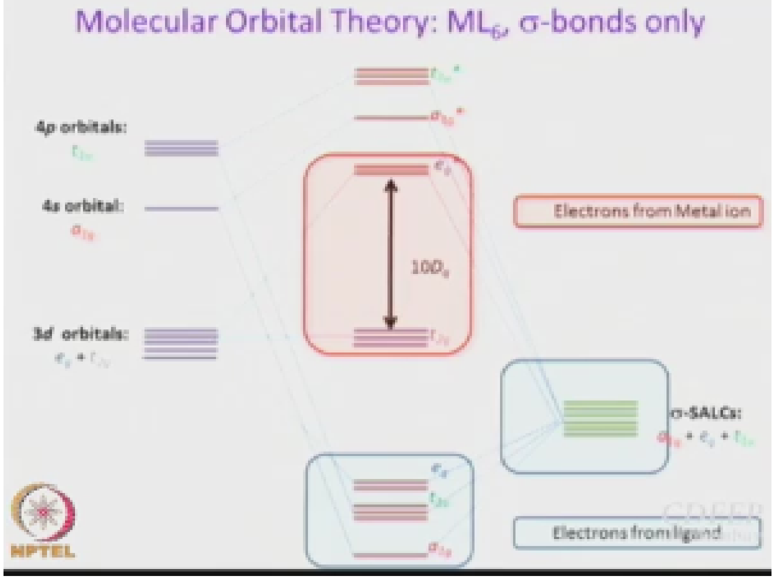

Molecular Orbital Theory: ML_6, σ-bonds only

And to start with we say that we will talk only about sigma bonds. But before that I want to ask you a question. In crystal field theory what is 10D q, 10D q? the difference in energies between e g and t 2g orbitals, okay? So splitting. So this is how we do it in CFT.

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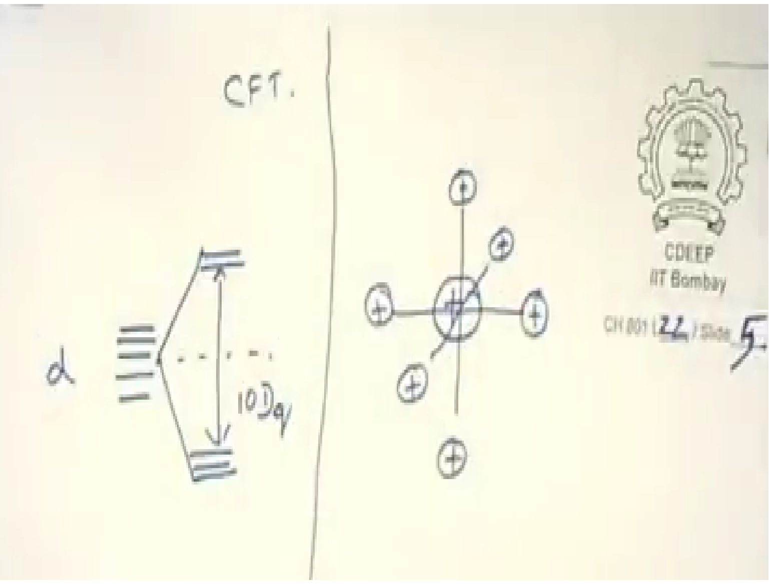

These are your d orbitals, right? Under crystal field they are going to split, 2 at the top 3 at the bottom. That we have not drawn to scale definitely. Looks very symmetric. Pardon me for that, I am teaching symmetry after all. This energy gap is called 10D q is it not? How do I write 10D q capital D small q or small d capital Q? This is called 10D q, right. So remember that. So 10D q is the energy difference between the t 2g set and the e g set, right and all these orbitals come from the metal ion. That is what CFT says. Let us see what MOT says.

Now we have already worked this out. So if you turn the pages of your notebook you will find that the sigma SALCs that we generated for the pendant atoms breaks down into a 1g + e g + t 1u, right? Now let us look at the atomic orbitals of the central metal ion. What do we have? See 3p and all do not participate in this kind of bonding, let us leave them out, okay? Let us focus on 3d, 4s and 4p. Whether or not there is any involvement of 4p we will see very soon, okay?

So here you see 3d orbitals we know already that they consist of the e g and the t 2g set, okay. 4s orbital I think everybody will agree with me is totally symmetric a 1g. What about 4p orbitals? P orbitals I think you worked out for something or the other. P orbitals are transformed together right? They belong to a 3-dimenisonal symmetry species. I was going to say point group again, so I checked in the last minute. 3-dimensional symmetry species and of course p orbitals are all ungerade, right antisymmetric with respect to inversion.

So the p orbitals, 4p orbitals belong to the t 1u set. Shubanghi, okay with this? Anchal? Everybody okay with this? Now, what do we have to do? We have to play matchmaker. Orbitals of same symmetry are going to combine with each other and when they combine they are going to give me a set of low energy orbital and set of high energy orbital, bonding and antibonding if you want to call them that, okay? Now see. What do you have?

We have sigma 1 g, e g and t 1u, right? Let us take sigma 1 g first, why am I saying sigma 1 g, a 1g, e g, and t 1u. Do you have a 1g orbital here? 4s. So see the a 1g LCAO is going to combine with 4s. Do you remember what the a 1g LCAO is? A 1g is very easy, even I can write it. Right? Right or wrong? Sigma 1 + sigma 2 + sigma 3 + sigma 4 + sigma 5 + sigma 6 what is the normalization constant? Root 6 or root 3? Okay very good.

Now, even without drawing the diagram if I draw 4s here does it not become apparent that 4s has the right kind of symmetry to form bonding and nonbonding kind of combinations with the LCAOs formed by this a 1g set, right? So if it is bonding then this is plus, these are all plus and the other combination is minus. This is plus so everything else is minus is it not? Right, so what have I done? I have just drawn the MO.

I have drawn the bonding MO as well as the antibonding MO, right? I just have to change the sign, okay. So I hope you do not mind if I say that the a 1g LCAOs are going to combine with 4s orbital, right? One low energy a 1g MO and one high energy a 1g * MO will be formed. Agree? How many nodes are there in this a 1g * MO? 1 or 6? 1, which is spherical, right? So it is just spherical node, okay. What next? E g okay? Is there anything like e g? 3d orbital.

3d orbital e g is going to combine with e g of sigma SALC but oops unfortunately for some reason I did have worked out t 1u first so please amuse me and let us work with t 1u. So t 1u. this t 1u SALC that is there is going to combine t 1u orbital of the central metal atom, metal ion, right. So t 1u and t 1u * MOs will be formed alright? Then now perhaps you can talk about e g. I was thinking that there is a some gadbad in the order. This is what it is.

I do not know why I animated it like this. Okay. Finally e g is going to combine with e g is it not. So you get 1 e g bonding, 1 e g * antibonding. Order of energies can only be done if you do the quantum mechanical calculation. Here we are only talking about the symmetries, okay. What is left? Is anything left on the SALC side? Have you used up all the SALCs? All SALCs are used up. Is anything left on the metal atoms, metal ion side? T 2 g is left?

So t 2 g remains as a nonbonding set. What is the meaning of nonbonding? T 2 g is localized completely on the metal ion right? but look at this. What is 10D q. This is 10D q now. So this concept of 10D q, this is 10D q the gap between t 2g and e g. the only difference between crystal field theory and molecular orbital theory at this state is that you do have 10D q, it is defined. Not the only difference.

But the difference between CFT approach and MOT approach is that in CFT the t 2g set as well as the e g set all belonged exclusively to the metal ion. Here, however, you see t 2g is a nonbonding set of orbitals on the metal ion, fine but e g *, what is e g *? It is an antibonding orbital, right? So it should have contributions from the metal ion as well as the ligands.

Of course, you can say that it is very close to the metal ion in energy, the way we have drawn it is very close to the energies of metal ion orbitals, pretty far away from the SALC orbital. So the contribution of the metal ion is more, okay? But you cannot deny the fact that it is really an antibonding orbital. So this is the additional information that we get from MOT over VBT over CFT rather.

We get a bonding and antibonding character in the orbitals and what we see is that this 10D q that we get that is going to be a transition from MOs not MOs nonbonding orbitals localized on the metal to antibonding orbitals that are delocalized over the metal and the ligands. So what kind of a transition will that be? The transition is from an orbital that is localized on the metal ion to another orbital that is delocalized to some extent over metal as well as ligand.

Yes, cannot hear, louder. So it is kind of a metal to ligand charge transfer transition, right. It is not pure DD transition anymore, okay and if you fill in the electrons then what will happen? Yes, sir. For that you have to do a little more quantum mechanical calculation, okay. That we are assuming. We are only talking about the symmetry aspect here. How many electrons would there be in the sigma SALCs.

So where will they go? 1, 2, 3, 4, 5, 6. 6 or 12 how many electrons will be there? 12 no? 12. So we are talking about this lone pairs, 12. So 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. So see all the electrons right 12 electrons go here. So where do the electrons from the metal get filled in? t 2 g and e g. So what is that? There is an agreement with crystal field theory. In crystal field theory where did the 3d electrons of the metal go, the remaining 3d orbitals.

It is just that the 3d orbitals got split into t 2g and e g sets. T 2 g is lower in energy. So suppose configuration is d 2? Then what will you have? You will have 2 electrons in the t 2g set in CFT. In MOT also you have 2 electrons in t 2g state. Is it not? Because these are all filled orbitals right. if you have 6 SALCs that means they have originated from 6 orbitals. 6 atomic orbitals on pendant atoms. And this 6 atomic orbitals are completely filled.

If you go back to the classical picture of dative bond, coordinate bond that involves what, a filled orbital, right? Both electrons come from the donor. These are the donors. So these are all doubly filled. So you have 6 here. Here also you have 6 MOs. So 12 electrons go here. So whatever is the electron configuration of the metal, that gets reflected purely in t 2g and e g. So that is an agreement between CFT and MOT, alright?

So what we see is that is unraveling to is unraveling in the way that we want it to unravel to be honest. There is a correspondence with crystal field theory. However, we are getting more information. We are developing a more generalized approach by using molecular orbital theory, right? That is the triumph of molecular orbital theory. So this is 10D q for you and of course okay that is what I talked about already. I just, in my excitement I forgot to press the button. I did not realize that I have animated it also. Okay, so you understand what I am saying, right.

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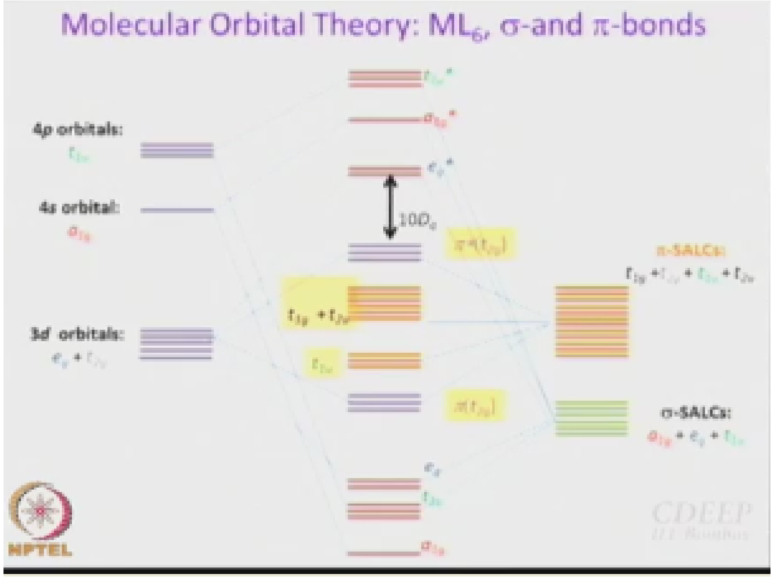

Molecular Orbital Theory: ML_6, σ-and π-bonds

Moving on, there is no reason why we should be happy only with sigma bond. This is highly possible and it happens that you have pi bonds also, okay and this is something that we have not worked out. Self-study problem for you. If you cannot do it, come to me we will do it together, okay? We have generated the sigma MOs right? Similarly, you can generate pi MOs as well. It is worked out in Cotton's book, right? Not MO sorry, pi SALCs.

When you generate pi SALCs you get t 1g + t 2g + t 1u + t 2u okay? Now what will happen? Sigma bonds have formed already. You have generated the energy diagram for sigma bonds. What is the symmetry of the nonbonding orbitals that you have, t 2g? Do you have t 2g here? You do, right? So what will happen? Pi bonds will form involving these t 2g orbitals of the metal and the t 2g SALC pi SALC, what question?

It was what? Yeah of course yes. But not necessarily back donation, you can have regular pi bond also. Back donation would be there when you have empty orbitals like it happens in carbonyl. In carbonyl complexes you have antibonding orbitals that are empty and that can accept electrons from the metal, that is back donation, okay? But here what will happen? This t 2g and this t 2g they are going to mix and once again you are going to have splitting like this.

This then is the complete energy diagram of a octahedral complex involving sigma bond as well as pi bond okay? Where is 10D q now? Sorry, we have to write these also. T 1g t 2u remain as like nonbonding SALCs you can say. So this is 10D q. So see there is a qualitative difference between the 10D q that you have in octahedral complexes with and without pi bonds.

If there is no pi bond, then this energy, then the t 2g orbital is a nonbonding orbital on the localized on the metal. E g * is antibonding orbital which is spread. Whereas if you have pi bonding also, then the t 2g that you have is no longer nonbonding. It is actually an antibonding orbital, okay and as expected the energy should be a little smaller than what you would have in absence of pi bonding, okay.

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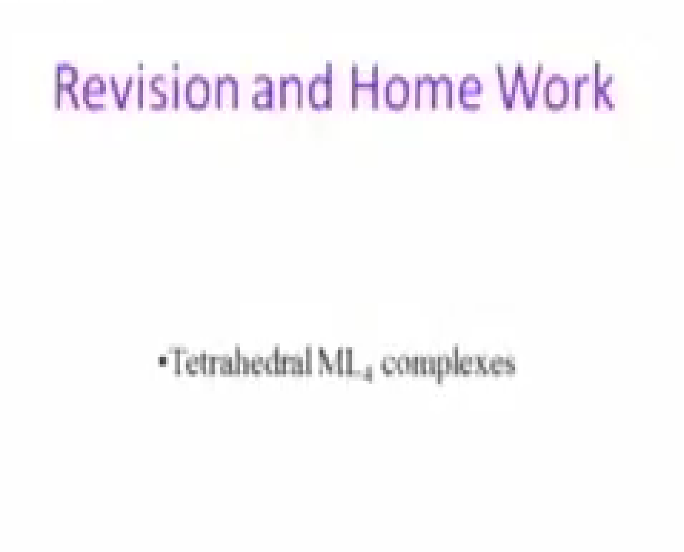

Revision and Home Work

- Tetrahedral ML_4 complexes

This is what I would like you to do, yes. What was that? **"Professor - student conversation starts"** t 1g for pi SALC not mixed with 4p orbitals. Because 4p orbitals are already betrothed or whatever that word is pronounced. **"Professor - student conversation ends".** They are already taken. They are committed. They are committed to sigma bonding. And sigma is stronger than pi so there is no reason why it should come out of the stronger commitment for an uncertain weaker commitment that has suddenly come its way.