Symmetry and Group Theory
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Lecture - 64
MOT Approach of Bonding: H2O, Ferrocene

What is the molecular orbital theory approach of bonding? You have molecular orbitals that in the simplest approximation are generated by linear combinations of atomic orbitals, okay?

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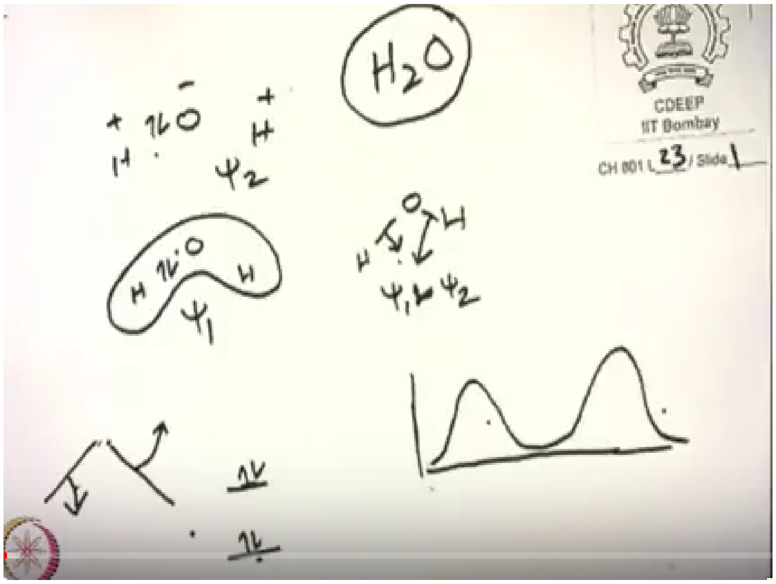

So in water, the lowest energy MO will obviously be something like this. So what I am asking you is, is this a bond? Is this a bond? No. If I put in 2 electrons here, is that a bond? No. Right? Okay, often I do not remember what the higher energy molecular orbitals look like, but let us say it looks something like this. So this is plus, this is minus, something okay? So this also will have 2 electrons, bond pairs. And then you have the lone pairs and oxygen, right?

So now the thing is this bond pair is in a particular MO that is delocalized over the molecule. This bond pair is another MO that is delocalized over the molecule. Now if you want to draw the structure like this then this bond, let me call this psi 1, let me call this psi 2. This bond will have contributions from psi 1 as well as psi 2. This bond will also have contribution from psi 1 and psi 2, is that understood?

Because both the molecular orbitals are delocalized from this hydrogen to that hydrogen through oxygen, okay. So that is why there is no problem okay? That is why we are fine with the 2 bond lengths being the same. The 2 bond lengths are the same because both have equal contribution from each MO, but they are not degenerate, the MOs are not degenerate. MOs are different from each other. So the picture is something like this.

If you work out the photoelectron spectra then this is something that you will get. Actually, not really. You are going to get some vibrational structure because they are bonding MOs, right? You are going to get 2 bands in the photoelectron spectrum because the electrons come from 2 different MOs but not 2 different bonds, okay? MOs and bonds are not synonymous with each other. Each bond has equal contribution from each of the bonding MOs, alright?

That was what I was saying. But what I like you to do really is that work out the SALCs of H2O. It is going to be interesting. Psi 1 and psi 2 are wave functions. Psi 1 is delocalized over the whole thing. We are talking about molecular orbital theory here. If it was valence bond theory then what you would have done is you would have worked out the psi for this bond, you would have worked out for the psi, you worked out the psi of this bond separately and you have assumed that this bond pair is localized between oxygen and this hydrogen.

The second bond pair is localized between oxygen and this hydrogen. That is what molecular orbital theory does away with. It allows this bond pair to get delocalized over the whole molecule and same is true for the second one. So each bond now has contributions from all the bonding molecular orbitals even though the molecular orbitals themselves have different energies.

So the bond that you get in molecular orbital theory, each bond, localized bond is really an (()) (04:19) and you are going to work out now another kind of metal complexes, something that we have talked about already, long ago and that is ferrocene. So ferrocene is an example of metal sandwich complex is it not? Metal sandwich complex. So, so far we had talked about simpler complexes.

Perhaps that is an oxymoron, simpler complexes but now we want to talk about this complex, complex, the metal sandwich complex and as you will see that it is not really as complex as you think that it might be. So you are going to work this out yourself. What is the structure of ferrocene? 5 membered ring on the top, 5 membered ring at the bottom and iron in between, okay? Let us take the staggered configuration, not the eclipse configuration.

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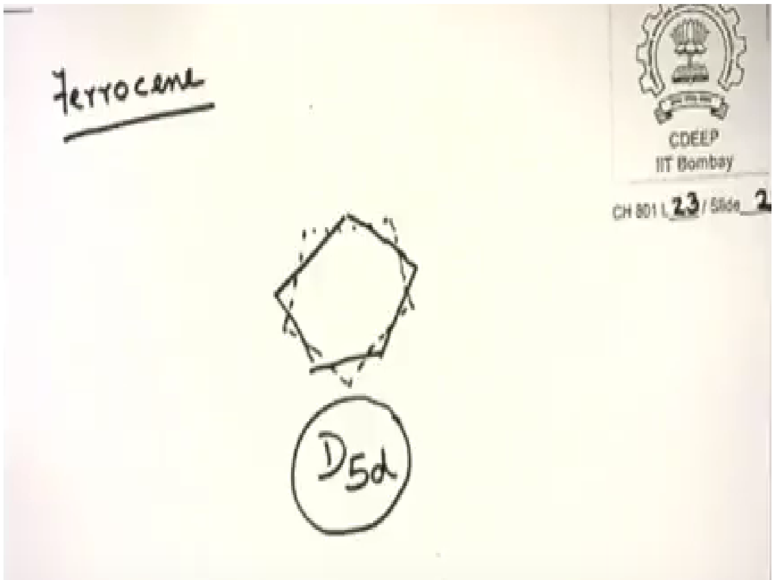

What is a staggered configuration? We are talking about ferrocene. Staggered configuration means this, right? What is the point group? D 5d. There is no sigma h right? D 5d. If it was eclipsed then what would have it been? D 5h. So we will work with D 5d, alright? How will you approach the problem? What is the central atom here? Iron. So and what are the orbitals that we can use for the coordinate bonds?

No, not about iron now, ferrocene; I mean the 5 membered rings. The p orbitals, right? Very good. So we are going to use the p orbitals to form the SALCs, right? Is that right or wrong? We are going to use, how many p orbitals will be there? 10. But there is some relationship, right? 5 membered rings are identical, right? So actually we can work with 2 identical sets of 5, alright.

So we will work with those 10 p orbitals, we are going to generate those SALCs and then we are going to match these symmetries of these SALCs with the orbitals that are there in the central metal ion, okay? What is the first thing I need to do? First thing I need to do is to look at the character table.

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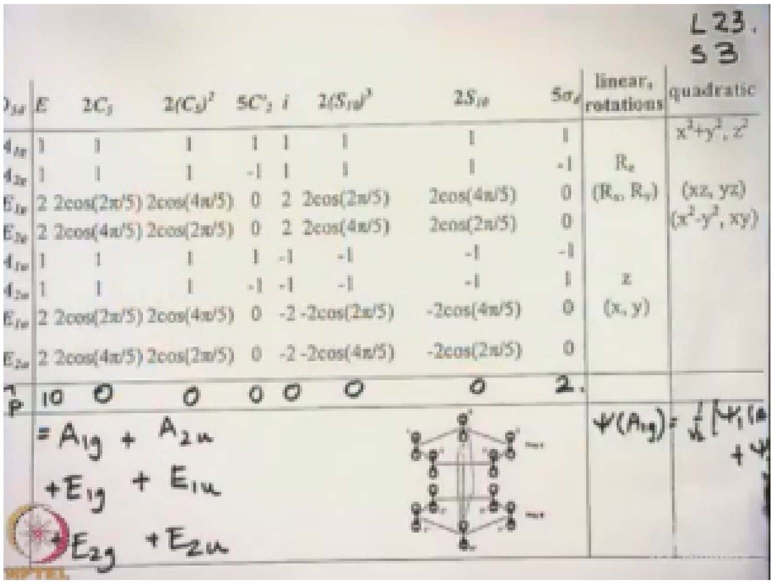

L23. S3

D_{5d}	E	$2C_5$	$2(C_5)^2$	$5C'_2$	i	$2(S_{10})^3$	$2S_{10}$	$5\sigma_d$	linear, rotations	quadratic
										x^2+y^2, z^2
A_{1g}	1	1	1	1	1	1	1	1		
A_{2g}	1	1	1	-1	1	1	1	-1	R_z	
E_{1g}	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	1	z	
E_{1u}	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	-2	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	(x, y)	
E_{2u}	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0	-2	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0		
Γ_p	10	0	0	0	0	0	0	2.		

$= A_{1g} + A_{2u}$
$+ E_{1g} + E_{1u}$
$+ E_{2g} + E_{2u}$

$\psi(A_{1g}) = \frac{1}{\sqrt{1}}[\psi_1$
$+ \psi$

Oh, it is just fit. So see this is ferrocene for you. Those figure is from Cotton’s book. These are the p orbitals. Do you see that the p orbitals are drawn in a little strange fashion. For the 5 membered ring on the top the plus lobes are pointing in. for the 5 membered ring at the bottom the plus lobes are once again pointing in, right. So they are not like this. They are rather like this, okay? It is a matter of convenience that is all.

All that will change is a definition of plus and minus because of that, okay. But before we go any further, let us use the 10 p orbitals that are there to construct the reducible representation. First one I will write 10. For C 5 what will be the character? What are we working with? We are working with those 10 p orbitals that are shown. Why 0? Because they change places. What about C 5 square?

But even before you go there why is it that C 5 and C 5 square are written separately? Why is that C 5 and C 5 square are written separately? They belong to different classes, right. You see characters are different but what I like you to do is convince yourself by yourself that they actually belong to different classes. Later on, not now. Moving on, C 2. What will happen when I apply C 2. Even the rings interchange places. So the character would have to be 0.

I, even without asking you I can write 0. S 10 definitely 0. Rings are changing place. S 10 cube S 10 fine. Sigma d, I got 3 answers; 0, 1, 2 which one is correct? Why 2? Because if I draw it like this, is this sigma d? Then see sigma d contains this p orbital and this p orbital is it not? No matter which sigma d you draw it is going to go through 2 p orbitals. So as a result of application of sigma d these 2 p orbitals are not going to change places is it not?

So that is why the character is 1; 2 just checking, alright? Now see our reducible representation in front of you. You have the character table in front of you and after some time I have almost the entire class in front of me. So let us work it out. Break it down into irreducible representations. What will it be? A 1g okay is there any other one-dimensional representation? No? A 2u is there. A 1g + A 2u + E 1g + E 2g + E 1u okay?

A 1g + A 2u + E 1g + E 1u + E 2g + E 2u, alright? Now of course you can go ahead and write this, write this out completely in the full form by working with all the 10 orbitals, okay. One of these, one of SALCs is right there in front of us. What is drawn here is also an SALC is it not? Right? Which SALC is this? Yes. Yes to both. That is right, this is also right. But this is the question I was asking. What is the symmetry of this SALC? Do you agree that is this A 1g?

Right? If you go ahead and quickly apply all the symmetry operations, character is going to be 1 for everything okay and that is basically why you have drawn it like this. Because unless the plus lobes are both pointing inwards or unless the minus lobes are both pointing inwards, you are never going to get symmetry with respect to inversion. It is never going to be gerade, right? If you drew it like this, then it would have been ungerade is it not?

If you just turn this around, the lower one, what will you get? Will it not be antisymmetric with respect to inversion? Right? So that is why we write like this. This is A 1g you are right. Now, so will you allow me to write this psi A 1g as psi 1A + psi 2A. What will be the normalization constant? What is psi 1A and what is psi 2A? Psi 1A is the totally symmetric SALC that you get of the top ring.

Psi 2A is the totally symmetric SALC that you get for the bottom ring if you consider the 5 membered ring separately. So this is a short form of writing it. Since I have two 5 membered rings anyway, right and I can handle the 5 membered ring separately, right? I can generate all the pi SALCs of 5 membered ring separately and then in terms of those I can write the SALCs of ferrocene. The only advantage of that is that you do not have to write out long expressions, okay? Do you understand? Do you agree with me?

Psi 1A + psi 2A, psi 1A is the A; A means totally symmetric SALC of the ring on the top and psi 2A is the totally symmetric SALC of the ring in the bottom, right? Any comment here? Do not forget that in all convention plus means both are pointing inwards, right? Not both are pointing in one direction. Do not get confused with that, alright?

So before we go any further what I would like to do is I would like to show you, you can work this out yourself because you have worked out benzene I think. We have worked out benzene in class. Then we have worked out naphthalene. So then you can work out the 5 membered ring also without much hassle.

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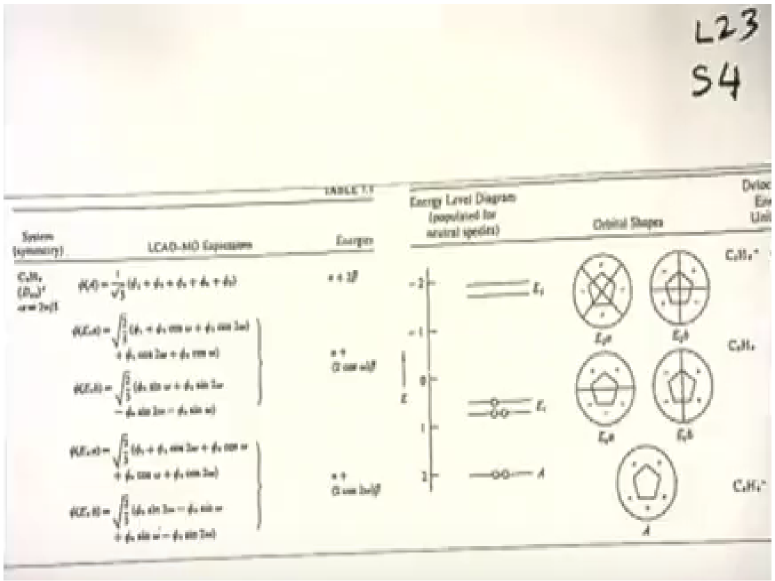

L23
S4

System (symmetry)
LCAO-MO Expressions
Energies
Energy Level Diagram (populated for neutral species)
Orbital Shapes

Can you read? You can read with a little trouble could you not? Once again, these are 2 pages from Cotton's book okay. A summary of C 5 H 5. The symmetry is D 5h I think everybody will agree. We are talking about each ring, if each 5 membered ring of ferrocene separately now, okay? If you just take a 5 membered ring, symmetry of that is D 5h okay? What will the character table look like? Character table will have complex characters.

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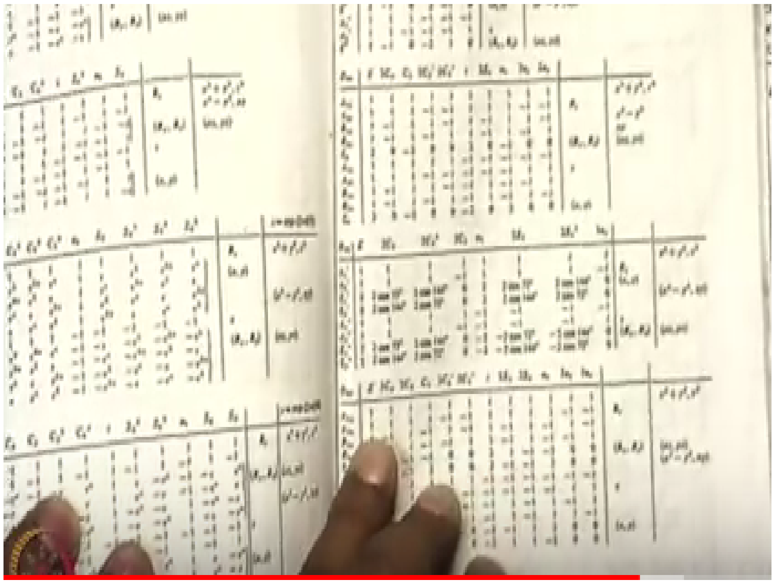

Not complex really. Complicated characters. 2 cos 72 degree **etc**. etc. okay? So here that is written as omega and these are the LCAOs that you get. You can work this out yourself and as a matter of fact is I encourage you to work it out yourself okay. So first one is 1 by root 5, phi 1 + phi 2 + phi 3 + phi 4 + phi 5 okay, all are plus. That is the one that we have used so far and of course that is bound to be totally symmetric, right like benzene.

It is just that there is one carbon atom less, one p orbital less. Was it not the case in benzene also? Sum over i phi i and this is what it will look like. Are you familiar with this kind of notation. We are just writing plus that we are looking down from the top which lobe do you see plus or minus, okay? All are plus. So this is the, symmetry of this molecular orbital is A, alright. Then next you have E 1a and E 1b.

Since both belong to the 2-dimenional representation E 1 they are going to be degenerate and see this is what, you can work this out once again. Root over 2 by 5 phi 1 + phi 2 cos omega + phi 3 cos 2 omega + phi 4 cos 2 omega + phi 5 cos omega and the second one is root over 2 by 5 phi 2 sin omega + phi 3 sin 2 omega – phi 4 sin 2 omega – phi 5 sin omega, right? And you know how to work out the energies as well. How do I work out the energies?

I solve the secular equation, right? But I do not have to solve the big secular equation. I can symmetry factorize it and I can work with that part of the determinant which is relevant to the kind of symmetry I am talking about. That is what we did for naphthalene, okay. So from there you get this, the energy for alpha + 2 cos omega beta. This is where you draw them, degenerate and this is what they look like plus, plus. This is the nodal plane and this side is 3 -.

The other one is where the nodal plane goes through one of the carbon atoms, right? So these are your E 1 orbitals and above that you have the E 2 orbitals. This is the form. This is what they look like. Instead of one node, you have two nodes. So you have plus minus, plus minus kind of arrangement. They are of higher energy. You can work out what the energy is. Alpha plus 2 cos 2 omega beta.

I encourage you to work this out by yourself, at least one or two examples, alright? But for today we are just going to use this, okay? So this is what, this is psi A, this is psi E 1a, psi E 1b. This is psi E 2a, psi E 2b and all these psi's would be there for the top ring as well as the bottom ring. So what we can do is that depending on the symmetry we can just represent the SALCs of ferrocene as linear sums of these SALC MOs that are there, makes sense?

And we have already worked out one. We have already worked out the first one, the simplest one. What is this psi A 2u going to be? What happens if I turn the other ring? I turn it around by 180 degrees. So now it is pointing inwards, the top one is pointing inwards, the bottom one is pointing outwards. Then it will definitely have u symmetry, right? Is it A 2u, can you verify quickly. There is no point in going up to i. A 2u is this, right?

Where does it change sign? C 2, will it change sign or not? If I apply C 2 will it change sign? Okay, think of one orbital. It is like this. What about the p orbital below? It is also like this, right? Both are pointing in one direction. This is C 2, right? You turn with respect to C 2, the orbital will be pointing upwards. So that is the change in sign. Understand what I am saying? Both the orbitals pointing downwards, right? And then you have the C 2 turned by 180 degrees.

The transformed orbital is going to point upwards which is -1 sign. Any question? So similarly, you work out for everything else. S 10 cube, S 10, sigma d; sigma d is very obvious right? These are the orbitals. You apply sigma d, there is no question of changing sign, okay? Or apply C 5 for that matter. C 5 is like this. No question of changing sign, right? Only when you apply inversion or when you apply this C 2 or anything to be with those symmetry operations, the sign is going to change, right? So how will I write psi A 2u in terms of psi 1A and psi 2A?

That is very easy, minus, okay? So if I add them, psi 1A and psi 2A if I add them then I get psi A 1g. If I subtract one from the other then I get psi A 2u, right? So these are the two. Now what will be psi E 1ga? I will show you those MOs again. This is E 1a, this is E 1b. This is E 2a, this is E 2b and do not forget you have another set of E 1a, E 2b; E 2a, E 2b on the ring that is above or below whatever you might want to take it.