Symmetry and Group Theory
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Lecture - 65
MOT Approach of Bonding: H2O, Ferrocene

So now you tell me, you had broken down that reducible representation, right? A 1g is accounted for, right. You have worked out the wave function for A 1g, right?

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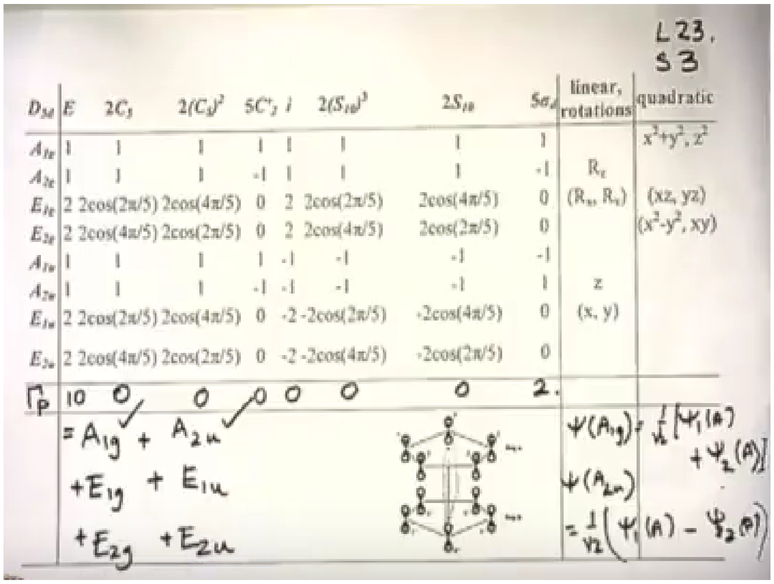

L23, S3

D_{5d}	E	$2C_5$	$2(C_5)^2$	$5C'_2$	i	$2(S_{10})^3$	$2S_{10}$	$5\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1		x^2+y^2, z^2
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.		

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

$\psi(A_{1g}) = \frac{1}{\sqrt{2}}[\psi_1(A) + \psi_2(A)]$

$\psi(A_{2u}) = \frac{1}{\sqrt{2}}(\psi_1(A) - \psi_2(A))$

We have found what is A 2u. Next we want to know what is E 1g, what is E 1u, what is E 2g, what is E 2u. How will I do it? For E 1g and E 1u what should I combine? Right.

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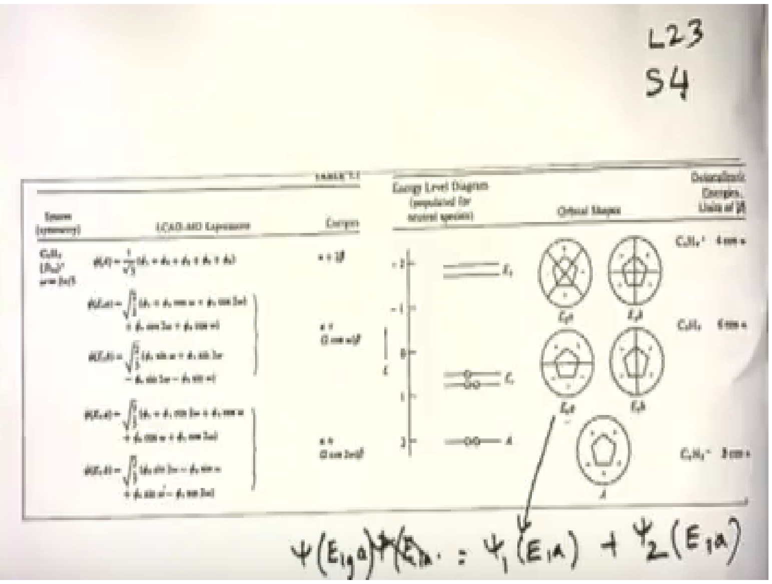

So tell me then what is psi E 1g a? In terms of the psi’s, this psi’s, these psi’s. Psi 1 E 1a, psi 2 E 1a, psi 1 E 1b, psi 2 E 2b. So that is why I do not want to write so much. See this is E 1a right, this combination. What is E 1a? This is, this one is plus, plus this one is minus and so on and so forth. So that linear combination that you are trying to say, half of it is already worked out. Psi 1 E 1a + psi 2 E 2a? What is that? Is it psi E 1. Do you agree with that?

Because in our convention this is plus and this is minus right, this is g, right? So psi E 1ga = 1 by root 2 psi 1 E 1a + psi 2 E 1a. What are we trying to generate? We are trying to generate the LCAO of the 2 rings together, right? When I try to do that, does it make sense to mix an a LCAO of this ring with say an E 1a LCAO of the other ring, no, right? So a will mix with a , E 1a will mix with E 1a, A 1b will mix with E 1b and so on and so forth, right?

Now what I am trying to tell you is this, this is your E 1a right? Let us say this is the top ring. I denote the top ring by a subscript 1. So this is what, this is psi 1 E 1a right? I denote the bottom ring by a subscript 2. That will also have a similar symmetry orbital, orbital of same symmetry. What will I call it? Psi 2 E 1a. And it makes sense to mix them and generate an LCAO because they are of same symmetry. If I mix these, what symmetry will I get?

If it is plus, then it is going to be gerade, right? So E 1 is already there, a is already there. It is going to become, it is just that I have not left any space for g, that is why I stopped. Something like this. Right or wrong? If it is plus then the p orbitals are both pointing inwards. Plus lobes inside and minus lobes inside, both of them, right? So when you mix that kind of LCAOs what we were saying earlier also is that then you are bound to get something that is symmetric with respect to inversion. Right or wrong? So think of this.

It is plus on this side, minus on this side, okay? And then you take the same thing, put it out. Now you have to visualize, but then you have to turn it around also so that plus is over plus, minus is over minus, right. That is the meaning of plus, okay. And since you are mixing E 1a kind of LCAOs, the resultant linear combination is also going to have E 1a kind of symmetry.

The only additional thing that will come is that if it is a plus combination, then the subscript g also will have to come in, right. Because by themselves, these rings do not have a center of inversion do they? Does this ring have a center of inversion, no? Where does the center of inversion come from? Center of inversion comes from the fact that you have taken 2 such rings and you have placed them like this, right?

Now this and this, they are related by a center of inversion, is it not? Now, is it, does it start making sense? You have this E 1a linear combination on the top. You have another E 1a linear combination at the bottom, sorry like this, okay? When you add them, add them means this p orbital pointing inwards, this p orbital also pointing inwards. Plus lobe pointing inwards, plus lobe pointing inwards.

That combination gives you the E 1a symmetry with an additional symmetric behaviors with respect to center of inversion. So that is why it is called psi E 1ga. Makes sense? So this is what the combinations are going to be. And now I have everything at a glance.

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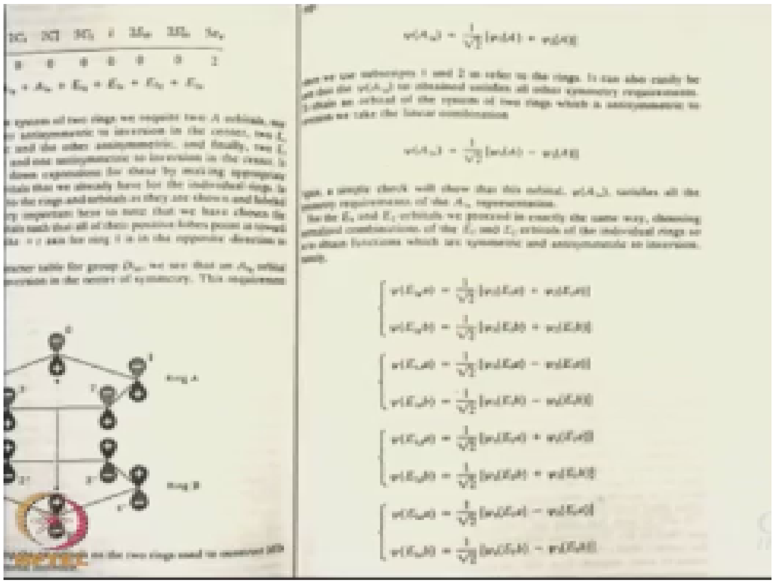

So this you all understood? Psi A 1g = 1 by root 2 psi 1A + psi 2A. Psi A 2u is 1 by root 2 psi 1A - psi 2A. What is this psi 1A? The linear combination on the top ring whose symmetry is A. When I combine it with the same linear combination of the bottom ring, right when the plus lobes point inwards that is plus then I get the linear combination that is symmetric with respect to inversion and when it is like this, minus, then I get the linear combination that is antisymmetric with respect to inversion; makes sense?

We are going back to what we had discussed a little earlier. Do you understand these two? If you understand these two then let us look at this. One by root 2 psi 1 E 1a + psi 2 E 1a. I am mixing the linear combinations of symmetry E 1a of the top ring and the bottom ring. When I add them, once again I get a symmetric function with respect to inversion. I get a gerade function; makes sense? Here when we added, it became gerade.

Here also when we add it becomes gerade. Rest of the symmetry remains the same and when we subtract psi 1 E 1a - psi 2 E 1a you get psi E 1ua because now this is what it is like, corresponding p orbitals, right? So let us see if you understand this. Have a look at this and tell me if you understand what is written there. What is there on the left hand side? On the left hand side, we have the SALCs of the 2 rings together.

That is what we need when we want to talk about ferrocene. What do you have on the right hand side, what are the stars, each * is an SALC of one of the rings, okay? We might as well write this out completely in terms of 10 p orbitals, right? all we are trying to do is since the 5 membered ring by itself is already a knows system, we are trying to use the information that is available from the isolated rings and using that we are trying to develop a description for ferrocene. So on the left hand side you have the LCAOs of the 2 rings together.

On the right hand side, you have the LCAO of the top ring separately and LCAO of the bottom ring separately. So the LCAO of the 2 ring system is represented as linear combinations of LCAOs of similar symmetry of the isolated rings. Please read this and tell me if that makes sense, then we will proceed. So this is E 1ga, this is E 1gb right? So what is a and what is b? When you work with the subgroup then degeneracy is lifted is it not?

And you have those complex numbers and all. We have done this earlier for this C 3h C plus kind of system. We worked with the full rotational subgroup and then we combined we got back the same, we got back the entire picture. That is why you should combine them eventually and you should work with the LCAOs that are there in the original group. It is just that since we have that a and b description, we are keeping the separation as far as possible.

Finally you have to combine. Now, so finally this is what we have to work with. We have generated more SALCs than we need. From there we can generate these. Now see 2 candidates for combination with the A 1g SALC, okay. What about A 2u? p z? p z is the only orbital, right? E 1g? E 1g you have d xz and d yz. You are looking for compatible orbitals. E 1u? p x p y right? Then E 2g?

Do I have a p x square - y square orbital? D x square - y square orbital and d xy orbital right, we have it. What was that E 2g. What about E 2u? Do you have anything of symmetry E 2u, no. So that E 2u SALC is useless, right? So knowing this what you could do is, I do not know if you can read. Okay, I will write. So these are the SALCs of the ring. You have A 1g, A 2u, E 1g, E 1u. Then this is E 2g, E 2u. Now tell me in this d what are the different symmetries that are there? A 1g, E 1g, E 2g. What about s? This is A 1g. What about p? Somebody said t. A 2u, E 1u, okay.

Now the problem becomes simple. What you have to do is you have to find the right match but then do not forget that just match of symmetry is not enough, the energies must be close enough. Otherwise, they are not going to combine, okay.

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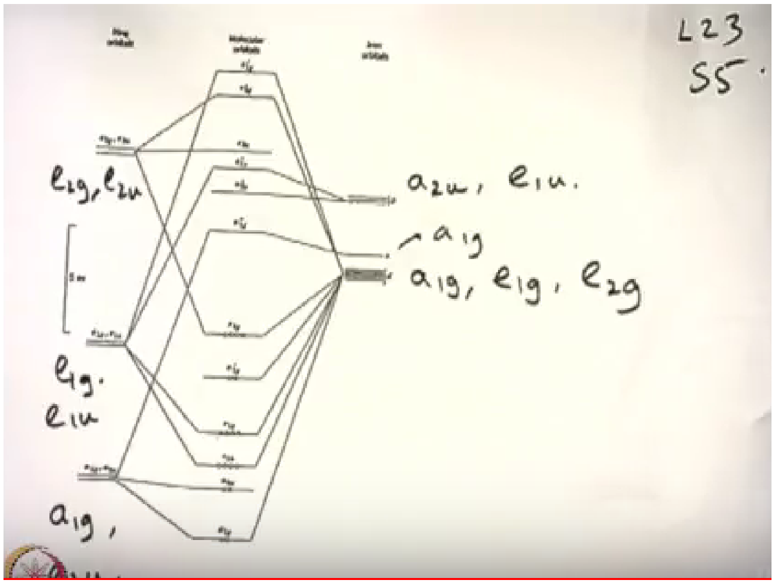

So knowing the symmetries of the orbitals on the metal and knowing the symmetries of the LCAOs you can generate all these MOs of ferrocene, right and you can see that some are going to be nonbonding because they are not going to have the right symmetry or because the energy is not going to be very close, okay? But once again, this is not a problem that can be solved only by symmetry. Computation is very much involved here, okay. So that (()) (15:31) a 1g, e 1g, e 2g.

What about s? This is a 1g. What about p? Somebody said t. a 2u, e 1u, okay. Now, the problem becomes simple. What you have to do is you have to find the right match, but then do not forget that just match of symmetry is not enough, the energies must be close enough. Otherwise they are not going to combine, okay.

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