Symmetry and Group Theory
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Lecture -46
Tutorial- 9

So, welcome to today's tutorial. In this tutorial we will be looking at how to create symmetry adapted linear combinations and we will also try to see if we can create a molecular orbital picture for pi bonding in aromatic ring systems that is one topic which we are not covered in regular classes. So, let me cover a little bit of that in today's tutorial. So, tutorial 9 where will be discussing about pi bonding in aromatic ring systems.

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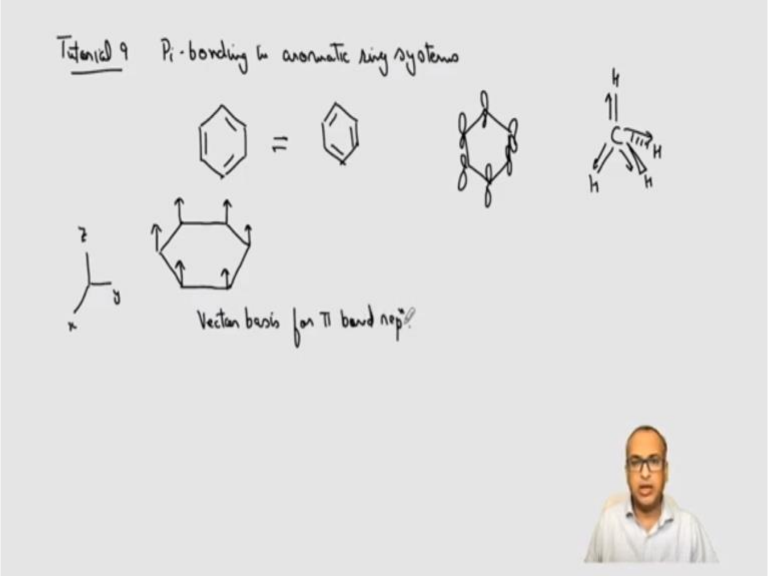

So, we are well aware of an example of benzene which is a famous aromatic ring system. There are several other examples, which we know that it is one of the kekule structures. And another one, which is the resonating structure is these. So, if you look at the ring system, it looks something like this. So, we have six sigma bonds between the adjacent carbon atoms and then we have pz orbitals, lying like this perpendicular to the plane of the board.

So, if benzene molecule it is a flat molecule if it is lying in the plane of the board. The pz orbital each of the pz orbital is perpendicular to the plane of the board. Now these pz orbitals each one of this has a single electron so that is how it makes three bonds and these three bonds are resonating in nature and the bond order between the adjacent carbon-carbon is one and a half.

So, one is coming from sigma bond, half of it is coming from pi bond. So, now let us see, how do we use group theory to actually look at how these pz orbitals will combine to give you a molecular orbital picture or the bonding picture for pi bonds? So, we have already looked at sigma bond examples in CH4 example, the similar thing will apply here also but pi bond we have not looked at so let us see, how do we look at pi bonds?

So, for pi bond, let me go back to CH4. So, in case of CH4 we actually made arrows like this to use our basis set. These were the four arrows. So, along the direction of the sigma bond starting from the central atom going towards pendant atoms. So, we used these for arrows as the basis set to create a reducible representation. In this case the arrows which we will use will be perpendicular to the sigma bonds.

Because these the pi bonds are actually formed by the perpendicular orbitals, so we will use something like this, so if this is my benzene molecule. If I am looking from the sideways, so the arrows will be like this. These will be the six arrows, which are perpendicular to this plane. And just for the reference, I have this is my x, y, z. This is called as vector-basis same as here, this is vector basis for pi-bond representation.

Now you can use this kind of approach in any of the system, we will later on see that let us say if we want to discuss the bonding of CO2 for sigma bonds we will take this type of arrows and for pi bonds we will take this type of arrows, perpendicular arrows. So, this is just an example, so now let us see that how do we take these arrows and create a basis set?

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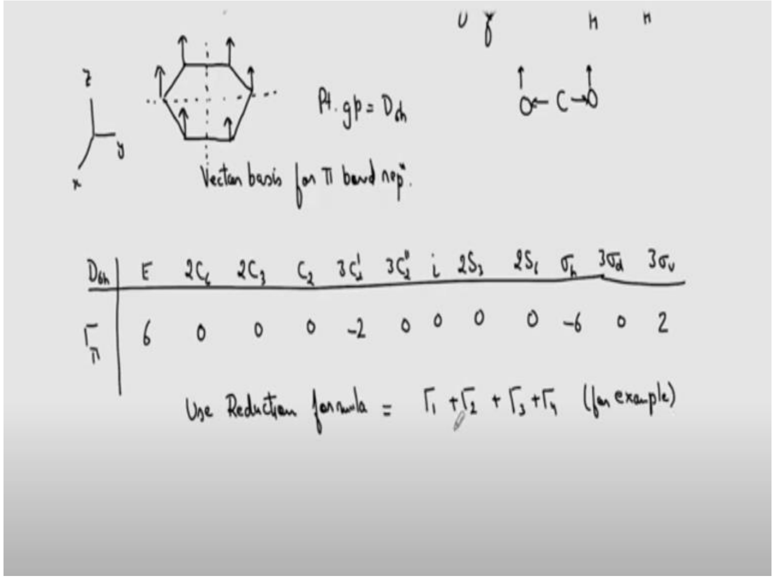

Pt. gp = D_{6h}

Vector basis for π bond repⁿ.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

Use Reduction formula = $\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$ (for example)

So, what is my D6 the point group here is, let me write down point group is D6h. So, let us see what happens to these arrows when we perform different symmetry operations under D6h point group? So, this is my D6h point group and these are my symmetry operations under this 2 C3, then I have C2, 3 C2 primes, 3 C2 double primes, we must know the location of each and every symmetry operation by now.

So, I am not going to tell you which is where now 2 S3, 2 S6, sigma h, 3 sigma d and 3 sigma v. Now this is my tau pi, now what happens to 6 vectors when I do E operation none of the vectors will change. So, I will say the character under E will come out to be 6, remember that we have discussed that if none of the vectors will change, it will be 6, number of vectors that will change will give you the value over here.

So, if 6 vectors remain unchanged 6, if 0 vectors remain unchanged that means all of them are changing the value will be 0. So, if I am doing C6 operation, I am rotating this by 360 by 6 that is 60 degrees, so if I rotate it by 60 degrees all of these will go to adjacent places. That means the character will come out to be 0. Similarly, if I do C3 operation will be 0, C2 operation will be 0 because all the vectors will be moving to alternate positions.

Now if I am doing C2 prime, so C2 prime is axis which is going through opposite vertices. So, if I am doing this, these vectors. So, this is let us say this is my C2 prime, so these four vectors will be replaced with each other so that means they will not contribute towards this reducible representation whereas these two vectors will contribute but they will become negative. So, I will have -2 corresponding to two vectors which are becoming negative.

Now similarly if I have a C2 double prime which are going through opposite bonds. Let us say this is my C 2 double prime then these three will be replaced with these three in the negative side. So, again, this will be zero, i everything will be replaced again, so zero, S3 it is a rotation reflection 0, rotation reflection 0. Sigma h is now the molecular plane of benzene all of the vectors will remain at their own position.

But they will go from plus 1 state to minus 1 state, so that means this will be -6. They will be reflected by the molecular plane. Sigma d, again this will be 0. Sigma v will be containing this C 2 prime, so this is my sigma v which is containing these two vectors, so these two vectors will not change so that means two whereas these four vectors will change their positions. So, this is my tau reducible for pi basis set.

Now what happens if I reduce this? So, how do I get the component irreducible representation? So, what I have to do is I have to use reduction formula. So, this is actually one of the questions in the assignment this week. So, I am not going to tell you the answer for this, but I will just tell you partial answer. So, you have to use reduction formula to solve this. So, now you know how to create a reducible representation for this.

Now, what you have to do is use reduction formula to find out what are the component irreducible representations. So, there will be four such reducible representations. For example, I do not know if it will be 4 or 2 or 5 or 6. Now this you can easily obtain by just using the reduction formula and find out what is the answer.

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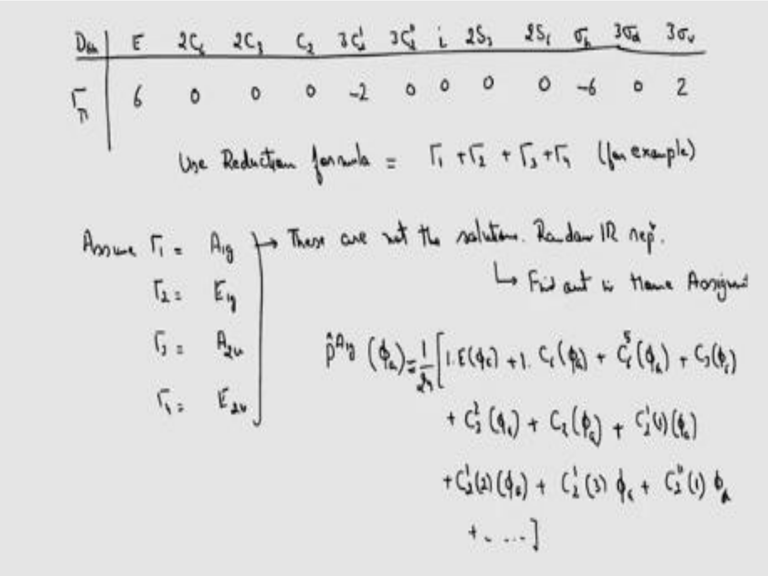

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

Use Reduction formula = $\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$ (for example)

Assume $\Gamma_1 = A_{1g}$
$\Gamma_2 = E_{1g}$
$\Gamma_3 = A_{2u}$
$\Gamma_4 = E_{2u}$

→ These are not the solutions. Random IR rep.
↳ Find out in Home Assignment

$$\hat{P}^{A_{1g}}(\phi_a) = \frac{1}{24}\Big[1.E(\phi_a) + 1.C_6(\phi_a) + C_6^5(\phi_a) + C_3(\phi_a) + C_3^2(\phi_a) + C_2(\phi_a) + C_2'(1)(\phi_a) + C_2'(2)(\phi_a) + C_2'(3)\phi_a + C_2''(1)\phi_a + \ldots\Big]$$

Now let us see when you want to create, so let us say that, assume I am not saying that it is correct because I am not telling you the answer for this. So, assumed tau 1 is A1g, what are the irreducible representation? So, it has A1g, let us say tau 2 is E1g, let us say tau 3 is A2u, tau 4 is E2u. I am just randomly writing 4 irreducible representations. These are not the solutions random IR representations.

So, these solutions you must find out in home assignment. So, I am not going to tell you whether these are correct solutions or not, these are not correct. I can just tell you that the whole set may not be correct some of them may be correct some of them may not be correct. So, now what will be the next step? Next step will be to apply projection operator using any of this A1g. Let us say if you are taking A1g and let us do incomplete projection operator.

And what will be the projection operator applied on any of the Phi a? Now what was my basis set? My basis set was, let me call these as phi a, phi b, phi c, phi d, phi e, and phi f. So, now I can use my projection operator corresponding to these four irreducible representations and use any of the basis vectors. So, how do we do that? So for that we need to go to the character table and carry out all these operations.

So, I will just tell you one of the operations let us do it for once. So, for A1g Li is 1 and the h value for D6h this will be thing 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 24 so this will be 24. Now what else for A1g? All the characters are positive. So, you will have 1 into E operating on phi a + 1 into C6 operating on phi a plus again, so you have to do it for all the operations.

Because, effect of C6 and the other operation which is generated by C6 will be different so you have to consider the other operation, which is actually C6^5 phi a, then what else do we have? So, this will be 24 such operations. So, C3 effect of C3 onto phi a and then effect of C3 square on to phi a. So, it is a tedious calculation. So, you can see that already, it is long but it is not difficult, C2 phi a.

Then I have 3 C2 but I will have to take each of them one by one, so C2 prime let us say 1 on to phi a, then C2 prime second operated on phi a, C2 prime third operated on phi a + C2 double prime 1 operated on phi a, and so on. So, you can write all 24 operations here and their effect onto phi.

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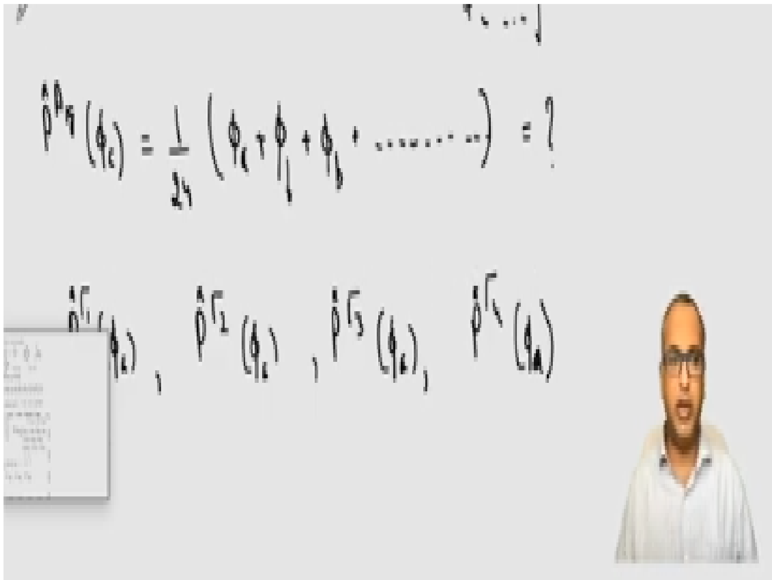

$$\hat{P}^{A_{1g}}(\phi_a) = \frac{1}{24}\left(\phi_a + \phi_f + \phi_b + \cdots\cdots\right) = ?$$

$$\hat{P}^{\Gamma_1}(\phi_a),\quad \hat{P}^{\Gamma_2}(\phi_a),\quad \hat{P}^{\Gamma_3}(\phi_a),\quad \hat{P}^{\Gamma_4}(\phi_a)$$

Now the answer to this, you will get is what will be the answer. So, let us try to see if we can actually find out what will be the answer. So, answer, will be projection operator A1g phi a 1 over 24. So, let us say this is E operating on phi a will give you phi a, C6 operating on phi a will give you rotate by 60 degrees. So, you will get, let us say where; so, anticlockwise rotation, so phi a will go to phi f.

So, you will have phi f over here. So, the new position is phi f. Now C6^5, so I will have phi b here, then C3 if I do C3 operation. So, the point is that you can find out what this is going to be? How many will be positive? How many will be negative? Are there is going to many positive or any negative? So, now you have to tell me what will be the answer to this once you complete the home assignment.

Now similarly you have to do, calculate the projection operator of A2u on phi a, then projection of E1g on phi a and projection of E2u on phi a. Of course, these values will be the actual or we can say let me just correct this. So, what you have to do is you have to actually calculate projection of tau 1 phi a, projection of tau 2 on phi a, projection of tau 3 on phi a, projection of tau 4 on phi a.

This overall will give you the bonding of phi system in resonating structures, so resonating or ring structures. This approach can be used for any of the ring system or any of the phi bonding system. The only care that you have to take is that the vectors have to be perpendicular, rest of the procedure is actually very much similar. So, for example, in case of CO2, I told that if you have to look for pi bonding.

So, you have to look for the basis vectors, which will be perpendicular to the axis, the internuclear axis. So, I think that is all this covers phi bonding in aromatic ring system and If you have any doubt, please do write to me on the discussion forum so that I can clear these doubts about this molecule and if there are any difficulties in generating these projections, please do let me know.

So, we can work it out again during discussion. That is all for today. This was a short tutorial because this particular topic was pending and so I thought I will cover this topic in this tutorial alright that is all, thank you.