

**Chemical Applications of Symmetry and Group Theory**  
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**Lecture – 27**

Hello and welcome to the second day of 6th week. So, we have been discussing about the projection operators, and in the previous class we discussed about the complete projection operator and also introduced the incomplete projection operator. So, incomplete projection operator is expressed in terms of the character of the representation.

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**Chemical Applications of Symmetry and Group Theory**

- Since we always can not deal with complete matrices hence to use more convenient information i.e. characters, we employ the so called “incomplete projection operator”.

$$\hat{P}^E = \frac{1}{h} \sum_R \chi(R) \hat{R}$$

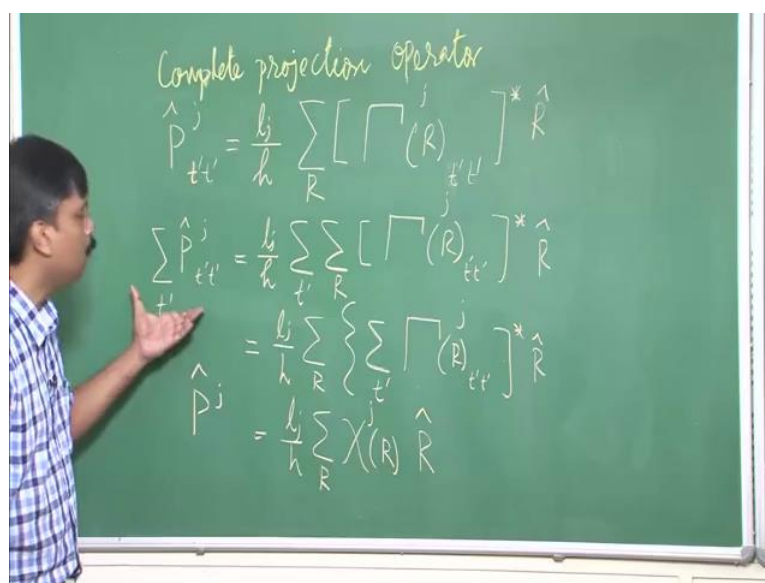
- Now let us see what happens when we apply  $\hat{P}^E$  to  $xz+yz+z^2$ .

$$\begin{aligned} \hat{P}^E(xz + yz + z^2) &= \frac{1}{6} \{ (2)(xz + yz + z^2) \\ &\quad + (-1) \left[ -\frac{1}{2}(1 + \sqrt{3})xz + \frac{1}{2}(\sqrt{3} - 1)yz + z^2 \right] \\ &\quad + (-1) \left[ \frac{1}{2}(\sqrt{3} - 1)xz - \frac{1}{2}(1 + \sqrt{3})yz + z^2 \right] \\ &\quad + 0 + 0 + 0 \} \\ &= \frac{1}{6} \{ [2 + \frac{1}{2}(1 + \sqrt{3}) - \frac{1}{2}(\sqrt{3} - 1)]xz \\ &\quad + [2 - \frac{1}{2}(\sqrt{3} - 1) + \frac{1}{2}(1 + \sqrt{3})]yz \\ &\quad + (2 - 1 - 1)z^2 \} \\ &= \frac{1}{6} (3xz + 3yz + 0z^2) \\ &= xz + yz \end{aligned}$$

So, incomplete projection operator is given by this particular expression. So, how do you get this particular form of projection operator, which is incomplete projection operator? So, this is very easily it can be formulated.

So, let us try to do that.

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First; so we had the complete projection operator. So, this one was written as in terms of the symmetry elements, so what we got there is this, and sum over R for the matrix elements S prime, t prime for a particular irreducible representation (Refer Time: 02:16) over all the symmetry operations. So, that was the complete symmetry projection operator, because it deals with all the matrix elements. And to start with we also got, when we go to the special case where we deal with only the diagonal elements so we get this one as, you take the diagonal elements as; t prime, t prime so that is what was our projection operator that we deal with in the last class.

So, if you sum over both the sides, over the element t prime. So, you get this is; equal to you can take this one out. So,  $l_j$  by  $h$ , and then you sum it over t prime and you already have a sum over R, and then you have the matrix elements; now this matrix element and the symmetry operations, they have nothing to interfere with each other. So, you can interchange the position. So, you can swap the position. So, what you have is, you can rewrite this as  $l_j$  by  $h$  and sum over R and then you can write separately sum over t prime of this.

Now, what this is corresponds to? It corresponds to the character of this jth irreducible representation. So, I rewrite this one as  $l_j$  by  $h$  sum over R, and this one is  $\chi^j$  of R for the jth irreducible representation, followed by the symmetry operation, and this particular one we can write as  $P^j$  simply because this you can see this is nothing but the sum of all

the projection operators; So, this  $P_j$  this is sum of all the projection operators individually that you can form.

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Complete projection operator

$$\hat{P}_{t't'}^j = \frac{h_j}{h} \sum_R [\Gamma^j(R)_{t't'}]^* \hat{R}$$

$$\sum_{t'} \hat{P}_{t't'}^j = \frac{h_j}{h} \sum_{t'} \sum_R [\Gamma^j(R)_{t't'}]^* \hat{R}$$

$$= \frac{h_j}{h} \sum_R \left\{ \sum_{t'} \Gamma^j(R)_{t't'} \right\}^* \hat{R}$$

$$\hat{P}^j = \frac{h_j}{h} \sum_R \chi^j(R) \hat{R} \quad \text{Incomplete } P_{ij} \text{ Op}$$

And the complex it will form a complete projection operator. So this is my expression for the so called incomplete projection operation. So, that is what we looked down here.

So, now whatever is the change, so write on your screen that  $j$  is assumed to be  $E$  because in the last class we already discussed about the projection operator for irreducible representation  $E$  for  $C_{3v}$  point group, so it can be anything. Now, since we have looked at the effect of the complete projection operator; on any given arbitrary function  $xz$  plus  $yz$  plus  $z$  square, and we saw that ultimately with two projection operators, two different function comes out to be the basis of the representation  $E$  and those were  $xz$  and the  $yz$ .

Now, here let us verify whether our this newly formed projection operator which is known as incomplete projection operator, in terms of the characters of the particular  $i$ th or  $j$ th irreducible representation that we are concerned with; whether they give the you know same result or not. So, what we do? We now easily can form this particular projection operator. So, what you need to do? You need to have a character table of that particular point group with you because you are going to use this character table. So, we are dealing with the representation  $E$ . So, you should know what the characters are for this particular representation, for  $C_{3v}$  point group.

So, find out character table for this  $C_{3v}$  point group, and now here you do the same thing here, that is you get the  $l_i$  and  $l_j$  value that remains the same, and instead of multiplying this effect of  $R$  on the function by the net diagonal matrix element; so directly you are multiplying with the character, corresponding to that particular symmetry operation. So, for identity you have a character 2, for  $C_{3v}$  point group and the  $E$  representation.

So,  $E$  and then  $E$  operator identity on this function and you get back the same thing and when you operate the  $C_3$  you get same result as we have same in the previous example of complete projection operator because the effect of  $R$  is not going to change and then you multiply by the character of  $C_3$ , which is minus 1, because you will see that  $C_3$  and  $C_3^2$ , they are clubbed under the same class. So, both of them have the same character.

So, you do it for  $C_3^2$  and then you do it for the  $\sigma_v$ s, which have the characters to be equal to 0 so, 0 multiplying with always ending up 0. So, when we simplify the whole thing, you get this  $xz$  plus  $yz$ ; again this is not surprising because that projection operator  $P_j$  which you are using right here, also as  $P_E$  that was formed by summing up the individual projection operator  $P_{11}$  and  $P_{22}$ . So, we are getting the same result because  $xz$  and  $yz$ , they are combined by this additional, so which means that  $xz$  and  $yz$  they together form the basis of the representation  $E$ .

Now, you can see the difference also. Difference was in the case of complete projection operator, each functions were in separately pointed out. So, they turned out to be the individual basis for  $E$  representation,  $xz$  and then  $yz$ , but here you are not getting them separate, but you are getting them as a combined function  $xz$  plus  $yz$ , which is again is not too surprising because here you are using only 1 operator; in the previous case you used two operators  $P_{11}$  and  $P_{22}$ , here you use only  $P_E$  right. So, one operator cannot give two functions that is very well understood.

So, here we are getting one, but in essence that solves for purpose because we know what are the component of this arbitrary function  $xz$  plus,  $yz$  plus,  $z^2$  from the basis of the irreducible representation  $E$  of  $C_{3v}$  point group.

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**Chemical Applications of Symmetry and Group Theory**

**Using Projection Operator to Construct SALCs**

**Use of Projection operators :** To determine the proper way to combine atomic wave functions on individual atoms in a molecule into Mos that correspond to molecular symmetry.

(Note: Valid MOs form bases for Irs of the molecular point group.)

We face the problem of writing SALCs when we deal with molecules having sets of symmetry equivalent atoms (e.g., the C atoms of benzene) each contributing atomic wave functions to the formation of MOs.

What we need to know are:

- (1) The IRs to which the any given set of equivalent AOs will contribute
- (2) The explicit form of the LCAOs that satisfy the symmetry properties of each representation .

So, now let us get in to the real business that is, how we use this projection operators particularly to form the SALCs? So, by now we know the actual use of the projection operator; we use some arbitrary function and all, but that must have by now given you a clear hint that, what this projection operator can actually do in real chemistry?

So, this projection operator is used to determine the proper ways, to combine atomic wave function on individual atoms in a molecule in to molecular orbitals that corresponds to particular molecular symmetry. So, here you must be remembering that; when we discussed about the relation between Group Theory and quantum mechanics, we said that the wave functions, which are the Eigen functions of an operator. Particularly Hamiltonian new operator in that case, they can form the basis for the irreducible representation for the molecule, and the particular point group to which it belongs to.

So, here when we talk about atomic wave function this also should be valid; more over is not only the wave function, but also the proper linear combination of those atomic wave function can also form the basis of the irreducible representation. So, we can actually go on to form the symmetry adapted linear combination, now we have a problem when we try to write down the you know symmetry adapted linear combination or in short SALCs, when particularly we deal with the molecule having equivalent atoms; say for example, in benzene that you have all the carbon atoms which are equivalent or in Sulfur

hexafluoride, all the fluoride atoms are equivalent or you take character MOCL 8, that kind of complex all the fluoride atoms are equivalent or say PF 5 at 3 flowing atoms in the equatorial plane and equivalent and the 2 in the axial reductions are equivalent.

So, in those cases we have something problem because each of this atom and hence both the atomic wave functions, they contribute to the symmetry adapter linear combination. So, we will see how? So, in order to found the SALCs, what do we need to know? So, first thing is that we need to know the irreducible representation to which, any given set of equivalent atomic orbitals we contribute.

So for example, if you take a benzene, so all the carbon atoms if you think about and the wave functions associated with the carbon atom or in other word all the atomic orbitals of each carbon atoms. So, how they are going to contribute to the formation of the particular irreducible representation that we are concerned about and second; the explicit form of the linear combination of atomic orbitals that satisfy the symmetry of the properties of each representation, that we have already mentioned earlier.

So, the ultimate the molecular symmetry that has to be satisfied by the linear combination of atomic orbitals that we are going to form. So this is comparatively easier to start with one dimensional irreducible representation.

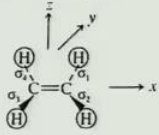
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**Chemical Applications of Symmetry and Group Theory**

**Constructing SALCs belonging to one dimensional representations: Sigma bonding in  $C_2H_4$**

Step1: We identify the point group:  $D_{2h}$

Step 2: We take 1s orbital as the basis for a representation ( $\Gamma$ ); we choose the coordinates and label the  $\sigma$  functions as shown below. Form the representation,  $\Gamma$ .



Step 3: We reduce the representation to irreducible representations

$$\Gamma = A_g + B_{1g} + B_{2u} + B_{3u}$$

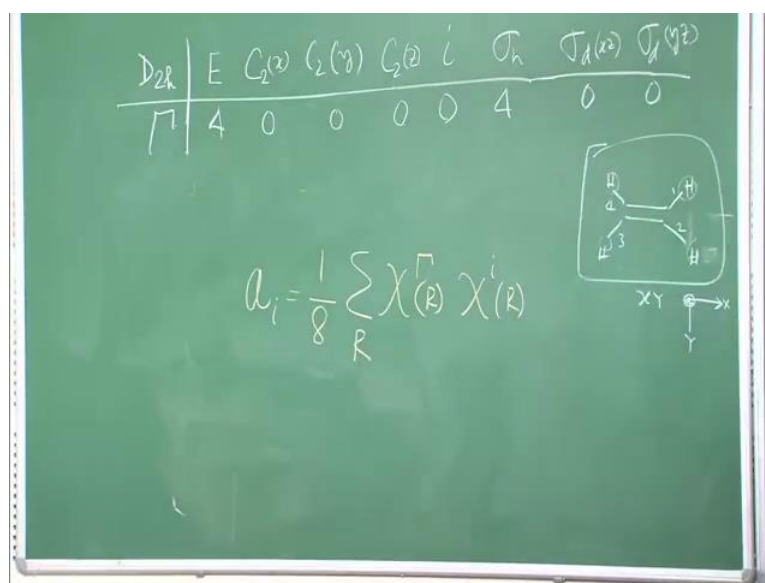
And then as we move on we will go to the complete case of two dimensional and three dimensional, it is not really complicated, but you know one dimensional is lot more easier. So, what do we do, when we try to find out the SALCs for any given molecules? So, the first thing; obviously, you have to find out the molecular structures and its symmetric meaning the point group of the particular molecule.

So, we will start with the construction of SALCs of in particularly this ethane molecules  $C_2H_4$  sorry ethylene molecule and you will particularly concentrate on the sigma bonds meaning CH 1s. So, once we identify this point group, which here is  $D_{2h}$ , which is very easy to find out and after finding out this one what we do? We take certain wave function as basic functions. So, we are considering (Refer Time: 16:20). Now what basis we can choose? The answer is anything that has to satisfy ultimately the symmetry conditions and that must be within that particular molecule.

So, what we do here? We choose the 1s orbital for each hydrogen atom. So, there are 4 hydrogen atoms. So, I consider total 4, 1s orbitals and based on that we will form a representation for this particular point group  $D_{2h}$ . So, we will choose the coordinates and these are the sigma bonds and we will level them as sigma 1, sigma 2, sigma 3, sigma 4, 5 and then we will ultimately use this coordinates as a bond vector, which is essentially sigma bonds to form the basis for this representation of  $D_{2h}$  point group. So, ultimately you will get a representation. So, you should be able to form this representation very easily.

So, I told you about the unshifted atom concept. So using that you can form the representation very easily. So, the number of basis function in my basis state is 4 and in  $D_{2h}$  point group what are the symmetry operations that I have? You have so  $D_{2h}$ .

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So, what you have is identity you have  $C_2 x$ ,  $C_2 y$ ,  $C_2 z$ . So the  $C_2 z$ , if you take them as molecular axis. So, if you just draw the structure, so, you are designing as the 1, 2, 3 and 4 and these are the 1s orbital's. So, we are talking about the sigma bonds here. So if I call this plane as my x y plane, then perpendicular to the z. So, this is my  $C_2 z$  and then  $C_2 y$ ,  $C_2 x$  are perpendicular that, and then you have i and you have sigma h, you have this sigma ts. So, you have one sigma plane here and one sigma plane here.

So, you have sigma d you can call; one as say yz and another is xz, so sigma d xz, sigma d yz. So, all together you have total 8 symmetry operations; now you have to find out about, find out the representation. So, if you think about all the symmetry, effect of all the symmetry operations on this basis function. So, basis functions are nothing but this 1s orbitals. So, identity will not change anything and if the basis function does not move upon the symmetry operation each basis function will contribute 1 to the diagonal, meaning 1 to the character. So, here there are 4 basis functions, all of them are un shifted will contribute total 4.

Now, if you think about  $C_2 x$ . So, this is my x and this is my y. So, let me draw it somewhere else, so, this is my X and this is my Y and this is my Z. So, this is X and this is Y. So, this one, what we make 1 will come 2, 2 will go to 1 and this 1 also. So, none of this basis functions will survive and what about this  $C_2$ . So, this will also 4, will be



interchanged with 1 and 3 will be interchange with 2. So, none of them will survive. So, there will be no contribution to the character.

So, both these and these will contribute 0 to the overall character, and  $C_2 z$ . So, that also it will rotate the molecule 180 degree about this Z axis. So, none of the basis function will stay at their place. So, that will also contribute 0 i will change every 1. Because 1 will come here, 3 will go here and this 1 will come here and 2 will come here and. So, there is no un shifted atom that will also contribute 0.

Now  $\sigma_h$ ,  $\sigma_h$  is nothing but the  $\sigma_{xy}$ . So, 1s orbital this is spherical symmetry. So, there is no separation of charge, therefore this plane will keep all the basics functions in that meaning it will contribute 1 1 each. So, together it will be 4 and then  $\sigma_d$  is doing the same thing, as the  $C_2$  plane as;  $C_2 x$ ,  $C_2 y$  and the other one is acting as  $C_2 x$ . So, both of them will contribute 0.

So, this is my representation. So, if I call this as  $\Gamma$  and that is what my intention was. So, the representation  $\Gamma$  is like this and you can see how easily I could find that out; I did not have to form a matrix or anything, greatly I could find the representation based on the characters and when you use this particular basis functions.

So, once you have found this  $\Gamma$ , then the next step you have to reduce this, reduce to the irreducible representation for the particular point group  $D_{2h}$ . So, in order to reduce that, you have to use the formula that we have already used that is, if you have to find out how many times a particular  $i$ th irreducible representation will occur. So, in this case see all of them are written in the way that, they form a class by themselves.

So, each 1 of them founds a class by itself. So, there are total 8 operations, 8 classes therefore, 8 irreducible representations, all of them will be one dimensional. So, here it will be 1 by 8, sum over R and then the  $\chi$  of this  $\Gamma$ , here we have named it was  $\Gamma$ , for each R and then  $\chi$  of the particular  $i$  for that particular operation. So, use this formula and get the irreducible representation that is contained within the representation  $\Gamma$  that you formed.

So, if you solved using this equation of  $a_i$  is equals to this, then you will see that you can find out  $\Gamma$  to be equals to  $A_g$  plus  $B_{1g}$  plus  $B_{2u}$  plus  $B_{3u}$  where, this  $A_g$ , B

1g, B 2u and B 3u are the irreducible representation of belonging to the point group D<sub>2h</sub>.

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**Chemical Applications of Symmetry and Group Theory**

• For each of the representations we have the following results

$$\hat{P}^{A_g}(\sigma_1) = (1)\sigma_1 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_4$$

$$= 2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \approx \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \quad \text{SALC}$$

$$\hat{P}^{B_{1g}}(\sigma_1) = (1)\sigma_1 + (1)\sigma_3 + (-1)\sigma_4 + (-1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (-1)\sigma_2 + (-1)\sigma_4$$

$$= 2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \approx \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$$

Similarly,

$$\hat{P}^{B_{2u}}(\sigma_1) \approx \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4$$

$$\hat{P}^{B_{3u}}(\sigma_1) \approx \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$$

So, in the next step what you have to do? So, here this is not A<sub>2</sub> prime. So, this is P of A<sub>g</sub>. So, we have taken this basis functions, in the bond vector sigma 1, sigma 2, sigma 3, sigma 4. So, you take any particular basis function out of the basis (Refer Time: 25:21). So, I choose sigma 1 and then form the projection operator for each one of those irreducible representation that, you just got after reducing gamma and then operate each one of projection operator on this particular basis function, which is sigma 1 in our case.

So, let us first operate P A<sub>g</sub> on sigma 1 and then after doing that by now you know how to operate the here, we are using in complete projection operator in terms of the character. So, after doing that we get this result. When I do the same thing for B 1g, I get this result and for B 2u this, and for B 3u this. Now you see what you are getting essentially, to start with this 4 basis functions, we are finding that this particular combination that, sigma 1 plus, sigma 2, sigma 3, sigma 4 is forming a basis for if, that not necessarily forming a basis for any other thing.

Similarly, for B 1g, you are getting a particular combination of sigma 1 minus, sigma 2 plus, sigma 3 plus, minus sigma 4 this forming a basis. And for B 2u and B 3u using that particular projection operator operated on sigma 1, you are getting this 4 set of combinations of this atomic orbital, that we started with as basic functions are coming

out to be the symmetry allowed combinations, that transform as the irreducible representation  $A_g$  or  $B_{1g}$  or  $B_{2u}$  or  $B_{3u}$  of the particular point group  $D_{2h}$ . So, in this way we can find out this are called symmetry adapted linear combinations.

So, we started with 4 functions and we got 4 SALCs. So, each one of them will transform as the respective irreducible representation. So, I will suggest you to verify if this particular function  $\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$  will form a basis of  $A_g$  or not. Similarly  $\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4$  will it form a basis for  $B_{2u}$ ? It is very easy to do you take this SALC that we got, operate all the symmetry operations and just see what is the symmetry property of this combination whether it is plus 1 or minus 1 and then you will get the characters and then you match with the character table for which particular irreducible representation it belongs to and you see that yes this will be correct.

Now, one thing you notice here when you form this SALCs, we really did not care about that term  $l_y$ ,  $l_z$  by  $h$ , or  $l_x$  by  $h$  because we are interested into a functional form, how this sigmas are related? So those coefficient that we left out, can be easily found out by while doing the normalization and which is not so important stuff, but to know which the particular atomic orbitals that can are combine, and in which particular way they can combine. So, that they can adapt to the symmetry of the final molecule; in our case this hydrogen 1s orbitals they are combining with a carbon to form the basis, of one of the irreducible representation of the  $D_{2h}$  point group. To which the final molecule  $C_2H_4$  belongs to. So, this is how we form the symmetry adapted linear combination. So, you can verify for other type of bonds and you can go to higher order of representation that is to two dimensional or three dimensional representations.

So, we will take this representation in the next class and we will also try to look at the energy contributions in case of like you know of the molecular orbitals and so on. So, we will try to look at the Huckel's Approximation and (Refer Time: 30:09). Till then I thank you for your attention and see you in the next class.