

**Symmetry and Group Theory**  
**Prof. Anindya Datta**  
**Department of Chemistry**  
**Indian Institute of Technology-Bombay**

**Lecture - 46**  
**SALC:CH4**

Now it is already 12:30. Give me 10 minutes, let me talk about CH<sub>4</sub>, methane. So CH<sub>4</sub> is a problem that is not very easily handled if you do not use the character table, okay.

**(Refer Slide Time: 00:25)**

The slide contains the following content:

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
SALC	4	1	0	0	2

$\Gamma_{SALC} = A_1 + T_2$

Below the table are several diagrams: a tetrahedral CH<sub>4</sub> molecule, two p-orbitals, and two cube diagrams illustrating the mapping of orbitals to the tetrahedral geometry.

On the right side, the following equations are written:

$$\phi_1 = \frac{1}{2}(1s_A + 1s_B + 1s_C + 1s_D)$$

$$\phi_2 = \frac{1}{2}(1s_A + 1s_B - 1s_C - 1s_D)$$

$$\phi_3 = \frac{1}{2}(1s_A - 1s_B + 1s_C - 1s_D)$$

$$\phi_4 = \frac{1}{2}(1s_A - 1s_B - 1s_C + 1s_D)$$

Which point is this? Tetrahedral T<sub>d</sub>. What I will do this, this is slide number, I am little lost now. What are the symmetry operations tell me; E then, how many C<sub>3</sub>? 8 C<sub>3</sub> very good. Then 6 C<sub>2</sub> or 3 C<sub>2</sub>? Why 6? 3 C<sub>2</sub> right? This, this and this and C<sub>2</sub> + C<sub>2</sub> -, they are one and the same. Then I no I. There would better be no I in a T<sub>d</sub> point group. If there is an I in T<sub>d</sub> point group all your stereochemistry would have gotten messed up, right?

The whole premise of stereochemistry is the absence of I in T<sub>d</sub> point group, okay. Then what else? Any alternating axis of symmetry? 6 S<sub>4</sub>. Then, how many sigma d's? This is an axis. This is one sigma d, this is one sigma d right? One pair for this, one pair for this, one pair for this. So 1 + 1 + 1 is not 4, it is 6 no? One pair for this axis, one pair for this axis that is 4 and one pair for this axis also, 6 right? 6 sigma d.

Now what I can do is, I can do as usual how many hydrogen atoms are there in CH<sub>4</sub>, 4 right? They are the pendant atoms, carbon is the central atom. So I can construct gamma SALC by using the 1s orbitals of hydrogen atom, right? Character of E will be 4. What will be the character of C<sub>3</sub>? 1 or 0 or 2? 1 not 2 because you are not, do not forget what we are doing. We are constructing symmetry adapted linear combinations of the pendant atoms right?

So we do not consider the central atom. We consider this and this and this and these, the 4 circles. We do not consider the orbitals of carbon. Are you okay. Understand what we are doing? First job is to construct the SALC of the pendant atoms. Shubangi, okay. So C<sub>3</sub> is going to be, character is going to be 1. What about C<sub>2</sub>? C<sub>2</sub> has to be 0 right? Thus this interchange is going to take place in this no matter which C<sub>2</sub> you use, 0. What about S<sub>4</sub>? Of course 0.

Sigma d. Remember how sigma d is? These are 2 bonds. Sigma d is like this, right? Sigma d contains 2 bonds. And the answer is not 3, answer is 2. Because once again we are considering the 2 hydrogen atoms, we are not considering the central carbon atom. We are right now only considering this symmetry adapted linear combinations, nothing else. Are you convinced that it should be 2 and not 3? Very good, 2; 4 1 0 0 2 and Td is not even an infinite group.

So we can use that old faithful. But looking at the kind of frown on some of our faces, I will write the answer. Yeah good, good thing that you can see your own face. But even before writing that answer I want to make a point. And this is a point that will perhaps make us understand why we have to do this in the first place. Now suppose you think of valence bond approach. You have 4 bonds right. Or suppose you think of localized molecular orbital approach.

Localized molecular orbital approach would be, first generate the 4 sp<sup>3</sup> orbitals okay and then combine each of the sp<sup>3</sup> orbitals with an atomic orbital of hydrogen. So you get 4 molecular orbitals which are separate right? What will the molecular orbitals look like? I will just draw the one for this. So maybe first generate the sp orbital of this and then combine it with the 1s orbital of hydrogen. This is carbon, this is hydrogen.

So we get a molecular orbital that looks like, something like this, okay? How many such molecular orbitals would be there? 4. And will they be all equivalent or no? They should be all equivalent. So this should be degenerate and what have we said in one of our earlier classes, many of our early classes that degeneracy and symmetry go hand in hand right? Right or wrong? Degeneracy and symmetry go hand in hand right.

So these 4 degenerate molecular orbitals should belong to one symmetry species, right? Right or wrong? They should all belong to the same symmetry species. What would be the dimensionality of that symmetry species? 4 right? We have 4 distinct molecular orbitals and if we take the localized demo approach then all 4 are equivalent. But they are separate right? So they should form a 4-dimensional representation.

**(Refer Slide Time: 06:55)**

9. The Cubic Groups

	$E$	$4C_3$	$4C_2$	$3C_2$	$i$	$6C_4$	$3C_2$	$\epsilon = \exp(2\pi i/3)$
$T_d$	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
$A_1$	1	1	1	1	1	1	1	$(2x^2 - y^2 - z^2, x^2 - y^2)$
$A_2$	1	1	1	1	1	1	1	$(xy, yz, zx)$
$E$	1	1	1	1	1	1	1	
$T_2$	3	0	0	0	0	0	0	

	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$i$	$\epsilon = \exp(2\pi i/3)$
$T_d$	1	1	1	1	1	1	$x^2 + y^2 + z^2$
$A_1$	1	1	1	1	1	1	$(2x^2 - y^2 - z^2, x^2 - y^2)$
$A_2$	1	1	1	1	1	1	$(xy, yz, zx)$
$E$	2	-1	2	0	0	0	
$T_2$	3	0	-1	1	-1	0	
$T_1$	3	0	-1	-1	1	0	
$T_2$	3	0	-1	1	-1	0	

Now look at the corrected table  $T_d$  which you had so nicely worked out in the mid-sem. Show me the 4-dimensional representation here.  $A_1$ ,  $A_2$ ,  $E$ ,  $T_1$ ,  $T_2$ . Do you see a 4-dimensional representation? No. What is the maximum dimensionality? 3. So what we are saying is that it is not possible that localized MO picture where you have 4 equivalent bonds like that is not possible, right? 4 MOs, 4 same, 4 MOs right which belong to the some symmetric species is not even possible, okay?

So localized MO picture fails the symmetry test. As we will see delocalized MO picture passes the symmetry test but also accounts for the fact that all 4 bond lengths are the same. Sounds oxymoronic, right? So all 4 bond lengths have to be the same. It is not as if in methane one bond length is more, 3 other bond lengths are different or something right? All 4 are the same. You have to explain that.

At the same time, you have to account for the fact that you cannot have 4 molecular orbitals which are degenerate, okay? This is what your localized molecular orbital cannot do and as we will see now, delocalized molecular orbital theory can actually do it. So let us get back there. So once again, so what am I doing? I am having too much of degeneracy in my slide numbers. Earlier one was 8, this one is also 8. This is not degeneracy, this is redundancy, ha.

What was I about to do? I was about to pay respect to the frowns and write the answer. Break this down, what you get is you get  $A_1 + T_2$ . 4 SALCs. One is  $A_1$  and the remaining 3 jointly form the basis for  $T_2$ . You can work it out. You can work it out using that example, that relationship  $\frac{1}{\sqrt{4}} \sum_R \chi_R \chi_{iR}$  and the answer you will get is  $\gamma$  SALC is  $A_1 + T_2$  okay.

So now we have to worry about what is  $A_1$  combination and what is  $T_2$  combination.  $A_1$  combination is very simple, is it not? We learnt to draw this tetrahedron inside a cube, let me do that. What I will do is, I will draw a solid circle for plus and a hollow circle for minus. So will you agree with me that this would be an  $A_1$  representation, totally symmetric representation. This will be the basis for a totally symmetric representation right?

What will it be then that SALC I will call it  $\phi_1$ , can you read? Zoom out a little bit.  $\phi_1$  is  $\frac{1}{\sqrt{4}} (S_A + S_B + S_C + S_D)$ .  $S$  the usual meaning A, B, C, D let us say are the names of the atoms, identifiers of the atoms, alright? What will be the normalization constant if I want this to be normalized? Half or  $\frac{1}{\sqrt{2}}$  or  $\frac{1}{\sqrt{4}}$ ? Okay, we have agreement up to here. Should I put the root sign or no? No root sign, right. If you try to normalize what will you get?

Cross downs will all cancel. So you are left with whatever is there outside right? So this square, if this is C, you are going to get C square multiplied by 1 + 1 + 1 + 1 is it not? Because when I say 1 S B, 1 S C, 1 S D are all normalized to 1 okay and they are orthonormal set right? So multiply them together, let us say this is C, you are going to get C square multiplied by 1 S A square + C square multiplied by 1 S B square + C square multiplied by 1 S C square + C square multiplied by 1 S D square.

Now all these are 1 right? So you get 4 C square equal to 1. So C square is one-fourth, C is half okay? You will get 1 by root 2 when you combine 2 way functions, right? Fine. So phi 1 equal to half and everything is plus. That is fairly easy. How do I construct the other one? How do I construct the T 2 set? I can think like this. It is triply degenerate, right? Which symmetry operation is triply degenerate? C 2, C 2, we have 3 C 2s right?

So there should be kind of symmetry with respect to C 2. So I can draw like this. These 2 can be plus and these 2 can be minus. Because this is symmetric with respect to this C 2 is it not? There are 3 C 2s and we are talking about degenerate set here. So let us see, let us try combinations that are symmetric with respect to the C 2s. So if I have 2 + and 2 - kind of combination, they will be symmetric with respect to C 2 okay.

So I will write those 2 + and 2 - combination phi 1, phi 2 sorry equal to half 1 S A + 1 S B - 1 S C - 1 S D. Phi 3 = 1/2(1 S A - 1 S B + 1 S C - 1 S D); phi 3, phi 4 sorry is equal to half 1 S A then what should it be, alright? So these are the SALCs that we have generated. First one is A 1. That phi 2, phi 3, phi 4 jointly belong to T 2. Let us see if that is correct or not. Remember what phi 2, phi 3, and phi 4 look like right? 2 + and 2 -.

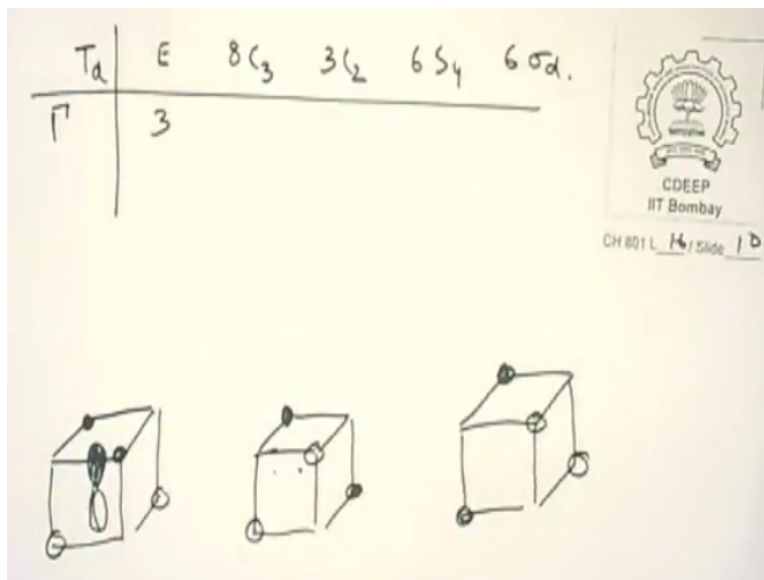
**“Professor - student conversation starts”** Sir? Yes sir. These are increasing order of notes. No. No increasing order of notes. They are same order of notes. All look like this. You just turn the few around. See, this is not a linear molecule no, it is a tetrahedron molecule, do not forget that. All I am doing is in a tetrahedral molecule I am saying that 2 are plus and 2 are minus. Now if I say this is plus, this is plus and these 2 are minus it remains the same. Number of notes does not change right. They are only turning. You are turning the whole box, okay. Why? Think like this.

But then A, B, C, D are degenerate, they are same. Do not forget. All are hydrogen atoms. You will get the same thing there. **“Professor - student conversation ends”**.

See all you have to do is set this to be plus okay, 3 atoms are left. Move the + sign from here to here to here. You got your 4. Now whether you start with this or you start with this or this or this it does not really matter. All are hydrogen atoms, is it not? You start from here no problem. But eventually it is 2 + and 2 -. That is all that matters. Now who has said that this is n, this is not A okay. So you cannot give too much of importance to the starting point.

Once you fix the starting point then the others become important, right? Okay. Let us see. Let us have a look at the character table then. Or shall we just sort out the oh why have I written there. It is sad. What will be the characters of these combinations? I will do it on a separate page.

**(Refer Slide Time: 17:23)**



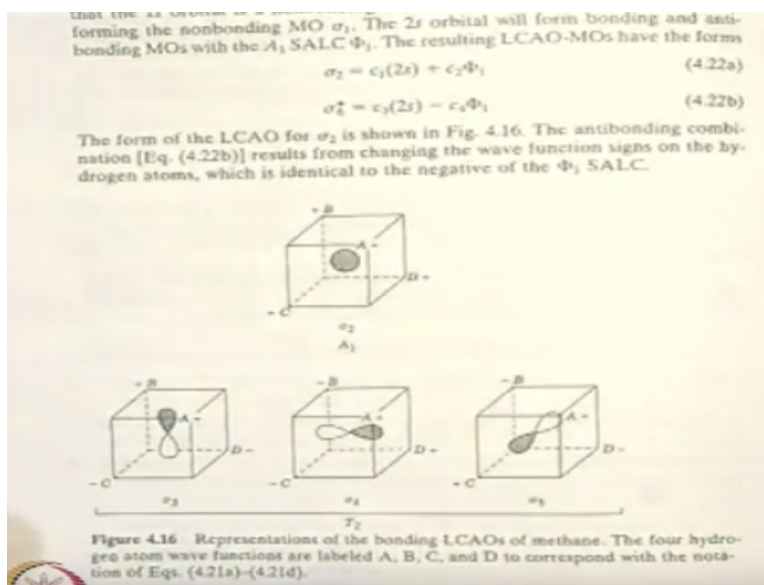
We are talking about something like this, right? This 4 and then you just turn everything around. This is a set, right? Now, what will be the gamma for this? Character for E will be 3, character for  $C_3$ ? What will be character for  $C_3$ ? It is a little difficult right? You have to look at the, you cannot do it just like this. You have to actually look at, no no you have to look at this and see how signs change and all. You can work it out. Anyway, it belongs to T 2.

Work it out if you want. It is a little too problematic, fine. So now what do we have? We have 2 kinds of SALCs. One is totally symmetric. The other is triply degenerate. Now, if you look at this, will you agree with me that symmetries of these match the symmetries of the p orbitals. Let me draw p orbital. This is the center of the box right? You have to pardon my bare artistic skills. This is what a p orbital on carbon will look like. So now see, matching? Okay.

And if you do not believe my diagram you should believe the character table. No? Now is it okay. Where do x and y and z belong? T 2 right; x, y, and z jointly form the basis for T 2. So will P x, P y, and P z also not jointly form the basis for T 2, right? So see we are matching symmetry. The 2s orbital of carbon is in the same symmetry species as the symmetry combinations A 1 okay and this T 2 SALC also finds a match in the P x, P y, and P z orbitals.

So this is what we should combine, A 1 with A 1, T 2 with T 2 alright. So you have 2 kinds of orbitals then. Let me just show you.

**(Refer Slide Time: 21:26)**



So these are the combinations that you get. Alright, this is the diagram that I wanted to draw but failed, right. No, did not fail. It is just that this is a little better because it is printed.

**(Refer Slide Time: 21:48)**

$\Gamma_{\text{SALC}}$	$\Gamma_2$	$\Gamma_1$	$\Gamma_2$	$\Gamma_2$	$\Gamma_2$
	4	1	0	0	2

This representation is identical to  $\Gamma_2$ , which we generated for a set of four hybrid orbitals in Section 4.2. Therefore, as before, it decomposes as  $\Gamma_{\text{SALC}} = A_1 + T_2$ . This means that we can form one totally symmetric SALC and a set of three degenerate SALCs.

The totally symmetric SALC is formed by taking all four hydrogen  $1s$  wave functions in a positive sense. Using labels A, B, C, and D to distinguish the hydrogen atoms, the normalized  $A_1$  SALC can be written as

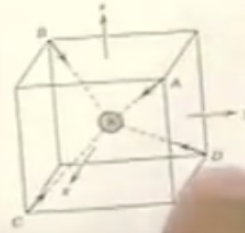
$$\Phi_1 = \frac{1}{2} [1s_A + 1s_B + 1s_C + 1s_D] \quad (4.21a)$$


Figure 4.15 Vector basis for a representation of hydrogen SALCs of  $\text{CH}_4$ .

Here you see this is the first SALC that we generated right, okay. This is how it is and you can see that it matches the symmetry of  $2s$ .

**(Refer Slide Time: 21:59)**

The three degenerate SALCs of  $T_2$  are constructed by taking all possible combinations of two hydrogen wave functions in a positive sense with two in a negative sense. The normalized  $T_2$  SALCs have the form

$$\Phi_2 = \frac{1}{2} [1s_A + 1s_B - 1s_C - 1s_D] \quad (4.21b)$$

$$\Phi_3 = \frac{1}{2} [1s_A - 1s_B - 1s_C + 1s_D] \quad (4.21c)$$

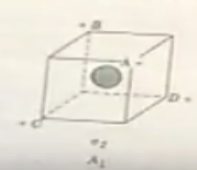
$$\Phi_4 = \frac{1}{2} [1s_A - 1s_B + 1s_C - 1s_D] \quad (4.21d)$$

On carbon, both the  $1s$  and  $2s$  orbitals have  $A_1$  symmetry. If we assume that the  $1s$  orbital is a nonbonding core orbital, then we may consider it as forming the nonbonding MO  $\sigma_1$ . The  $2s$  orbital will form bonding and antibonding MOs with the  $A_1$  SALC  $\Phi_1$ . The resulting LCAO-MOs have the forms

$$\sigma_2 = c_1(2s) + c_2\Phi_1 \quad (4.22a)$$

$$\sigma_2^* = c_3(2s) - c_4\Phi_1 \quad (4.22b)$$

The form of the LCAO for  $\sigma_2$  is shown in Fig. 4.16. The antibonding combination [Eq. (4.22b)] results from changing the wave function signs on the hydrogen atoms, which is identical to the negative of the  $\Phi_1$  SALC.



These are the other SALCs okay, right or wrong? Now if I want to generate the molecular orbitals, what will I do? These are the molecular orbitals that you get by combinations of  $A_1$  atom,  $A_1$  atomic orbital for the central atom and the  $A_1$  SALC.  $\Phi_1$ . What was  $\Phi_1$  remember, capital  $\Phi_1$ .

**(Refer Slide Time: 22:35)**




As a summarizing example, consider the ~~degenerate~~  $T_d$  representation of methane. It is reasonable to assume that the bonds are formed by interactions of the  $1s$  orbitals on the four hydrogen atoms with  $2s$  and  $2p$  orbitals on the carbon atom. The carbon  $1s$  electrons are assumed to be nonbonding. The four hydrogen atoms in their sigma interactions with carbon may be represented by a set of four tetrahedrally oriented vectors pointing toward the central atom (Fig. 4.15). These are taken as the basis for a representation in  $T_d$  to determine the symmetries of hydrogen SALCs. From a consideration of shifted and nonshifted vectors, the following reducible representation emerges:

$T_d$		$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{\text{SALC}}$		4	1	0	0	2

This representation is identical to  $\Gamma_u$ , which we generated for a set of four hybrid orbitals in Section 4.2. Therefore, as before, it decomposes as  $\Gamma_{\text{SALC}} = A_1 + T_2$ . This means that we can form one totally symmetric SALC and a set of three degenerate SALCs.

The totally symmetric SALC is formed by taking all four hydrogen  $1s$  wave functions in a positive sense. Using labels A, B, C, and D to distinguish the hydrogen atoms, the normalized  $A_1$  SALC can be written as

$$\Phi_1 = \frac{1}{2} [1\psi_A + 1\psi_B + 1\psi_C + 1\psi_D] \quad (4.21a)$$


This was capital phi 1 right, all plus. So what I am doing essentially is I am combining the  $2s$  orbital of carbon which is also  $A_1$  with the  $A_1$  orbital with the  $A_1$  SALC that I get from the pendant atoms. In one case it is plus, in another case it is minus. I do not know what is  $C_1$  and  $C_2$ .  $C_1$  and  $C_2$  remain to be determined okay. And there is something that I cannot determine from simple symmetry allowance.

That is where your computational chemistry CH 4 2 phi comes in. CH 4 2 phi is not computational chemistry but chemical bonding nevertheless. CH 4 2 phi is CH phi 04, phi 04 is definitely a computational chemistry course. That is where they come in for determination of the coefficients. But this is the kind of combination that I need, right. So I already constructed 2 MOs. Then where are the other combinations. This you agree that I have to combine the other 3 SALCs with the  $p$  orbitals, right?

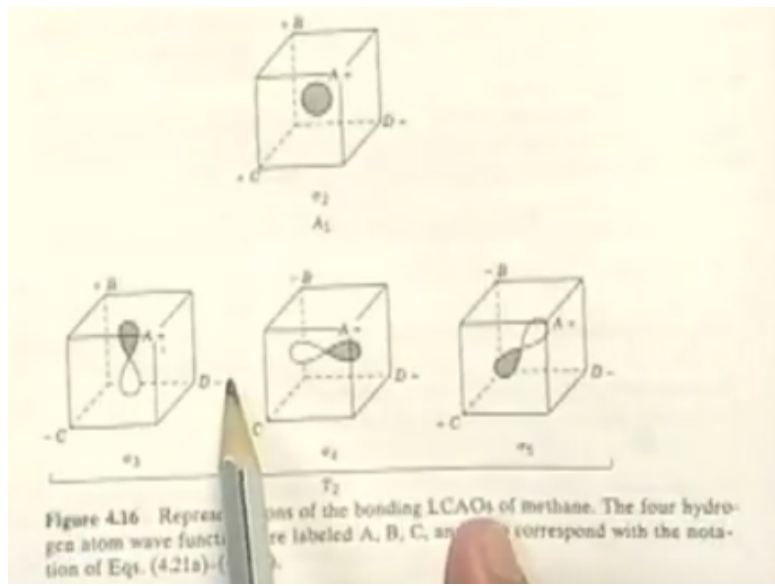
**(Refer Slide Time: 23:53)**

$$\begin{aligned} \sigma_3 &= c_5(2p_x) + c_6\phi_2 & (4.22c) \\ \sigma_3^* &= c_5(2p_x) - c_6\phi_2 & (4.22d) \\ \sigma_4 &= c_9(2p_y) + c_{10}\phi_3 & (4.22e) \\ \sigma_4^* &= c_9(2p_y) - c_{10}\phi_3 & (4.22f) \\ \sigma_5 &= c_{13}(2p_x) + c_{14}\phi_4 & (4.22g) \\ \sigma_5^* &= c_{13}(2p_x) - c_{14}\phi_4 & (4.22h) \end{aligned}$$

MOs  $\sigma_3$ ,  $\sigma_4$ , and  $\sigma_5$  are degenerate and necessarily have the same antibonding MOs  $\sigma_3^*$ ,  $\sigma_4^*$ , and  $\sigma_5^*$  are likewise degenerate and have the same energy. In summary, of all the MOs we have defined for  $\text{CH}_4$ , the bonding MOs are based on the LCAO-MOs

If you do that this is what you get. Moreover what I do is I know which one matches the symmetry of P x, which one matches the symmetry of P y, which one matches the symmetry of P z. Understood or not?

**(Refer Slide Time: 24:13)**

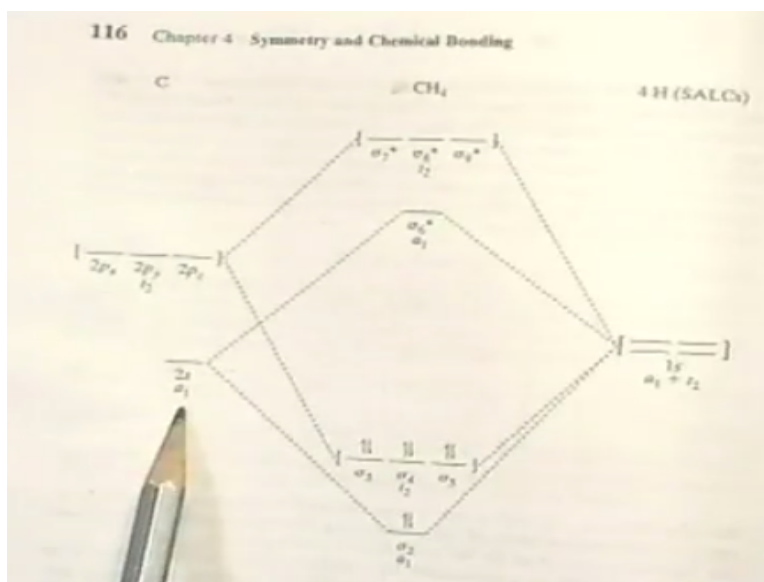


So take this example. A is +, C and D are -. The way that I have drawn it, that has matching symmetry with this P z orbital only. Not with P x or not with P y. So there is no point why there is no point in combining P x and P y with this SALC, right? I will only combine it with z right? Similarly, let us say this is x direction, then this second SALC where A and D are + and B and C are - that would have the same, would have compatible symmetry with your P x only. There is no point in invoking P y and P z for that.

So see what symmetry is helping us do is that it is helping us decrease the number of terms in every linear combination. If you try to perform a linear combination of atomic orbitals without any symmetry consideration, then you have to combine everything with everything, right? You get a huge number of terms. So essentially symmetry helps us simplify the problem by restricting the number of terms in every linear combination, understood?

So this then are the other molecular orbitals. These are all sigma orbitals, right.  $C 5 2 p z + C 6 \phi 2$  and so on and so forth. When you do that, now I will show you the energy level diagram.

**(Refer Slide Time: 25:45)**



See what happens. You are all familiar with energy level diagrams right? The energy level diagrams you have been drawing from I do not know class 12 maybe. So this is the situation. This is the central atom, carbon  $2s$  of  $a_1$  symmetry and  $2 p x, 2 p y, 2 p z$  of  $t_2$  symmetry and you have generated the SALCs from  $1 s$  and we broke them down into a  $1 + t_2$ . So a  $1$  set will combine with a  $1$  set, you get  $1$  here and this is the antibonding  $1$ .

And then  $t_2 z$  combines with  $t_2 z$ . You get a triply degenerate level here and you get a triply degenerate antibonding level here, okay? Before I start filling in the electrons is there a question? There should be at least one valid question here. No question? Which one? Because we generated that way right? When we generated the SALCs we saw that one is a  $1$  the other is  $t_2$ .

So whenever it is  $t_2$  that means they are jointly forming the basis for the  $t_2$  symmetry and when they jointly form the basis of some symmetry species we have said that they have to be degenerate. No, this is schematic, do not worry about that. In any case these are the energies that are more important. That is the question I was looking for. The honest answer is we cannot really draw quantitatively here.

This is only a qualitative picture you know looking at the number of nodes okay. But if you really want to put numbers here, then you have to go all the way and do the computation okay. This is only the expected scheme looking at the symmetry and number and number of nodes and all that, fine. So now what is it that we have got? We fill in the, how many electrons will be there? How many electrons? 4 for hydrogen. How many for carbon? 4 from carbon.

The  $n = 2$  electrons, right. So 18 all. 1, 2, 3, 4, 5, 6, 7, 8 alright? What is total sigma bond order? 8 electrons all in one EMOs. So one is 8. Is there any other combination? No, line of thinking is right. It is 4, 8 by 2 right? Then what is the definition of bond order? Number of bonding electron pairs. You can put it that way okay. Number of bonding electron pairs is 4, 4 bonds. But you see one bonding pair has a different energy compared to the other 3.

So that is where we become compatible with the symmetry argument. We do not have 4 degenerate orbitals alright. But then the question that comes now is does this mean that one carbon hydrogen bond is different from the other 3, no? Why not? Because do not forget what we are doing. Here we are talking about delocalized molecular orbitals. All molecular orbitals are actually delocalized over all the 5 atoms, right? What does this look like, this a  $2^2$ ? What would it look like, remember.

**(Refer Slide Time: 29:32)**

...ion  
 y). In other words, for  $\text{BeH}_2$  we should not expect to find two  
 electrons with exactly the same energy, contrary to the suggestion of  
 localized MO models.

...ons are delocalized across the molecule, as the general MO ap-  
 proach, then the concept of bond order between two adjacent atoms  
 must be assessed in that context. In the case of  $\text{BeH}_2$ , the VB  
 MO models clearly indicate that both Be-H bonds are in every  
 ant, each being a single bond (bond order = B.O. = 1). The ap-  
 proach in no way contradicts this. To arrive at the same conclu-  
 sion realize that the two pairs are in bonding MOs that extend  
 over both Be-H bonds. This results in a total bond order of 2 over  
 the Be-H bonds, or B.O. = 1 for each bond. In essence, each single  
 bond is formed by sharing half the electron densities of both the  $\sigma_p$   
 and  $\sigma_s$ .

...ring of levels in MO schemes such as Fig. 4.14 deserves some  
 attention. In speaking, the relative energies of MOs cannot be predicted  
 by simple calculations, subject to experimental verification. In the ab-  
 sence of such information, we can arrive at a tentative ordering of MOs for  
 molecules on the basis of some generally observed results. The follow-  
 ing may be used as guides to establishing a tentative ordering:

- MOs always lie lower in energy than the antibonding MOs  
 formed from the same AOs.
- MOs tend to have energies between those of bonding and  
 antibonding MOs formed from similar AOs.
- MOs tend to have less effective overlap than sigma interactions.
- MOs tend to have higher energies than sigma interactions.

... special circumstances for two orbitals of different symmetries to have  
 the same energy, a condition called accidental degeneracy. This, however, is more the ex-  
 ception than the rule. One should generally assume that different symmetries imply differ-  
 ent energies.

$T_2$	$E$	$6C_2$	$3C_2$	$A_1$
$\Gamma_{\text{SALC}}$	4	1	0	0

This representation is identical to  $T_2$ , which we gener-  
 ally use in Section 4.2. Therefore, as before, if  $\phi_1$   
 is  $A_1 + T_2$ . This means that we can form one totally sym-  
 metric SALC from three degenerate SALCs.

The totally symmetric SALC is formed by taking  
 the wave functions in a positive sense. Using labels A, B,  
 C, and D for the hydrogen atoms, the normalized  $A_1$  SALC can be  
 written as

$$\phi_1 = \frac{1}{2} (1s_A + 1s_B + 1s_C + 1s_D)$$

Fig. 4.15.  $T_2$  basis  
 functions for the four  
 hydrogens in methane.

This is what it would look like. So a 2, I am sorry a 1 is spread over A, B, C, D and carbon. It is there everywhere. It is not one of the bonds. It is not C a bond or it is not C b bond. All we are saying is that it contributes equally to all the 4 bonds. That is what is important to understand. Are you okay with this? You understand what we are saying? This molecular orbital here contributes equally to all the 4 CH bonds. It is delocalized.

**(Refer Slide Time: 30:13)**

Figure 4.16 Representations of the bonding LCAOs of methane. The four hydro-  
 gen atom wave functions are labeled A, B, C, and D to correspond with the nota-  
 tion of Eqs. (4.21a)-(4.21d).

Similarly, each of these bonds that we get, each of these bonds are also completely delocalized over all, all atoms are involved is it not, right? So each of these molecular orbitals contributes equally to all the 4 CH bonds. So eventually the electron density between carbon and any given

hydrogen atom is the same, okay? So this is something important. This is something that we sometimes miss when we talk about molecular orbital description. Please understand this.

A molecular orbital is not a bond, okay? A molecular orbital is not a bond. Molecular orbital is actually distributed over, molecular orbital is distributed over the entire molecule, right? So every molecular orbital effectively contributes to every bond that is there. By bond I mean individual bonds in the VV picture right. So that is why, so it is best to think in terms of electron density. Contribution of each molecular orbital to the electron density between any 2 atoms, carbon atom and the hydrogen atom is the same, okay?

That is why all the 4 CH bonds are equivalent. This is not a bond, these are not bonds. These are molecular orbitals. Is that point taken? Now, so next. Once again, what we had, not we, what Max Plank had said was experimental results are the only truth. Everything else is poetry and imagination. So I better show you some experimental result if I am to tell you that this is the right picture and not your valence bond picture, not the localized demo picture. And that comes in the form of, almost done, 2 minutes. That comes in the form of photoelectron spectroscopy.

What is photoelectron spectroscopy? What you do essentially is that you shine the molecule with light and you shine it with light which has sufficient energy to ionize the molecule, alright. If you ionize it and the electron is then liberated right, liberated from, it becomes a free electron. Once it becomes free electron it will have some kinetic energy, right? So this is the relationship.

**(Refer Slide Time: 32:34)**

or UV radiation.\* If the energy of the incident radiation,  $h\nu$ , is known and the kinetic energy, KE, of electrons ejected from a particular MO is measured, then the ionization energy of the electrons, IE, is given by

$$IE = h\nu - KE \quad h\nu = IE + KE$$

The higher the ionization energy, the lower in energy lies the MO from which the electrons were ejected. The photoelectron spectrum of  $CH_4$  (Fig. 4.18) shows a large band at approximately 13.5 eV and a smaller band at approximately 23.0 eV. The larger band corresponds to ejection of the three electron pairs in  $t_2$  bonding MOs—namely,  $\sigma_3$ ,  $\sigma_4$ , and  $\sigma_5$ . The smaller band arises from ejection of electrons from the lower-lying  $a_1$  MO,  $\sigma_2$ , and therefore requires greater ionization energy. Both bands have considerable vibrational fine structure, characteristic of electrons ejected from bonding MOs.

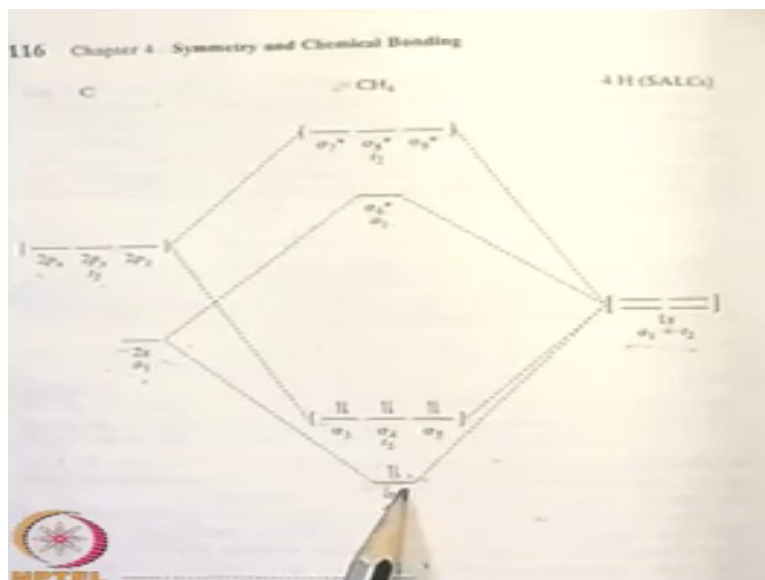
Figure 4.18 does not show the band arising from the two electrons in the core level  $\sigma_1$ , which is essentially a  $1s$  orbital on the carbon atom. This ionization energy is considerably higher (approximately 291 eV) than the energies required to eject electrons from the bonding MOs. X-ray photoelectron spectroscopy<sup>1</sup> is needed to observe the ionization band arising from  $\sigma_1$ .

The absence of four equal-energy pairs can be seen as a necessary consequence of methane's  $T_d$  symmetry. Since the highest-dimension irreducible representations of  $T_d$  are triply degenerate ( $T_2$  and  $T_2'$ ), there can be no higher than threefold degeneracy among the MOs. In other words, the fourfold degeneracy among electron pairs that VB and localized MO models suggest is not allowed by the symmetry of the molecule.

So actually I should write  $h\nu = IE + KE$ . The total energy supplied, first of all ionizes the electron, exit to a level where it just about loses the attraction and then some residual kinetic energy is imparted to it. So it is like the first stage of sending this Mangalyaan out of the earth's orbit. You give it sufficient energy so that it loses its attraction for earth and then you give it a little more it gets some kinetic energy. What she was involved in it?

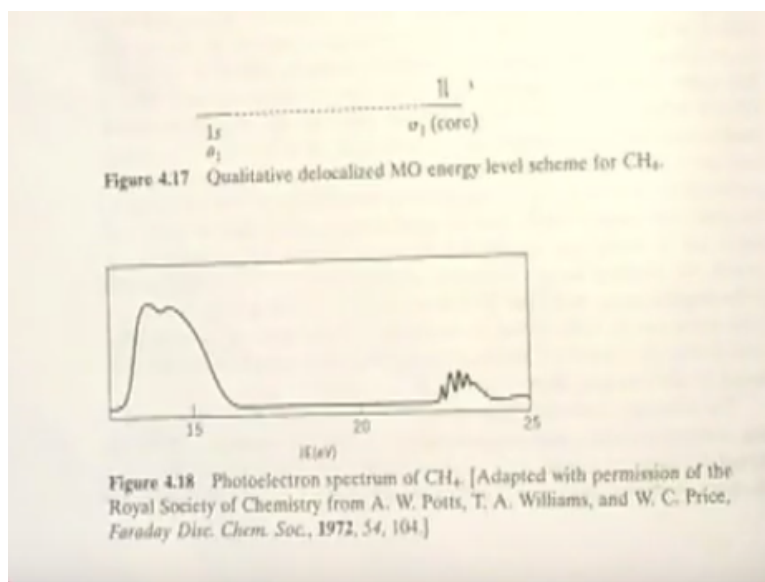
Then why she is being congratulated for it? Alright. Downward velocity? downward velocity is different. This is escape velocity, alright. Okay. So this is what you do and then you plot the intensity versus ionization energy. Ionization energy, what would, what is the meaning of ionization energy? Let us take this, these MOs for example. If I completely ionize this, the energy required to ionize it would give us the difference between, that infinite level and this, right?

**(Refer Slide Time: 33:58)**



So which would have more ionization energy? This or this? This would be more right? And these 3 molecular orbitals would have less ionization energy.

(Refer Slide Time: 34:08)



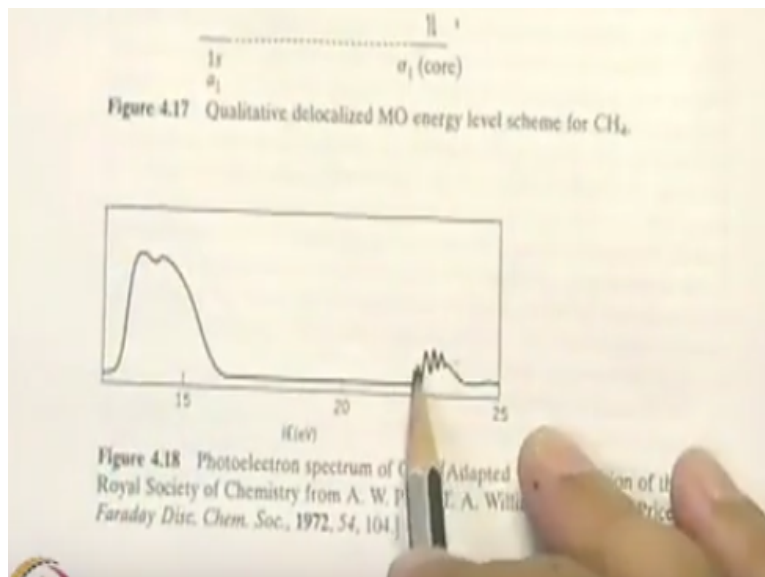
Now if you look at the photoelectron spectrum, this is intensity versus ionization energy. What do you get? Look at this intensity, actually area under the curve and look at this area under the curve. This is approximately 3 times this okay? Is this lower or is this higher? Lower. This is like maybe 12 electron volts. And this is more like maybe 22 electron volts or something. This 22 electron volt band is 3 times less intense compared to the 15 electron volt band.



Is it not consistent with the qualitative picture that we have developed? One bonding MO is lower in energy and then we have a triply degenerate bonding level, triply degenerate MOs are there. So this is the experimental results. So whatever I had drawn there, that gained some support from here, right?

And if you are an experimentalist, now you can kind of thump your nose to theoreticians at this point of time because what you can do is you can simply now write the energies from the experimental values, okay and then tell the theoreticians get me these energies if you can, okay? That is what happens very often, okay. To conclude, what we see is this picture that we developed of the localized demos using symmetry seems to be giving us some correct result.

**(Refer Slide Time: 35:43)**



This one point you see this structure here, what does that stand for? That is basically vibronic structure. That is a bound state is it not. Bonding means is a bound state. It is going to vibrate. So when it vibrates, you get this vibrational structure. Because the potential energy will be something like this. You can have this transition also. Well still from here to up somewhere here. So vibrational structure is a marker of bonding molecular orbitals.

We will come back to this maybe in the next class, okay? So we see that molecular orbital delocalized molecular orbital is the way to go and symmetry helps. But I think you have realized by now that one difficulty we have is see BH 2 even CH 4 are okay but how much time did it

take us and we are overshot by 35 minutes today. How much time did it take us to do this treatment if you have to actually look at character tables, look at orbitals and do it.

You cannot do it for really big molecules. So for that once again we want to develop a machine. A machine that will do the dirty work, difficult work for us and that machine of course is provided once again from the power of great orthogonality theorem. So next day, actually I was planning to discuss carbon dioxide but maybe we can come back to it later on. Next day let us do this. Let us discuss something called projection operator.

We will derive the expression for projection operator and you will see this projection operator is like a magic machine that takes in some arbitrary function and spits out linear combinations. After all what we are trying to do is we are trying to develop symmetry after linear combinations. So this machine that we develop, the projection operator will do that for us. All we have to do is we have to mechanically use character tables. But before that we better derive it.

So we will derive what is called the complete projection operator. Then we will see that that also is too much of hassle. So we will derive what is called the incomplete projection operator and that is what is going to help us throughout the remaining lectures that are there in this course.