Symmetry and Group Theory

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Lecture -45
Valence Bond Theory

So, in the previous lecture we were trying to understand the relation between symmetry and chemical bonding. So, in this lecture let us continue the discussion and see, what are the two most popular theories which describe chemical bonding.

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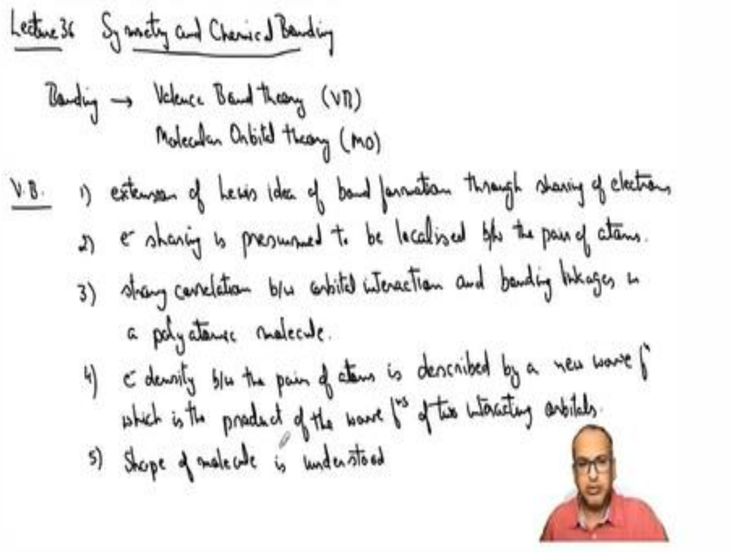

Lecture 36 Symmetry and Chemical Bonding

Bonding → Valence Bond theory (VB)
Molecular Orbital theory (MO)

V.B.
1) extension of Lewis idea of bond formation through sharing of electrons
2) e^- sharing is presumed to be localised b/w the pair of atoms.
3) strong correlation b/w orbital interaction and bonding linkages in a polyatomic molecule.
4) e^- density b/w the pair of atoms is described by a new wave f^n which is the product of the wave f^{ns} of two interacting orbitals.
5) Shape of molecule is understood

So, we go to lecture 36 and we will continue our discussion of symmetry and chemical bonding. So, bonding can be described by again this you must have already read in your first or second year of BSc. So, it is valence bond theory and second is molecular orbital theory. So, this is also denoted as VB and then this one is MO theory. So, now let us discuss first the valence bond theory and then we will also we will try to use symmetry arguments to develop the bonding wave functions in valence bond theory.

So, let us discuss what are the salient features of valence bond theory? So, basically, it is an extension of Lewis idea of bond formation through sharing of electrons. So, electrons are shared to form a bond then electron sharing is presumed to be localized between the pair of atoms which are interacting to form the bond. Then what is the next point it is the orbital interaction and the bond linkages.

So, there is a strong correlation between orbital interaction and bonding linkages. So, this is only to refresh the previous lectures which you must have read about valence bond theory and that is in a diatomic for a polyatomic molecule. Then, electron density between the pair of atoms is described by a new wave function, which is the product of the wave functions of two interacting orbitals.

And fifth is shape of the molecule, how do you define the shape of the molecule? The shape of the molecule is understood from VSEPR theory.

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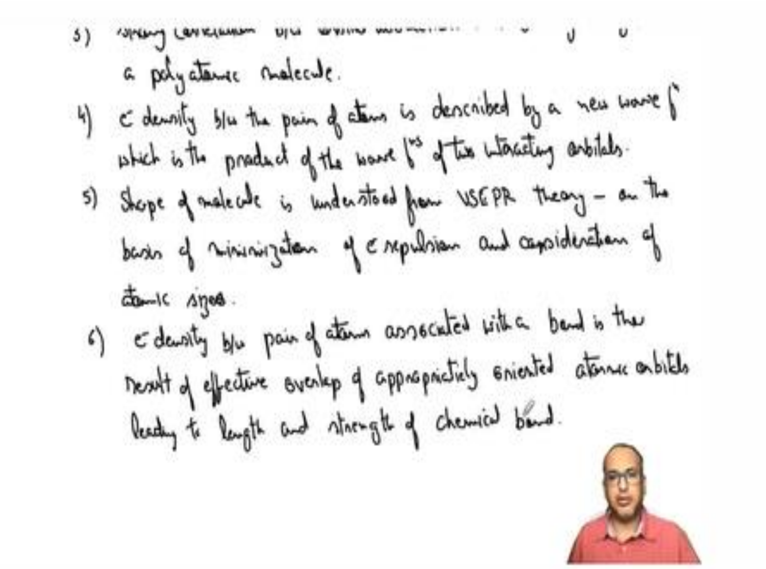

3) Strong correlation b/w
a polyatomic molecule.

4) e^- density b/w the pair of atoms is described by a new wave f^n which is the product of the wave f^{ns} of two interacting orbitals.

5) Shape of molecule is understood from VSEPR theory – on the basis of minimization of e^- repulsion and consideration of atomic sizes.

6) e^- density b/w pair of atoms associated with a bond is the result of effective overlap of appropriately oriented atomic orbitals leading to length and strength of chemical bond.

I am not going to go into details of what that is, that is we will just briefly say on the basis of minimization of electronic repulsion, and consideration of atomic sizes, and I think the last point is electron density between pair of atoms associated with the bond is the result of effective overlap of appropriately oriented, so, this is very important that they must be appropriately oriented.

Because then only they will be able to define the shape of the molecule, atomic orbitals. And, this is where the problem is because atomic orbitals are oriented along Cartesian coordinates and they do not generally orient as per the shape of the molecule. We can say leading to a particular length and strength of a bond.

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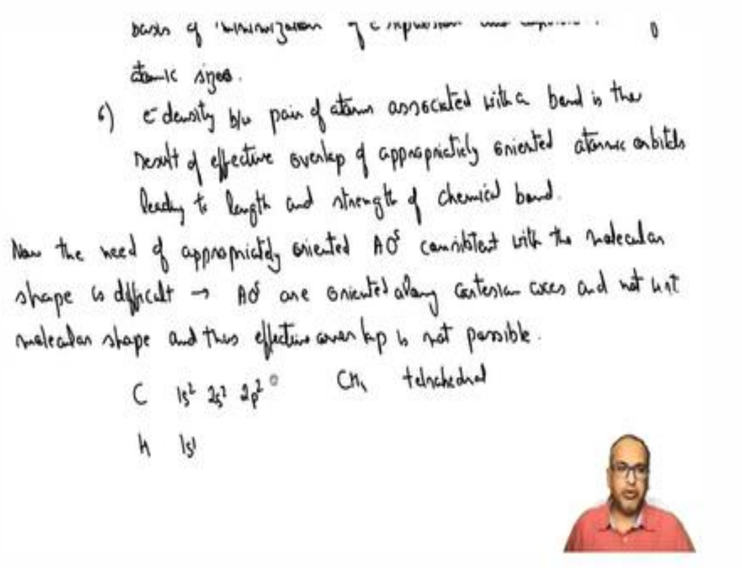

basis of minimization of e^- repulsion [illegible]

atomic sizes.

c) e^- density b/w pair of atoms associated with a bond is the result of effective overlap of appropriately oriented atomic orbitals leading to length and strength of chemical bond.

Now the need of appropriately oriented AO^s consistent with the molecular shape is difficult → AO^s are oriented along Cartesian axes and not w.r.t molecular shape and thus effective overlap is not possible.

C $1s^2\ 2s^2\ 2p^2$ CH$_4$ tetrahedral

H $1s^1$

So, why this is required? So, consider that you have atomic orbitals, which you want to overlap or interact with other atomic orbitals and then resulting in to a given shape of the molecule, right? So, now this is not always these atomic orbitals are as I said, not always oriented along the shape of the molecule. So, we can say now the need of appropriately oriented atomic orbitals consistent with the molecular shape is difficult.

This is because atomic orbitals are oriented along the Cartesian axis and not with respect to molecular shape and thus effective overlap is not possible. So, let us consider a case of carbon, so the electronic configuration of carbon can be understood as 1s2, 2s2, 2p2. So, now I am trying to form bond between CH4, we know that the shape of the molecule is tetrahedral. So, that means all four bonds all four, CH bonds must be equivalent.

Now, if four hydrogen bonds come with four s orbitals, then the combination happens between this s orbital and the empty p orbitals. So, now all the bonds forms will not be same if we just combine atomic orbitals of carbon with atomic orbitals of hydrogen. So, hydrogen has 1s1, so these are not effective overlap and this will not intuitively lead to a tetrahedral shape. So, then now what do we do where what is the solution for this?

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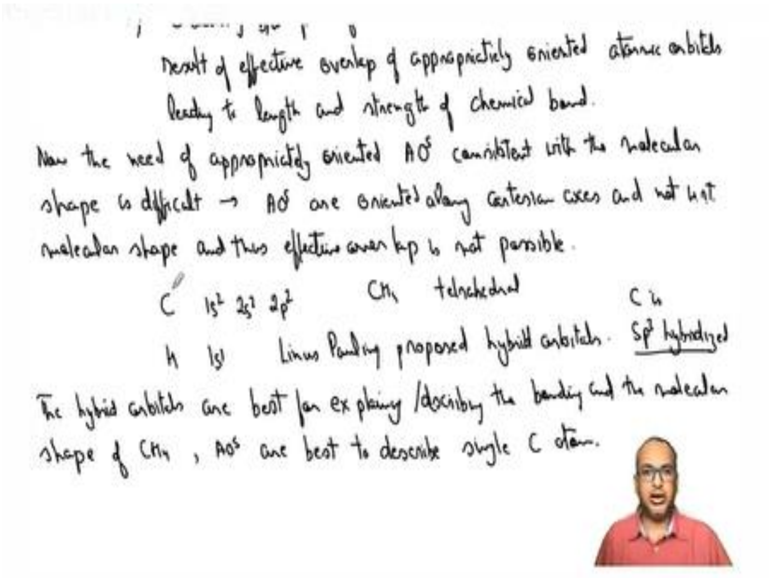

result of effective overlap of appropriately oriented atomic orbitals leading to length and strength of chemical bond.

Now the need of appropriately oriented AO's consistent with the molecular shape is difficult → AO's are oriented along cartesian axes and not wrt molecular shape and thus effective overlap is not possible.

C $1s^2\ 2s^2\ 2p^2$ CH_4 tetrahedral C is

H $1s^1$ Linus Pauling proposed hybrid orbitals. sp^3 hybridized

The hybrid orbitals are best for explaining /describing the bonding and the molecular shape of CH_4, AO's are best to describe single C atom.

So, Linus Pauling actually came up with solution and he proposed hybrid orbitals like we have learned that how carbon is sp3 hybridized in CH4. So, carbon is sp3 hybridized leading to tetrahedral shape and carbon is sp3 hybridized or sp2 in other molecules or sp hybridized other molecules. So, there is a concept of hybridization where atomic orbitals mix and match leading to formation of hybrid orbitals, which are now equal in energy.

And, thus they interact with the atomic orbitals of hydrogen leading to formation of tetrahedral shape. So, we can say that the hybrid orbitals are best for explaining or for describing the bonding and the molecular shape of CH4, whereas atomic orbitals of carbon are best to describe single carbon atom, so this we can understood. Now, so let us now see how symmetry and group theory arguments can be used to develop what atomic orbitals can be mixed to give you a hybrid orbital, which will satisfy the tetrahedral shape of the molecule.

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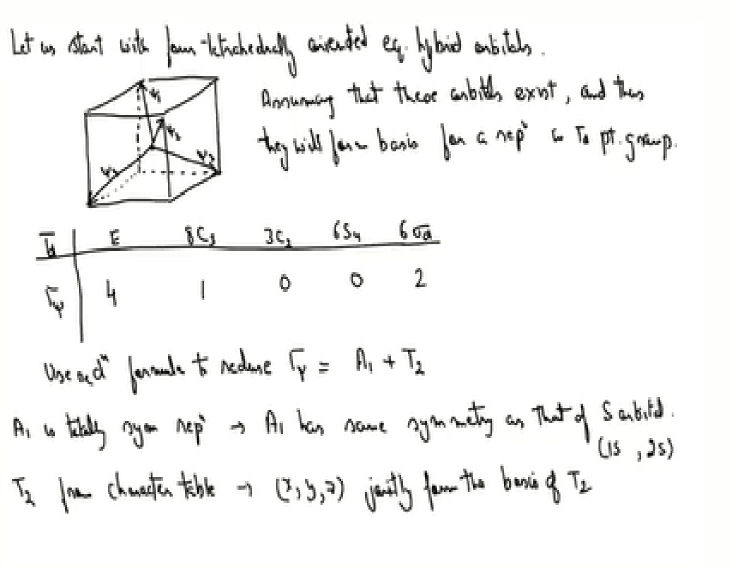

Let us start with four-tetrahedrally oriented eq. hybrid orbitals.

Assuming that these orbitals exist, and thus they will form basis for a rep^n in T_d pt. group.

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

Use red^n formula to reduce $\Gamma_\psi = A_1 + T_2$

A_1 is totally sym rep^n → A_1 has same symmetry as that of S orbital. (1s , 2s)

T_2 from character table → (x, y, z) jointly form the basis of T_2

So, let us go there, so let us start with four tetrahedral oriented equivalent hybrid orbitals. So, we start with the assumption that these hybrid orbitals exist and we will represent them with vectors psi 1, psi 2, psi 3, psi 4. Let us see, so for a tetrahedral I am going to draw cube it will be easier to understand. In the centre of the cube is the atom and then you have 4 hybrid orbitals, which are now represented by the arrows.

Now these arrows are oriented as a tetrahedral, so this angle will be the standard 109 degree 28 minutes between this. Now let us represent them with psi 1, psi 2, psi 3, psi 4. So, now here we are assuming that these orbitals are already existing orbitals exist and thus they will form basis of for a representation in Td point group. So, now let us create representation under Td point group, so this is my Td point group.

I am going to write the operations classified into different classes E, 8 C3, 3 C2 and I have 6 S4, 6 sigma-d. Now, tau psi for psi 1 psi 2, psi 3, psi 4, now we will use the same rule where we will say that on carrying out a symmetry operation if none of these change then they will contribute to trace are if any of this will change then it will not contribute towards the trace. So, then E will have a trace of 4, each of the C 3 will have a trace of;

So only one of the; psi 1 or psi 2 will not change because that will be the C3 axis. So, I will say 1, C2 everything will change so 0, S4 everything will change so 0, sigma d 2 will not change. So, now if I use reduction formula to reduce tau psi and this will result into A1 + T2. So, now we know that we have 4 hybrid orbitals which give us the representation as tau psi tau, psi upon reduction gives me A1 + T2.

Now, A1 is the totally symmetric representation, this means that A1 has same symmetry as that of S-orbital, it can be 1s as well as 2s both of them will have same symmetry S-orbital. Now, what about T2? So, T2, if we look at the character table so from character table we see that x, y, and z jointly found the basis of T2.

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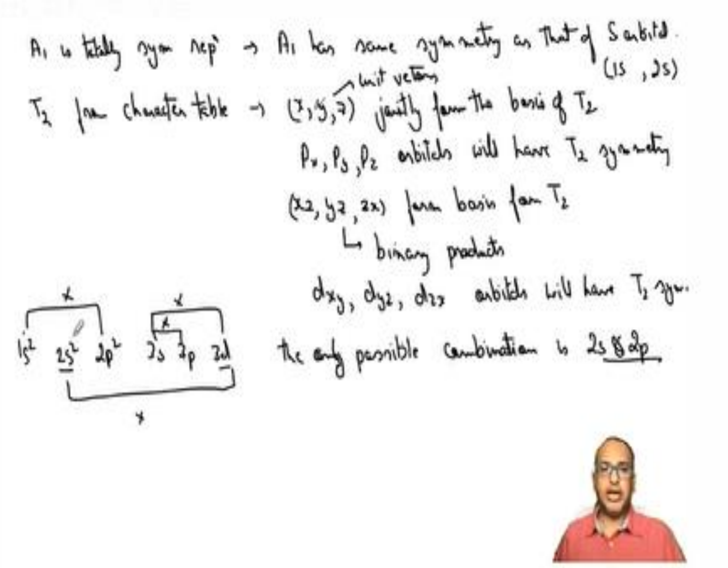

A_1 is totally sym rep → A_1 has same symmetry as that of S orbital.
(1s, 2s)
unit vectors
T_2 from character table → (x, y, z) jointly form the basis of T_2
P_x, P_y, P_z orbitals will have T_2 symmetry
(xz, yz, zx) form basis for T_2
↳ binary products
d_{xy}, d_{yz}, d_{zx} orbitals will have T_2 sym.
$1s^2$ $2s^2$ $2p^2$ $3s$ $3p$ $3d$
the only possible combination is 2s & 2p

That means that I can say; Px, Py, Pz orbitals will have T2 symmetry. Now, if you also see that xz, this is again from character table yz and zx they will also form basis for T2. So, this comes from the unit vector transformation and this comes from the binary products, so this is from unit vectors and this comes from binary products as the basis. So, this tells you that dxy, dyz and dzx orbitals will have T2 symmetry.

Now, there is a confusion between what to combine, so 1s orbitals cannot combine with so we can say let us say what we have so we have principal quantum number as 1s2 then we have 2s2 and 2p2. So, we have 2s orbitals here and 2Px, 2Py, 2Pz orbital here, then we have 3s orbital which is empty, 3p orbital which is empty and 3d orbital, I mean, there is no point considering combination of 3d orbital with 2s orbital.

Because there will be a lot of difference in the energy, this will be very high in energy, so you cannot combine this with this. Similarly, this s and this p cannot be combined; so we only have to combine s and p or s and d orbital, because A1 has s symmetry and T2 has either px, py, p z or dxy, dyz, dzx. So, either you can combine see this combination is meaningless because there is no electron in that.

So, if we are trying to combine so this does not work so if you are trying to combine this also does not work if you are trying to combine this also does not work, this also does not work, the only possible combination is 2s and 2p orbitals. So, we have 1s orbital and 3p orbitals, which can now combine to give you 4 hybrid orbitals psi 1, psi 2, psi 3, psi 4.

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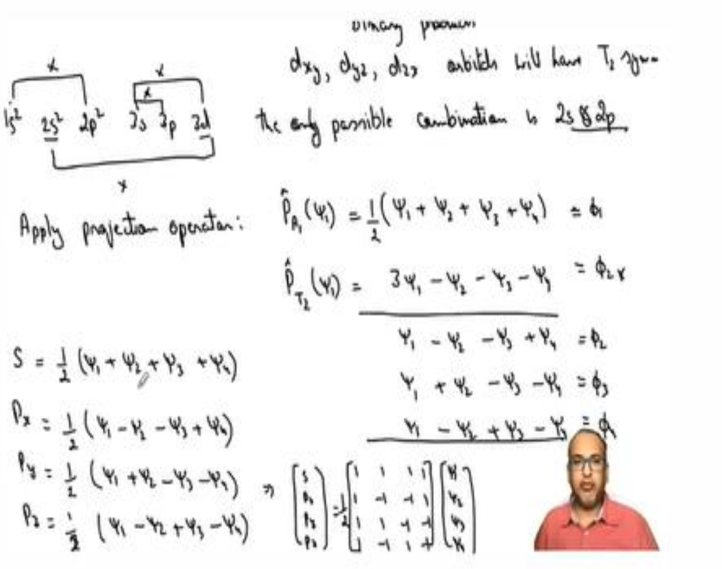

d_{xy}, d_{yz}, d_{zx} orbitals will have T_2 sym-

$1s^2$ $2s^2$ $2p^2$ $3s$ $3p$ $3d$

the only possible combination is 2s & 2p

Apply projection operator: $\hat{P}_{A_1}(\psi_1) = \frac{1}{2}(\psi_1 + \psi_2 + \psi_3 + \psi_4) = \phi_1$

$\hat{P}_{T_2}(\psi_1) = 3\psi_1 - \psi_2 - \psi_3 - \psi_4 = \phi_2$

$\psi_1 - \psi_2 - \psi_3 + \psi_4 = \phi_2$

$\psi_1 + \psi_2 - \psi_3 - \psi_4 = \phi_3$

$\psi_1 - \psi_2 + \psi_3 - \psi_4 = \phi_4$

$S = \frac{1}{2}(\psi_1 + \psi_2 + \psi_3 + \psi_4)$

$P_x = \frac{1}{2}(\psi_1 - \psi_2 - \psi_3 + \psi_4)$

$P_y = \frac{1}{2}(\psi_1 + \psi_2 - \psi_3 - \psi_4)$

$P_z = \frac{1}{2}(\psi_1 - \psi_2 + \psi_3 - \psi_4)$

$$\Rightarrow \begin{bmatrix} S \\ P_x \\ P_y \\ P_z \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \end{bmatrix}\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

So, now if we apply projection operator, so I am not going to go into the complete calculation you should be well versed with this now, so if we apply projection operator, I will have to do P A1 on to psi 1, this will give me psi 1 + psi 2 + psi 3 + psi 4 and then upon normalization you can say that this will be half. So, similarly if I do P T2 on psi 1, you will see that I am leaving this exercise for you to do at home.

So, you will get 3 psi 1 - psi 2 - psi 3 - psi 4. So, what are the other two orbitals? So, if we now try to do it for psi 2, you will get the similar combination with 3 psi 2 - psi 1 - psi 3 - psi 4 again.

So, they will not be orthogonal to each other this and this let us call this as phi 1 and phi 2. So, these two are let us say this is phi 1, this is phi 2, so phi 1 and phi 2 are orthogonal, so you can take the dot product and take the summation overall psi's and it does go to 0.

But the other phi is which you will get upon projecting out onto psi 2 psi 3 psi 4 will not be orthogonal to each other. So, now what to do here? So, if we carefully see this is actually instead of a combination of 4 psi orbitals we have what we have is 3 here and 3 here so 6 psi orbitals are interacting each other. So, like that is not a favourable case because you have more than expected orbitals.

So, now if you see that this can be broken down into linear combination of 3 independent orbital, so psi 1 - psi 2 - psi 3 + psi 4, psi 1, psi 1 + psi 2 - psi 3 - psi 4 and - psi 2 + psi 3 - psi 4, right? So, if you take this summation, you will get this back. So, now I can call these as phi 2, phi 3 and phi 4 and not this one. So, now if you see that these are orthogonal to each other as well as orthogonal to this one.

So, 2 positives and 2 negatives, so these will these 2 will be orthogonal and then here if you see that there again there are 2 positives and 2 negatives, so this will also be orthogonal. So, you can test it out. Now, if we see that this one has a symmetry so phi 1 has a symmetry of S orbital. So, I can equate the symmetry and I can say that this is my half psi 1 + psi 2 + psi 3 + psi 4. Similarly, I can say Px, Py and Pz will have symmetries corresponding to rest of the 3 phi's 1 by 2.

So psi 1 - psi 2 - psi 3 + psi 4, then I have psi 1 + psi 2 – psi 3 - psi 4 then I have psi 1 - psi 2 + psi 3 - psi 4. Now, if I try to write this in matrix form, I can always say S, Px, Py, Pz is equal to psi 1 psi 2 psi 3 psi 4 and this will be my half I can take out side this is 1 1 1 1, 1 - 1 - 1 1, 1 1 -1 – 1, 1 - 1 1 – 1. So, now if I want to write in terms of psi, what are the combinations of S and P orbitals, so I can always say that;

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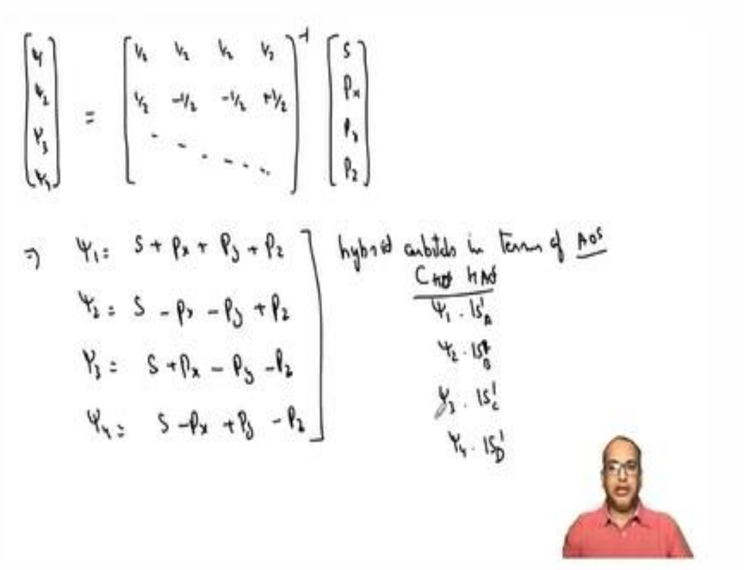

$$\begin{bmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{bmatrix} = \begin{bmatrix}\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2}\\ - & - & \cdots & \cdots\end{bmatrix}^{-1} \begin{bmatrix}s\\ p_x\\ p_y\\ p_z\end{bmatrix}$$

$$\Rightarrow \left.\begin{aligned}\psi_1 &= s + p_x + p_y + p_z\\ \psi_2 &= s - p_x - p_y + p_z\\ \psi_3 &= s + p_x - p_y - p_z\\ \psi_4 &= s - p_x + p_y - p_z\end{aligned}\right]$$

hybrid orbitals in terms of AOs

C hyb HAO

$\psi_1 \cdot 1s'_A$

$\psi_2 \cdot 1s'_B$

$\psi_3 \cdot 1s'_C$

$\psi_4 \cdot 1s'_D$

Psi 1 psi 2 psi 3 psi 4 is equal to half, half, half, half, half, minus half, minus half, plus half, and inverse of this, so this is the one so you can write the rest of the components, so you have S, P x, P y, P z right? I can always say that now this implies so I can write psi 1 is equal to if I expand this take this reverse I can always write this as psi 1 is equal to S + P x + P y + P z, psi 2 as S - P x - P y + P z, psi 3 as S + P x - P y - P z, psi 4 is S – P x + P y - P z.

So, now you have expressed hybrid orbitals which you assume to start with that they exist in terms of atomic orbitals. Now, you know the symmetry of these orbitals from there you have not reduced that what atomic orbitals should combine to give you four hybrid orbitals, which will be oriented along in a tetrahedral fashion so, that you can combine now these Psi's with the hydrogen atomic orbitals.

So, now if we want the formation of the bonds, so you can express those bonds in terms of psi 1 into 1S1, psi 2 into 1S1 of A B, psi 3 1SC, psi 4 1SD, these are the hydrogen atomic orbitals and these are the carbon hybrid orbitals. So, using this you can form four bonds which will now define the correct molecular shape, so this is an example of how valence symmetry and group theory can be used for to explain bonding under valence bond approach.

So, now in the next class we will go forward with this chemical bonding and will look at the localized and de-localized molecular orbital picture and how symmetry and group theory can be used to describe bonding in those cases, all right, that is all for today, thank you.