Symmetry and Group Theory
Dr. Jeetender Chugh
Department of Chemistry and Biology
Indian Institute of Science Education and Research, Pune

Lecture -50
Delocalized MO Theory Part- II

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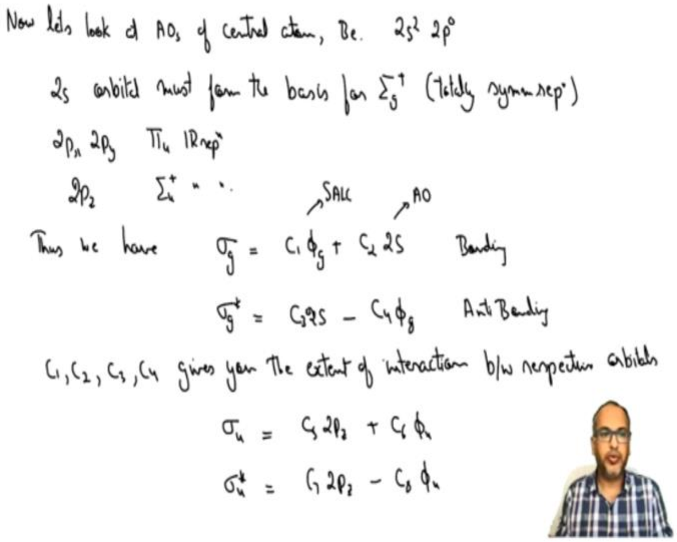

Now lets look at AOs of central atom, Be. $2s^2\ 2p^0$

$2s$ orbital must form the basis for Σ_g^+ (Totally symm rep^n)

$2p_x\ 2p_y$ Π_u IRrep^n

$2p_z$ Σ_u^+ " "

Thus we have $\sigma_g = C_1 \overset{\nearrow \text{SALC}}{\phi_g} + C_2 \overset{\nearrow \text{AO}}{2S}$ Bonding

$\sigma_g^* = C_3 2S - C_4 \phi_g$ Anti Bonding

C_1, C_2, C_3, C_4 gives you The extent of interaction b/w respective orbitals

$\sigma_u = C_5 2p_z + C_6 \phi_u$

$\sigma_u^* = C_7 2p_z - C_8 \phi_u$

So, now that we have determined the SALCs, now, let us look at atomic orbitals of central atom, which is Beryllium here. So, the central atom has valence shell as 2 S 2 and 2 P 0. So, now what is the symmetry for 2 S? So, 2 S under B infinity h point group, we see that the 2 S orbital. It is a spherically symmetric orbital so it must form the basis for sigma g plus that is the totally symmetric representation.

And 2 P orbitals, let us say 2p x, 2p y orbitals. They form the basis of pi u as the IR representation and 2p z forms the basis for sigma u plus IR representation. So, now that you have the symmetry of SALCs and symmetry of the central atom, so you know that which orbitals will combine with what orbitals and which will remain as non-bonding. So, these will remain as non bonding the p x and p y, 2 S will combine with phi g, 2p z will combine with phi u.

So, thus we have let us write down sigma g as C 1 times phi g, which is the SALC coming from the two hydrogens, this will combine with C 2, 2 S. This is the SALC and this is the atomic orbital. Also, sigma g star can be written as C 3 2 S minus C 4 phi g. So, again, this is atomic orbital and the SALC. So, this will form because summation will give you bonding and this will give you anti-bonding.

Now C 1, C 2, C 3, C 4 reflect the extent of interaction we can write down C 1, C 2, C 3, C 4 gives you the extent of interaction between respective orbitals. How strongly they are overlapping and all? So, similarly the interaction between 2p z and phi u will give you sigma u which is equal to C 5 2p z + C 6 phi u. This will give you bonding, and sigma u star give you C 7 2p z minus C 8 phi u. Now let us try to draw it pictorially and see how if you get a picture clear?

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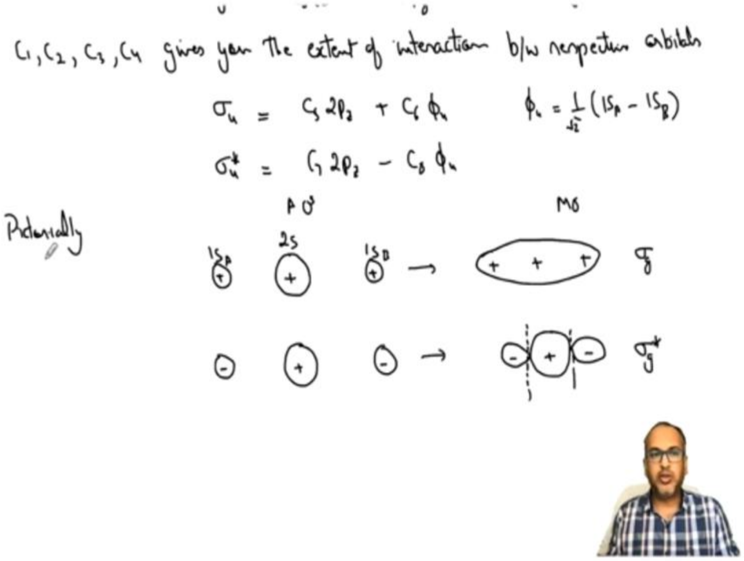

C_1, C_2, C_3, C_4 gives you the extent of interaction b/w respective orbitals

$\sigma_u = C_5 2p_z + C_6 \phi_u \qquad \phi_u = \frac{1}{\sqrt{2}}(1s_A - 1s_B)$

$\sigma_u^* = C_7 2p_z - C_8 \phi_u$

Pictorially

So, you can say, so we have our let us start with sigma g. So, sigma g has a 2 S orbital, which is the central atom. Let us draw the phase also so start with positive phase and then you have plus 1 S plus 1 S. So, remember that we had, if you see here phi g is positively phased. And 2 S is also positively faced. So, this plus sign means that the phase is positive the negative sign means the phase is inverted.

So, now, this is the combination so this particularly gives rise to orbital which is something like this. Actually, this is we should not write sigma g here we should write sigma g on these side. Because this is the MO these are the individual atomic orbitals. So, you see directly atomic orbital combination is used, there is no hybridization happening here, so we will write all of them with positive phases, this is the combined MO.

So, you can write atomic orbitals in this the molecular orbital. The next one was sigma g star where we had this as positive and phi u this is negative and this is negative. We had phi g with a negative sign. So, here phi g, phi g is what? Phi g was 1S A plus 1S B so both of them have to have same signs but we have overall phi g negative, so both the 1S A and 1S B go negative here. So, we will write 1S A and 1S B.

So, both of them will go negative and what is the result here? The result is, there is a node formation. So, this node represents that there is no electron density here, this is plus, minus, this is sigma g star. Now for sigma u what did we have? So, we had 2p z with positive phase and phi u, so phi u was 1 over root 2, 1S A minus 1S B. So, that means the 2 S orbitals were with opposite phase in phi u.

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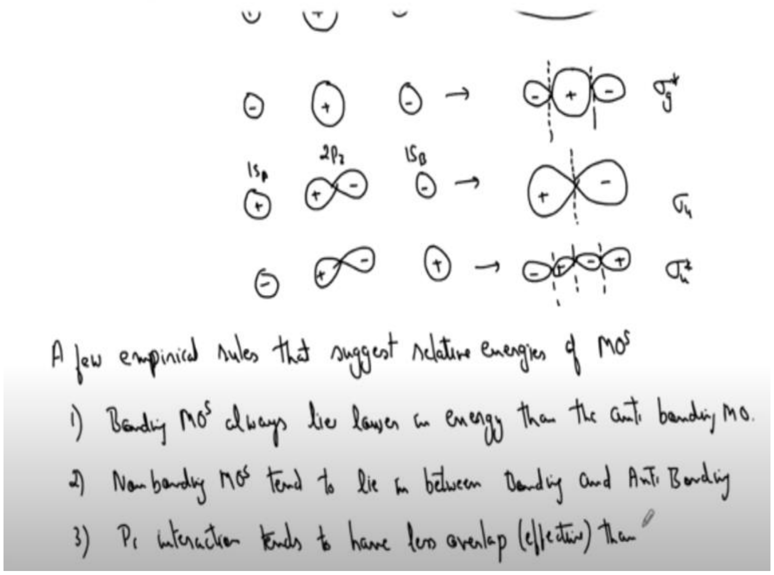

A few empirical rules that suggest relative energies of MOs

1) Bonding MOs always lie lower in energy than the anti bonding MO.

2) Non bonding MOs tend to lie in between Bonding and Anti Bonding

3) Pi interaction tends to have less overlap (effective) than

So, let us write down, so you have 2p z with positive and negative and 1S A was positive and 1S B was Negative. So, how does it look? So, you have built up of electron density or build up of the wave function here in the negative phase. So, both the lobes will increase in size both the lobes of p z will increase in size. So, this is 2p z now and this is 1S A, this is 1S B. You have something like this.

So, you have positive enhancement and negative enhancement also, will give rise to increase in lobe. So, this will give rise to bonding and there is one node which was originally present in 2p z, so there is no electron density here. So, now next one is sigma u star, so sigma u star if you see that 2p z remains same. And then there is a negative sign for phi u that means these two will go opposite in sign.

Let us see how it works? So, you have plus and minus. Now this side the negative will come and this side positive will come. Now again there is a negative phase of wave matching with positive phase so that means there would be a node formation here. So, that means there will be total four lobes present. This is plus, minus plus, minus plus and there are three nodes present, sigma u star. Now, how do we arrange this in terms of energy?

We have got 4 orbitals for molecular orbitals, 2 of them are bonding, 2 of them are anti-bonding. And then we will also have some non-bonding coming from 2p x and 2p y. So, let us see, how do we arrange these. So, the MO theory beautifully describes the relative energy of these orbitals? So, there are empirical rules. So, we will write down those rules, a few empirical rules. So, again remember that for explicit energy calculation you have to resort to quantum mechanical calculations.

You cannot calculate explicit energies here. You can only tell about relative energies, a few empirical rules that suggest relative energies of molecular orbitals. So, first rule is that bonding MOs always lie lower in energy than the anti-bonding MO. So, that means sigma g will be stable as compared to sigma g star, sigma u will be stable as compared to sigma u star. So, that is one.

So, you can already see that advantage of delocalized MO theory, over localized MO theory or valence bond theory, where we can explicitly write down the relative energies. So, non-bonding MOs tend to lie in between bonding and anti-bonding. Because non-bonding is not taking part in these kinds of bond formations, so they tend to remain where they were for the individual atom. So, in some cases there is interaction with the outer atoms.

And they tend to destabilized or stabilized in certain cases but typically they tend to lie between bonding and anti-bonding there is no change. So, third is pi-interaction tends to have less effective overlap then the sigma interaction.

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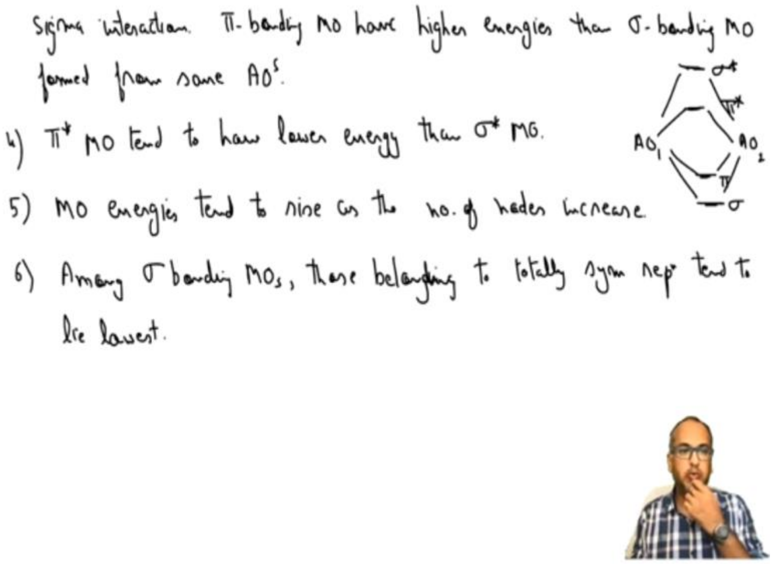

sigma interaction. π-bonding MO have higher energies than σ-bonding MO formed from same AO^s.

4) π^* MO tend to have lower energy than σ^* MO.

5) MO energies tend to rise as the no. of nodes increase.

6) Among σ bonding MOs, those belonging to totally sym rep tend to lie lowest.

So, if the interaction is less effective that means the stabilization energy will also be less. So, that would mean that pi bonding MO have higher energies than sigma bonding MO, even though if they are formed from same atomic orbitals. So, fourth point is that pi star MO tends to have lower energy then sigma star MO. See if the stabilization energy is less the destabilization energy is also less.

Let us say if two atomic orbitals, atomic orbital 1 and 2 are giving rise to a sigma orbital and a sigma star. The stabilization is more as compared to if the same thing will give rise to pi's, pi bonding versus pi star, so that is what I mean here. That the sigma even though they are forming from the same atomic orbitals, if it is a sigma interaction the stabilization and the destabilization of anti-bonding both will be higher as compared to pi-interaction.

Because of less effective overlap because pi orbitals overlap sideways whereas sigma orbitals overlap in head-to-head. So, fifth is, molecular orbital energies tend to rise as the number of nodes increase. Sixth is, among sigma bonding Mos, those belonging to totally symmetric representation tend to lie lowest. So, these empirical rules would define the relative energy. So, let us see the case of BeH2 we have already developed the MO diagram.

So, let us see, we have already developed the molecular orbitals, let us see how they are arranged in a MO diagram now?

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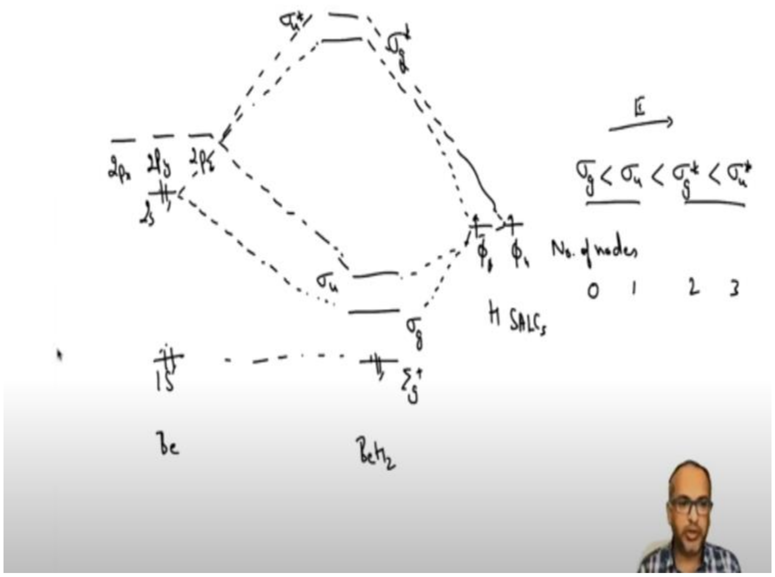

So, we have for beryllium, we have 2 S which is filled and then we have 2p x, 2p y, 2p z where 2p x and y are of different symmetry then 2p z. And then for hydrogens we had SALCs, as phi g and phi u. So, we get two hydrogens each with one electron. so now we have seen that the S orbital will combine with phi g so this will give rise to and then you can also say that you have on beryllium you also have 1 S orbital with two filled electrons which will also be of sigma g plus.

But depending on which will have better energy which compares in energy to phi g the combination will take place so this will typically remain as non-bonding. So, you have sigma g plus, this is now for BeH2 molecules. This is Be now this will combine with phi g to give rise to sigma g. And then this will also give rise to sigma g star. Now 2p z will combine with phi u. Because of same symmetry again, so this will give rise to sigma u and sigma u star.

So, now you see that I have arranged sigma g at the lowest with sigma u with sigma g star and sigma u star. This is in increasing energy, why did I do that because if you remember that the number of nodes if I write here number of, so, first of all, these are bonding these are anti bonding so as per rules they have to be lower in energy as compared to this. Now number of nodes present will dictate which one will be more stable as compared to whether sigma g is more stable or sigma u is more stable?

So, sigma g has zero nodes sigma u has 1 node, 2 node, 3 node. So, let me see if I am writing it correctly, so sigma g has 0 nodes, sigma u has 1 node, sigma g star has 2 nodes, sigma u star has 3 nodes. So, the number of nodes will also define the energy so that is how they are arranged now sigma g, sigma u, sigma g star, sigma u star. So, there should not be any confusion now. We will see more examples if time permits will discuss, otherwise, I would suggest you to take home assignment.

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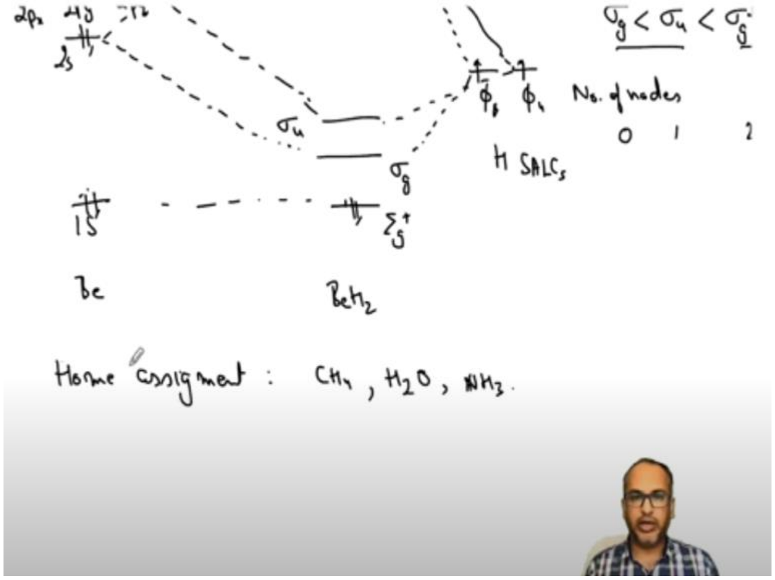

And do it for CH4, try to develop the MO diagram we have already done it for Valence Bond treatment, so it should not be a problem, and take more molecules, take H2O, NH3 and try to develop this MO diagram for all of this and see if you get any difficulty, of course, we can discuss once you have the difficulty. That is all for today, thank you.