Symmetry and Group Theory
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Lecture -48
Localised MO Theory

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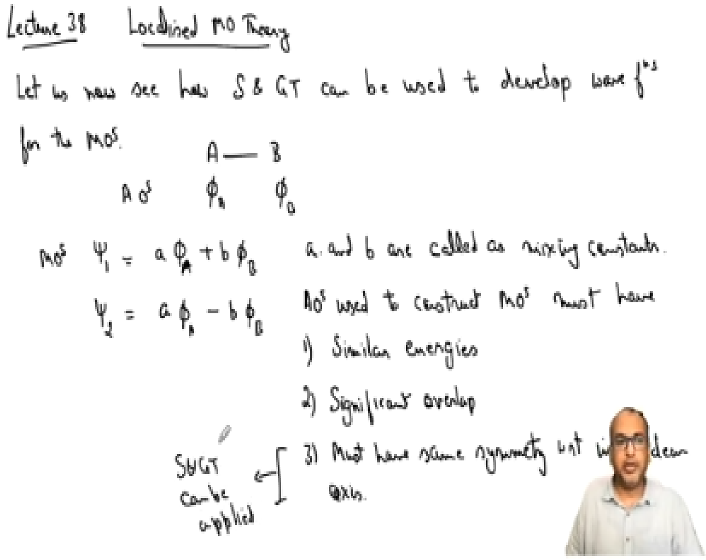

Lecture 38 Localised MO Theory

Let us now see how S & GT can be used to develop wave f^ns for the MOs.

A — B

AOs ϕ_A ϕ_B

MOs $\psi_1 = a\phi_A + b\phi_B$

$\psi_2 = a\phi_A - b\phi_B$

a and b are called as mixing constants.

AOs used to construct MOs must have

1) Similar energies

2) Significant overlap

3) Must have same symmetry wrt [illegible] axis.

SGT can be applied

So, in the last few lectures we have been discussing chemical bonding, so how symmetry and group theory can be used to develop wave functions for different bonds, under valence bond theory. And we have also discussed the comparison between valence bond theory and molecular orbital theory. So, now let us see how under molecular orbital theory we can develop wave function to describe the chemical bonding.

So, under MO theory, we will be first discussing localized molecular orbital theory. Localized MO theory, we will see what are the problems with this and then we will move to delocalized MO theory which is much more general. So, we have also seen the linear combination of atomic orbitals approach when we were discussing the MO theory basics; So, now let us see let us now see how symmetry and group theory can be used to develop wave functions for the molecular orbitals.

So, we will first look at the localized one between two atoms of a diatomic molecule. So, let us consider a diatomic molecule something like this. Let us say that the atomic orbital of this is phi 1 or phi A and atomic orbital of B is phi B, so these are atomic orbitals. Now the molecular orbitals, we have learnt that, will be obtained by linear combination of these, so linear combination of two orbitals can be obtained in a very simple and straight forward way.

We do not really need to apply projection operator although if we even if we apply projection operator, we will get the same thing. So, if we see that psi 1 if these are our molecular orbitals, so psi 1 can be written as a times phi A plus b times phi B and whenever 2 orbitals are combining, they will give you 2 molecular orbitals. So, then psi 2 will be phi A minus b times phi B, so where A and B are called as mixing constants.

Now atomic orbitals used, not all orbitals of atom A can be combined with all orbital B. So, there are certain criteria which can participate in this linear combination approach. So, let us list down those criteria, so atomic orbitals used to construct MOs must have. So, first is similar energies, see if the energies are not in the similar range, it is not possible for the two atomic orbitals to combine, so for example, atomic orbital from one principal quantum number cannot be combined with atomic orbital from second principal quantum number.

So, n has to be at least similar. Similarly S orbital of a principal quantum number is difficult. I mean you can still combine but it is difficult to combine with d orbital for example, because d orbitals have higher energy than S orbitals. So, a better mixing is between S and P orbitals, for example, that is general rule of thumb; So, idea is that you have to have similar energies of course apriori you do not know which orbitals would have similar energy.

But there are certain basic rules the way I said that the similar principal quantum number, or between S and P orbitals the energy differences much less than as compared to s and d orbitals so accordingly you can choose. And of course you have to take the valence orbitals from balance shell. So, orbitals from penultimate shell you cannot take because those are complete shell those will not participate in chemical bonding.

So, they should also have significant overlap. How do we know whether to orbitals are having significant overlap? That we can calculate the Slater's overlap integral, that we have seen earlier. Now the third and most important point here is all points are important. But most important in terms of symmetry and group theory rules that they must have same symmetry with respect to inter nuclear axis. So, this last requirement specifically points out that symmetry and group theory rules can be applied.

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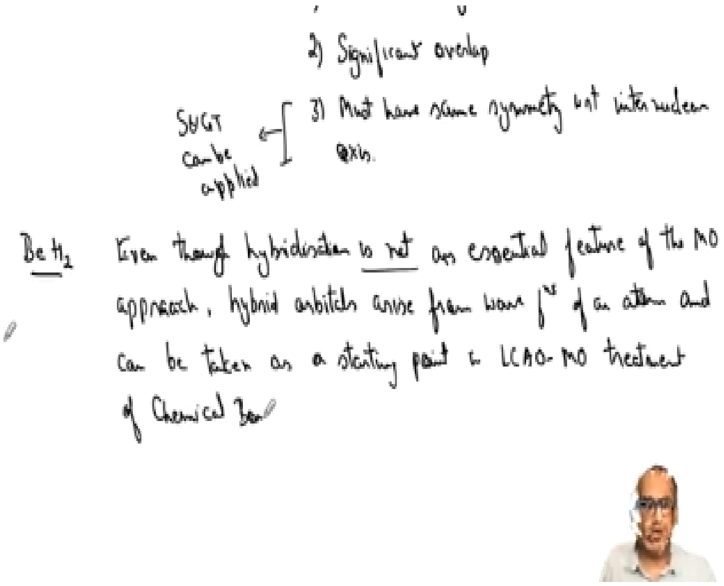

2) Significant overlap

SnGT can be applied ← 3) Must have same symmetry wrt internuclear axis.

BeH_2 Even though hybridisation is not an essential feature of the MO approach, hybrid orbitals arise from wave f^n of an atom and can be taken as a starting point in LCAO-MO treatment of Chemical Bon

So, now let us take an example, and see how to do this. So let us take an example of BeH2. So, now one important point is that even though hybridization of central atom, in this case central atom is Beryllium, hybridization is not, so I will underline this, not an essential feature of the MO approach. That we have learnt when we will looking at the differences between MO and VB theory. So, in balance bond theory the hybridization is an essential approach.

Whereas in case of MO theory it is not an essential feature of MO. So, hybrid orbitals, we can say hybrid orbitals arise from wave functions of an atom and can be taken as a starting point. And we will see that if we take hybrid orbitals as a starting point, it is the bonding descriptions is easier, then if we take the atomic orbitals. Starting point in linear combination of atomic orbitals MO approach or a MO treatment of chemical bonding. See this is not required, but if we do this if we take the hybridization here, it makes our life little easier.

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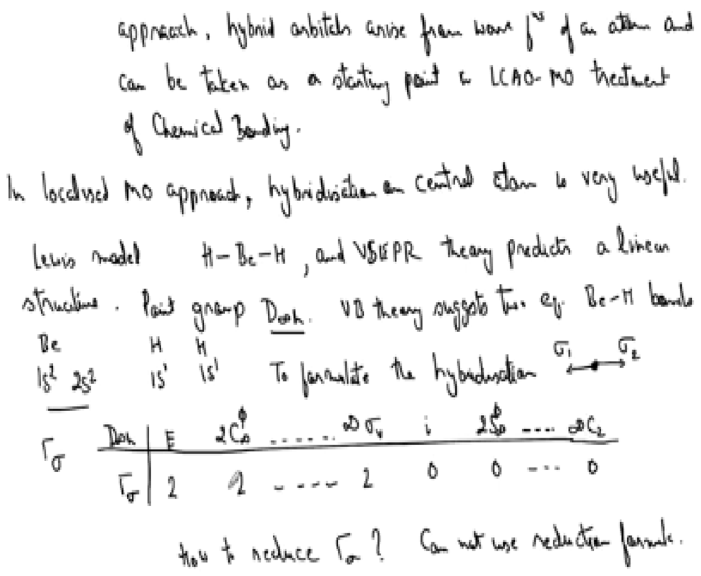

approach, hybrid orbitals arise from wave f^n of an atom and can be taken as a starting point in LCAO-MO treatment of Chemical Bonding.

In localised MO approach, hybridisation on central atom is very useful.

Lewis model H–Be–H, and VSEPR theory predicts a linear structure. Point group $\underline{D_{\infty h}}$. VB theory suggests two eq. Be–H bonds

Be $1s^2\ 2s^2$ H $1s^1$ H $1s^1$ To formulate the hybridisation $\sigma_1 \leftarrow \bullet \rightarrow \sigma_2$

Γ_σ

$D_{\infty h}$	E	$2C_\infty^\phi$	……	$\infty\sigma_v$	i	$2S_\infty^\phi$	----	∞C_2
Γ_σ	2	2	----	2	0	0	---	0

how to reduce Γ_σ? Can not use reduction formula.

So, then in localized MO approach hybridization on central atom is very useful. So, we will try to develop using this. So, now in BeH2 example, the Lewis model is, if we try to draw the structure of this using Lewis model, so of course I am not going to go into these details because these are very preliminary and you must have an idea of how this Lewis model or VSEPR theory tells you the structure of the molecule.

So, the structure would be something like this, and VSEPR theory predicts a linear structure. So, if it is a linear structure what will be the point group? So, we should be aware of this thing now, how to calculate point groups. So point group of the molecule will be D infinity h. So, I am not going to go into details of how to determine the point group. We have already covered a lot of lectures on this.

So, also VB theory, valence bond theory suggests to equivalent Be-H bonds. Because the structure is linear and it is the two bonds has to be of similar type or similar energy or so these will be equivalent. So, now to form just like in VB, so we will create hybrid orbitals for Be. So, Be atomic structure is 1S 2, 2S 2. This is for Be and for hydrogens we have 1S1 and two hydrogens we have 1S1.

So, to formulate hybridization remember what we did what is the next step to formulate the hybridization, we will convert this bonding into vector diagram. So, you start from the central atom and go outwards towards the pendant atoms, these are called as pendant atoms. So, now this would be, we can call it as phi 1 and phi 2. Now based on this under D infinity h point group we will create tau phi, which will be tau reducible, so how do we do that?

So, let us list it down so we have D infinity h now this is a infinity point group. So, we will see how to work with infinity point group but this will be just by inspection and not by following any rules as such, but later on in this course we will see if we are encountered with infinity point groups how to simplify those and go to a smaller point group.

We will see that so let us not jump the guns, so E, 2C infinity, then call it as phi, so if this is phi so let us not create confusion so let us call this as sigma. So, let us call this is sigma1, sigma 2. Now also so we cannot list down all the atom because all the symmetry operations, so we will just list down a few 2S phi infinity b, infinity C 2, so now tau sigma. So, because these are two sigmas as the basis functions;

So, for this tau there will be E will have 2 cross 2 matrix so we will write the trace as 2. C infinity will be passing through these two bonds. So, none of this will change so both of them will contribute to the trace, similarly for sigma v, again sigma v nothing will change sigma 1 and sigma 2 will remain at their own places. So, 2 i everything will change so zero s infinity everything will change so zero.

In C 2 axis C 2 axis is perpendicular to this, so again sigma 1and sigma 2 will change, so this will be 0. So, now you cannot use so next step is to reduce this how to reduce tau sigma? Now you cannot use a reduction formula, why you cannot use reduction formula? Remember that in reduction formula we have to actually see the calculations for all symmetry operations. We cannot list all symmetry operations, so it will not be possible to use it, however by just simple inspection of character table;

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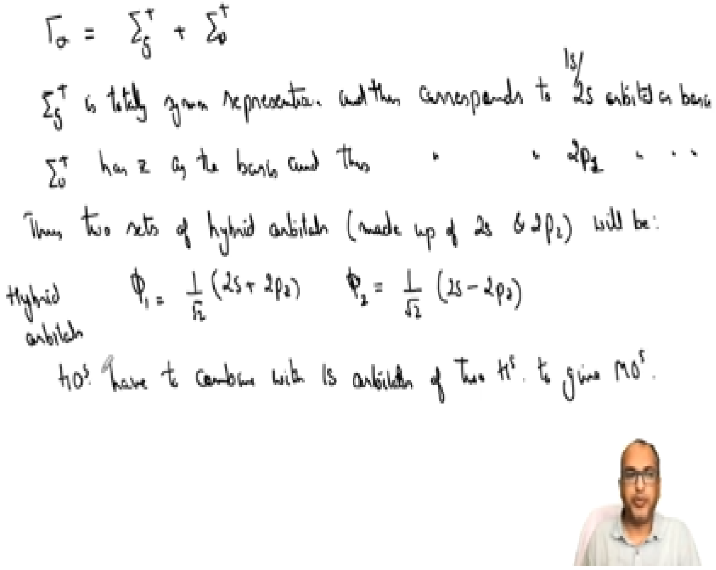

$\Gamma_\sigma = \Sigma_g^+ + \Sigma_u^+$

Σ_g^+ is totally sym representation and thus corresponds to 1s/2s orbitals as basis

Σ_u^+ has z as the basis and thus " " $2p_z$ " " "

Thus two sets of hybrid orbitals (made up of 2s & $2p_z$) will be:

Hybrid orbitals $\phi_1 = \frac{1}{\sqrt{2}}(2s + 2p_z)$ $\phi_2 = \frac{1}{\sqrt{2}}(2s - 2p_z)$

HO's have to combine with 1s orbitals of two H's to give MO's.

We can see that if we create a sum of two IR representations that are tau sigma can be broken down into sigma g plus and sigma u plus, this is by just inspection. We have not done any calculation this is just hit and trial, so just look at the character table and see which two IR representations will give you a summation so that it will give rise to tau sigma. So, that is why we said that we cannot use reduction formula we will simply use our logic by just inspection.

So, now if we see sigma g plus is totally symmetric representation, so sigma g and sigma u are the Mulliken symbols and remember that in infinity point groups we have different Mulliken symbols. So, that is why I have written this, so you can go back to the discussion of Mulliken symbols and see what does it mean for sigma g and sigma u plus. All the rules were described earlier so it is a totally symmetric representation.

And thus, corresponds to 2s orbitals as basis. So that means 2s orbital will form basis for totally symmetric representation, of course you can also say 1s orbital, but 1s orbital will not take part in bonding it is only the 2s orbital which will take part. So, that is why we are considering only words 2s. So similarly, sigma u plus has this information is again from the character table as z as the basis and thus corresponds to 2p z orbital as basis.

So, now we know that the S orbital 2s orbital of beryllium and 2p z orbital of beryllium are transforming the basis for tau sigma. So, that means our hybrid orbital will come from the 2s and

2p z orbitals. Thus, two sets of hybrid orbitals, which will be made up of 2s and 2p z, will be, so again you cannot use projection operator here because again for projection you have to do the calculation for all the symmetry operations.

Its summation overalls R, which you cannot do because it is a infinity point group. So, again this is a simple case, so we can deal with this without having to use projection operator. So, if you want a combination of these two leading to hybrid orbitals, you can see that we can use phi 1 as 1 over root 2 this is after normalization, 2s plus 2p z and phi 2 is the second hybrid orbital these are not yet molecular orbitals these are only hybrid orbitals.

So, the other combination will be the subtraction of this 2s minus 2p z. So, this will be your hybrid orbitals. Now we know that these hybrid orbitals have to combine with these hybrid orbitals have to combine with 1s orbitals of two hydrogens to give you molecular orbitals. So, let us see how does that work.

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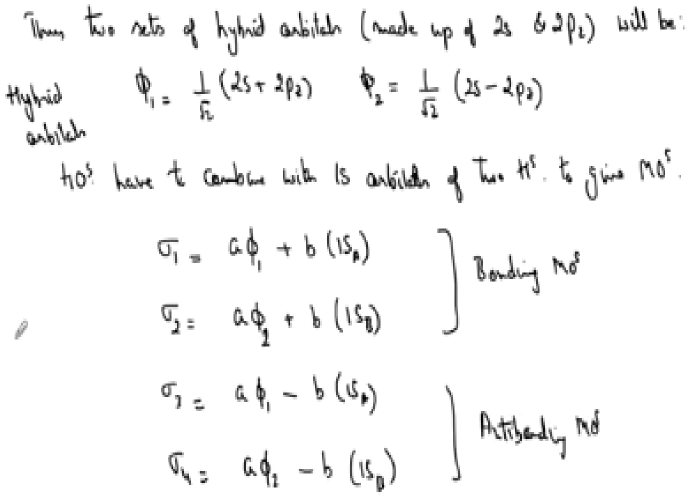

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$$\left.\begin{aligned}\sigma_1 &= a\phi_1 + b(1s_A)\\ \sigma_2 &= a\phi_2 + b(1s_B)\end{aligned}\right\}\text{Bonding MO's}$$

$$\left.\begin{aligned}\sigma_3 &= a\phi_1 - b(1s_A)\\ \sigma_4 &= a\phi_2 - b(1s_B)\end{aligned}\right\}\text{Antibonding MO's}$$

So, we can say that the two molecular orbitals as, so you can say sigma 1 which combines with a times phi1 plus b times 1S A, this is coming from hydrogen. Similarly sigma 2 can be written as a times phi 1 or phi 2 one this one plus b times 1S B this is the second hydrogen. Now these two together will create bonding orbitals bonding molecular orbitals. Now sigma 3 if something is combined in pause plus then that should also be a minus a phi 1 minus b 1S A. And sigma 4 will be a phi 2 minus b 1S B and these will be antibonding molecular orbitals.

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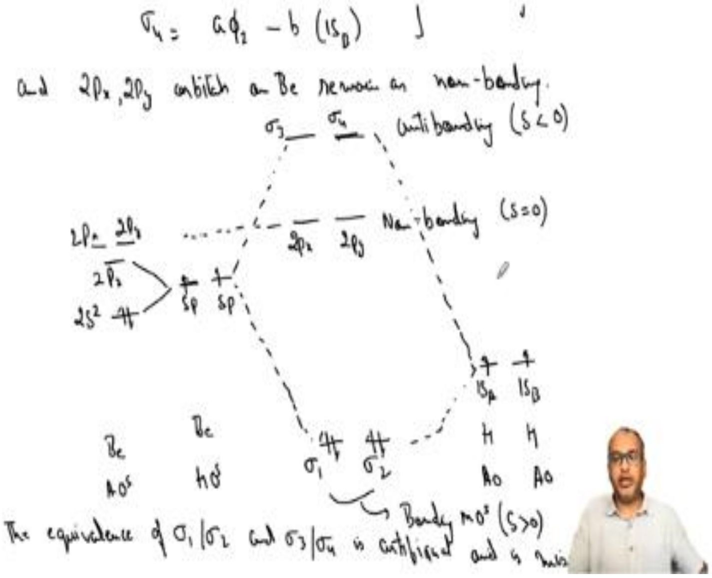

$\sigma_4 = a\phi_2 - b\,(1S_B)$

And $2P_x, 2P_y$ orbitals on Be remain as non-bonding.

The equivalence of σ_1/σ_2 and σ_3/σ_4 is artificial and is mis

So, it is still a localized molecular orbital because, we are still considering the electron which are defining the bond between the two atoms. Between beryllium and hydrogen and between the beryllium and other hydrogen we have still not considered the delocalization part. So, it is still localized molecular orbital. So, and so beryllium is left with 2p x and 2p y which were not part of the tau reducible, so these will not take part in bonding.

And then these will these orbitals on beryllium remain as non-bonding. So, again we have only considered the symmetry arguments to identify which orbitals will combine with what orbitals; and which will form bonding which will form antibonding and which will remain as non-bonding. So, now let us try to draw the molecular orbital diagram of this. So we saw that we have 2S 2 which is filled with 2 electron, this is for Beryllium atomic orbitals.

And you have well we do not know to start with what is the P z P x P y. These will not be degenerate, because z has different symmetry then x and y but we do not have any idea of whether this will be lower or higher in energy so I am just writing it like that only. So, 2P x, 2P y but these are all empty, these are the Beryllium atomic orbitals. Now these two combined to give you 2S p orbitals Sp hybrid orbitals this is Beryllium hybrid orbitals.

Now what is this? This is S p and S p now both are of same energy, so both of them will contain one one electron each. What about hydrogens? So, hydrogen is 1S so there are two hydrogens, so 1S A and 1S B this is for hydrogen, hydrogen and these are atomic orbitals and atomic orbitals it has electrons each. Now these have to combine with these because, they are of same symmetry it cannot combine with p 2, p x and 2 p y S orbitals of this hydrogen cannot combine.

So, this will remain as non-bonding. So, 2p x, 2p y these are non-bonding. So, this you can also calculate from slaters overlap integral the overlap between these two if you calculate the integration equal to be 0. So, that is why this will be non-bonding. Remember that condition S equal to 0, non bonding, so this will be S equal to 0. And S is positive means bonding S is negative which will be negative. Now what is left?

So, you have to combine these two now because of similar symmetry. So, now you have sigma 1, sigma 2, coming from here sigma 1, sigma 2 and equal destabilization will happen leading to antibonding formation. Well, you cannot predict the absolute energies from group theory but you can only estimate the relative energies. Also, in this particular case, let me finish this first, so you have four electrons over here so four will fill these two bondings;

So, these are bonding orbitals bonding molecular orbitals, but localized. So, S is greater than 0, these are antibonding S is negative. So, now we have listed sigma 1, sigma 2, and sigma 3, sigma 4 as with equal energy. So, we can say that the equivalence of sigma 1, sigma 2 and sigma 3, sigma 4 is artificial. See there is no rule which predicted that they should have same energy but we have just listed down them as same energy.

We do not know to start with whether they will indeed have same energy or not, so the equivalence of this is artificial and thus misleading. So, now in this particular case we have constrained the electrons to localized orbitals and that is how we got localized MO approach. But there is a problem that we do not know the relative energies of these orbitals whether these will be same, this will be same or not or sigma 1 will have higher energy or lower energy;

So, all of this basically you cannot describe the electronic spectra using the localized MO theory approach. Because the energies have to match and accordingly you have to explain the transitions. So, any transition from here to here will give you a line and if those energies are not as predicted by this approach. Then you will not be able to equate those energies with what you get from experimentally in electronic spectroscopy.

So, if you cannot do that then you need to go to a more general approach which is delocalized molecular orbital approach, where we do not constrain electrons to localized bonds. And we will see that how do we do that in delocalized MO theory in next class. That is all for today, so thank you very much.