

Symmetry and Group Theory
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Lecture -49
Delocalized MO Theory Part- I

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Lecture 29 Delocalized MO Theory

- DMs yield energies that are consistent with electronic spectra and ionization energies.
- This approach requires abandoning the VB notion of chemical bond i.e. chemical bond as the sharing of a pair of e⁻s by two adjacent atoms.
- In this approach, we try to find out bonding, anti-bonding, and non-bonding orbitals as LCAO of ordinary AOs on all atoms of the molecule.
- Hybridisation is not a starting assumption here.

So, in the last lecture we were discussing localized MO theory where we saw that how MO's developed using localized theory start with valence bond kind of approach, where we start with the hybrid orbitals of the central atom. And then we go on develop MO theory, but one of the major issues was that there was accidental degeneracy of those MO orbitals that we saw. Let us now see how delocalized MO theory works better and it yields energies that are much more consistent with the electronic spectra and ionization energy of a molecule.

So, let us start our discussion today with delocalized MO theory. So, or MO description of chemical bonding. So, we will see that these delocalized MO's yield energies that are consistent with or we can say more consistent with electronic spectra and ionization energies. Using group theory, you cannot calculate the exact energy. But you can only tell the relative stabilization destabilization of different orbitals, we will see that today.

So, for calculations of course you will have to set up the actual equations and solve the integrals and some of the integrals you get help from group theory rules that some of the integrals will get cancelled out. So, that is the only help group theory will do. But for actual calculation of energies, you cannot use this theory to calculate the energies which has to be explicitly calculated. So, group theory will not help you calculate the actual energy numbers.

So, this particular approach requires abandoning the VB or valence bond notion of chemical bond. What is that notion? That the electron pairs subside between the shared atomic orbitals or between the interacting atoms. Chemical bond has the sharing of a pair of electrons by two adjacent atoms. So, this thought we have to get rid of, when we are discussing delocalized MO theory.

So, what we will do instead of VB notion, so in this approach we try to find out bonding, anti-bonding, and non-bonding. So, ideally the aim is still saying that we need to find out bonding, anti-bonding, nonbonding orbitals. But here it is done as the linear combination of atomic orbitals of ordinary atomic orbitals on all atoms. So, there is no hybridization to start with all atoms of the molecule.

So, explicitly we will just write hybridization which is actually the product of wave functions. So, that is not a starting point here, so this has to be very clear.

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→ In this approach, we try to find out bonding, anti-bonding, and non-bonding orbitals as LCAO of ordinary AOs on all atoms of the molecule.
 → hybridization is not a starting assumption here.

Approach → Match the symm of central atom (in MX_n type systems) with that of linear combination of orbitals of outer X atoms (pendant atoms) called SALCs.

$$\psi_{MO} = a\psi_{AO}(M) \pm b\psi_{SALC}(nX)$$

$$\psi_{SALC} = c_1\psi_1 \pm c_2\psi_2 \pm \dots \pm c_n\psi_n$$

So, what is the approach so I will just give you a brief approach and then we will write down step by step and then again, we will take the beryllium hydride example so, that we can compare it with localized MO approach. So, the approach in short is, match the symmetry of central atom. For example, in MX₄ type systems, with, so you already know what is the atomic orbital of central atom.

So, you have to match the symmetry of that central atom atomic orbital with that of linear combination of orbitals of outer X atoms. So, these outer atoms like this one is called a central atom this M is called a central atom and X is called as pendant atoms. And we have seen this approach these are called as SALCs. So, we create SALCs using outer X atoms and then we match the symmetry of central atom with those SALCs.

And combine them to form molecular orbitals. So, thus we can write let us say if this is the wave function of molecular orbital. So, we can say that this is a combination of course symmetry matched combination of atomic orbital of central metal atom or central atom and plus/minus any combination with appropriate coefficients with SALCs of nX atoms. So, this is the general picture of MO theory.

Where we can say that the psi SALC is nothing but c₁psi₁ plus c₂psi₂ plus c_npsi_n. So, this is a linear combination, this can be plus or minus. And the appropriate coefficients also have to

be and then these again have to be normalized and orthogonal, all those things which we have already learned.

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$$\psi_{MO} = a\psi_{AO}(M) \pm b\psi_{SALC}(MX)$$
$$\psi_{SALC} = c_1\psi_1 \pm c_2\psi_2 \pm \dots \pm c_n\psi_n$$

We use GT rules to determine the group of possible SALCs, formed from pendant atom AOs. And then determine the SALC that will combine with which AO to form MO.



So, where is the group theory application coming in. So, using group theory, so we say that we use group theory rules to determine the symmetry of possible SALCs formed from pendant atom atomic orbitals. So, let us again compare this with valence bond approach, so in case of valence bond approach we did not do SALCs like this. So, instead what we did, we picked up the atomic orbitals of central metal atom or central atom and then we created the hybrid orbitals of those.

And then we match the symmetry of those hybrid orbitals with the atomic orbitals of pendant atoms, pendant atoms atomic orbitals and those were matched. In case of localized what we did? So, we did hybridization here at the central atom and we did the SALCs of the external and then we matched this thing the symmetries. In case of MO theory, we are taking atomic orbitals here and we are creating SALCs of pendant atoms and then so there is no hybridization involved here.

So, in d localized MO that is the basic difference. So, maybe in the end we will just write down the summary of all three so that it is very very clear. But let us go on with what we were saying that how group theory rules are used in MO approach. So, group theory rules to determine the symmetry of possible SALCs formed from pendant atoms atomic orbitals. And then determine

the SALCs that will combine with which atomic orbital, of course this is on central atom, to form MO's. So, let us define the steps one by one on how to proceed with this. So, let us see.

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SALC

We use GT rules to determine the group of possible SALCs formed from pendant atom AOs. And then determine the SALC that will combine with which AO to form MOs.

Steps

- 1) Use directional properties of potentially bonding orbitals on the outer atoms (shown as vectors) as a basis for rep of the SALCs in the point group of the molecule.
- 2) Generate a red. rep for all possible SALCs by noting which of the vectors are shifted or not shifted by each class of symm. operation of the pt. group.
- 3) Decompose the Γ_{red} into component IR reps using reduction formula (or by inspection of character table).

So, use directional properties of potential or potentially bonding orbitals on the outer atoms or pendant atoms. In some books you will see it is written as outer atoms, in some books it will be pendant atoms. This will be shown as vectors, we will see that when we will describe it, as a basis for representation of the SALCs in the point group of the molecule. So, we will explicitly see what it means.

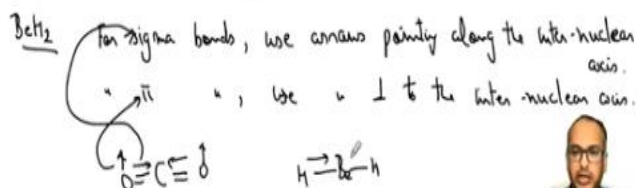
But let us first list down what we are going to do. So, that you have some idea of this thing. So, second step is, once you have determined what is the basis you are going to take, then you will generate a reducible representation. Generate a reducible representation for all possible SALCs and this we will not write explicit matrices under each symmetry operation; we will simply do this by noting which of the vectors are shifted or not shifted by each class of symmetry operation of the point group.

So, once you have generated the reducible representations what will be the next? Next, we will have to decompose the reducible representation. So, decompose the tau reducible into its component irreducible representations. Now this can be done using reduction formula or by inspection. If it is an easy case you can just simply do it by inspection or by inspection of

character table, like we did in the case of d infinity h where using reduction formula was not as feasible.

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- 4) determine the sym of potentially bonding MO on central atom by inspecting unit-vector and direct product transformations listed in the character table.
- 5) Central atom AO and pendant atom SALCs with the same symmetry will form both bonding and anti-bonding MO's. (LCAO-MO)
- 6) Central atom AO and pendant atom SALCs with unique symmetry will remain as non-bonding.



So, we simply did it by inspection. So, next is, what is the next step? Now fourth is determine the symmetry of potentially bonding atomic orbitals on central atom. And this is done by inspecting unit vector and direct product transformations. For example, if you are looking at the symmetry of p x orbital, then you have to see that what is the symmetry of x unit vector transformation and if you are looking for a d orbital symmetry.

So, corresponding direct product of xy has to be taken in consideration, transformation this is of course you have to look at the character table, listed in the character table. So, next step would be central atom atomic orbital and pendant atom SALCs with the same symmetry will form both bonding and anti bonding. You can say anti-bonding MO's or else or we can say linear combination of atomic orbitals MO's.

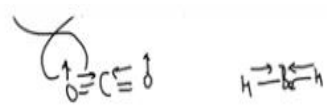
Because this is a linear combination there is no product involved here. Again, so central atom atomic orbital and pendant atom SALCs with unique symmetry let us say some of this cannot match. So, those will be with unique symmetry will remain as non-bonding that is very obvious, non-bonding. So, this should be very clear. So, now let us take the example of BeH₂ again, we have already discussed this example in localized MO theory.

So, now let us see what is the difference when we take delocalized MO theory. So, we said that we have to start with directional let us see we have to so the first step is use directional properties of potentially bonding orbitals on the outer atoms as a basis for representation. So, what is that directional property what do I mean. So, we will say for sigma bonds use arrows pointing along the inter-nuclear axis and for pi bonds we use arrows perpendicular to the inter-nuclear axis.

For example, if you want to consider the case of CO2 let us say, then the directional property would be something like this. So, you have to consider these arrows, so we will draw it on here. These arrows as the basis set now these are the two outer or the pendant atoms and this is the central atom. So, we are considering the formation of SALCs using these two orbitals which are the pi orbitals of this.

Now you have to consider perpendicular arrows which are perpendicular, but for sigma bonds you have to consider like this. So, these arrows are for sigma bonds and these arrows are for pi bonds. So, this should be very very clear. Now for in case of BeH2, we only have sigma bonds so we will consider BeH2. So, we will consider only these arrows which are along the inter-nuclear axis. And we will use these two arrows to create a tau reducible under d infinity h point here.

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$D_{\infty h}$	σ_g	$2\sigma_g$...	σ_u	i	$2\sigma_u$...	σ_g
Γ_{red}	2	2		2	0	0		0

$\Gamma_{red} = \Sigma_g^+ + \Sigma_u^+$

Apply PO for the two IR reps on $1s_A$ & $1s_B$ orbitals of H_A & H_B .

$\rho_g^{\sigma} (1s_A) = \frac{1}{\sqrt{2}} (1s_A + 1s_B) = \phi_g$

$\rho_u^{\sigma} (1s_A) = \frac{1}{\sqrt{2}} (1s_A - 1s_B) = \phi_u$



So, let us see what do we have. So, $D_{\infty h}$ point group E , $2C_{\infty}$, $\infty \sigma_v$, i , $2S_{\infty}$, ∞C_2 , this we have already seen. So, this is τ reducible using these arrows as the basis and under E these arrows would not change, under C_{∞} also these arrows would not change. So, you will get to σ_v the arrows would not change, i that is both arrows will change $0, 0$.

Now this τ reducible by inspection, it reduces to σ_g plus σ_u plus, this also we have seen in the last lecture. Now either you can apply projection operator or you can again by inspection you can do that. But standard in this particular case it is difficult to apply, but you can still do that. So, apply projection operator for the two IR representations on $1S_A$ and $1S_B$ orbitals of H_A and H_B .

See actually you do not need to apply projection operator. Because if you are combining $1S_A$ and $1S_B$, you know that if you combine these orbitals in 1 is to 1 ratio you will get totally symmetric. And if you subtract one from the other you will get σ_u as the basis. So, you can just simply do that or you can go methodically and then you can actually apply projection operators, which will be difficult, but you can still manage to do that.

So, if you do that summation σ_g plus applied on the $1S_A$, you will get after normalization $1/\sqrt{2} (1S_A + 1S_B)$. And we can call this set of SALCs ϕ_g . So, g because this is coming from gerade symmetry. Now again projection operator from σ_u plus applied on $1S_A$ or $1S_B$, you can apply on any of this after normalization, it will give you $1S_A - 1S_B$ and this we will call as ϕ_u , this is just for nomenclature.

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$$\Gamma_{\text{red}} / \begin{array}{cccccc} 2 & 2 & & 2 & 0 & 0 & 0 \end{array}$$

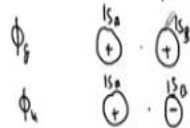
$$\Gamma_{\text{red}} = \Sigma_g^+ + \Sigma_u^+$$

Apply PO for the two IR reps on $1s_A$ & $1s_B$ orbitals of H_2 & H_2^+ .

$$P_1^{\Sigma_g^+}(1s_A) = \frac{1}{\sqrt{2}}(1s_A + 1s_B) = \phi_g$$

$$P_2^{\Sigma_u^+}(1s_A) = \frac{1}{\sqrt{2}}(1s_A - 1s_B) = \phi_u$$

Pictorially, SALCs can be represented as



Now what happens we can also draw this pictorially. So, pictorially, this will be easy to see, SALCs can be represented as so you have ϕ_g which is plus, this is $1s_A$ combined with plus of $1s_B$. So, same phase of the two orbitals are combining to give you ϕ_g , whereas opposite phase which is represented as plus and minus this has nothing to do with electron, electronic charge or something. So, this is plus this is just the phase of the wave function with a negative phase, this is again $1s_A$ and $1s_B$.