Ligand Group Orbitals and Walsh Diagrams

For complicated molecules (more than diatomic), need to first combine subset of atoms (molecular fragment), then combine subsets.

Simpler case: AH_2

Linear example: H–A–H

First take: H – · – H

* note, the resulting two orbitals are nearly identical in energy because of the large internuclear distance (poor overlap).

Then combine:

1s + H_2 LGO

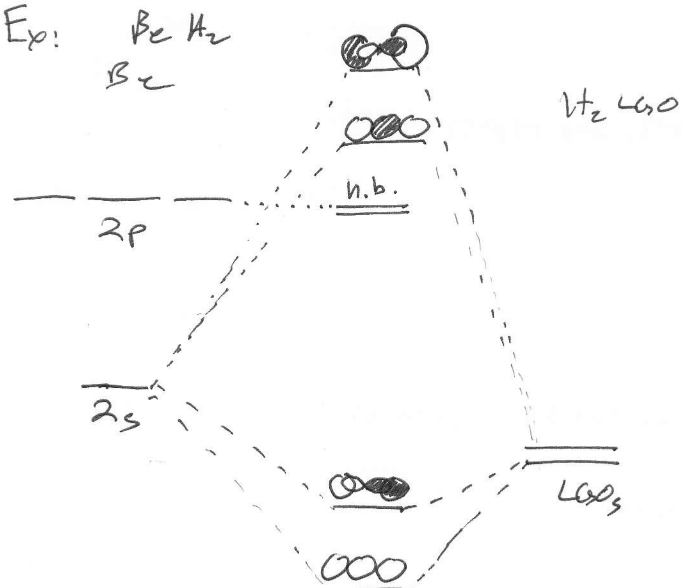
$2p_z$ + H_2 LGO

again, combine based on symmetry overlap, energy matching.

$2p_x$, $2p_y$ orthogonal to both LGOs.

Ex: BeH_2

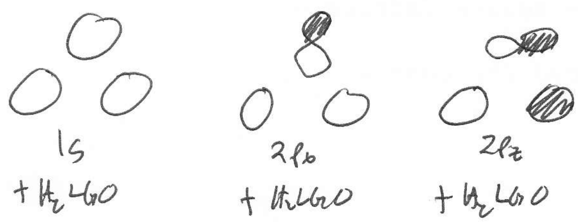
Be



what about bent geometry? H–A–H

Take same H_2 LGOs

Combine based on symmetry.



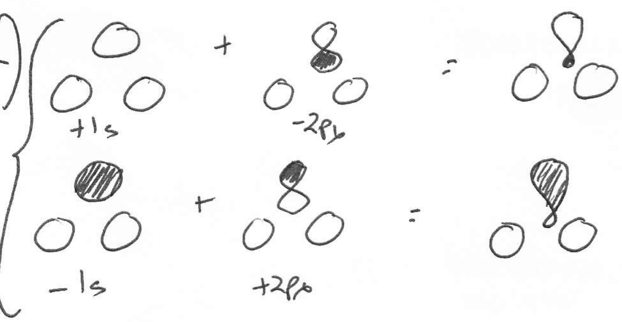
3 a.o.s/LGOs
= 3 MOs

1)

strong bonding

for s-p mixing odd number of a.o.'s/LGOs, need to take all possible combinations.

2)

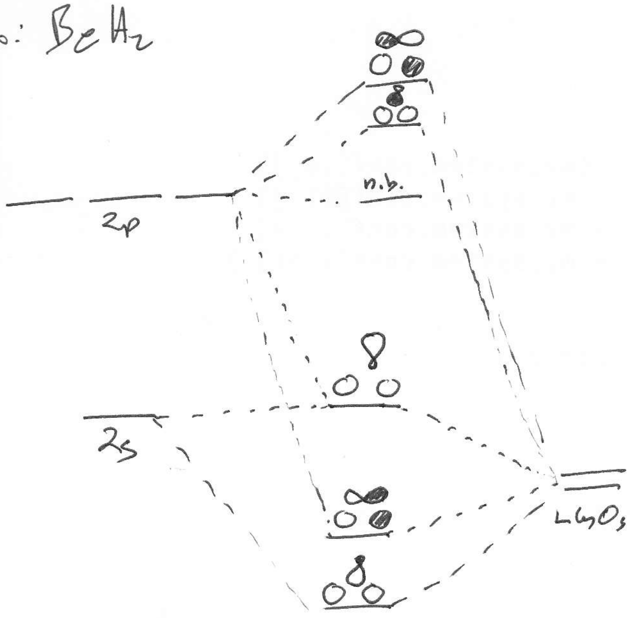


essentially non-bonding (slightly bonding or antibonding).

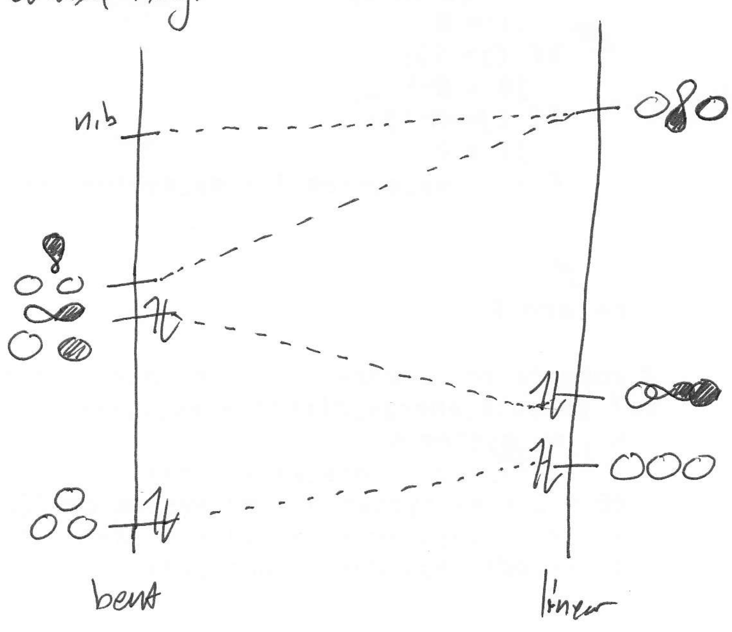
3)

strong antibonding

Ex: BeH_2



Walsh Diagram. (BeH_2)

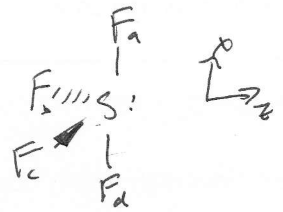


For more complicated molecular fragments, use projection operator method

③

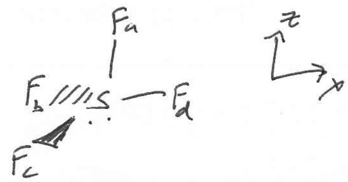
Consider AX_4 molecules:

Ex: SF_4 → possible geometries.



see saw

C_{2v}



trigonal pyramidal

C_{3v}

For C_{2v} configuration:

Generate LGOs for F_4 fragment

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

* caution: isolobal analogy is often, but not always applicable.

we can simplify this by taking an isolobal approach, in which we assume each half filled 2p orbital of F can be represented in symmetry by a s orbital (F_4 fragment has same LGOs as H_4 fragment). (i.e.

always assuming the p orbital points along the bond.

From this:

$$\begin{array}{lcccc} & E & C_2 & \sigma_v(xz) & \sigma_v'(yz) \\ \Gamma_{F_4} = & 4 & 0 & 2 & 2 \end{array} \rightarrow \Gamma_{F_4} = 2A_1 + B_1 + B_2$$

4 a.o.'s = 4 irreducible representations = 4 LGOs.

Now we apply the projection operator to generate LGOs.

$$\hat{P}^{\Gamma_i} = \text{const.} \sum \underbrace{\chi(R)^{\Gamma_i}}_{\text{character of symmetry operation for } \Gamma_i} \underbrace{\hat{R}}_{\text{symmetry operation.}}$$

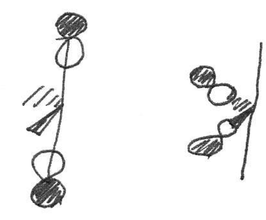
$$\hat{P}^{A_1}(F_a) = \text{const.}\left[1\cdot(F_a) + 1\cdot(F_d) + 1\cdot(F_a) + 1\cdot(F_d)\right]$$

$$= \text{const.}\left[F_a + F_d\right]$$

$\hat{P}^{A_1}(F_d)$ = same result.

$$\hat{P}^{A_1}(F_b) = \text{const.}\left(1\cdot(F_b) + 1\cdot(F_c) + 1\cdot(F_c) + 1\cdot(F_b)\right)$$

$$= \text{const.}\left[F_b + F_c\right]$$



A_1

$$\hat{P}^{B_1}(F_a) = \text{const.}\left(1\cdot(F_a) - 1\cdot(F_d) + 1\cdot(F_a) - 1\cdot(F_d)\right]$$

$$= \text{const.}\left[F_a - F_d\right]$$

$$\hat{P}^{B_1}(F_b) = 0$$

B_1

$$\hat{P}^{B_2}(F_a) = 0$$

$$\hat{P}^{B_2}(F_b) = \text{const.}\left[1\cdot(F_b) - 1\cdot(F_c) - 1\cdot(F_c) + 1\cdot(F_b)\right)\right]$$

$$= \text{const.}\left[F_b - F_c\right]$$

B_2

Combine w/ symmetry matched a.o.'s (read off symmetry functions from character table: $3s = A_1$, $3p_z = A_1$, $3p_x = B_1$, $3p_y = B_2$).
Form MO diagram as before.

How about C_{3v} geometry?

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(xz, yz)$
Γ_{4F}	4	1	2		

$\Gamma_{F_4} = 2A_1 + \underline{E}$ ↳ doubly degenerate ⟼ 4 LGOs.

$$\hat{P}^{A_1}(F_a) = \text{const.}\,[1\cdot(F_a) + 1\cdot(\overset{C_3}{F_a} + \overset{C_3^2}{F_a}) + 1\cdot(F_a + F_a + F_a)]$$

$$= \text{const.}\,[F_a]$$

$$\hat{P}^{A_1}(F_b) = \text{const.}\,[1\cdot(F_b) + 1\cdot(F_c + F_d) + 1\cdot(F_b + F_c + F_d)]$$

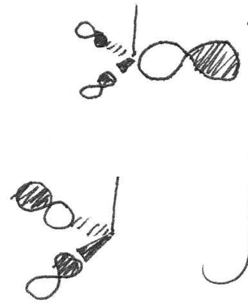
$$= \text{const.}\,[F_b + F_c + F_d]$$

A_1

$$\hat{P}^{E}(F_a) = \text{const.}\,[2\cdot(F_a) - 1\cdot(F_a + F_a)] = 0$$

$$\hat{P}^{E}(F_b) = \text{const.}\,[2\cdot(F_b) - 1\cdot(F_c + F_d)]$$

$$= \text{const.}\,[2F_b - F_c - F_d]$$



E

$$\hat{P}^{E}(F_c) = \text{const.}\,[2\cdot(F_c) - F_b - F_d]$$

$$\hat{P}^{E}(F_d) = \text{const.}\,[2\cdot(F_d) - F_b - F_c]$$

addition yields

subtraction yields $= \text{const.}\,[F_c - F_d]$

Drawing MO diagrams and Walsh diagram for SF_4 complicated, but possible.