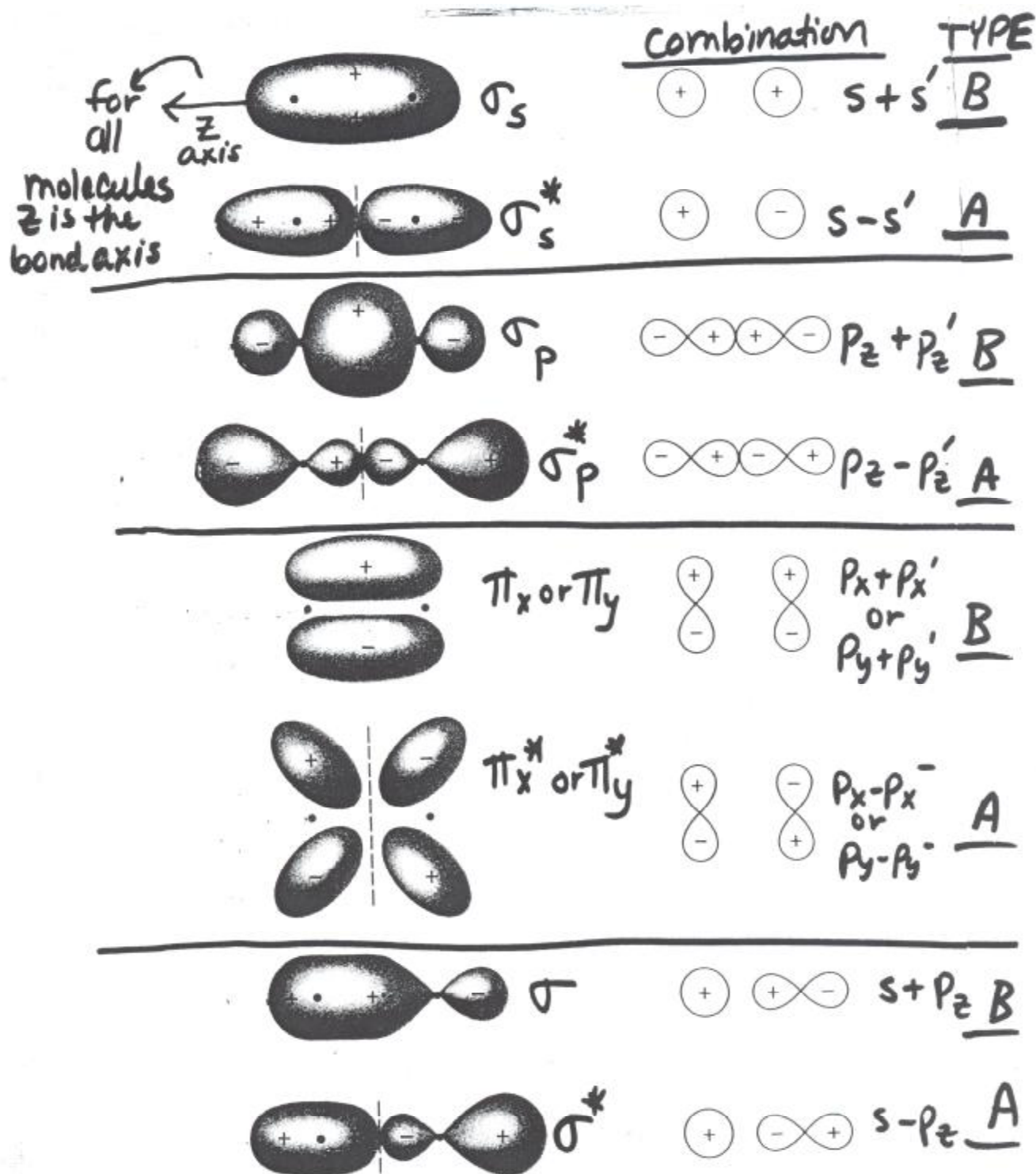


## Ten Important Types of Overlap in General HomoDinuclear M.O.'s



Are there any other possibilities that have gone unmentioned?

Five $s+p_x$  $s+p_y$  $p_x+p_y$  $p_x+p_z$  $p_y+p_z$ Five $s-p_x$  $s-p_y$  $p_x-p_y$  $p_x-p_z$  $p_y-p_z$ 

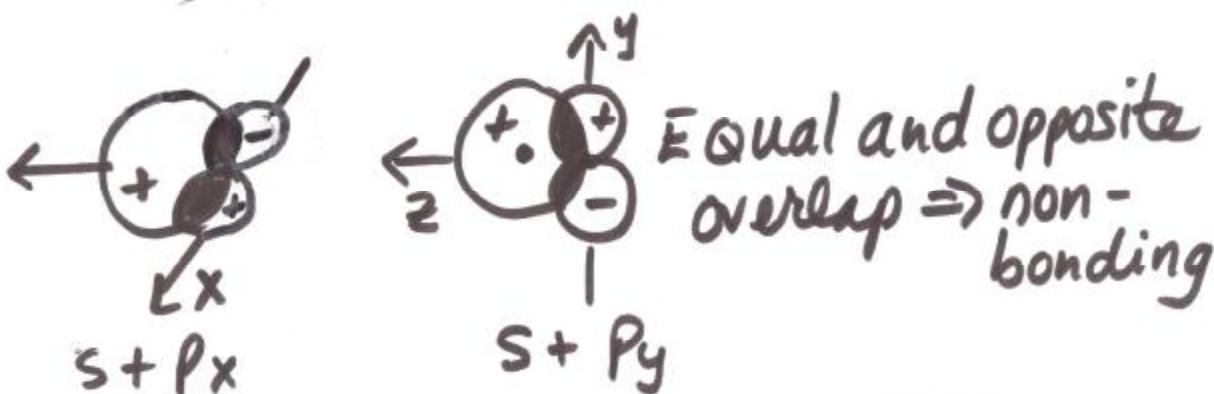
Q.

What about these?

A.

They are zero overlap

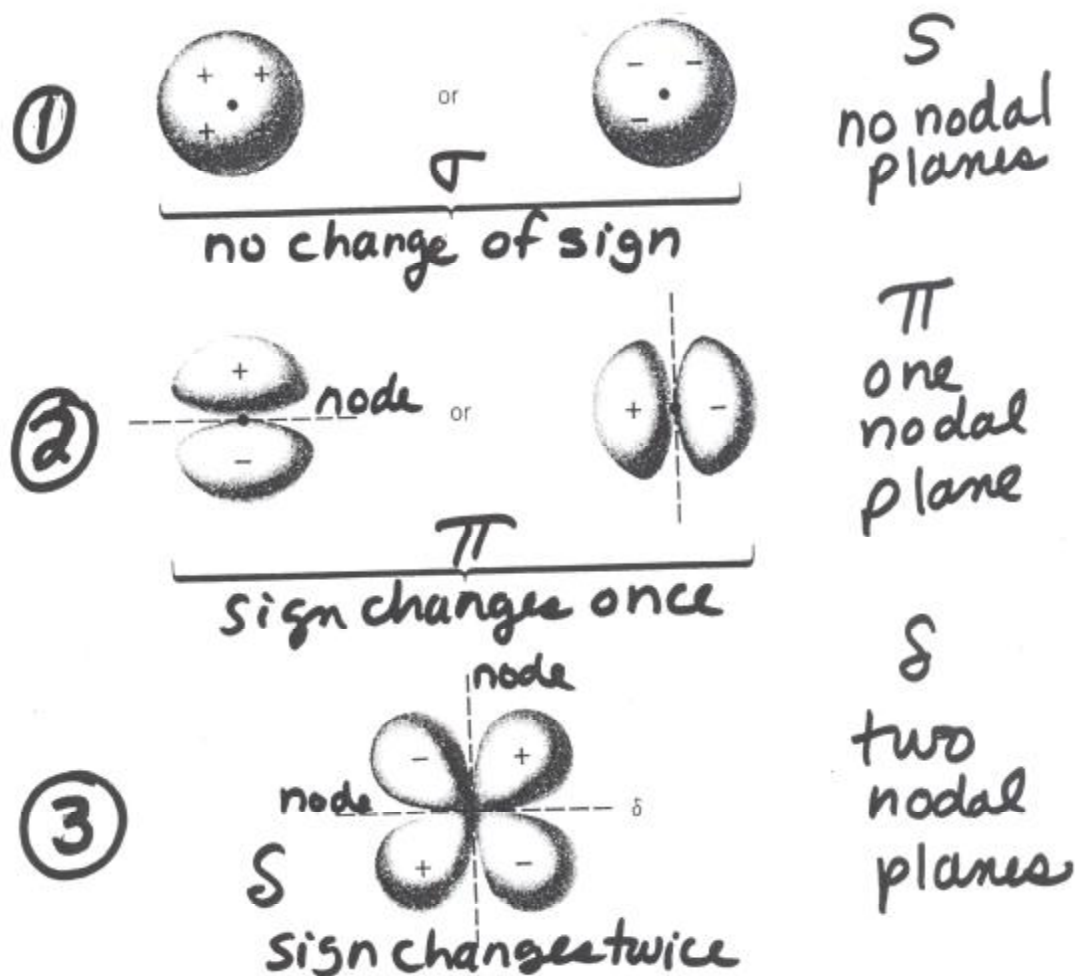
We define internuclear bond axis as the  $z$  axis. Convention



Whereas...



Due to the three different types of atomic orbitals depicted below, we also have three different types of M.O.'s\*



\*These three types of a.o.'s can combine with one another to give m.o.'s that have zero ( $\sigma$ ), one ( $\pi$ ), or two ( $\delta$ ) nodal planes

$\sigma, \pi, \delta$	bonding
$\sigma, \pi^*, \delta^*$	antibonding

## Examples of Diatomic M.O. Treatment

(1) F<sub>2</sub> Molecule:

F is  $2s^2 2p^5$  valence electrons

Buried, next to nucleus does not participate in bonding

Remember effective nuclear charge increases left → right in periodic table (adding protons to atoms whose electrons are going into the same shell)

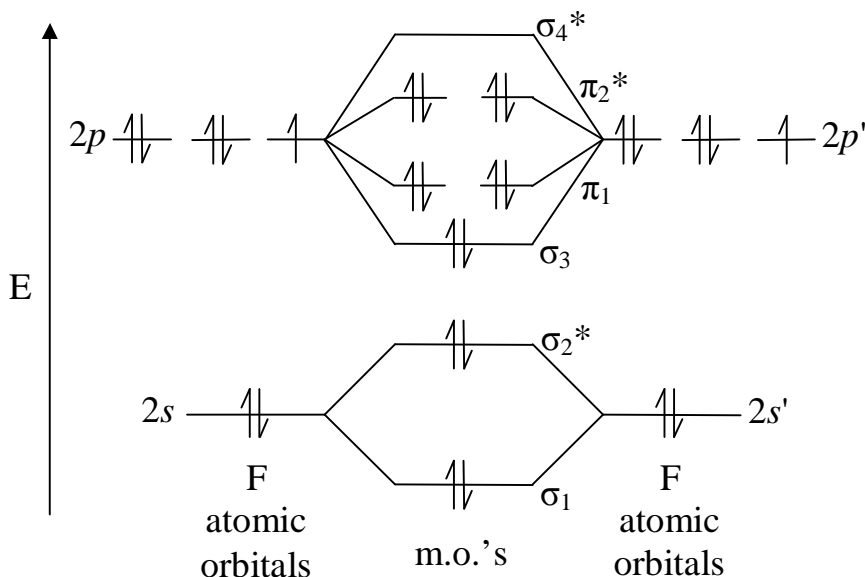
F- effective Nuclear Charge is high

→ 2s/2p orbital energies are therefore quite different (p orbitals are more shielded than s orbitals)

1s – very low in energy

2s – still very low in energy

2p – higher energy due to being more shielded from nuclear charge so their relative I.E. is less



Fill the diagram with the 14 valence electrons (7 from each F)

$F_2$

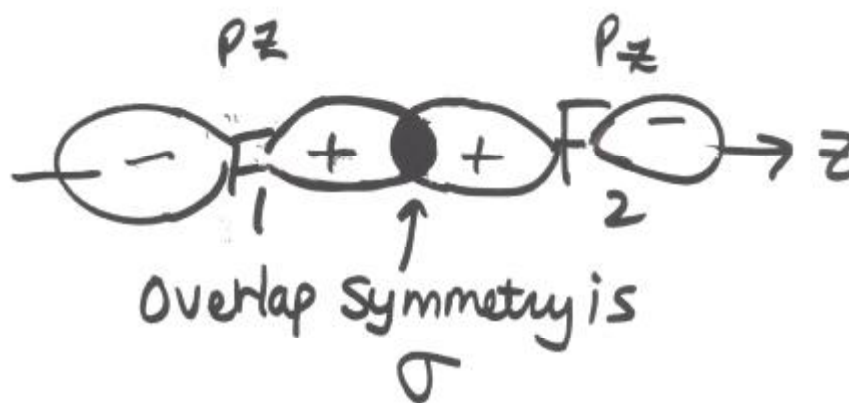
Electronic Configuration is :

$\sigma_1^2 \sigma_2^{*2} \sigma_3^2 \pi_1^4 \pi_2^{*4}$  ( $\sigma$  levels are non degenerate)  
( $\pi$  levels are doubly degenerate)

Net bonding is:

$\sigma_1^2 \sigma_2^{*2} \sigma_3^2 \pi_1^4 \pi_2^{*4}$

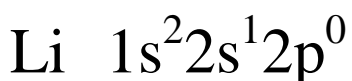
one  $\sigma$  bond based on the  $2p_z \dots 2p_z$  overlap



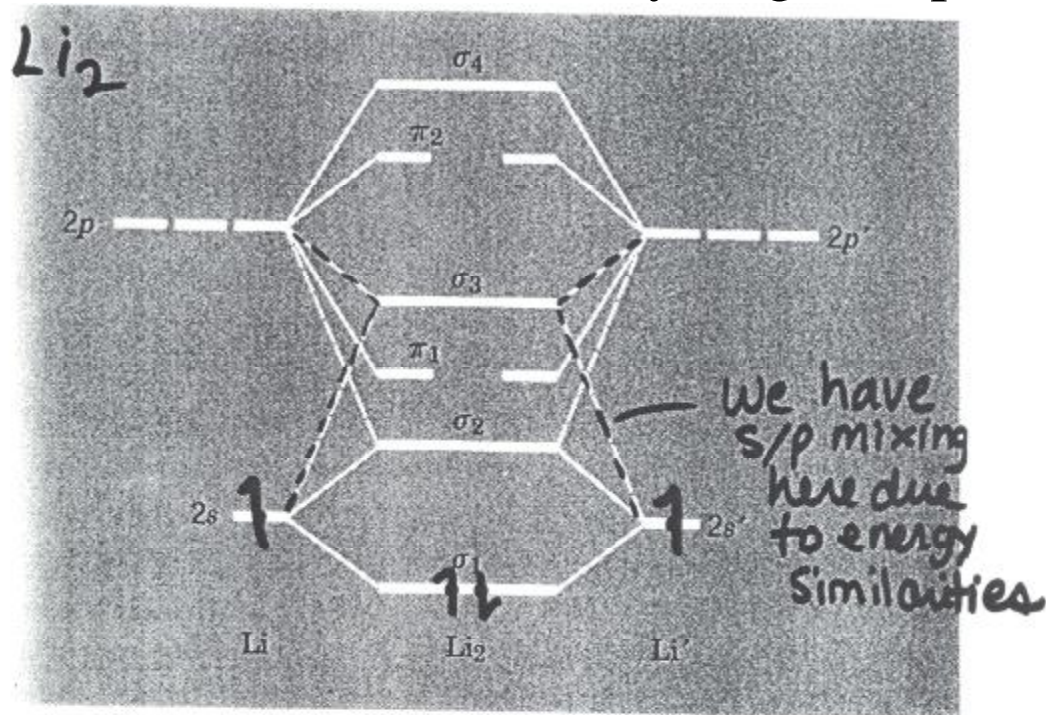
Bond order in MO theory is:  
 $(\text{\# of bonding electrons} - \text{\# of antibonding electrons})/2$   
 $\swarrow$   $2e^-$  per bond

### Example 2 $\text{Li}_2$

Main difference between  $\text{Li}_2$  and  $\text{F}_2$  is that the 2s and 2p separation is much lesser in  $\text{Li}_2$



Need to understand why  $\sigma^3$  goes up

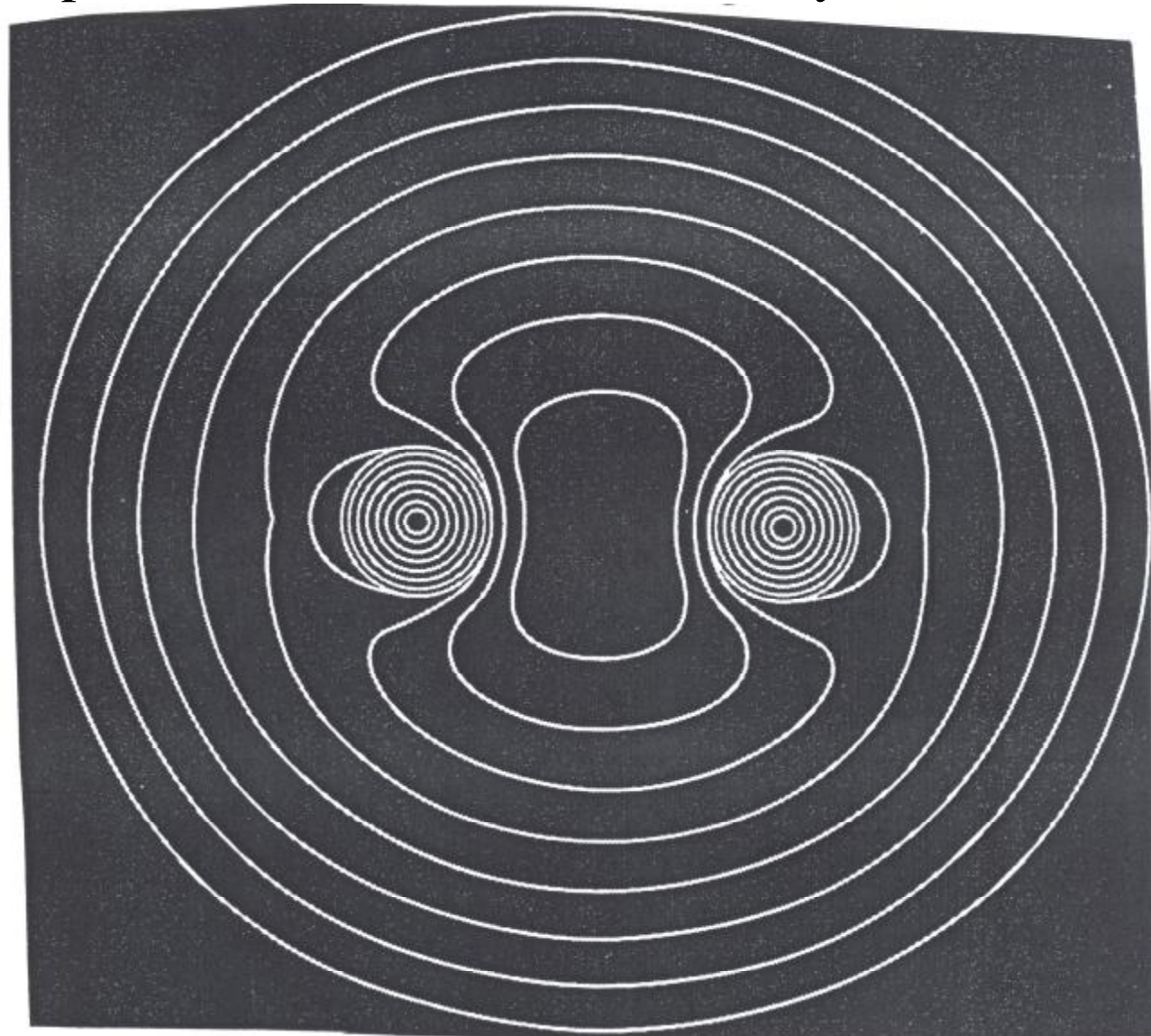


The electronic configuration is  $\sigma_1^2$  based only on s...s overlap. It is a weak bond because s...s overlap is poor (compared say to s-p  $\sigma$  overlap)



$\text{Li}_2$  ( $\sigma$ )

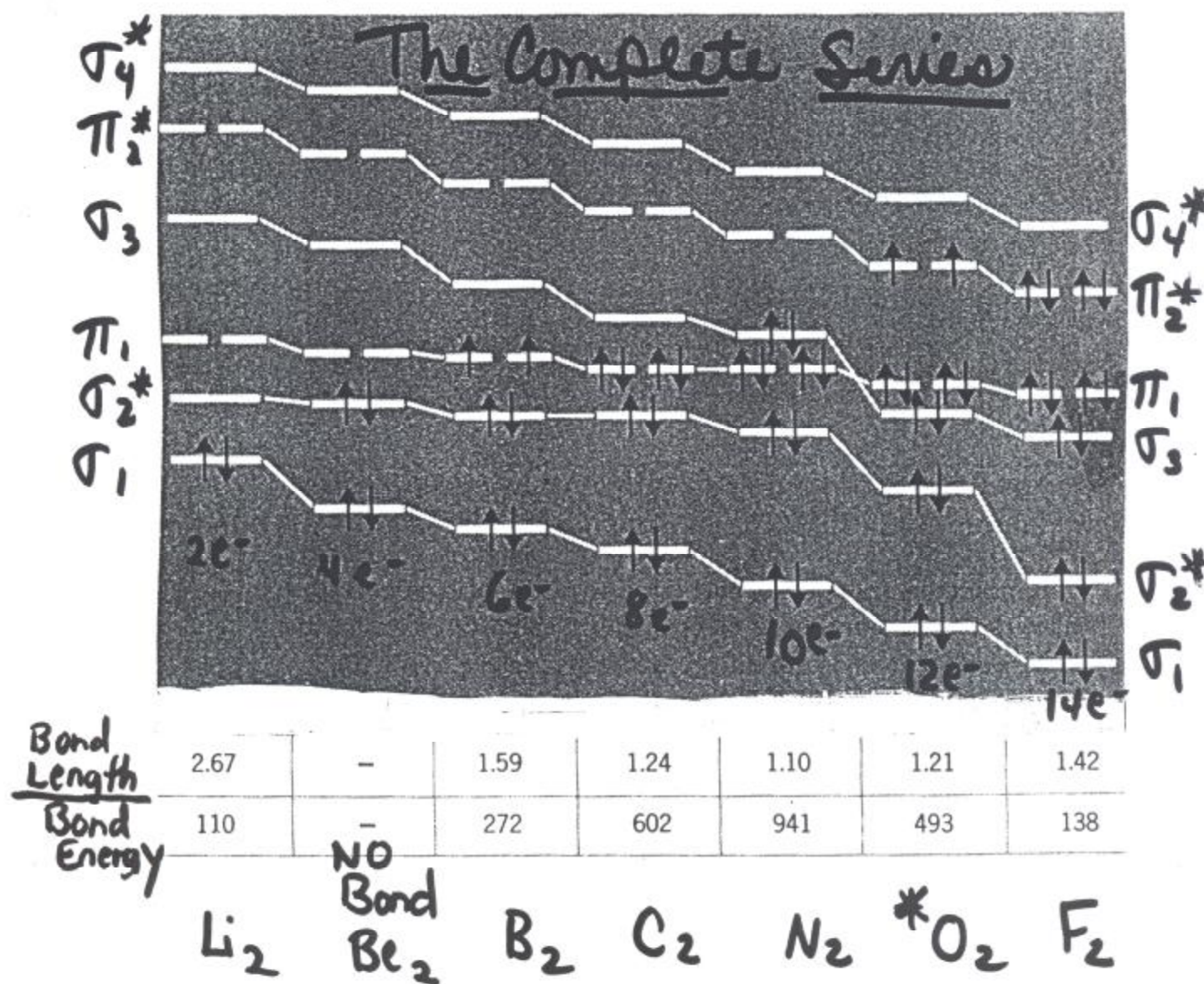
Weak s...s bond looks like this in terms of the electron density contour. Each new contour line as you go in from perimeter is a double of  $e^-$  density



Note: this bond doesn't depend on any of the higher energy M.O.'s

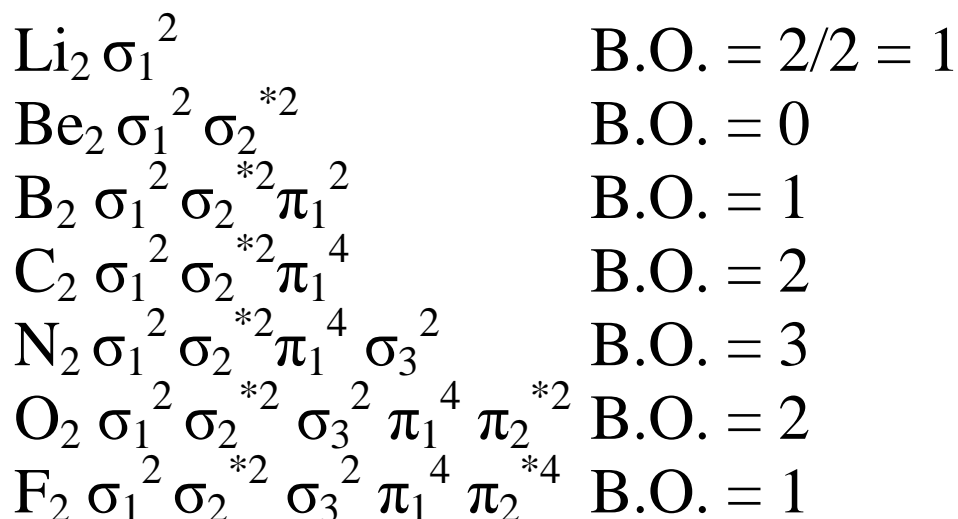
The difference in the separation of 2s and 2p lead to different energy orderings for  $\text{Li}_2 \rightarrow \text{F}_2$

\*Crossing of  $\pi$ , and  $\sigma_3$  occurs at  $\text{O}_2$  when mixing becomes unimportant.





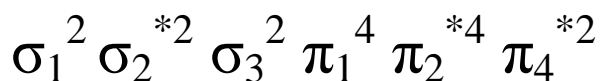
What are the bond order for the series?



- $\text{N}_2$  has highest bond order ( $:\text{N}\equiv\text{N}:$ ), the shortest, and the strongest bond
- $\text{O}_2$  is a double bond and a paramagnetic molecule because the last two electrons go in the  $\pi$  set unpaired
- \*  $\text{O}_2$  Lewis Structure is correct, but it does not predict two unpaired electrons.

Q. What about  $\text{Ne}_2$ ?

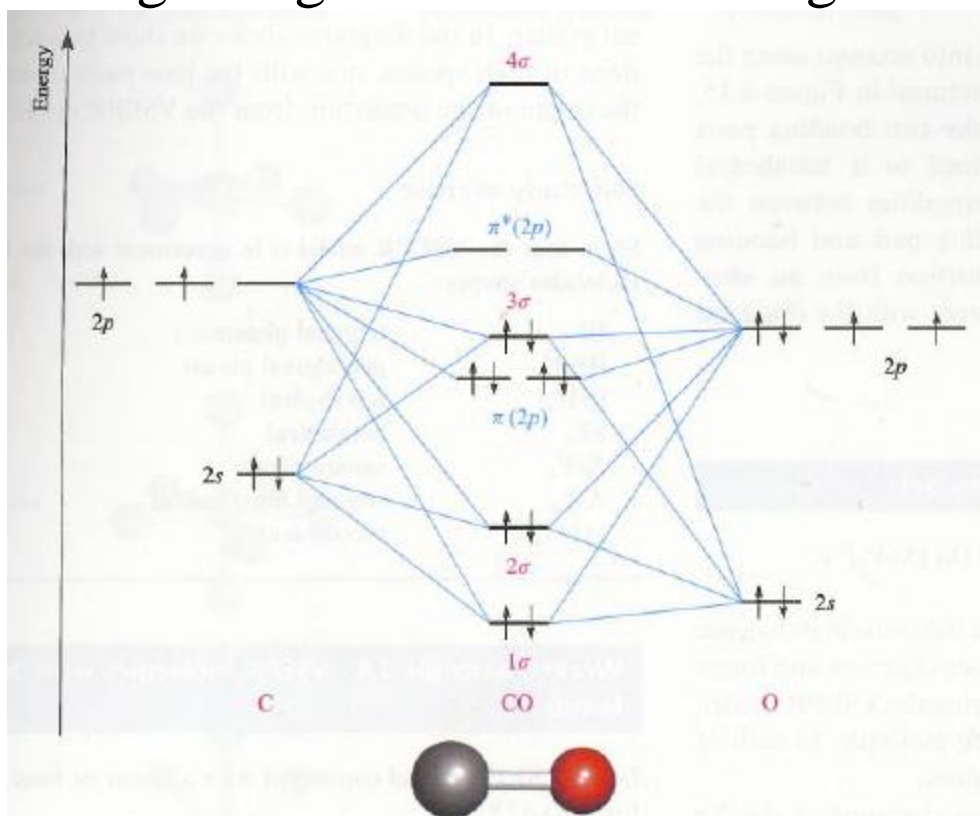
A. This is an unstable molecule:



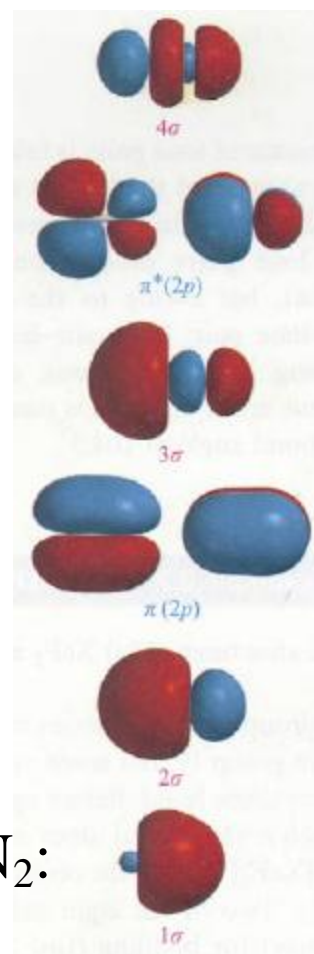
16 valence electrons (B.O. = 0)

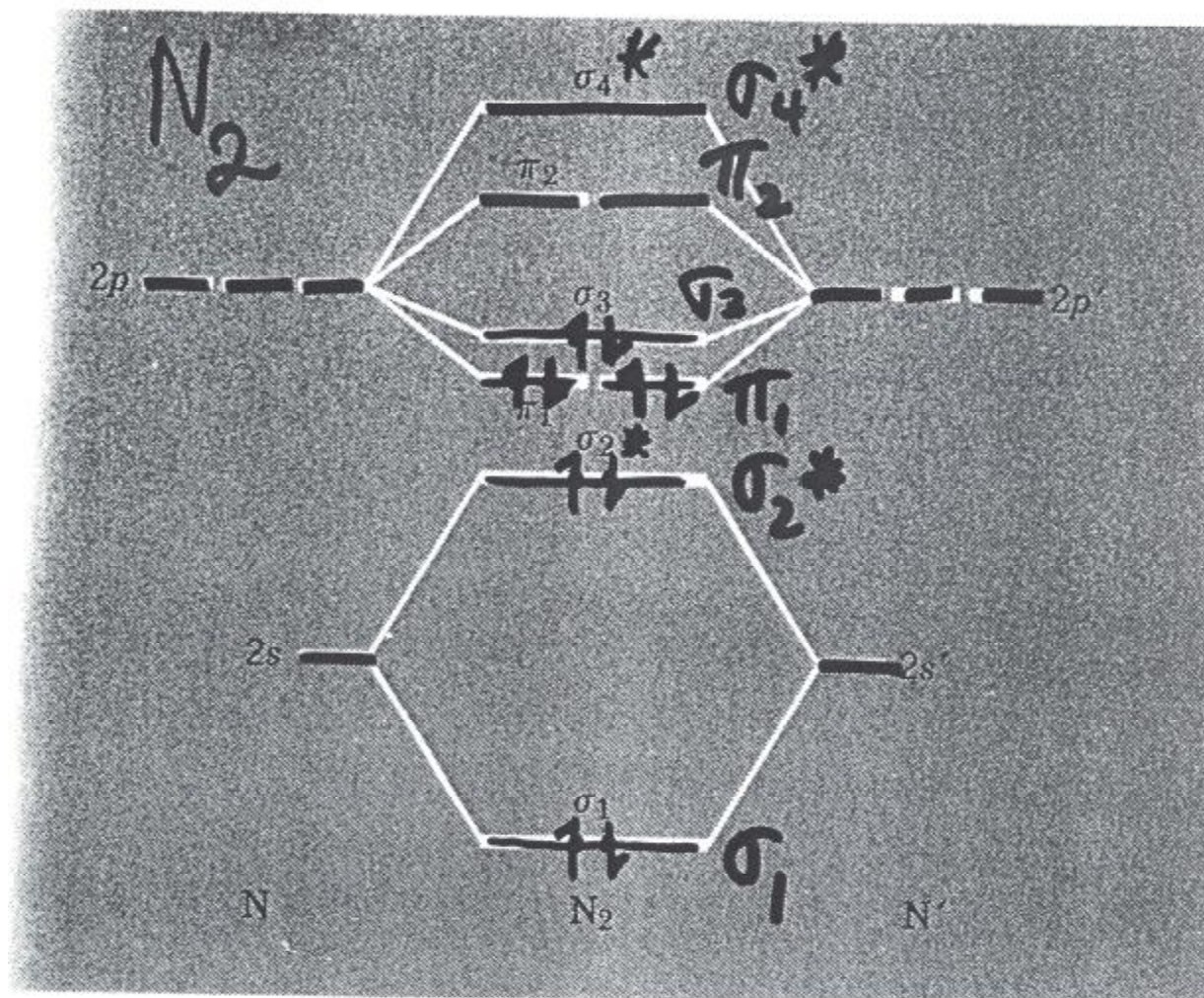
## Heteronuclear Diatomic Molecules

AB rather than  $\text{A}_2$  means that the atomic orbitals no longer begin at the same energies.



Contrast M.O. Diagram for CO with  $\text{N}_2$ :



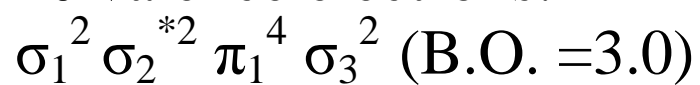


$N_1$   
a.o.'s

M.O.'s  
 $N_2$

$N_2$   
a.o.'s

10 valence electrons:



M.O. Diagrams for the Isoelectronic  $\text{N}_2$  and  $\text{CO}$  molecules are very different. They help explain the different reactivities of  $\text{N}_2$  vs  $\text{CO}$  in a way that Lewis Diagrams never could (or formal charges!)

### $\text{N}_2$

- (1) Highest  $e^-$  are in a strongly bonding orbital  $\sigma_1^2 \sigma_1^{*2} \pi_1^4 \sigma_3^2$ ,  $p_z$ - $p_z$   $\sigma$  orbital
- (2) As a consequence  $\text{N}_2$  is very stable,  $\text{N}_2 \xrightarrow{-e^-} \text{N}_2^+$  weakens the N-N bond. I.E. is very high

### $\text{CO}$

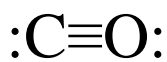
- (1) Highest  $e^-$  are in a slightly antibonding orbital  $\sigma_1^2 \sigma_1^{*2} \pi_1^4 \sigma_3^{*2}$  (higher in energy than the starting a.o.'s)
- (2) As a consequence  $\text{CO}$  is not as stable,  $\text{CO} \rightarrow \text{CO}^+$  actually leads to a strong  $\text{C}\equiv\text{O}$



What does ionization of  $\text{N}_2$  versus  $\text{CO}$  have to do with their activation?

(meaning destroying the molecule or even attaching it as a “ligand” to metals through lone pair)

A. Lewis basicity of  $\text{CO}$  is much higher than  $\text{N}_2$



↗  
This end binds to Lewis acids such as  $\text{M}^+$  ions very easily. The highest energy l.p. is  $\sigma^{*3}$  which is primarily C-based.

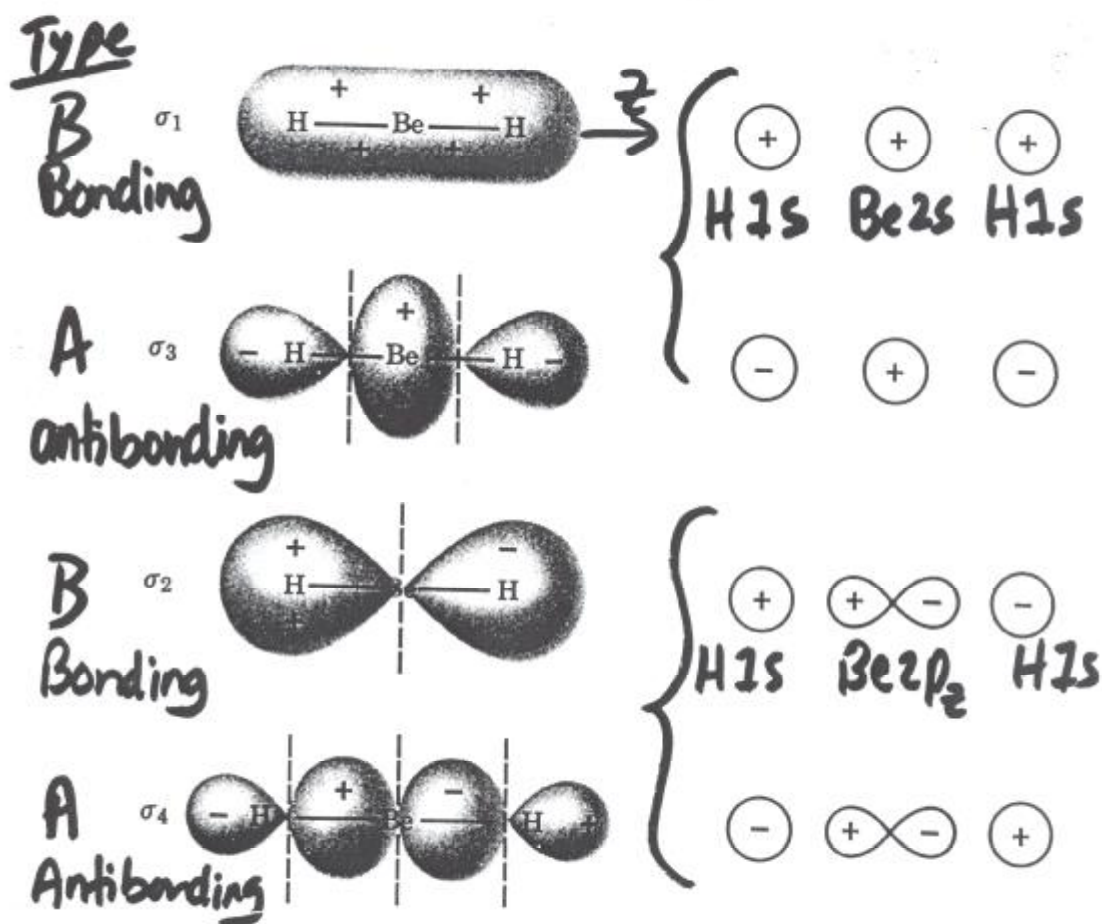


↗  
Very difficult to get this lone pair to donate

(buried in energy!)

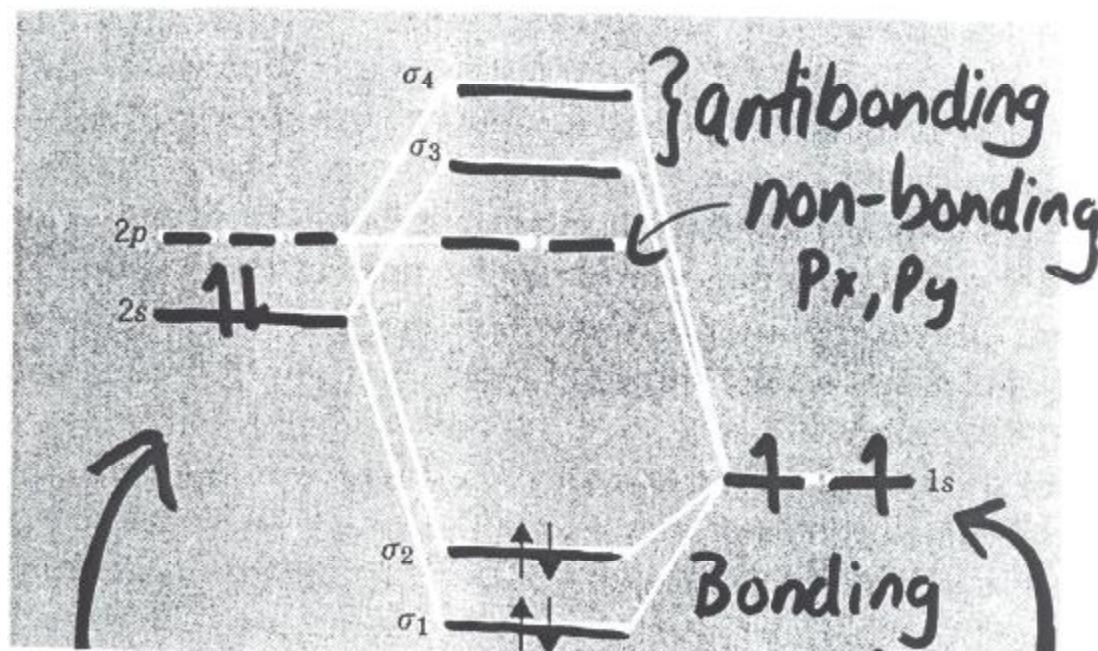
## Extrapolation of M.O. Theory Diatomic to Polyatomic

Linear Triatomics like  $\text{BeH}_2$  which can form only  $\sigma$  orbitals



- 1) In each bonding orbitals, B, The  $e^-$  density is continuous over adjacent atoms, in antibonding orbitals, A, there is a node.
- 2) In each bonding orbital, the electron pair is spread out (delocalized) over entire molecule.

## BeH<sub>2</sub> M.O. Diagram



Main  
Features

Be atom

Two H atoms

One 2s and three 2p orbitals lie at much higher energy than H 1s and they are close together due to lower effective nuclear charge

Two equal energy 1s orbitals are placed in the diagram. They are low in energy due to higher effective nuclear charge.

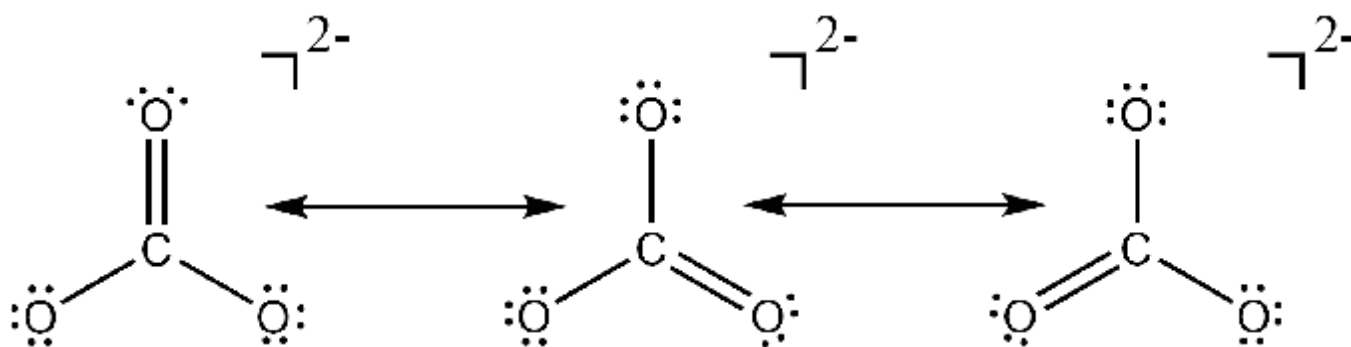
### Bonding in H-Be-H

$\sigma_1^2 \sigma_2^2 = 4$  Bonding electrons Distributed over two Be-H bonds. So two single bonds.

## Trigonal Planar Molecules



Recall, we invoked  $\pi$ -bonding in  $CO_3^{2-}$  and  $NO_3^-$  as part of “resonance” structures like these:



Q. But how does M.O. theory account for  $\pi$ -bonding?

More to the point: Can M.O. theory explain the one  $\pi$  bond in the above structure needing to be in 3 places at the same time?

A. YES!!!

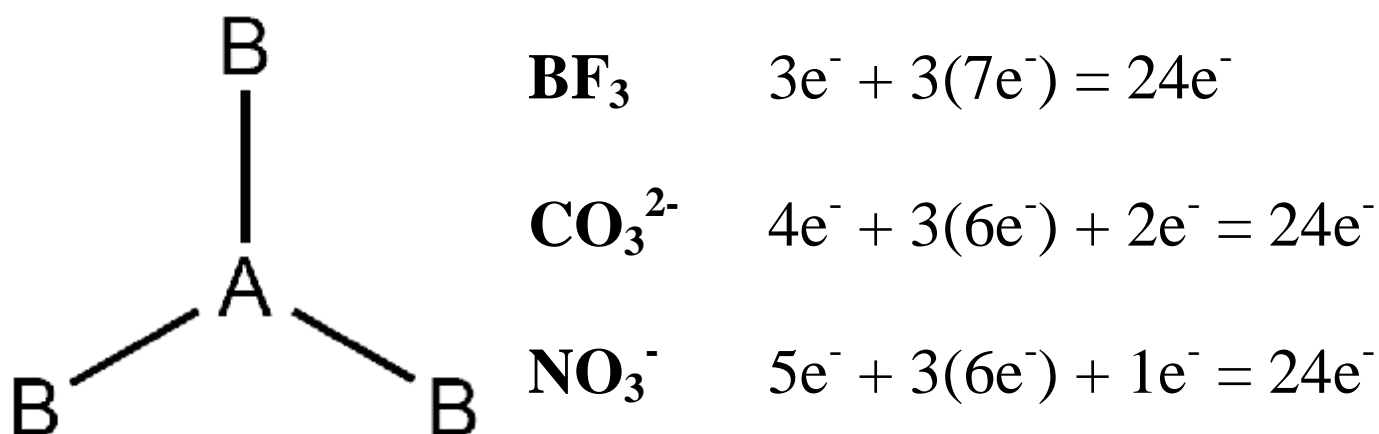


## M.O. Treatment of $AB_3$ planar molecules.

For example  $BF_3$ ,  $NO_3^-$ ,  $CO_3^{2-}$

Requires two different groups of atomic orbitals to be considered.

- 1) Hybrid Orbitals on central atom, A, and on B that will be used to make  $\sigma$ - bonds (A-B bonds) and used to house lone pairs (in plane)
- 2) Group Orbitals on outer atoms, B, that are made of  $p_z$  orbitals (out-of-plane) that can overlap with the  $p_z$  orbital on central atom A.

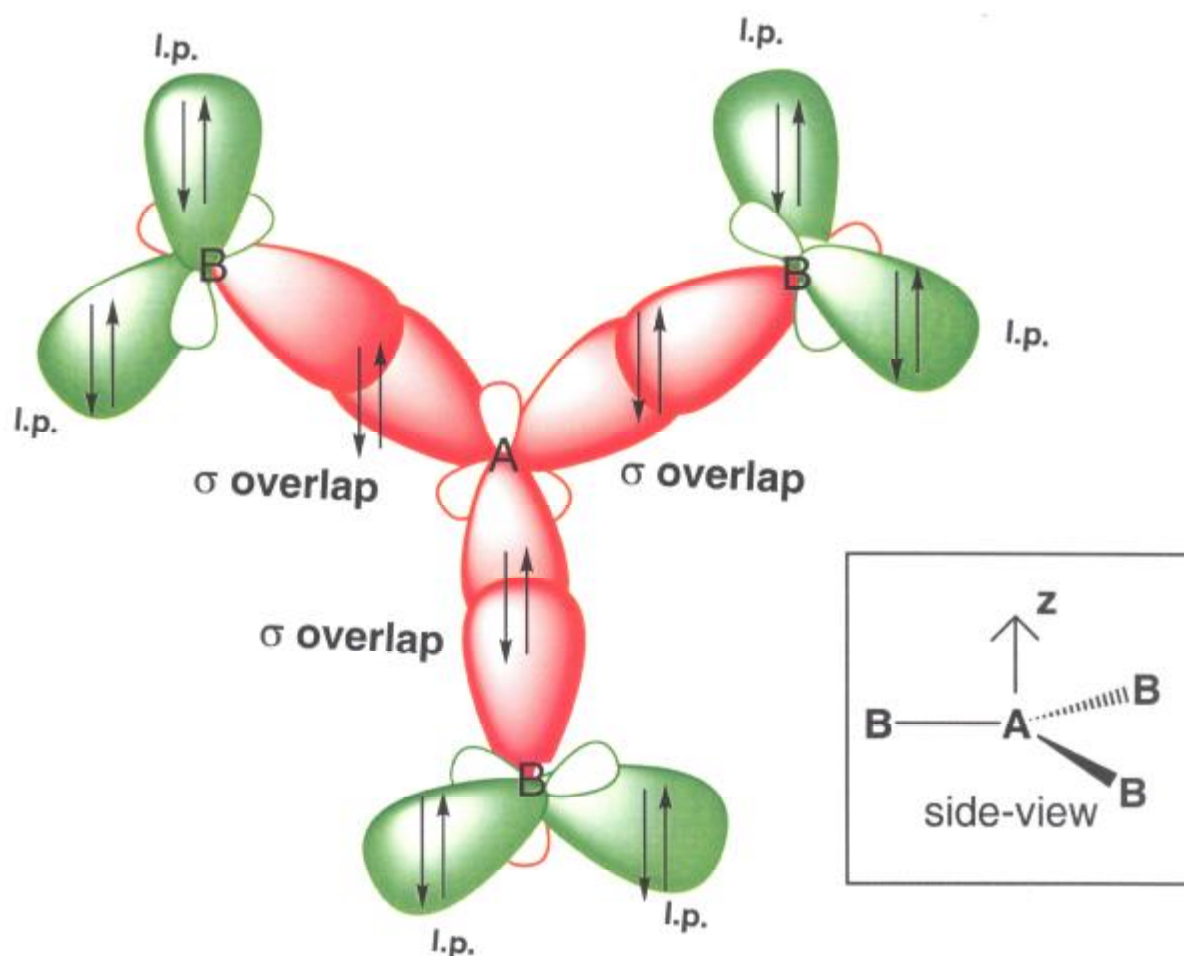


The xy plane is the plane of molecule

The z axis comes out of paper

# STEP 1      $AB_3$      M.O. Treatment

Use  $s$ ,  $p_x$  and  $p_y$  orbitals to make hybrids on all of the atoms

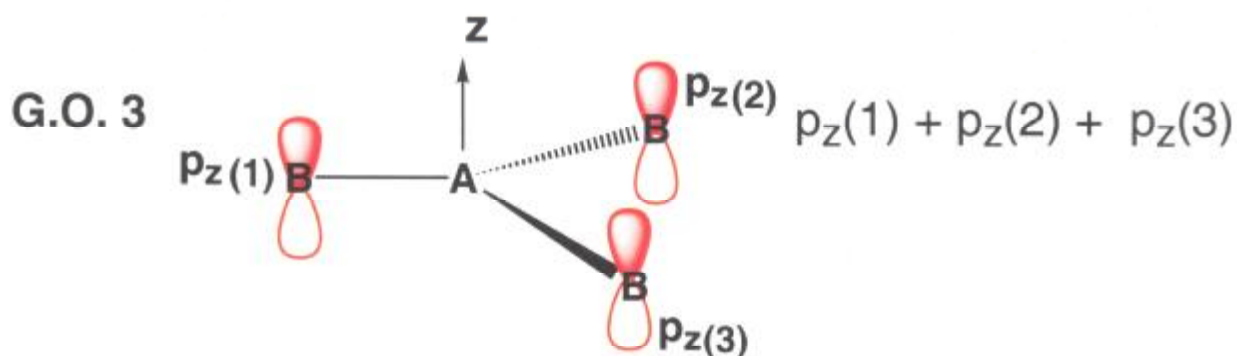
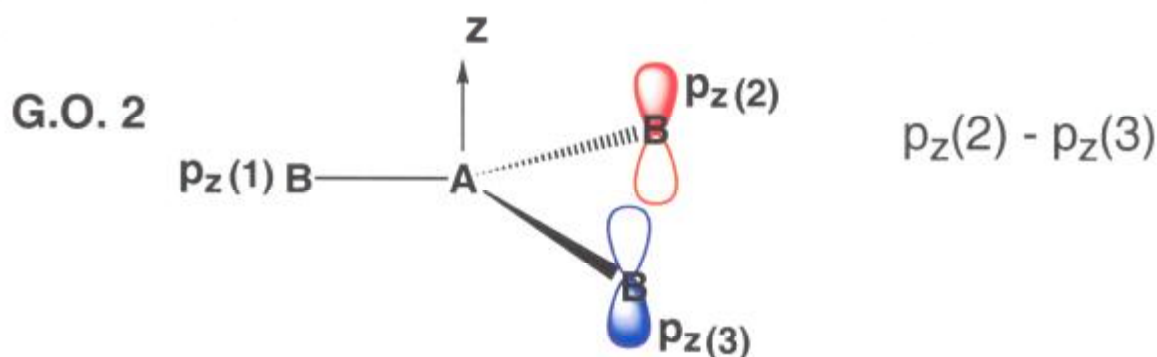
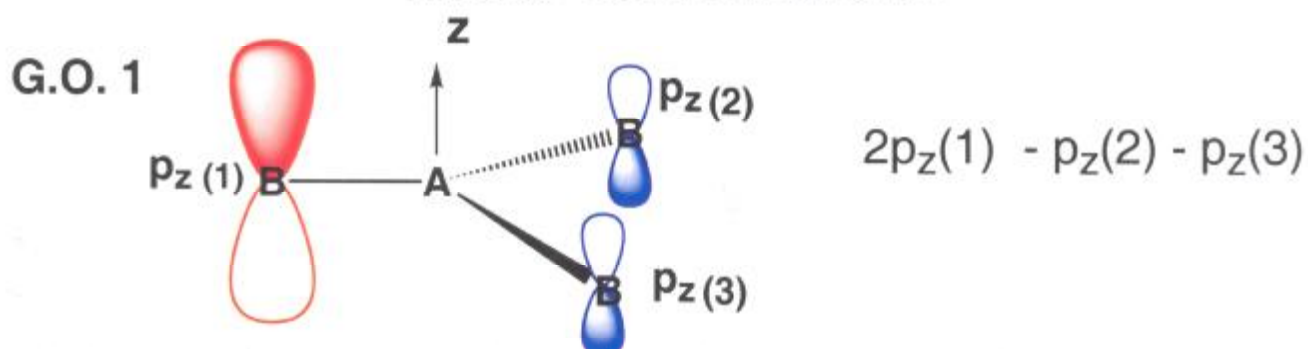


Network of  $sp^2$  hybrids involved in A-B  
bonding or lone pairs (non-bonding)  
in the  $xy$  plane

After all of the bonding pairs and lone pairs  
are placed in the  $sp^2$  hybrids in the  $xy$  plane,  
how many electrons are used?  $18 e^-$

## STEP 2 $AB_3$ M.O. Treatment

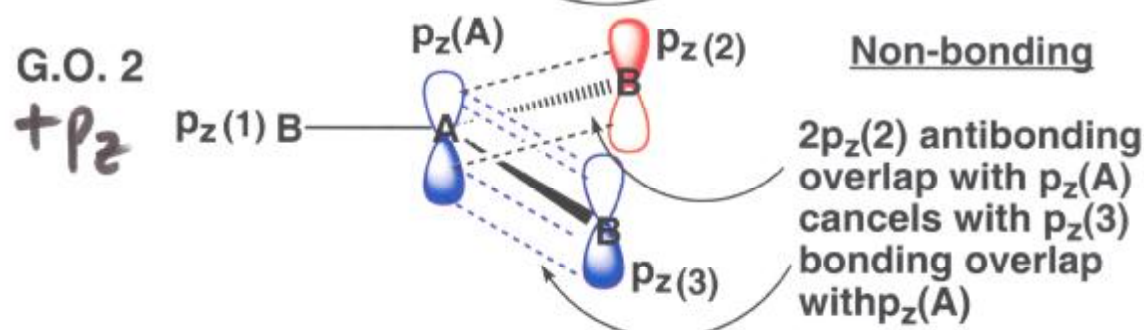
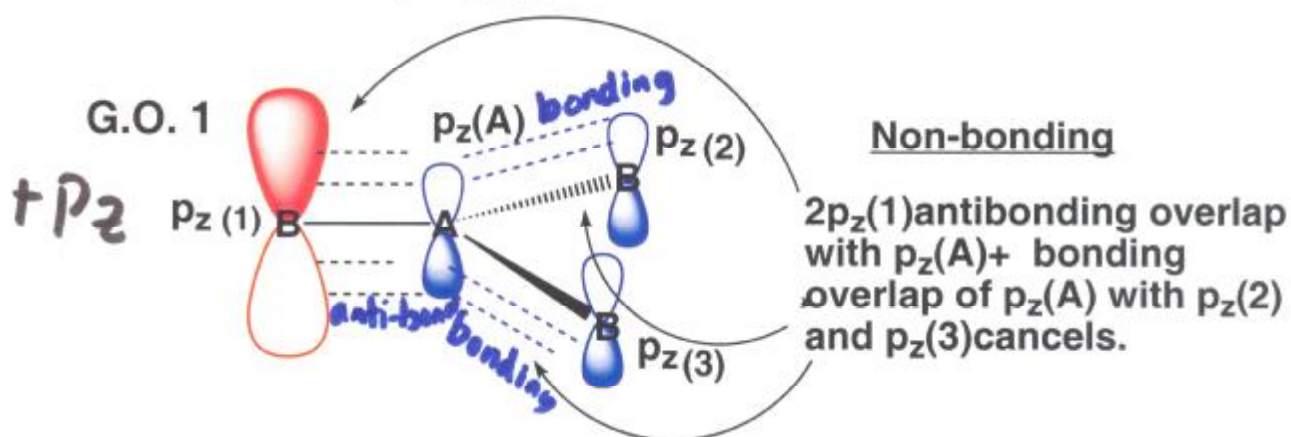
Take remaining unhybridized  $p_z$  orbitals on B atoms and group them by making linear combinations



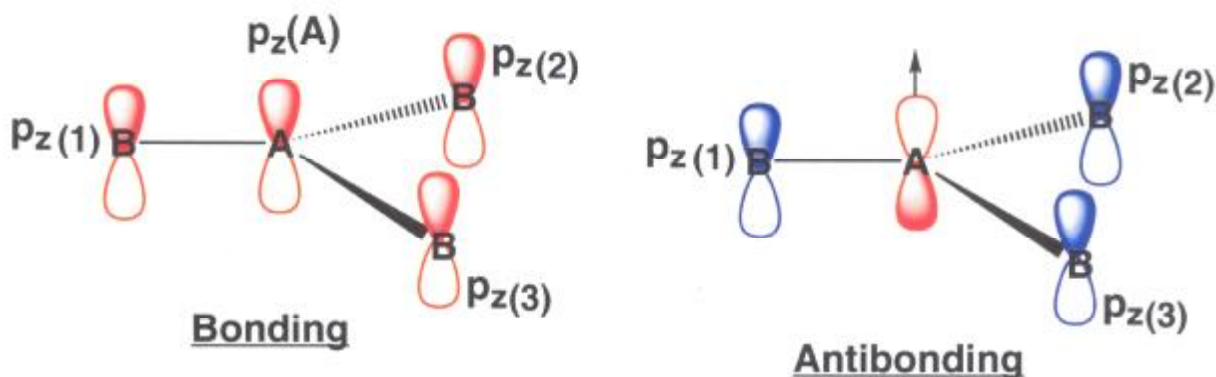
You obtain three group orbitals that can overlap with the  $p_z$  orbital on A to form  $\pi$ -bonds, only one of which is a bonding one

### STEP 3 $AB_3$ M.O. Treatment

Take  $(24 \text{ valence } e^-) - (18 e^-) = 6 e^-$  and use them to make  $\pi$ -bonds by overlap of the central atom, A,  $p_z$  orbital and the three G.O.'s



G.O. 3  
 $+p_z$  Bonding and antibonding Combinations

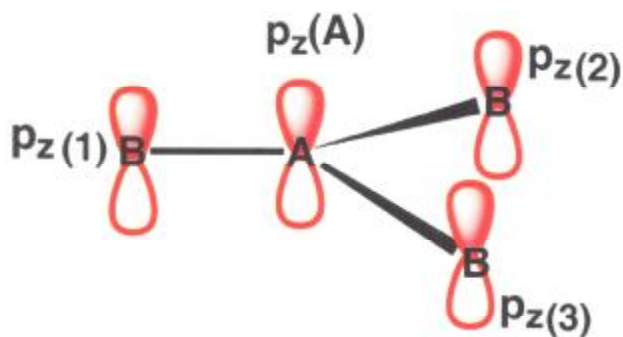


You get four molecular orbitals

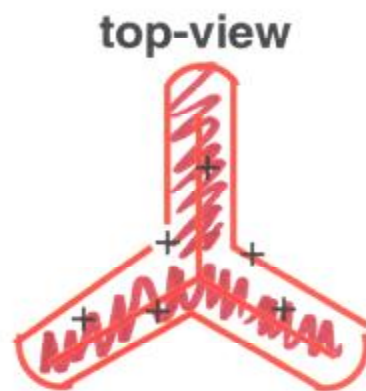


## The $\pi$ M.O.'s in $AB_3$ Molecules that Affect Bonding

### Bonding and antibonding Combinations



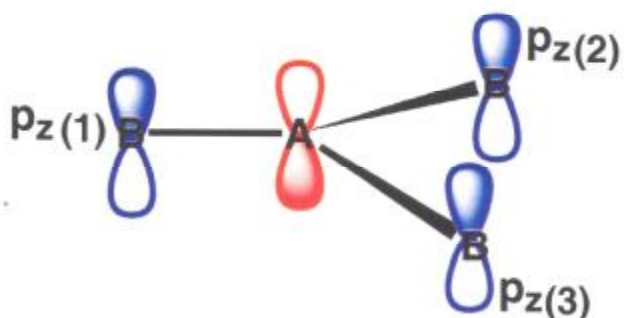
$\pi$  Bonding M.O.



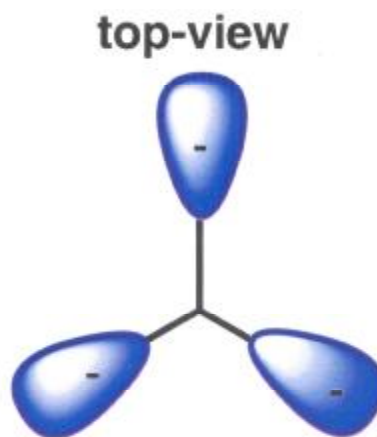
one continuous molecular orbital

if there are two electrons in this orbital, then this will be one  $\pi$ -bond delocalized over three A-B bonds with a  $1/3$  bond order for each A-B  $\pi$ -bond.

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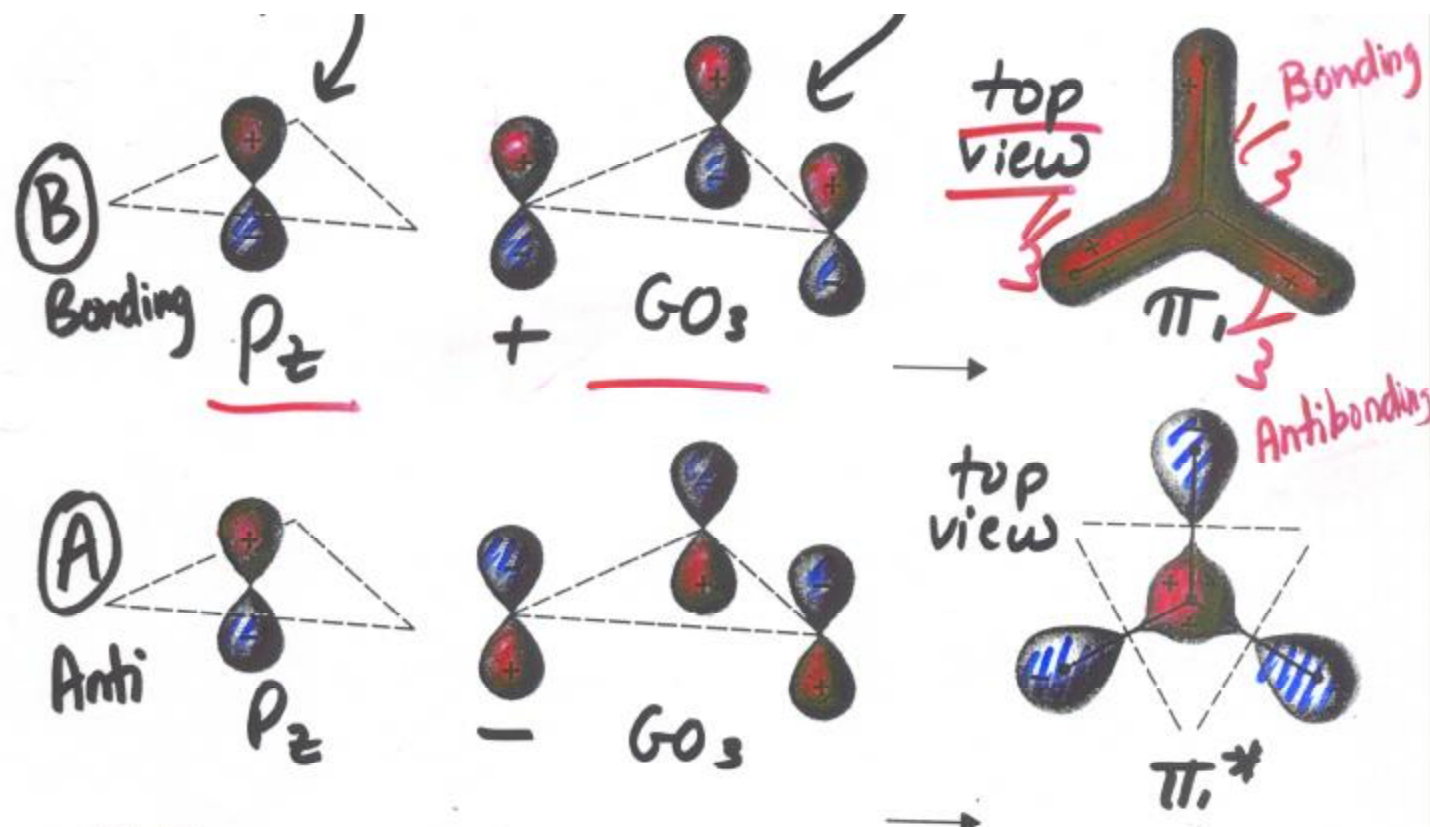


$\pi^*$  Antibonding M.O.



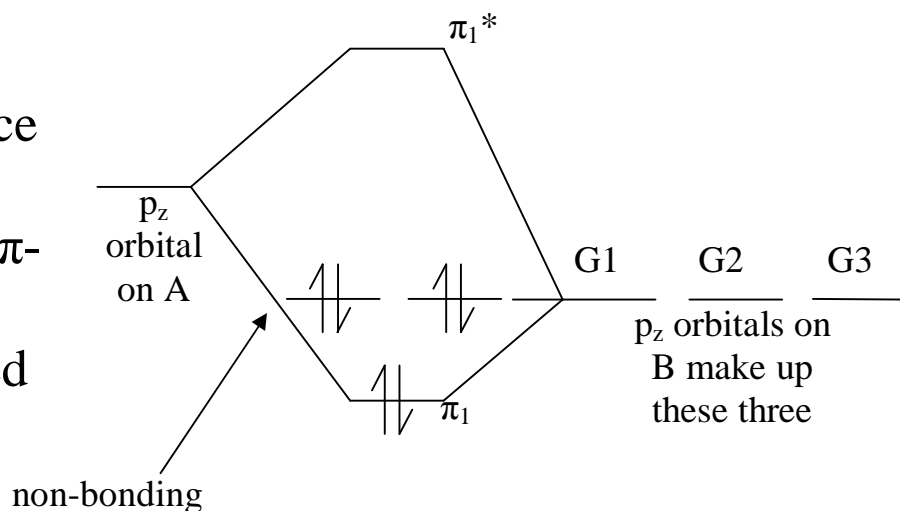
if this M.O. is empty, then it doesn't affect the bonding at all.

Diagrams showing how  $\pi$ - bonding and  $\pi$ - antibonding M.O.'s arise from overlap of G.O.'s with the  $p_z$  Orbital of A.

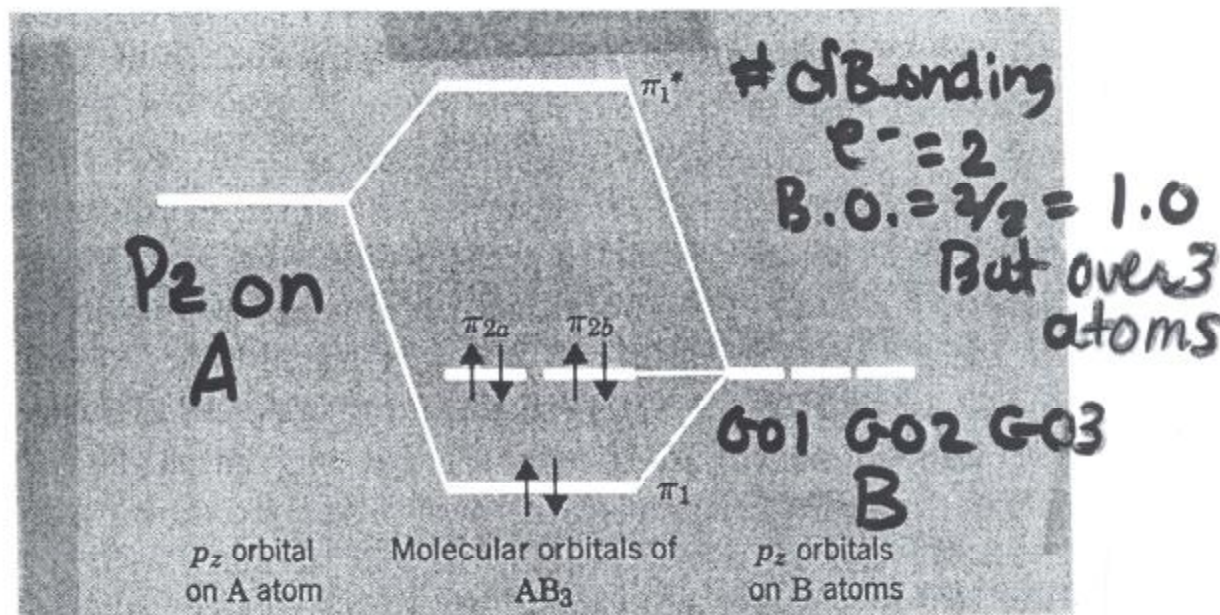


$\text{BF}_3$   
 $\text{CO}_3^{2-}$   
 $\text{NO}_3^-$

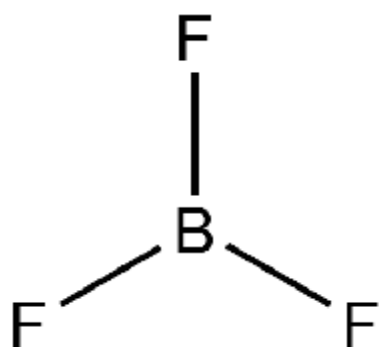
Only 6 valence electrons are available for  $\pi$ -bonding. The  $18e^-$  before this are involved in  $\sigma$  interactions ( $24e^-$  systems).



The part of the M.O. Diagram that depicts the  $\pi$ - bonding is:

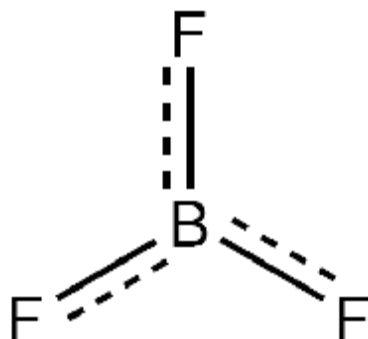


if  $BF_3$  then:



each of these is a single bond based on  $sp^2$  overlap

and



there is  $1/3$  of a  $\pi$  bond (1  $\pi$  bond over 3 atoms)

Note, we did not draw a complete M.O. diagram here with all of the orbitals and interactions. It is too complicated to try and get the relative energies of the starting orbitals and M.O.'s correct.

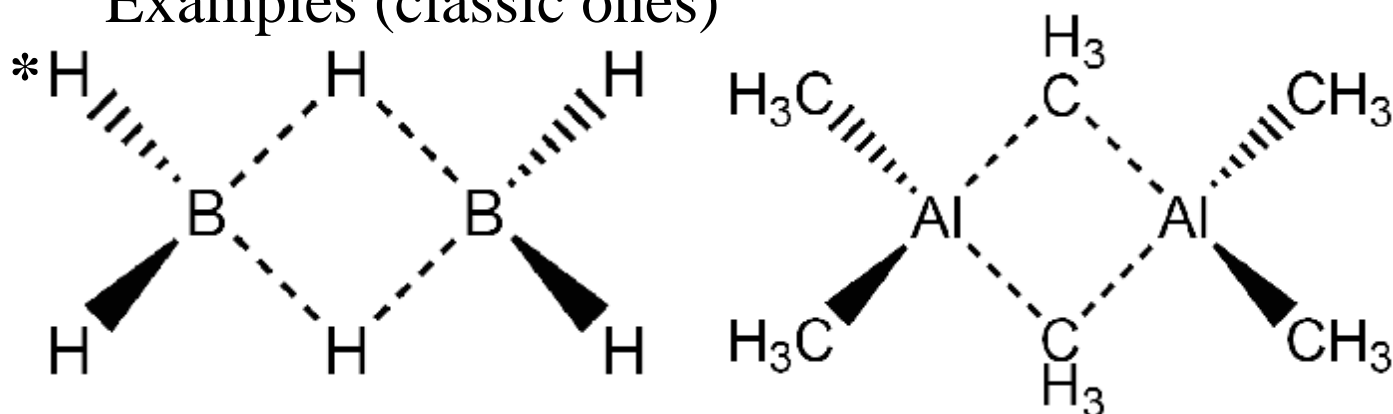
Nevertheless, we succeeded in developing a qualitative picture of the bonding that holds true for these types of molecules.



## Multi-Center Bonding in Electron Deficient Molecules

This happens when you don't have enough electrons to have a two-electron bond between all adjacent atoms.

Examples (classic ones)



There are eight adjacent pairs of atoms in these molecules but count electrons...

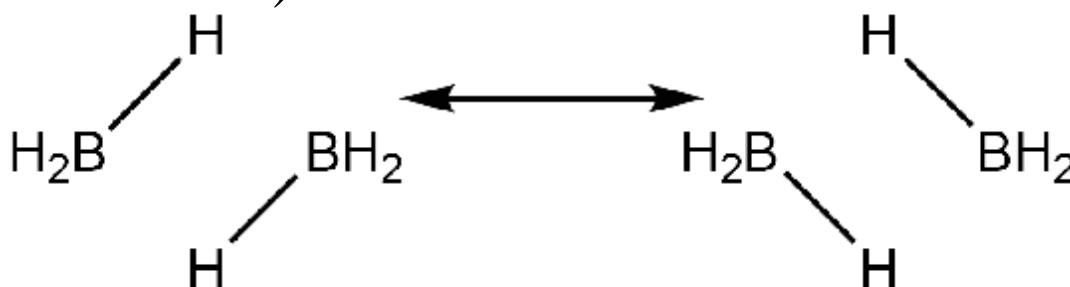
2B  $6e^-$  (3 each)

H  $6e^-$

$12e^-$

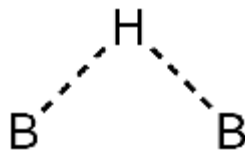
You need  $16e^-$  to make  
8 bonds but you have  
only  $12e^-$  which is only  
enough for 6 bonds

\*These are not planar  
(note that  $BH_3$  and  $Al(CH_3)_3$  are not really the way the formulae indicate)



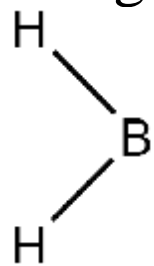
Consider these two resonance forms (canonical forms)

This implies that in each  
electron pair is shared  
distributed over) two B•••H bonds.



bridge, that one  
between (or

This would lead to a bond order of  $\frac{1}{2}$  for each B•••H  
 bridge bond but still result in the other two



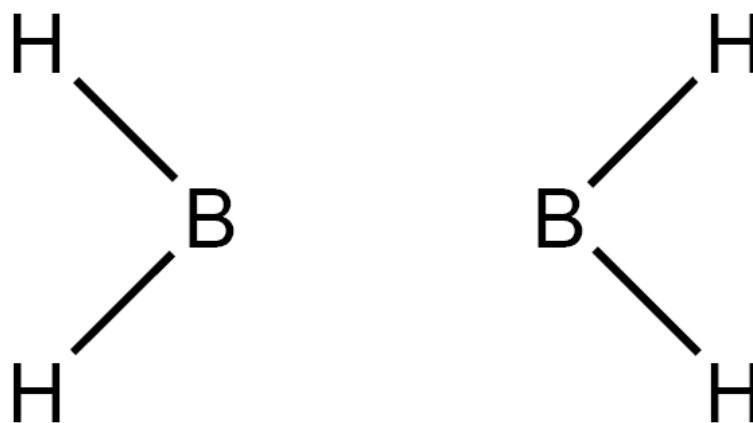
bonds being normal  $2e^-$  bonds.

Q. Doesn't this seem a little artificial to you?

A. Yes. There is a better way to think about this with M.O. theory

B has  $sp^3$  hybridization for tetrahedral Boron

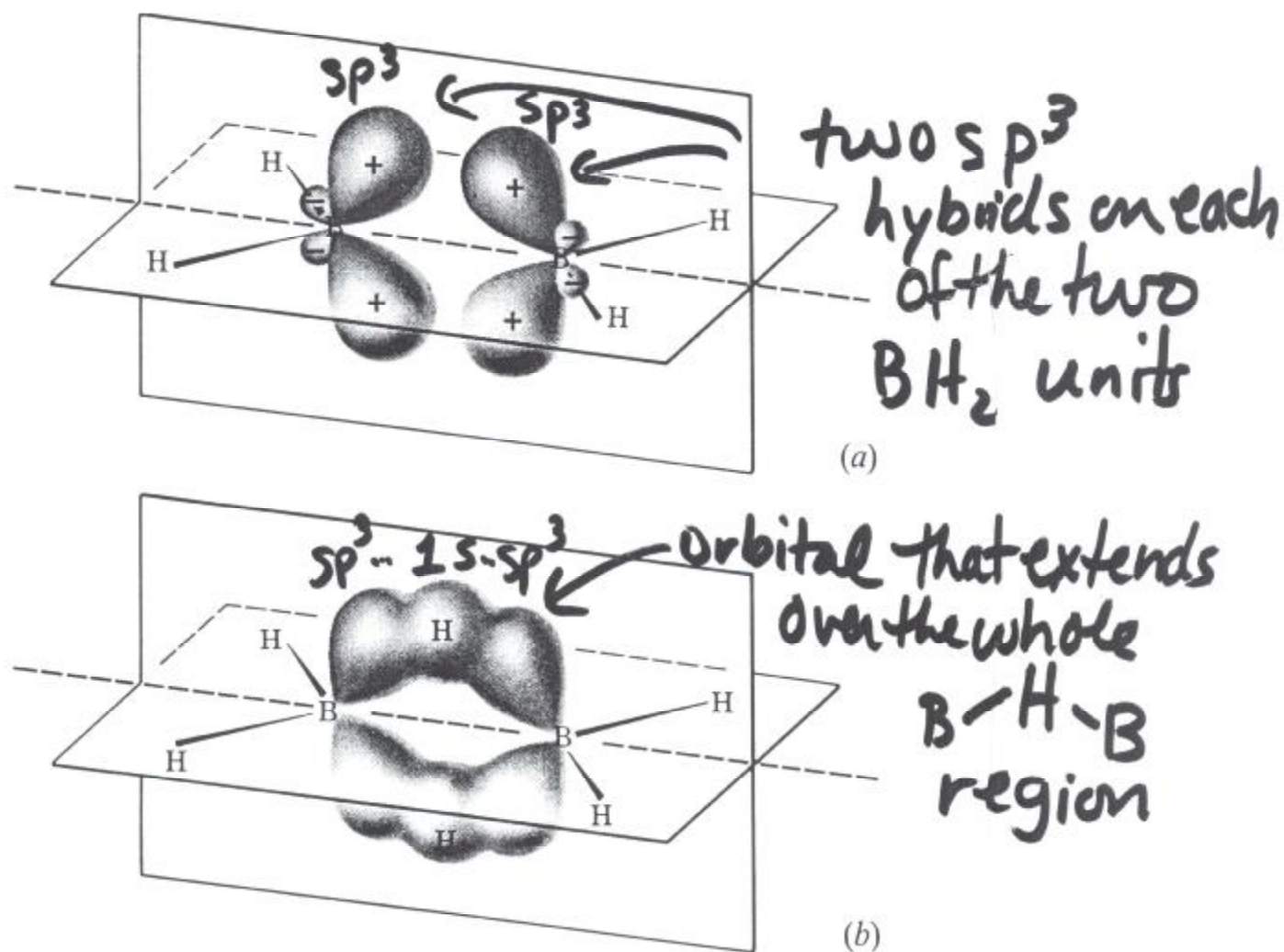
- $BH_2$  has two ordinary bonds made from two of the four  $sp^3$  hybrids and the H 1s orbitals.



These  $BH_2$  fragments are coplanar

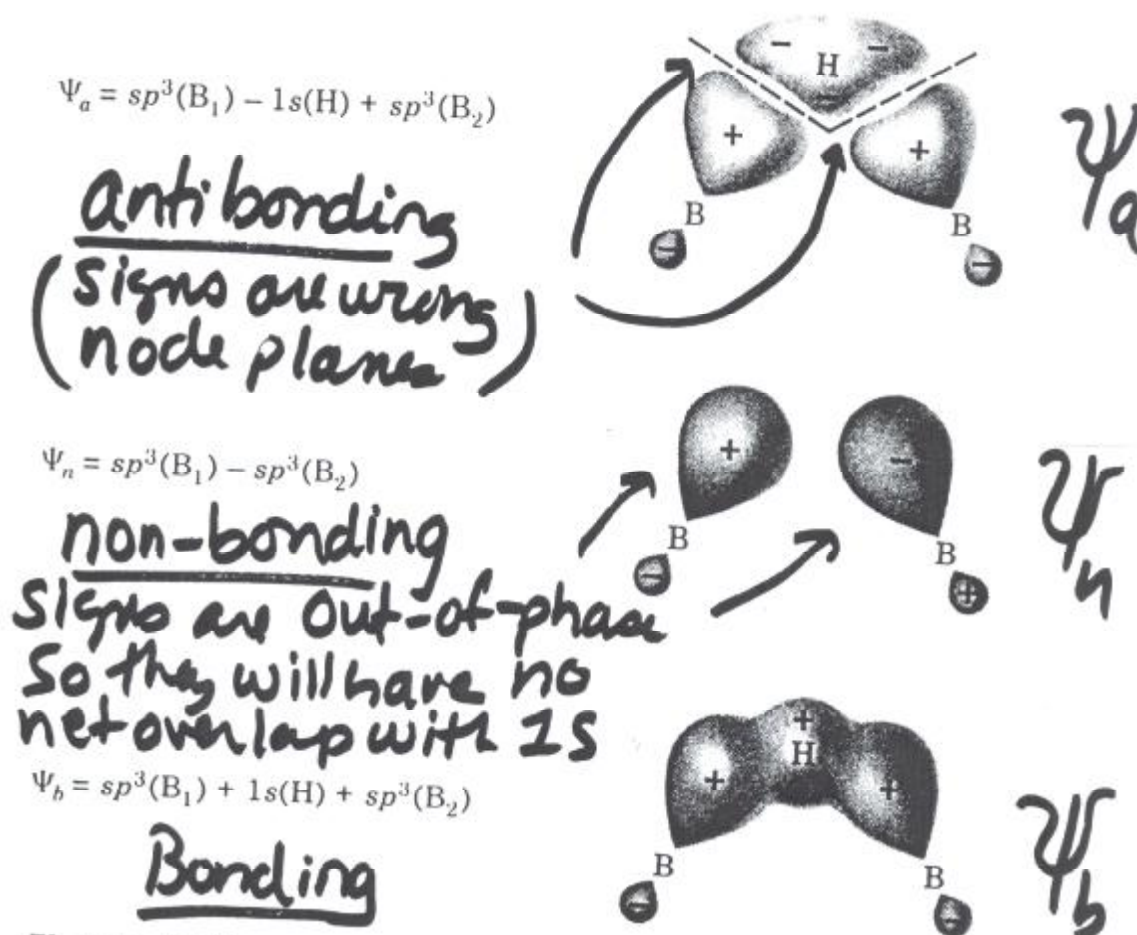
- the remaining two  $sp^3$  hybrids overlap in a perpendicular orientation with the bridging H atoms

# Formation of three-center two-electron Bonds in $B_2H_6$



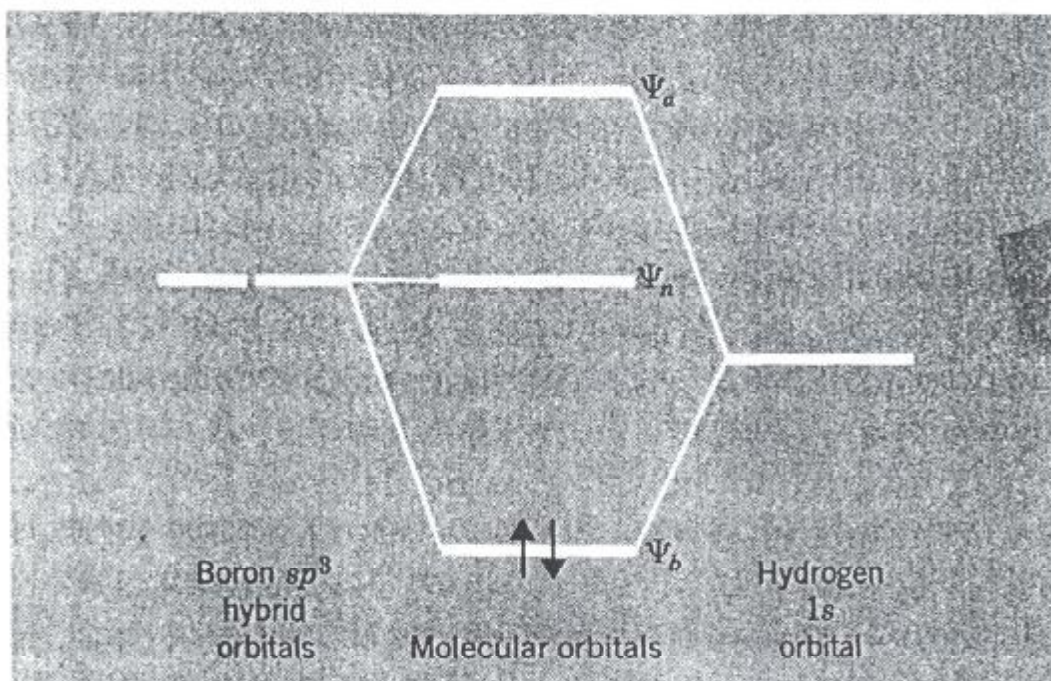
**Figure 3-33** The formation of 3c-2e bonds in  $B_2H_6$ . The orientation of two coplanar  $BH_2$  groups, with  $sp^3$  hybrids on B atoms, is shown in (a). When the bridging H atoms are placed as in (b), continuous overlap within each  $B-H-B$  arch results in two separate 3c-2e bonds.

# Combinations of B $sp^3$ hybrids and H $1s$ orbital



**Figure 3-34** The formation of three distinct three-center MO's in a B—H—B bridge system.





**Figure 3-35** An energy-level diagram for the three MO's of Fig. 3-34 that are formed in a three-center B—H—B bridge bond of  $B_2H_6$ .