Carbon Monoxide

LUMO = lowest unoccupied molecular orbital.
$\Rightarrow 1\pi^*$ is largely C character

HOMO = highest occupied molecular orbital.
$\Rightarrow 3\sigma$ is largely C character
(actually non-bonding…C lone pair)

Carbon monoxide is reactive at the C atom, not the O atom!

$3\sigma^*$

$1\pi^*$ $1\pi^*$
LUMO

$2p$

3σ
HOMO

$2p$

1π 1π

$2s$

$2\sigma^*$

B^2

2σ

$2s$
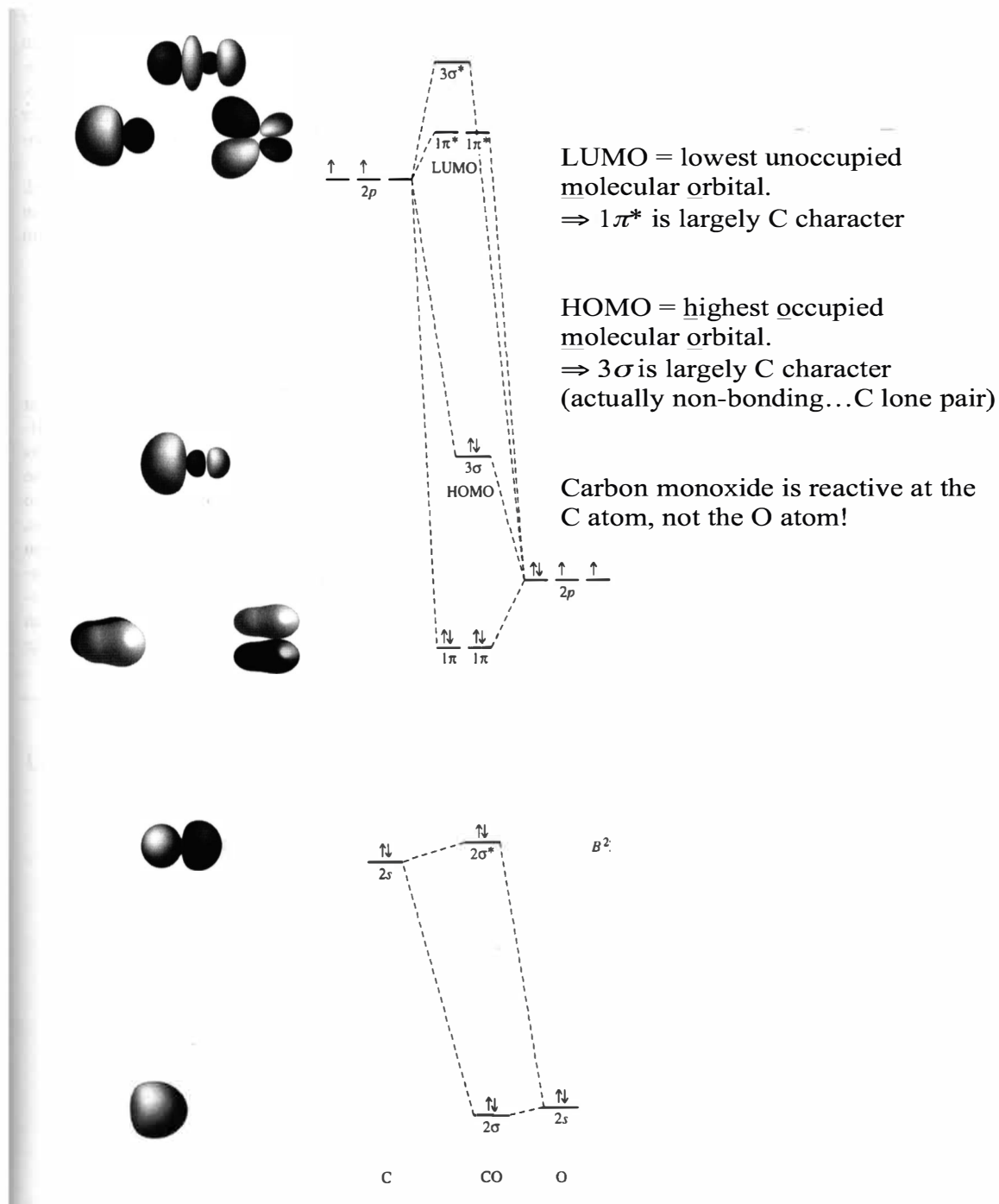
C   CO   O

N_1
a.o.'s

M.O.'s
N_2

N_2
a.o.'s

10 valence electrons:

$\sigma_1^2 \sigma_2^{*2} \pi_1^4 \sigma_3^2$ (B.O. =3.0)
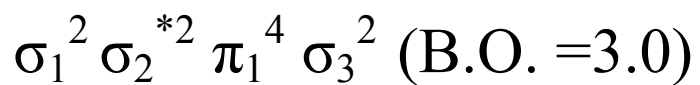
M.O. Diagrams for the Isoelectronic N_2 and CO molecules are very different. They help explain the different reactivites of N_2 versus CO in a way that Lewis Diagrams never could (or formal charges!)

<u>N_2</u>

(1) Highest e⁻ are in a bonding orbital $\sigma_1^2\sigma_1*^2\pi_1^4\sigma_3^2$, s/$p_z$-s/$p_z$ σ orbital

(2) As a consequence N_2 is very stable, $N_2 \xrightarrow{\text{-e⁻}} N_2^+$ weakens the N-N bond. I.E. is very high
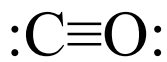
<u>CO</u>

a. Highest e⁻ are in an orbital $\sigma_1^2\sigma_1*^2\pi_1^4\sigma_3^2$ that is higher in energy than the starting a.o.'s

(1) As a consequence CO is not as stable, CO $\rightarrow$ CO$^+$ is not as unfavored

Q. What does ionization of N_2 versus CO have to do with their reactivity?
For example attaching it as a "ligand" to metals through lone pair

A. Lewis basicity of CO is much higher than N_2

:C≡O: :N≡N:

This end binds to
Lewis acids such
as metal cations
M^{n+} ions very
easily. The lone
pair on C carbon is
at high energies
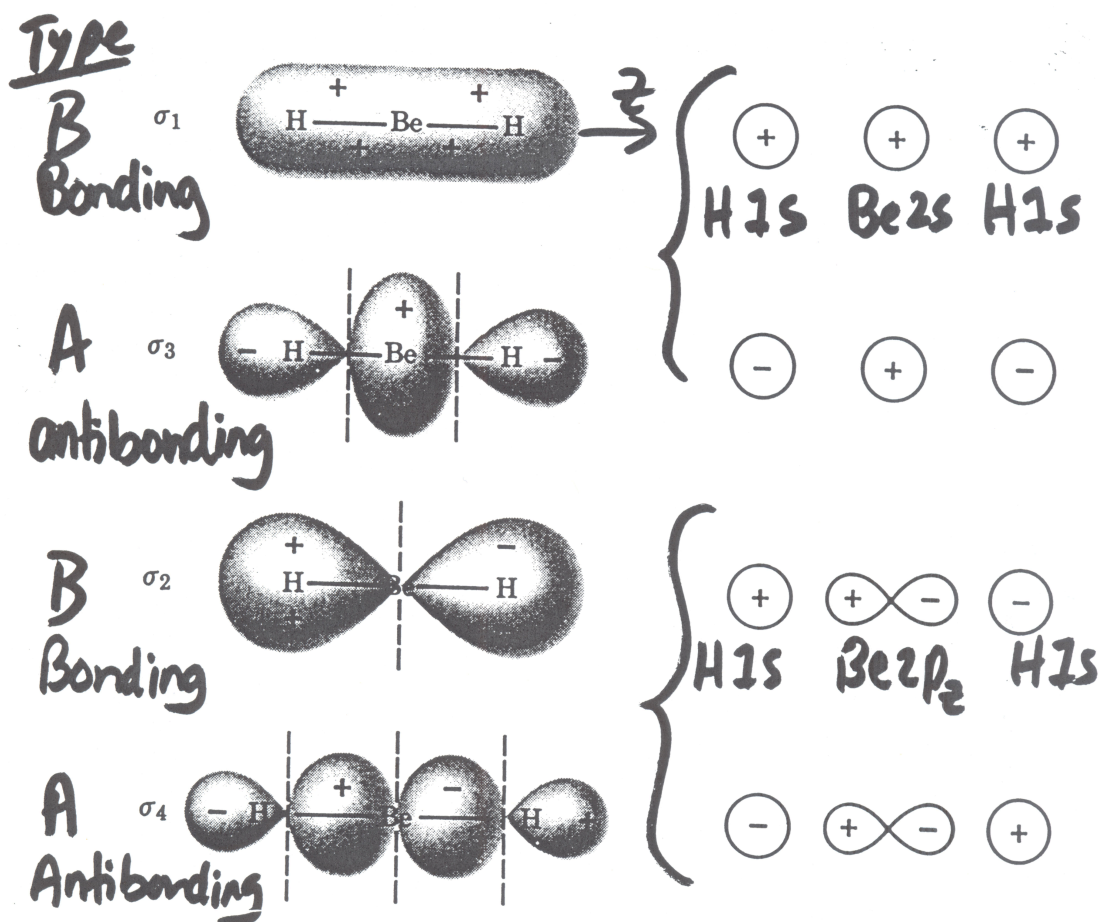and therefore is
exposed to act as a
Lewis Base.

Very difficult to
get this lone pair
to donate

(low in energy and
not accessible!)

Extrapolation of M.O. Theory Diatomic to Polyatomic

Linear Triatomics like BeH_2 which can form only σ orbitals

Type

B σ_1 Bonding

H —— Be —— H

H 1s   Be 2s   H 1s

A σ_3 antibonding

H — Be — H

B σ_2 Bonding

H —— Be —— H

H 1s   Be 2p_z H 1s

A σ_4 Antibonding

H — Be — H

1) In each bonding orbital, 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$_2$ M.O. Diagram
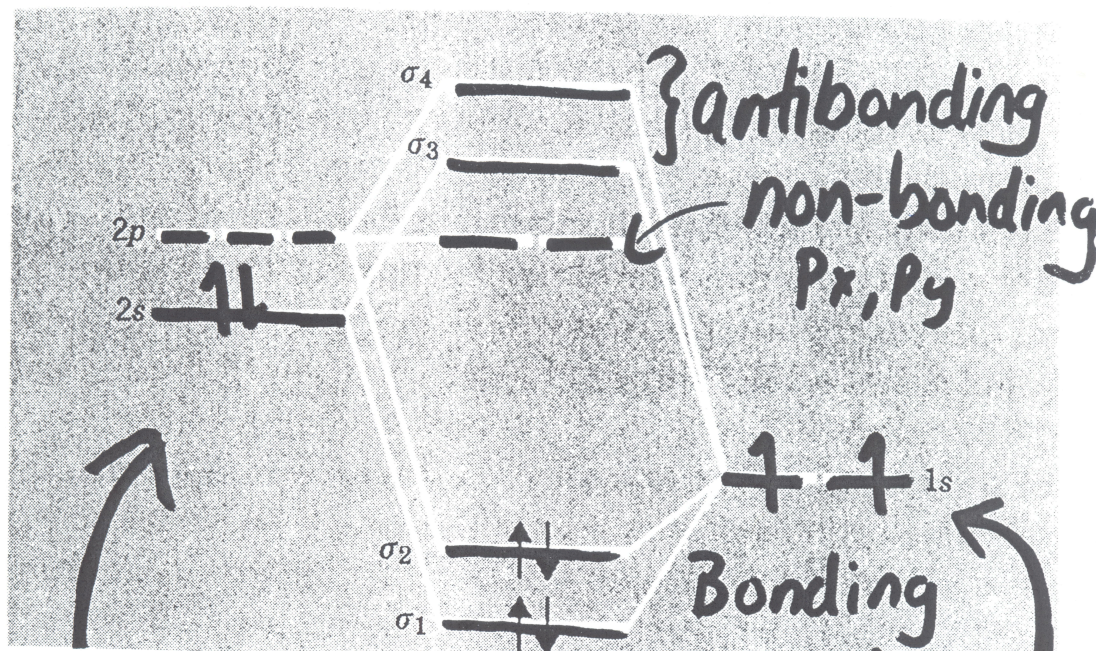
Main Features

Be atom

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 H atoms

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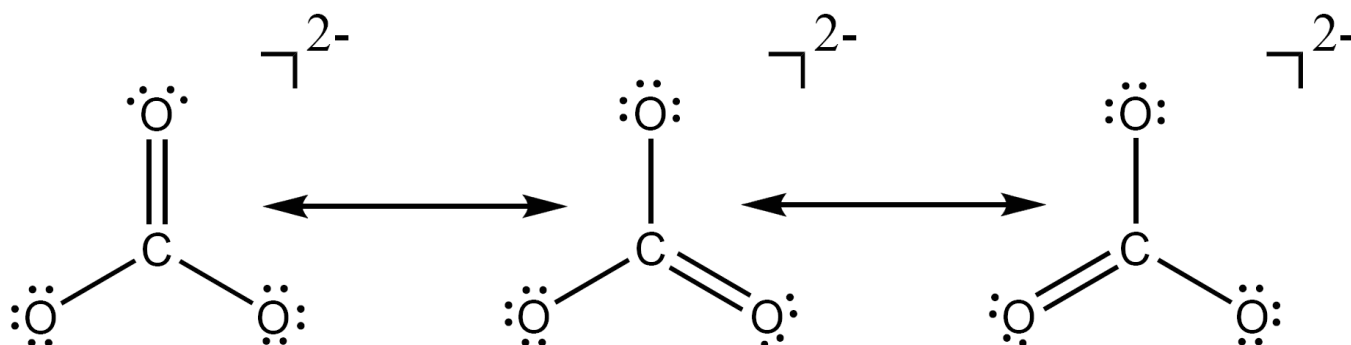They are lower in energy due to higher effective nuclear charge.

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

$$\mathbf{AB_3} \qquad\qquad BF_3 , CO_3^{2-} , NO_3^-$$

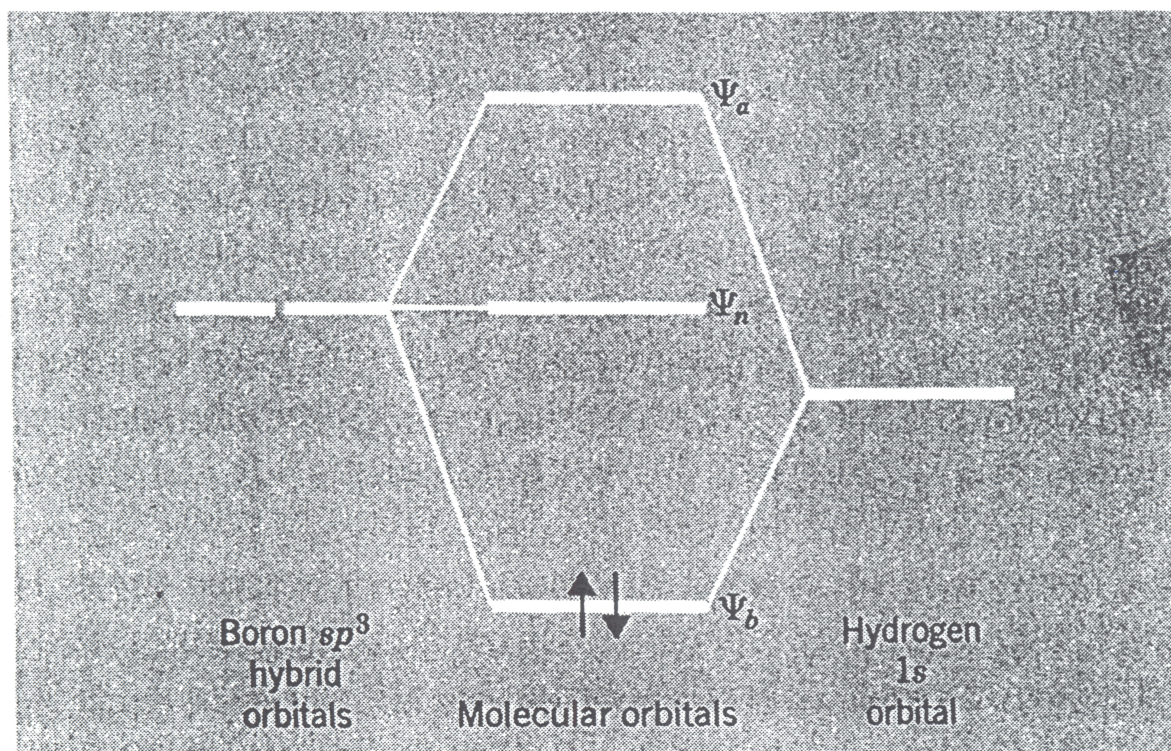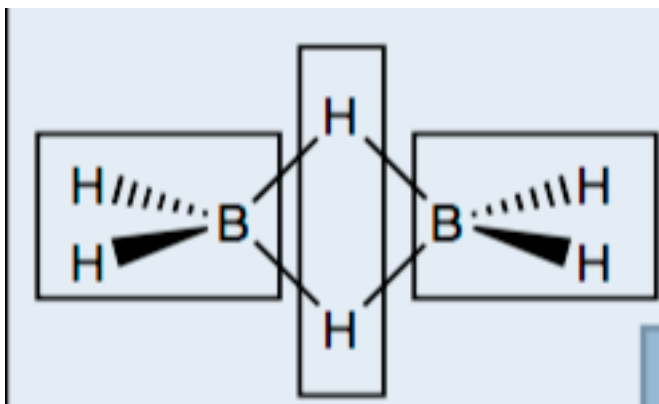Recall, we invoked π-bonding in CO_3^{2-} and NO_3^- as part of "resonance" structures like these:

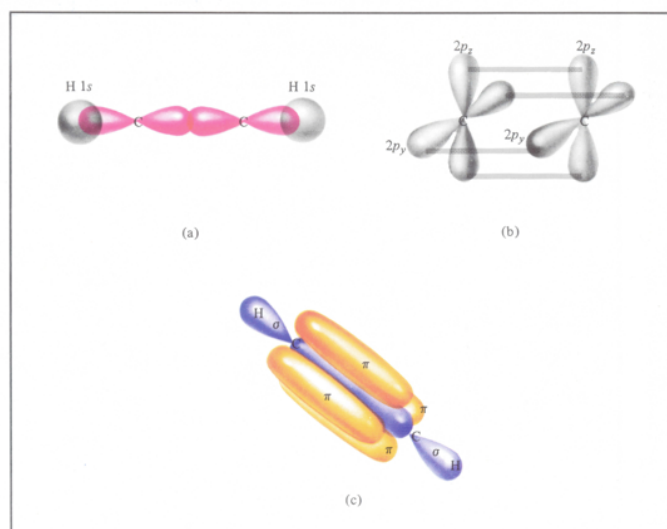**Q.** But how does M.O. theory account for π-bonding?
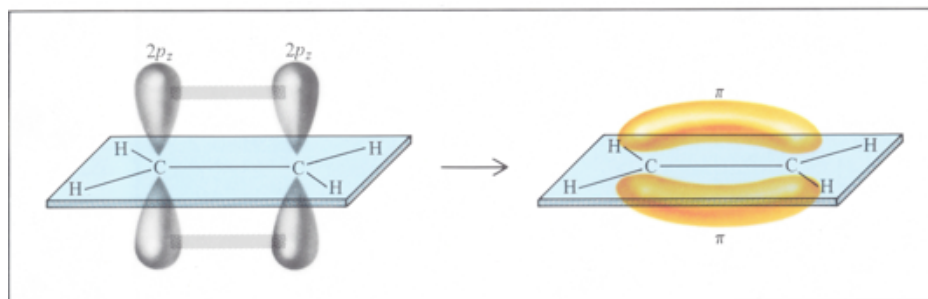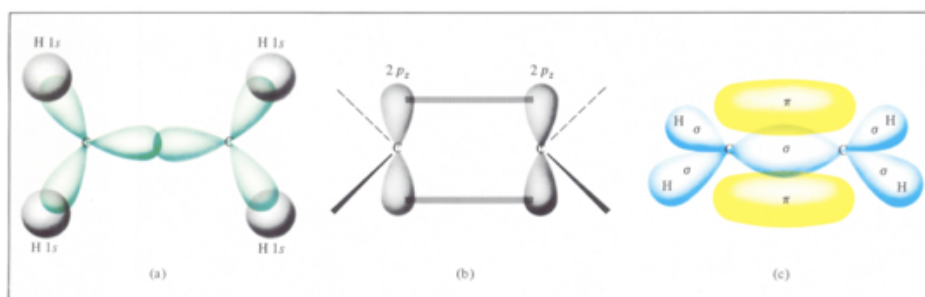
More to the point: Can M.O. theory explain the one π bond in the above structure needing to be in 3 places at the same time?

A. YES!!!

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.
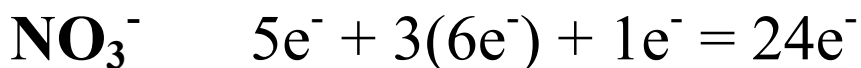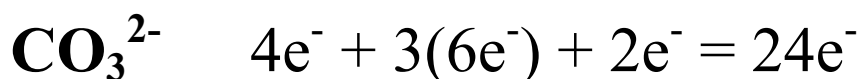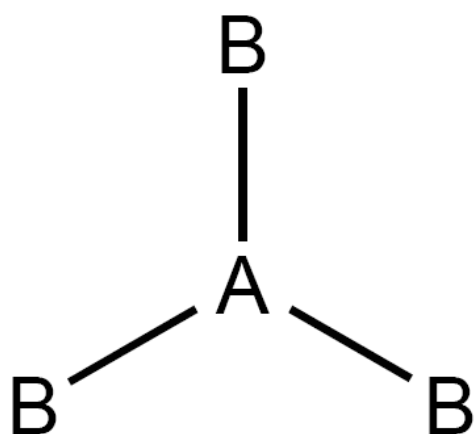
M.O. Treatment of AB_3 planar molecules.
For example BF_3, NO_3^-, CO_3^{2-}

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 σ- bonds (A-B bonds) and used to house lone pairs (in plane)
2) **G**roup **O**rbitals 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.
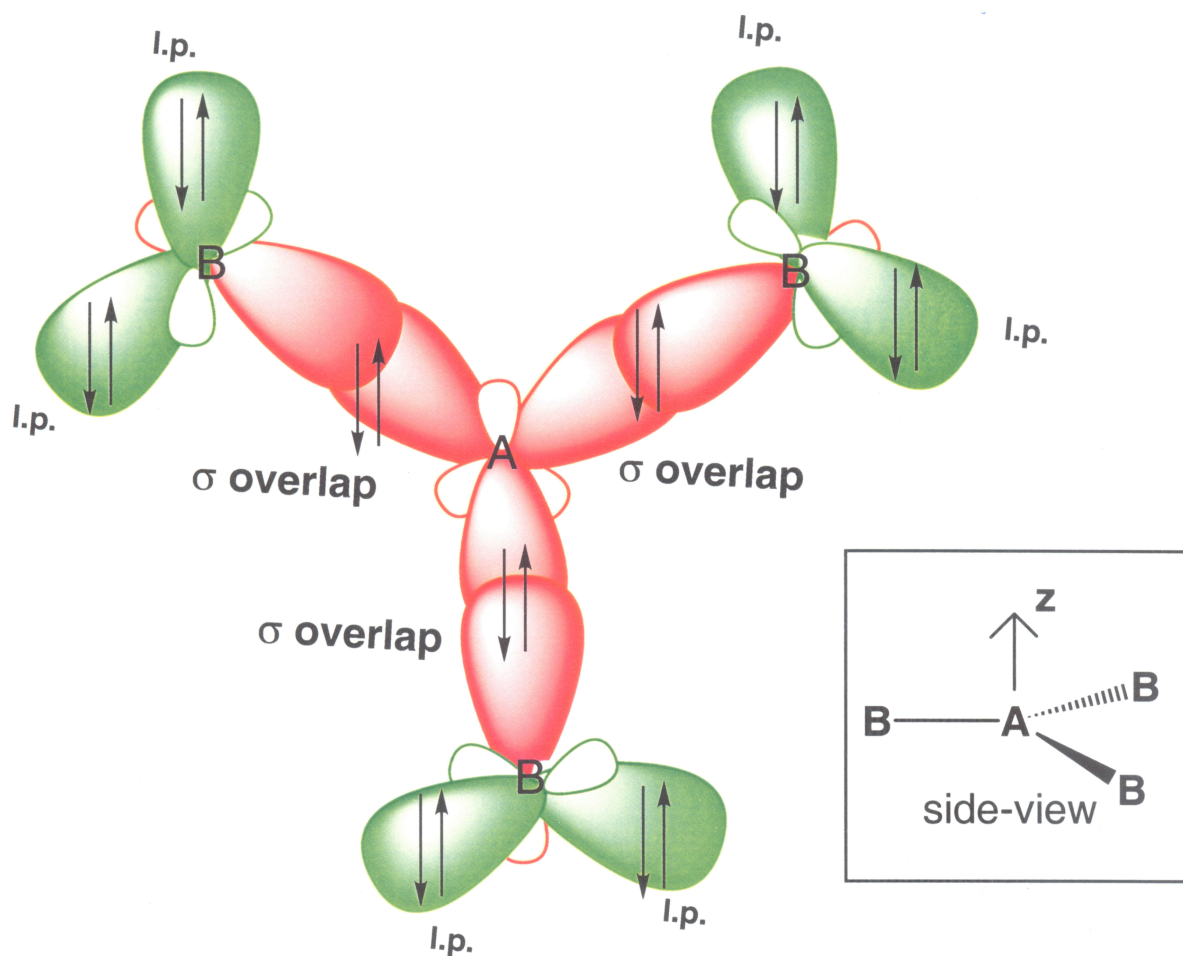
$$
\begin{array}{c}
B \\
| \\
| \\
A \\
B \quad\quad B
\end{array}
$$

BF$_3$ $3e^- + 3(7e^-) = 24e^-$

CO$_3^{2-}$ $4e^- + 3(6e^-) + 2e^- = 24e^-$

NO$_3^-$ $5e^- + 3(6e^-) + 1e^- = 24e^-$

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$^-$
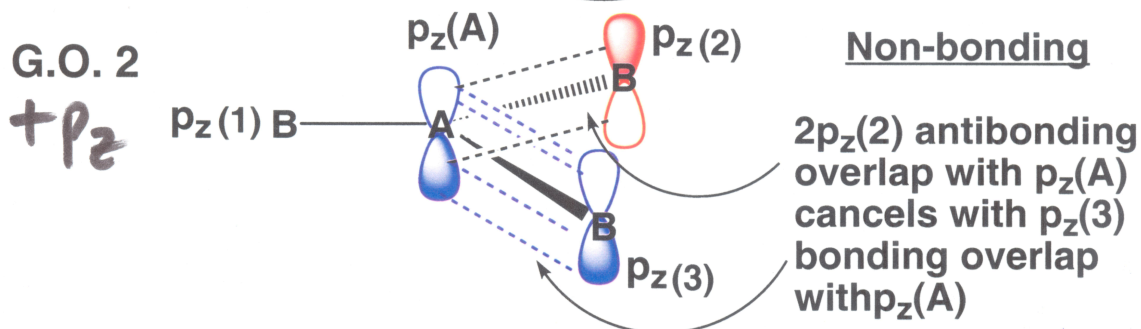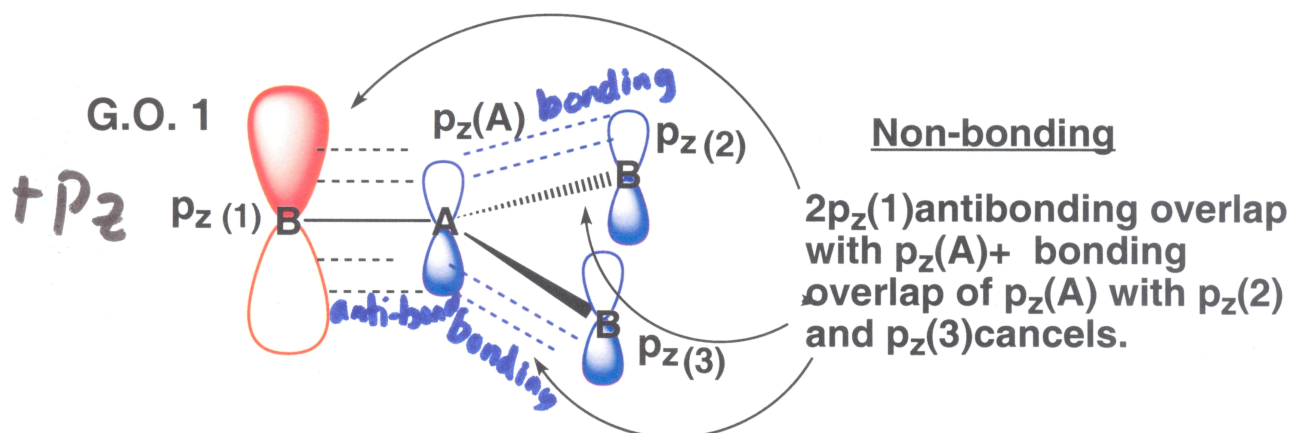
STEP 2   AB$_3$ M.O. Treatment

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

G.O. 1

$2p_z(1) - p_z(2) - p_z(3)$

G.O. 2

$p_z(2) - p_z(3)$

G.O. 3

$p_z(1) + p_z(2) + p_z(3)$
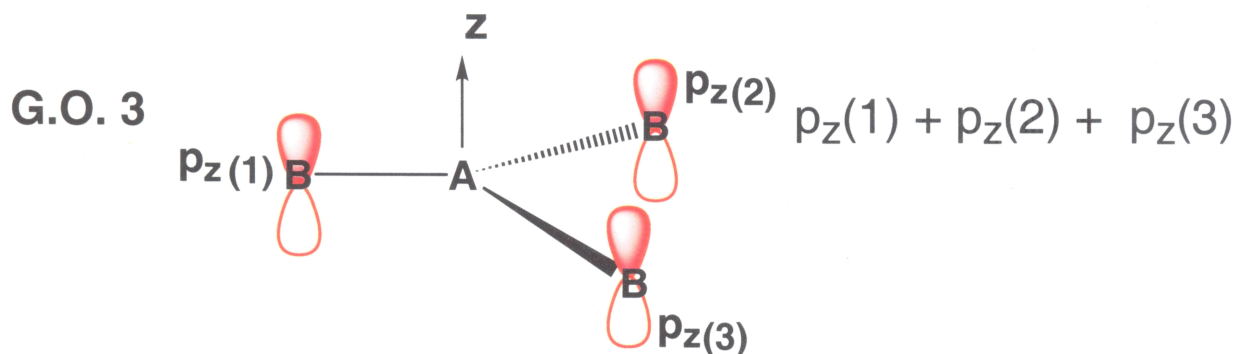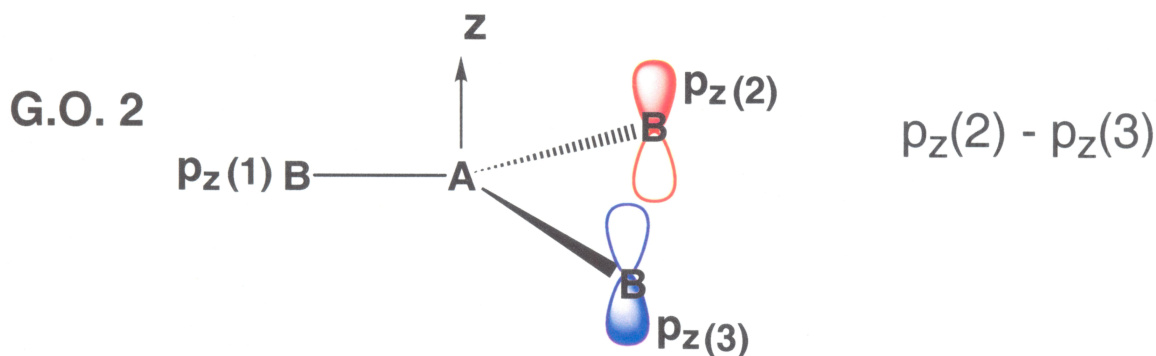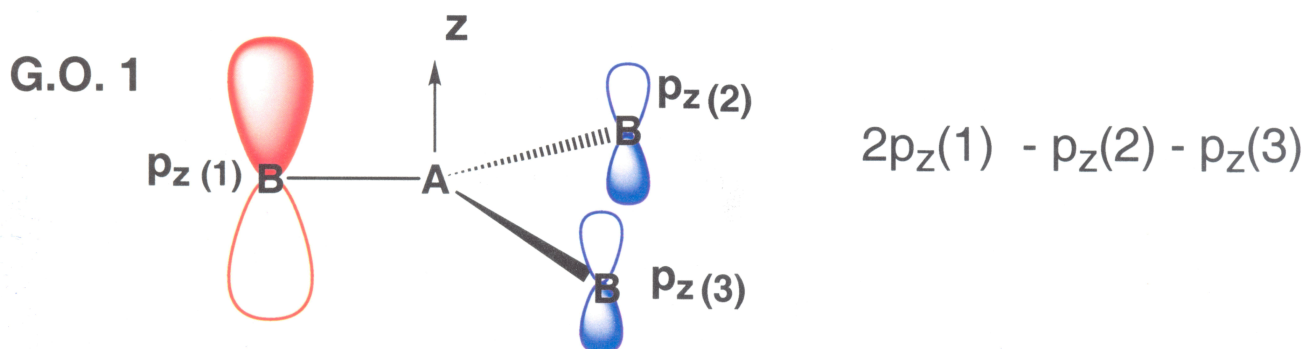
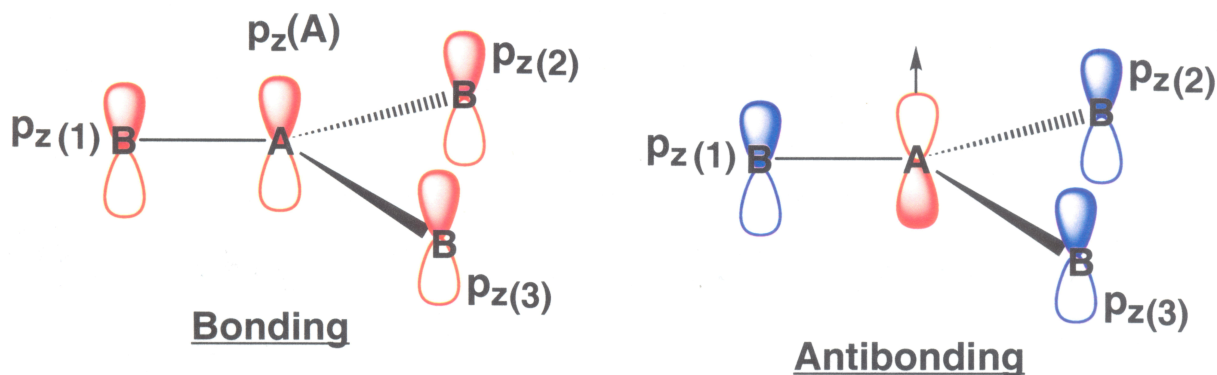You obtain three group orbitals that can
overlap with the p$_z$ orbital on A to form
π-bonds, only one of which is a bonding one

STEP 3   AB₃   M.O. Treatment

Take (24 valence e^-)-(18 e^-) = 6 e^- and use them to make π-bonds by overlap of the central atom, A, p_z orbital and the three G.O.'s
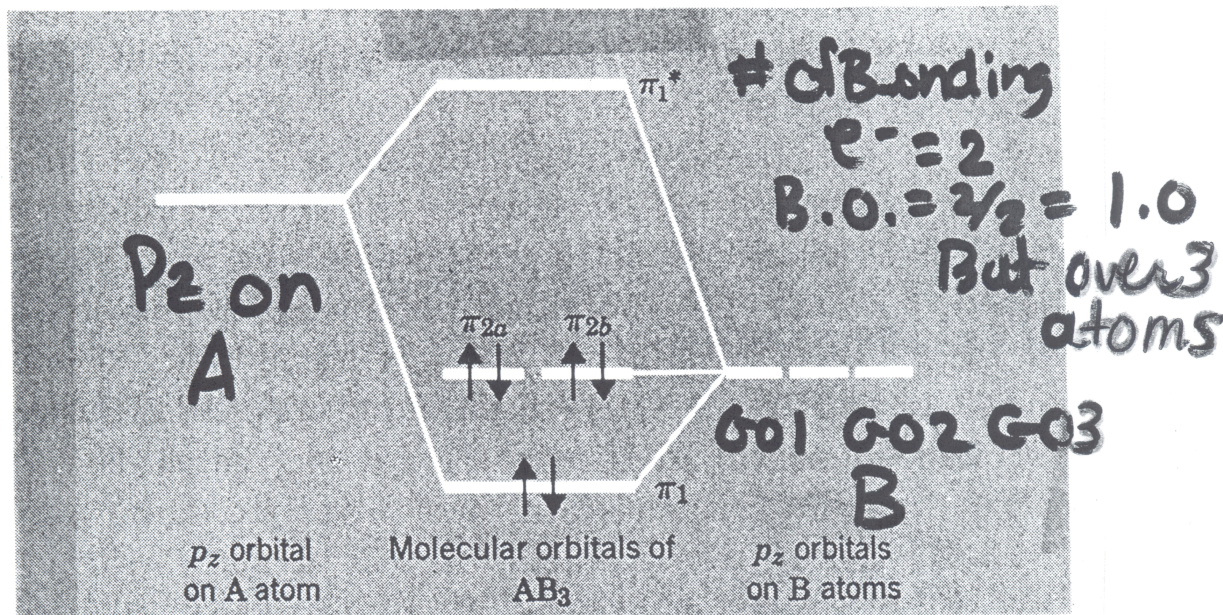
G.O. 1

$+P_z$

$p_z(A)$ *bonding*

Non-bonding

$2p_z(1)$antibonding overlap with $p_z(A)$+ bonding overlap of $p_z(A)$ with $p_z(2)$ and $p_z(3)$cancels.

G.O. 2

$+P_z$

Non-bonding

$2p_z(2)$ antibonding overlap with $p_z(A)$ cancels with $p_z(3)$ bonding overlap with $p_z(A)$

G.O. 3

$+P_z$ **Bonding and antibonding Combinations**

Bonding

Antibonding

You get four molecular orbitals

The part of the M.O. Diagram that depicts
the π- bonding is:

π_1^*

# of Bonding
e⁻ = 2
B.O. = 2/2 = 1.0
But over 3
atoms

GO1 GO2 GO3
B

P_z on
A

π_{2a} π_{2b}

π_1

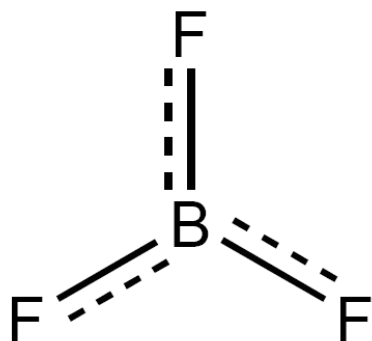| p_z orbital on A atom | Molecular orbitals of AB_3 | p_z orbitals on B atoms |

if BF_3 then:

F
|
B
F   F
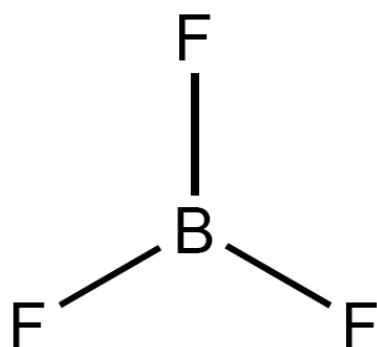
each of these is a single bond
based on sp^2 overlap

and

F
‖
B
F   F

there is 1/3 of a π
bond (1 π 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.
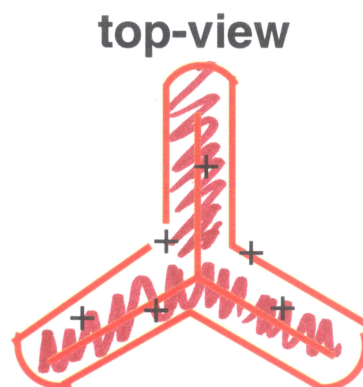
The π M.O.'s in AB$_3$ Molecules that Affect Bonding
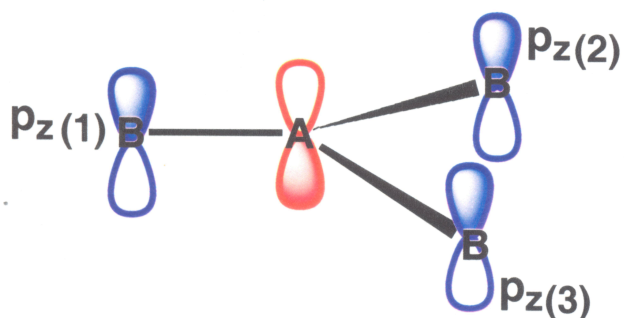
Bonding and antibonding Combinations

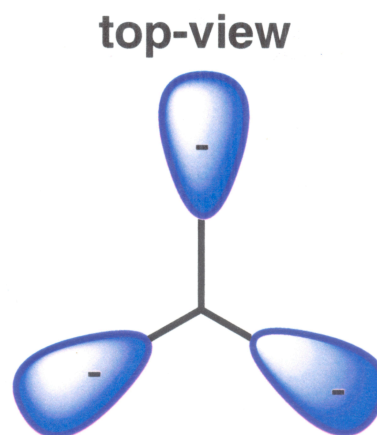π Bonding M.O.

top-view
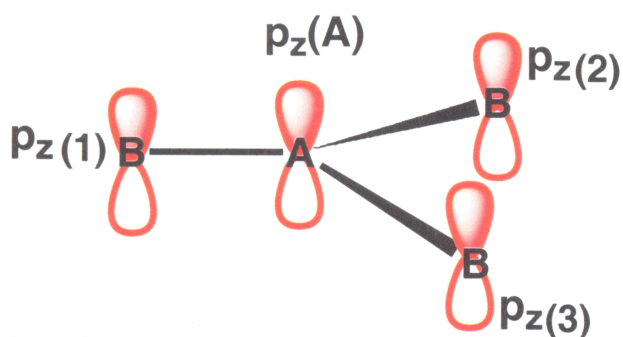
one continuous molecular orbital

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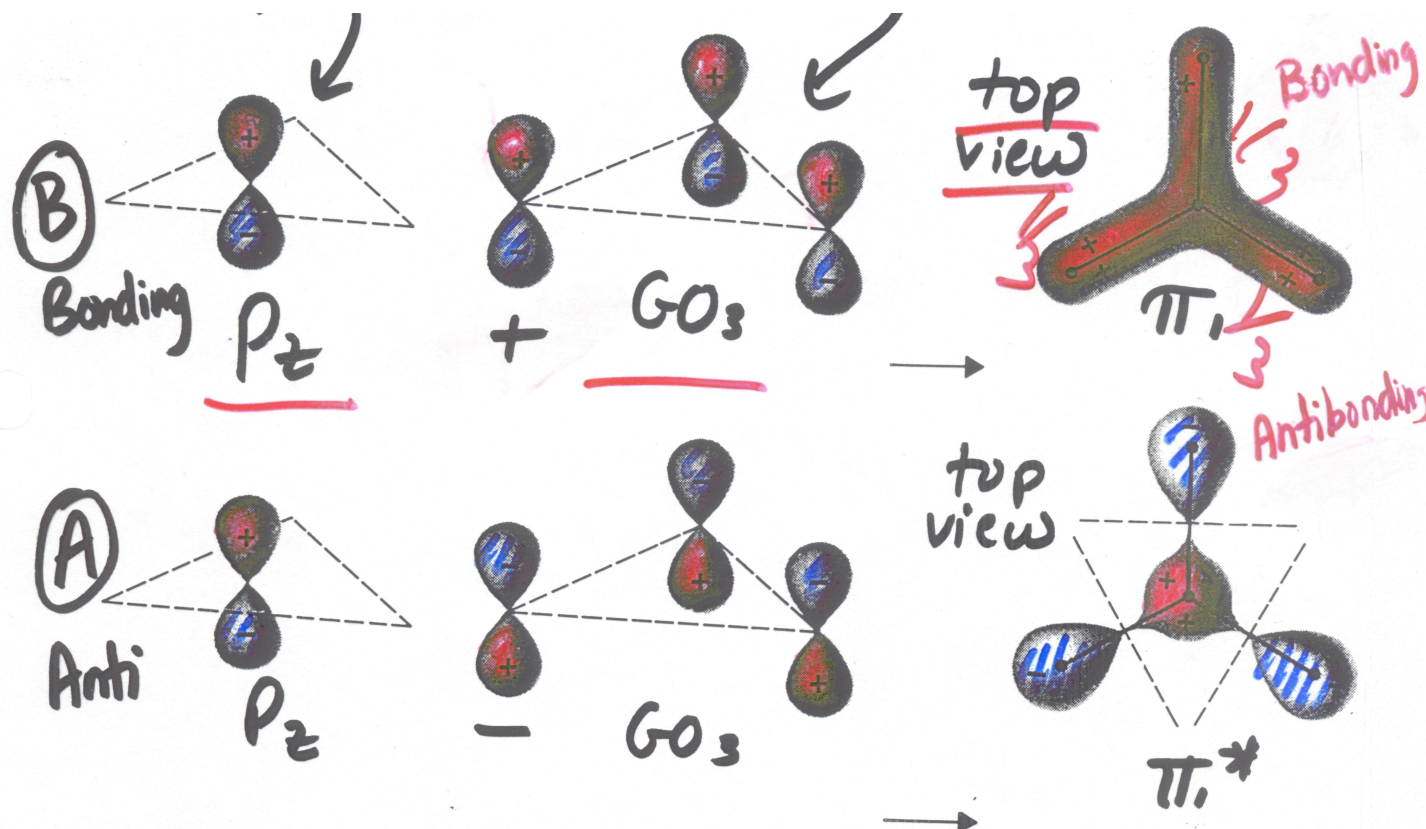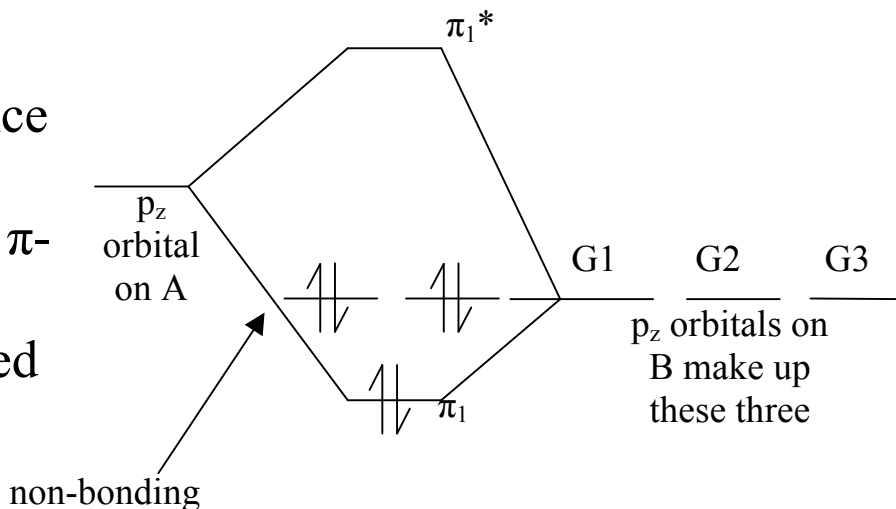

$\pi*$ Antibonding M.O.

top-view

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

Diagrams showing how π- bonding and π- antibonding M.O.'s arise from overlap of G.O.$_3$ with the p$_z$ Orbital of A.

BF$_3$ Only 6 valence
CO$_3{}^{2-}$ electrons are
NO$_3{}^{-}$ available for π-
bonding. The 18e$^-$ before this are involved in σ interactions (24e$^-$ systems).

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)

*H⸝⸝⸝B(H)(H) ... B ... Al ... Al structures
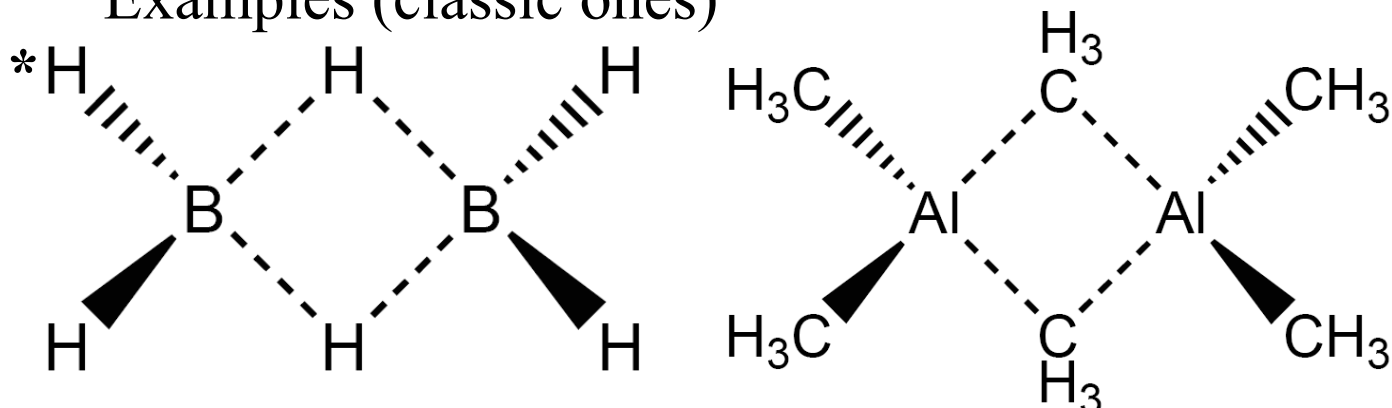
There are eight adjacent pairs of atoms in these molecules but count electrons…

2B 6e⁻ (3 each)
H 6e⁻
   12e⁻
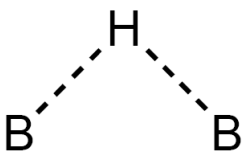
You need 16e⁻ to make 8 bonds but you have only 12e⁻ which is only enough for 6 bonds

*These are not planar
(note that BH_3 and $Al(CH_3)_3$ are not really the way the formulae indicate - they are dimers of this formula)

H_2B ⟷ H_2B (resonance structures with bridging H)
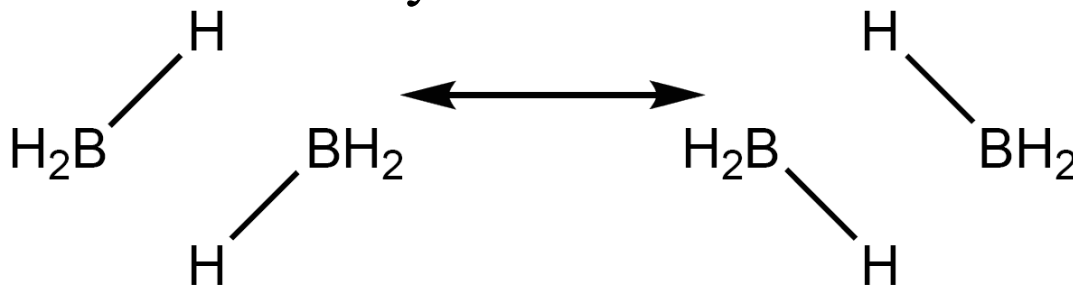
Consider these two resonance forms (canonical forms)

This implies that in each $\overset{\displaystyle H}{\underset{\displaystyle B \qquad\quad B}{\diagup\;\;\diagdown}}$ bridge, that one

electron pair is shared between (or distributed over) two B•••H bonds.

This would lead to a bond order of ½ for each B•••H bridge bond but still result in the other two terminal

bonds being normal 2e⁻ bonds.

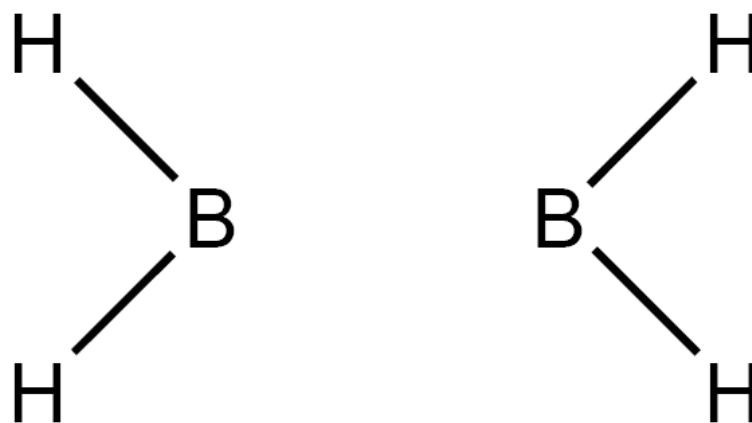$$\begin{array}{c} H \\ \diagdown \\ \quad B \\ \diagup \\ H \end{array}$$
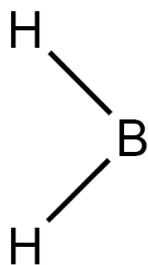
Q. Doesn't this seem a little artificial to you?

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

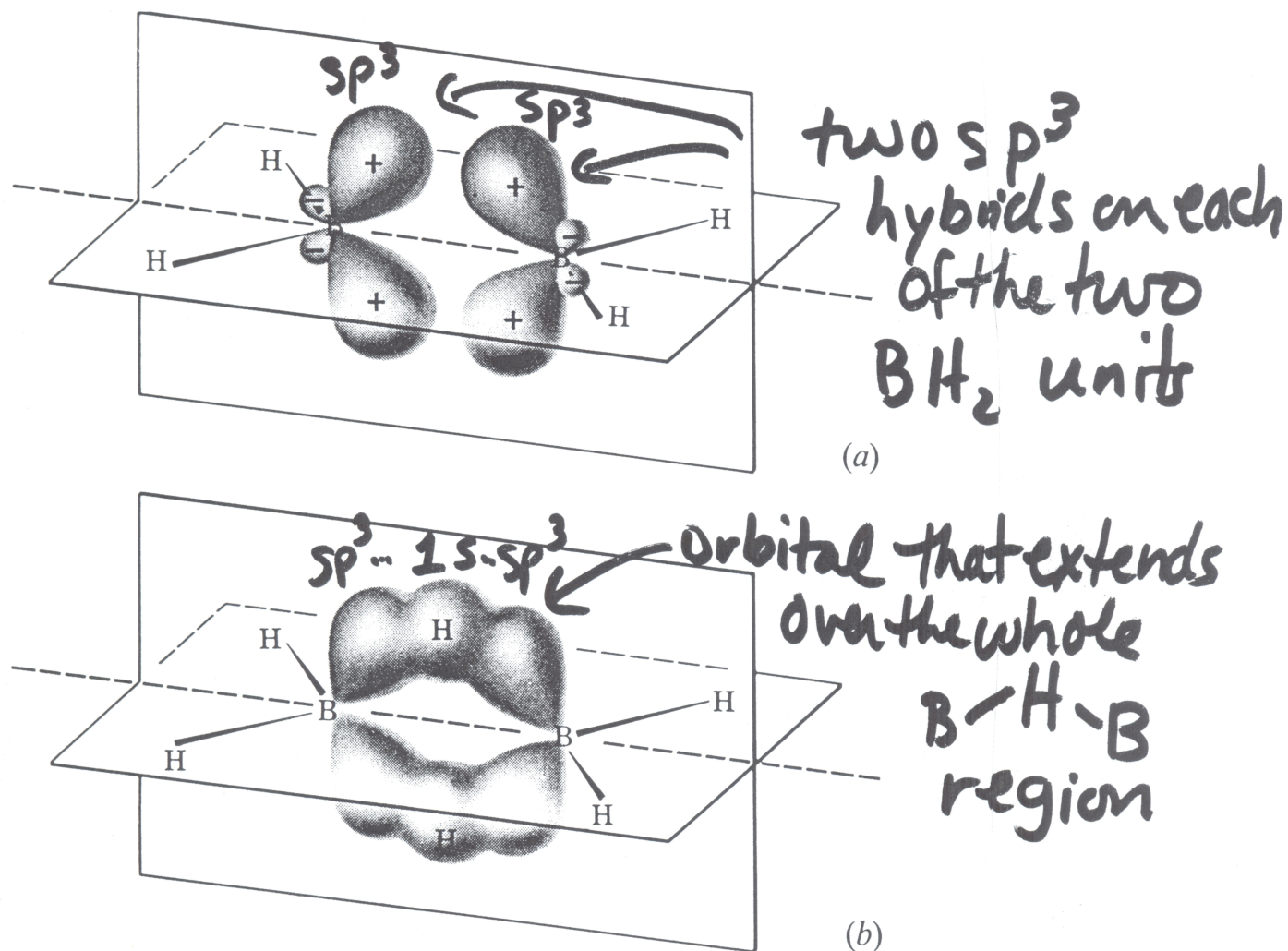B has sp^3 hybridization for tetrahedral Boron

- 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 because the geometry around the B atom is tetrahedral

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

(a)

(b)

Handwritten annotations:

two sp^3 hybrids on each of the two BH_2 units

Orbital that extends over the whole B–H–B region

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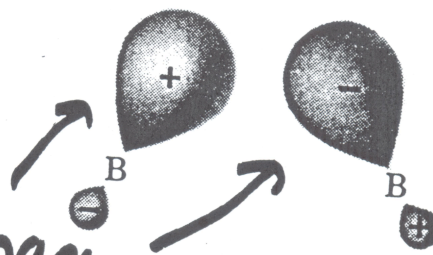
Combinations of B sp^3 hybrids and H 1s orbital

$\Psi_a = sp^3(B_1) - 1s(H) + sp^3(B_2)$

$\underline{antibonding}$
$\left(\begin{array}{l}\text{Signs are wrong} \\ \text{node plane}\end{array}\right)$
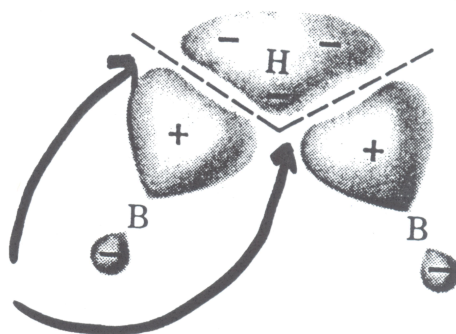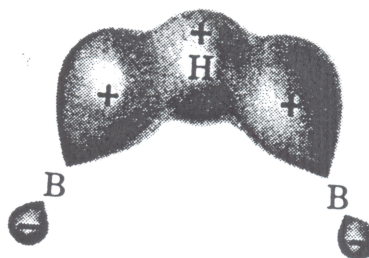
$\Psi_n = sp^3(B_1) - sp^3(B_2)$

$\underline{non-bonding}$
Signs are Out-of-phase
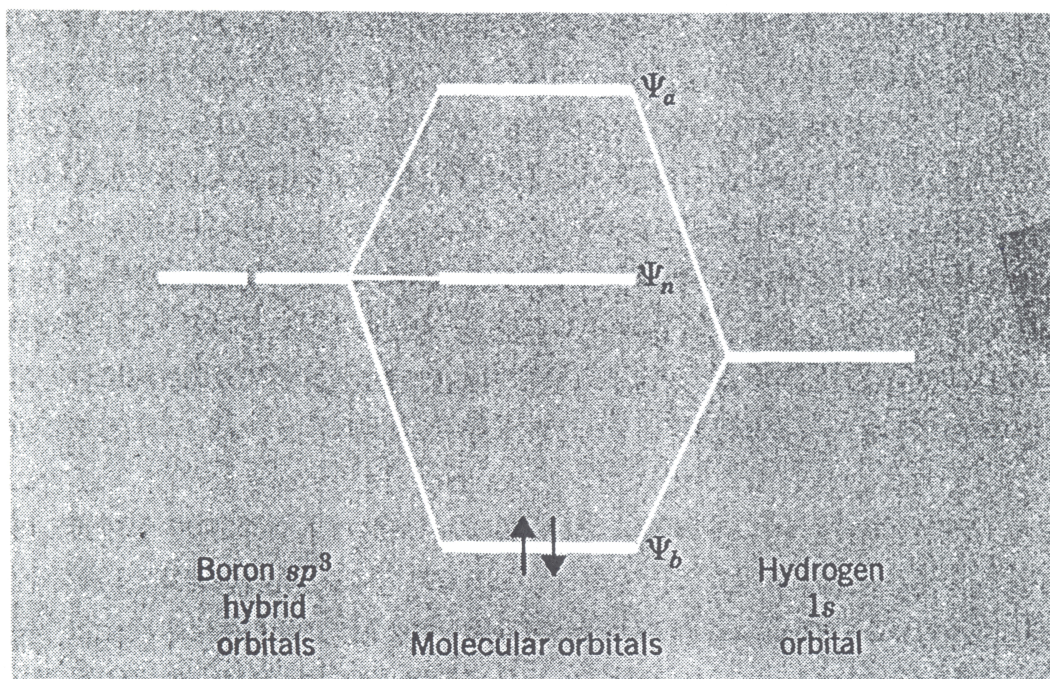So they will have no
net overlap with 1S

$\Psi_b = sp^3(B_1) + 1s(H) + sp^3(B_2)$

$\underline{Bonding}$

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.