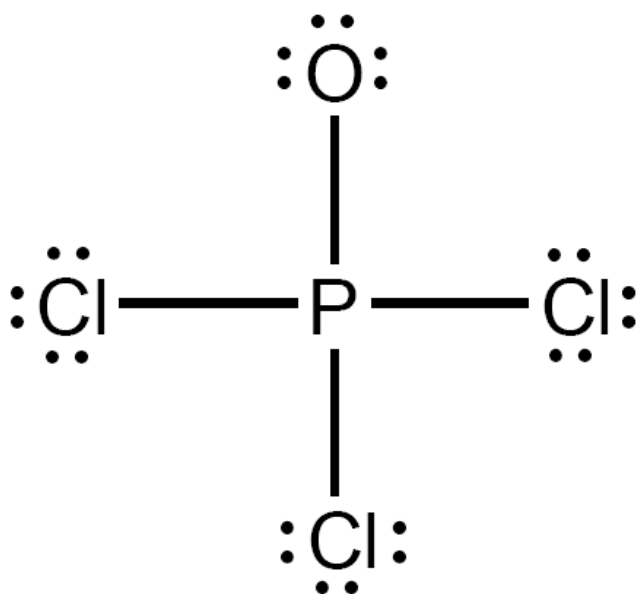Example 2
OPCl₃

pick central atom **A**
P is the central atom
(there are two odd ones, but the least electronegative one is the central atom)

O	6e⁻	6e⁻
P	5e⁻	5e⁻
Cl	7e⁻ x 3	= 21e⁻
		32e⁻

P usually has 8e⁻
or 10e⁻ around
the central atom

Lewis Structure
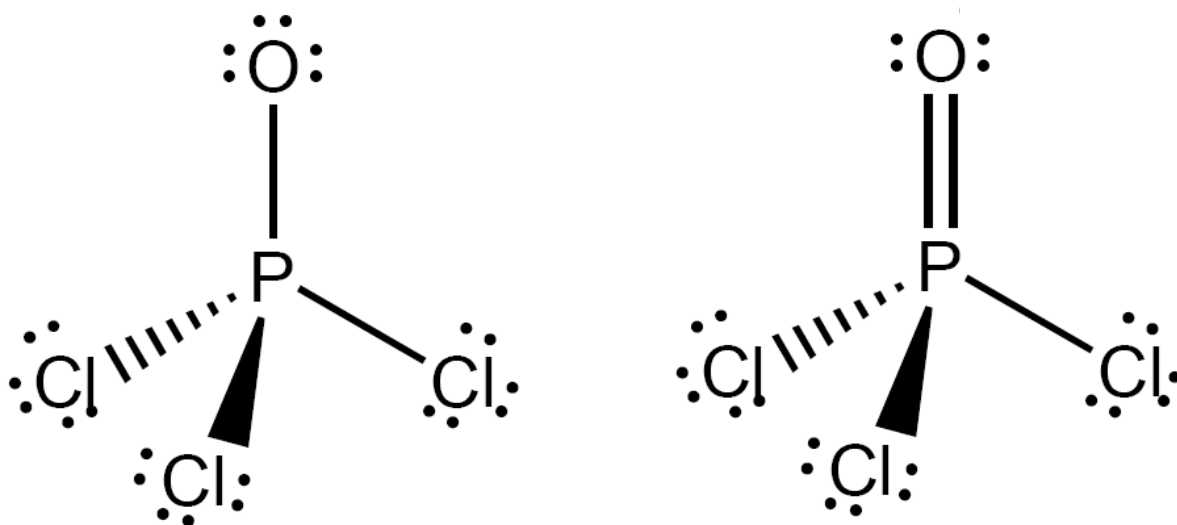(a possible one that works but you need to check it)

2) occupancy factor

   $OPCl_3$ or AB_3B' which is PCl_3O

   $(x+y) = 4$

3) for an occupancy factor of 4, sp^3 works well for P

4) VSEPR predicts tetrahedral

formal charge is often invoked to help choose the correct Lewis Structure. It works sometimes, but it is not always accurate.

Why?

Because it <u>assumes</u> that all <u>atoms</u> <u>have</u> the <u>same</u> <u>EN</u>.

Do the formal charge calculation on the above two structures. Which one is the best structure?

Q. Does formal charge ever fail to make sense?

A. Yes!   Look at CO

Lewis structure of CO
C   4e⁻
O   6e⁻   = 10 valence e⁻

:C≡O: is the only way to have a
complete octet (1 σ, 2π bonds)

Formal Charge $^{-1}$:C≡≡O:$^{+1}$ but O is more
                                                E.N. than C!

This formal charge implies a huge dipole moment

:C≡≡O:
⟵————+

but, in fact, CO has one of the smallest dipole
moments of any molecule (0.12 Debye units)

Bond lengths and Covalent radii

Covalent radius

In X-X molecules, if the bond distance is 1.988 A° as it is for C1 – C1, the <u>covalent bonding radius</u> would be ½ of this number.

Table 3-2 on page 97. (in A°)

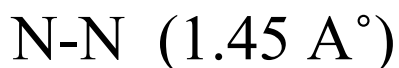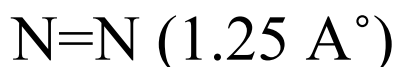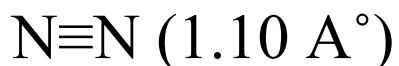| H 0.28	C 0.77	N 0.70	O 0.66	F 0.64
	Si 1.17	P 1.10	S 1.04	Cl 0.99
	Ge 1.22	As 1.21	1.17	Br 1.14
	Sn 1.40	Sb 1.41	1.37	I 1.33

These were obtained in a similar manner to Cl-Cl.

From this table, then, we can predict bond lengths:

C-Si   0.77 + 1.17   =   1.94 A°
                                  (1.87 A°) experiment
P-Cl   1.10 + 0.99   =   2.09 A°
                                  (2.04 A°) experiment
Etc.,

- <u>Multiple Bonds</u> are <u>shorter</u> than single bonds:

    N≡N (1.10 A°)

    N=N (1.25 A°)

    N-N (1.45 A°)

- also <u>hybridization affects covalent radii</u>

s orbitals have better overlap at short distances so the bonds get shorter with more s orbital character

<u>van der Waals Radii</u>

These are not covalent or ionic

These distances are the closest approach between atoms that are not bonded. Occurs in the liquid and solid states. There is a limit of contact based on repulsive forces.

Table 3-3

Table 3-3   van der Waals Radii of Nonmetallic Atoms (in Å)

H	1.1–1.3					He	1.40
N	1.5	O	1.40	F	1.35	Ne	1.54
P	1.9	S	1.85	Cl	1.80	Ar	1.92
As	2.0	Se	2.00	Br	1.95	Kr	1.98
Sb	2.2	Te	2.20	I	2.15	Xe	2.18

Radius of a methyl group, 2.0 Å

Half-thickness of an aromatic ring, 1.85 Å

The van der Waals distances values reflect a combination of attractive <u>and</u> repulsive forces.
Three contributions:
a) Dipole ···· Dipole
b) Dipole ···· Induced dipole
c) Fluctuating dipoles or London Forces

Delocalized Bonding
Molecular Orbital Theory

Main aspects:

(1) bonds exist when orbitals on different atoms overlap so as to concentrate electron density between the atoms

(2) electron density and not electron pairs is emphasized

(3) allows for three types of orbital overlap:
    (a) positive overlap – bonding
    (b) negative overlap – antibonding
    (c) zero overlap - nonbonding

1.40
1.54
1.92
1.98
2.18

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Example

Positive overlap

$s + s$

$p_z + s$

$p_x + p_x$

$d_{zx} + p_x$

Negative overlap

$p_z + p_z$

$-p_z + s$

$p_x - p_x$

$d_{zx} - p_x$

Zero overlap

s p_x or p_y

s d_{xy}

p_y $d_{x^2 - y^2}$

p_x p_y

Figure 3-15   Some common types of orbital interaction leading to positive, negative, and zero overlap.

Consider H_2^+ Molecule
$1e^-$

Two ways to describe overlap (which is proportional to $(e^-\ density)^2$)

(1) Simple "sum of the squares" of the atomic orbitals

<u>or</u>

(2) "Square of the sums" of the atomic orbitals

<u>Localized</u> versus <u>Molecular Orbital</u> approach

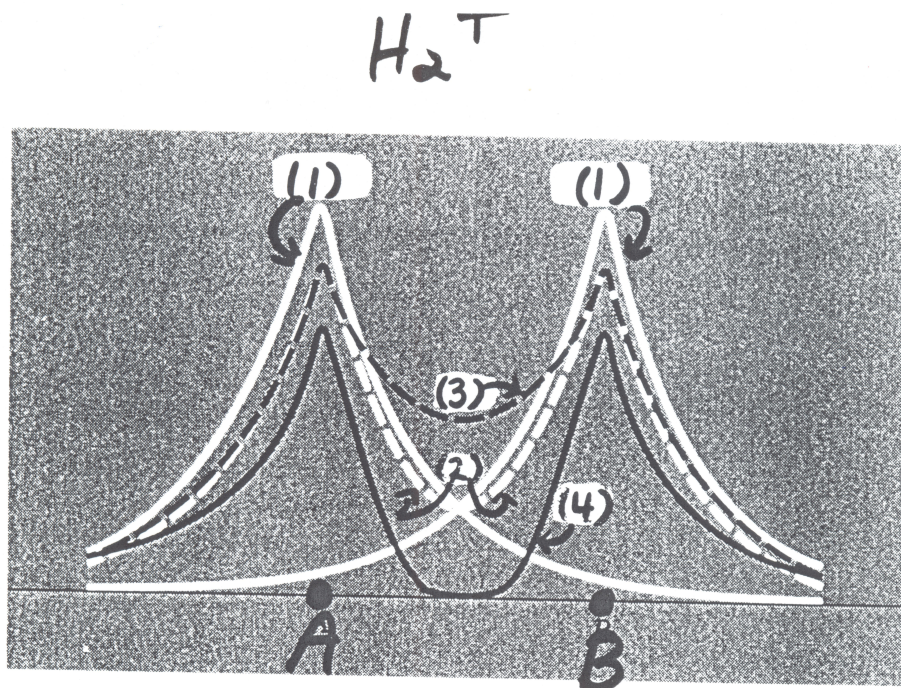Φ_A Φ_B <u>Atomic wavefunctions</u>
For H 1s orbitals

Φ_A^2 Φ_B^2 <u>Squares of the wavefunctions</u>
are proportional to overlap

Bonding then is either proportional to
(1) $(\Phi_A^2 + \Phi_B^2)/2$ or
(2) $(\Phi_A + \Phi_B)^2/2 \rightarrow (\Phi_A^2 + 2\Phi_A \Phi_B + \Phi_B^2)/2$

(2) is > (1) by $\Phi_A \Phi_B$

$H_2{}^T$

These plots depict the electron density in the region of space between atoms A and B

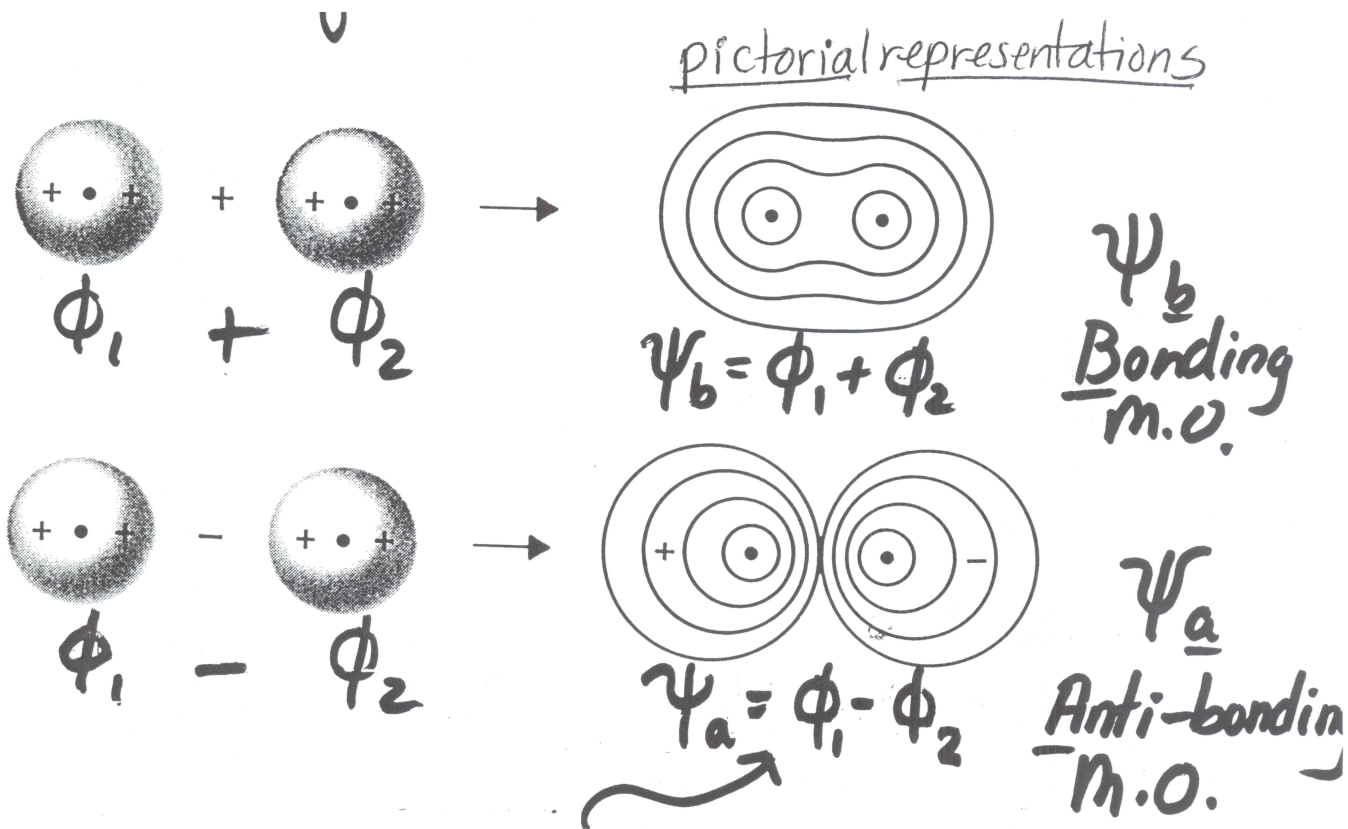|	
Atomic **Orbitals**	(1) white curves are individual atomic wavefunctions Φ_A, Φ_B
Localized **Bonding**	(2) dotted white curve represents the "sum of the squares" $\Phi_A{}^2 + \Phi_B{}^2/2$
M.O. **Bonding**	(3) dotted black curve represents the "square of the sum" of $\Phi_A + \Phi_B$ namely, $(\Phi_A + \Phi_B)^2/2$
M.O. **Antibonding**	(4) solid black curve represents the square of the difference $(\Phi_A - \Phi_B)^2/2$

Molecular Orbital Treatment
Diatomic Molecules …. continued

H_2 and He_2

As before: add & subtract wavefunctions

pictorial representations

$\phi_1 + \phi_2$

$\Psi_b = \phi_1 + \phi_2$

Ψ_b <u>Bonding</u> m.o.

$\phi_1 - \phi_2$

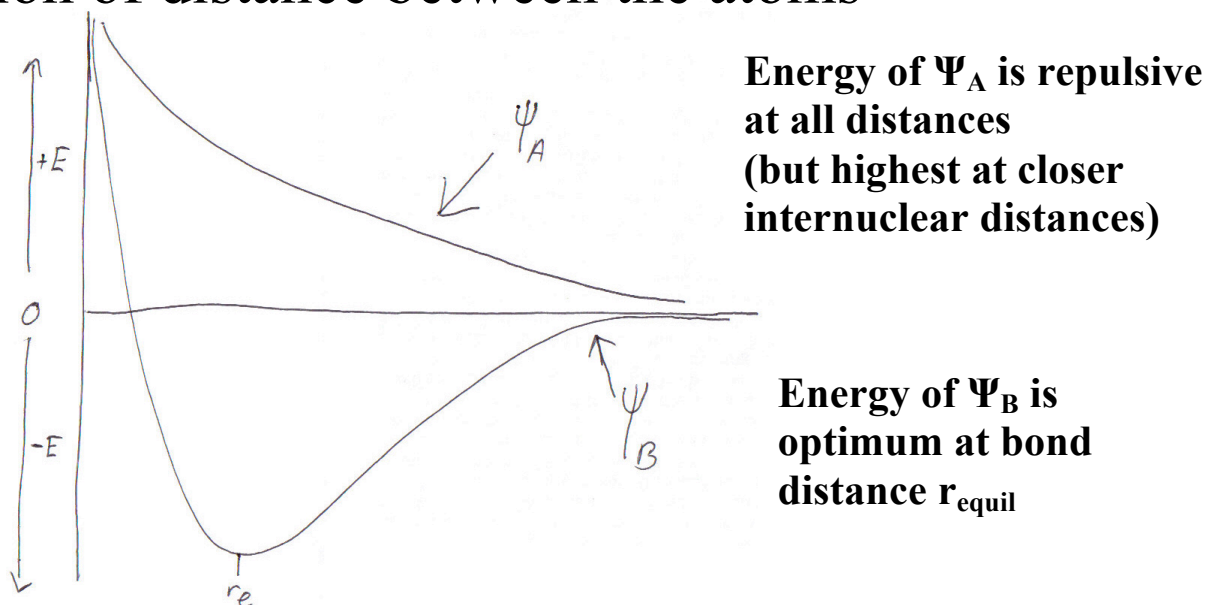$\Psi_a = \phi_1 - \phi_2$

Ψ_a <u>Anti-bonding</u> m.o.

The sign changes here
Between the nuclei $\rightarrow$ nodal
plane where e⁻ density is zero

Now:

Put electrons into Ψ_b and Ψ_a just as we do for atomic orbitals.

What are the relative energies of Ψ_a and Ψ_b?
One can represent this by a plot of the energies as a function of distance between the atoms

Energy of Ψ_A is repulsive at all distances (but highest at closer internuclear distances)

**Energy of Ψ_B is optimum at bond distance r_{equil}**

There is another, preferred, method for depicting the energies of M.O.'s than the above diagram

→   **Molecular Orbital Diagrams**

M.O. Diagrams
(1) Put the relative energies of the atomic orbitals on
      opposite sides of the diagram
(group "like" atoms together if there is more than one)

(2) The Diagram shows the energies of the
      molecular orbitals at only one energy, namely r_e.

$E_a = E_b$ for interactions of two orbitals at same starting energy
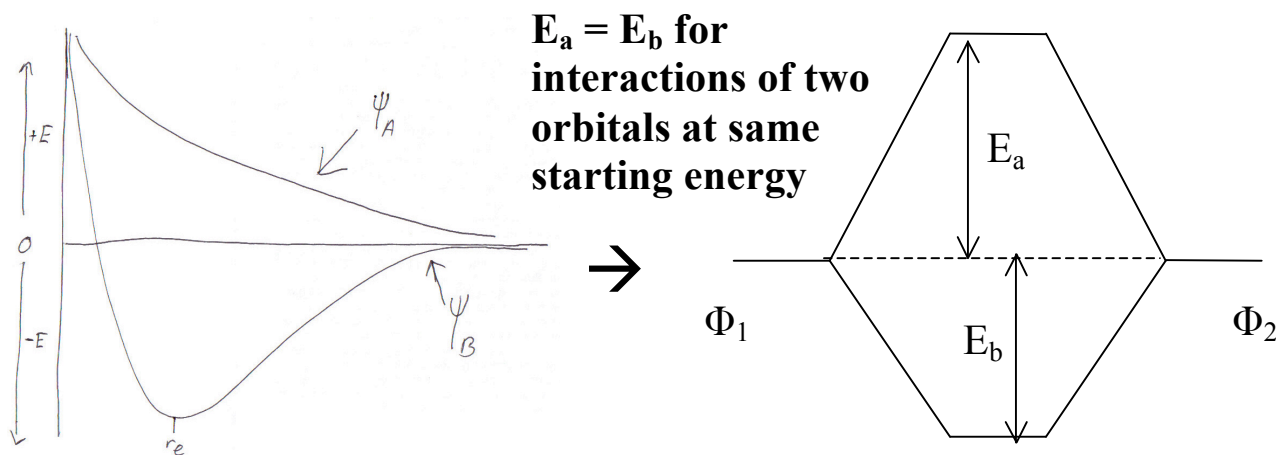
(3) Put electrons into the Molecular Orbitals following the same rules as for atomic filling (Pauli Exclusion Principle, Hund's rule)

Electrons are denoted by arrows ⇅ or dots ··

Contrast the Molecular Orbital Energy Level Diagrams for H_2 and He_2 : Φ_1 & Φ_2 are 1s atomic orbitals
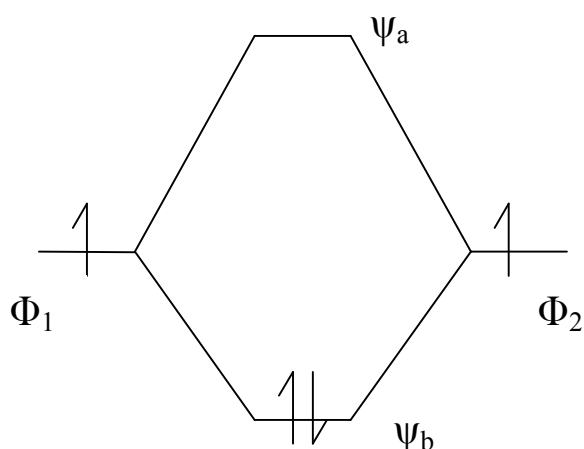
H_2 2e⁻
Stable, forms
a single bond:
H-H
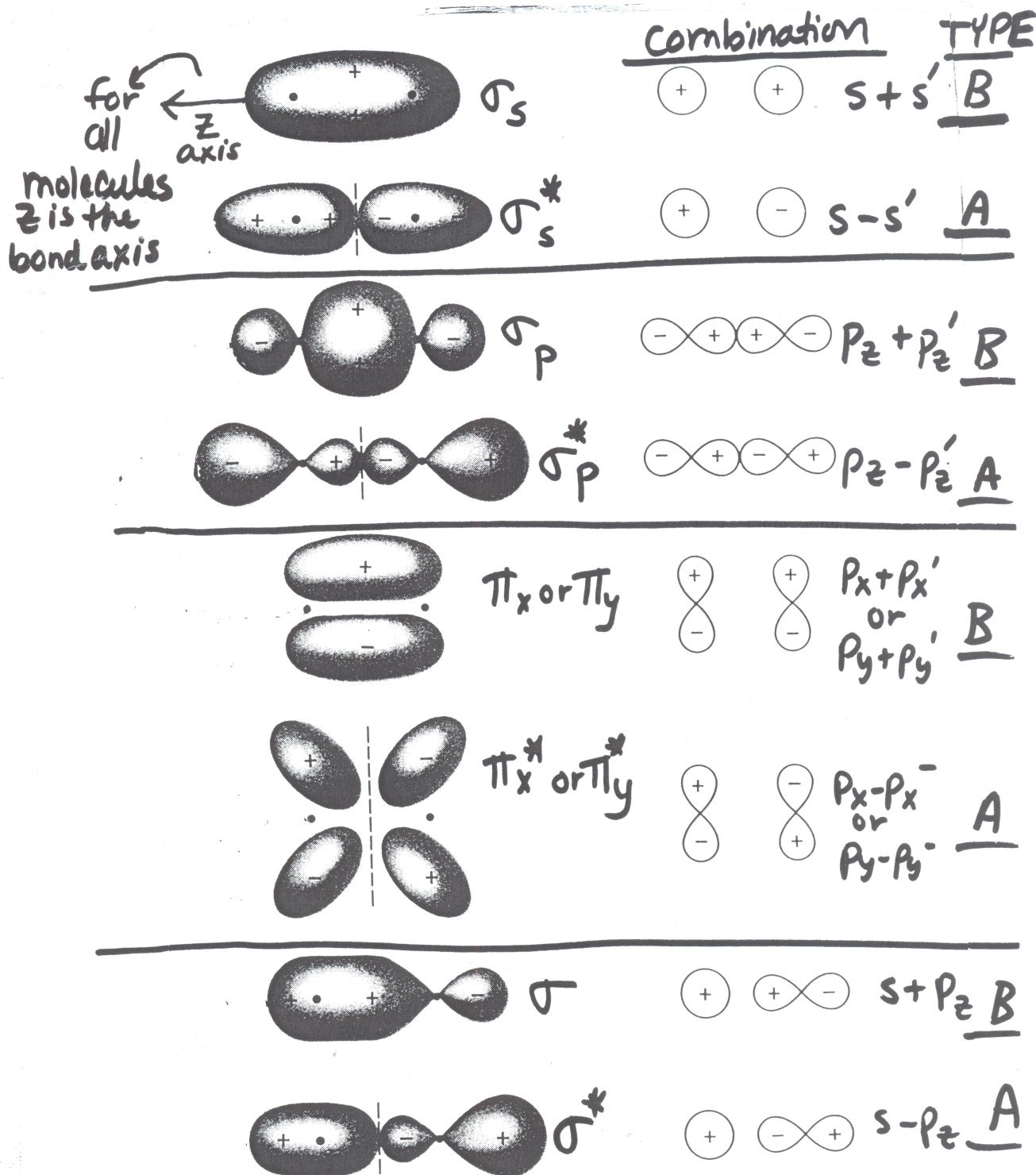$\Psi_b{}^2 \Psi_a{}^\circ$ is
Electronic conf.
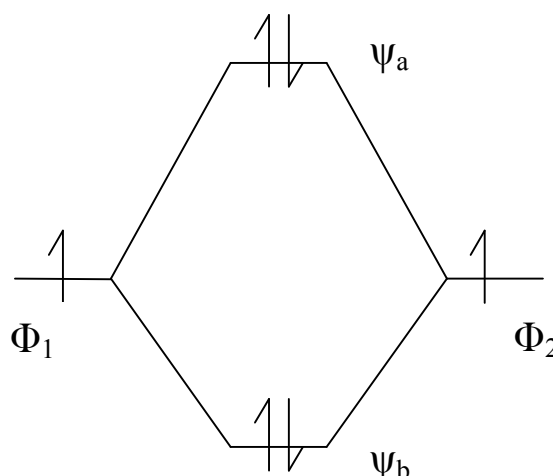
He_2 4e⁻
Unstable, no bond:
He X He
(same number of
bonding electrons and
antibonding e⁻)

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

	Combination	TYPE
σ_s	$(+)$ $(+)$ $s + s'$	B
σ_s^*	$(+)$ $(-)$ $s - s'$	A
σ_p	$(-)(+)(+)(-)$ $p_z + p_z'$	B
σ_p^*	$(-)(+)(-)(+)$ $p_z - p_z'$	A
π_x or π_y	$p_x + p_x'$ or $p_y + p_y'$	B
π_x^* or π_y^*	$p_x - p_x^-$ or $p_y - p_y^-$	A
σ	$(+)$ $(+)(-)$ $s + p_z$	B
σ^*	$(+)$ $(-)(+)$ $s - p_z$	A

for all molecules
z is the bond axis

z axis

Are there any other possibilities that have gone unmentioned?

Five	Five	**Q.**
$s+p_x$	$s-p_x$	What about these?
$s+p_y$	$s-p_y$	
p_x+p_y	p_x-p_y	**A.**
p_x+p_z	p_x-p_z	They are zero overlap
p_y+p_z	p_y-p_z	

We define internuclear bond axis as the z axis. Convention

Equal and opposite overlap ⇒ non-bonding

$s + P_x$

$s + P_y$

Whereas...

has a positive overlap

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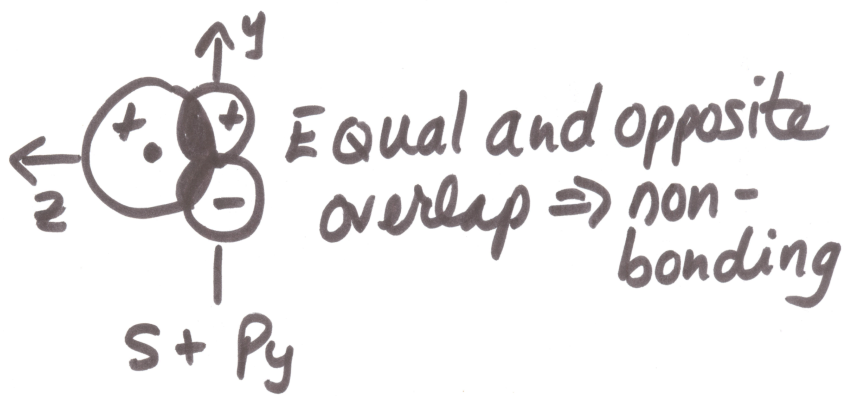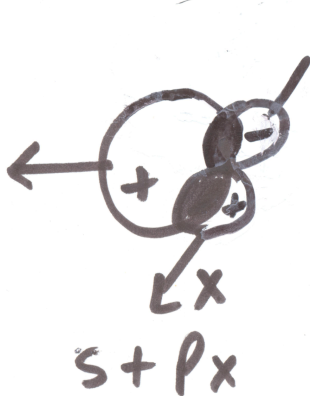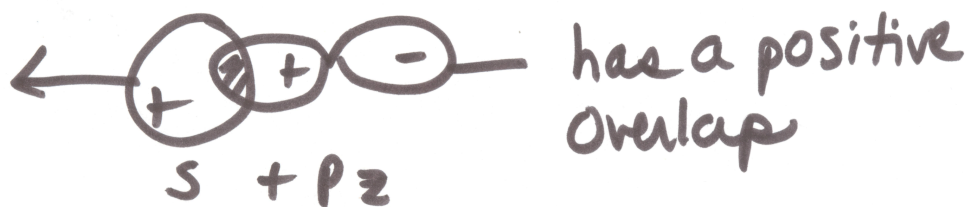
Due to the three different types of atomic orbitals depicted below, we also have three different types of M.O.'s*

① σ no change of sign — S no nodal planes

② node or π sign changes once — π one nodal plane

③ node node δ sign changes twice — δ two nodal planes
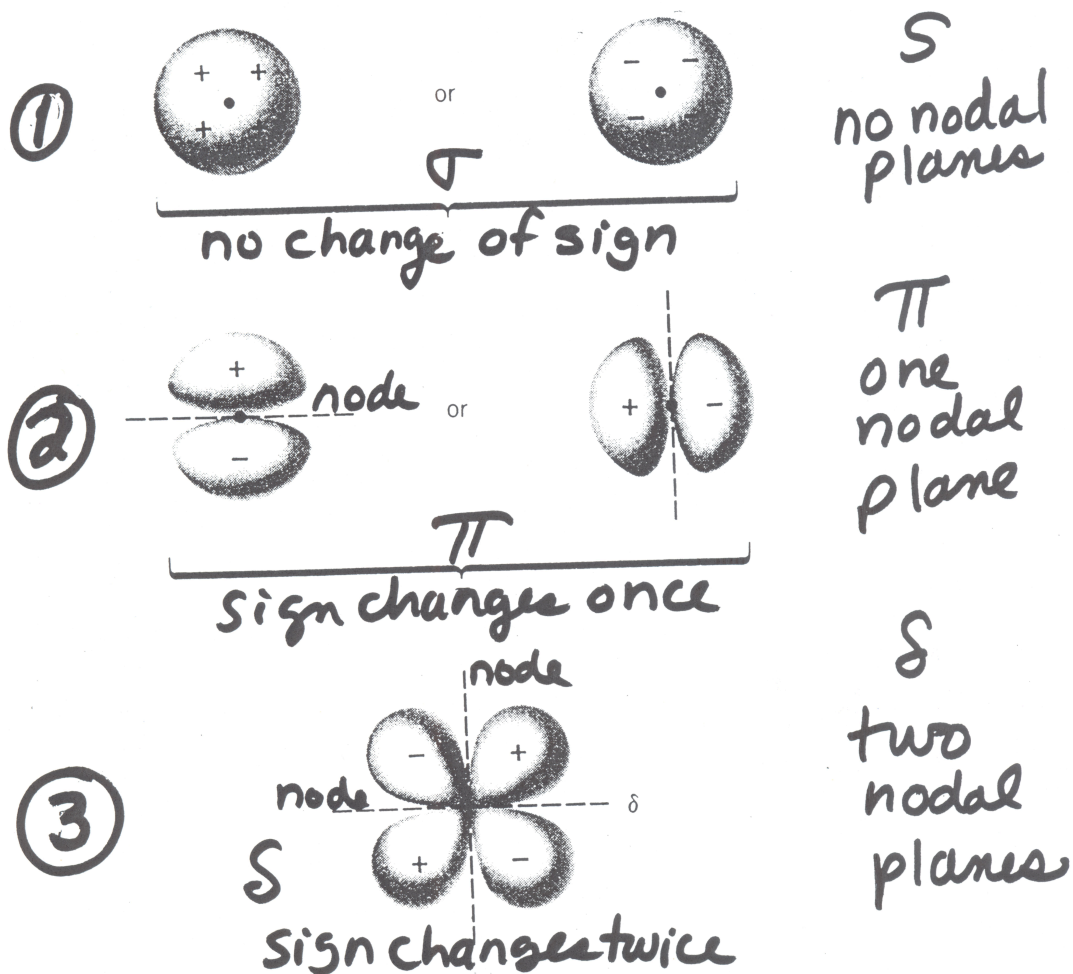
*These three types of a.o.'s can combine with one another to give m.o.'s that have zero (σ), one (π), or two (δ) nodal planes

$$\sigma, \pi, \delta \qquad \text{bonding}$$
$$\sigma, \pi^*, \delta^* \quad \text{antibonding}$$

Examples of Diatomic M.O. Treatment

(1) F_2 Molecule:

F is $1s^2 2s^2 2p^5$ (only $2s^2 2p^5$ are valence electrons)

1s electrons are buried, close to the nucleus and do 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 atom Effective Nuclear Charge is high
→ 2s/2p orbital energies are, therefore, quite different

1s – very low in energy
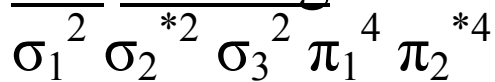2s – still very low in energy
2p – highest in energy
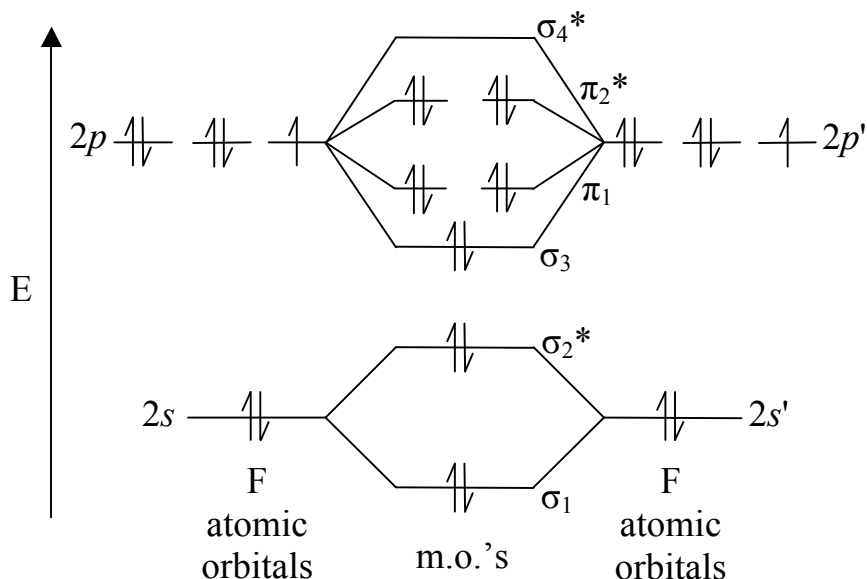
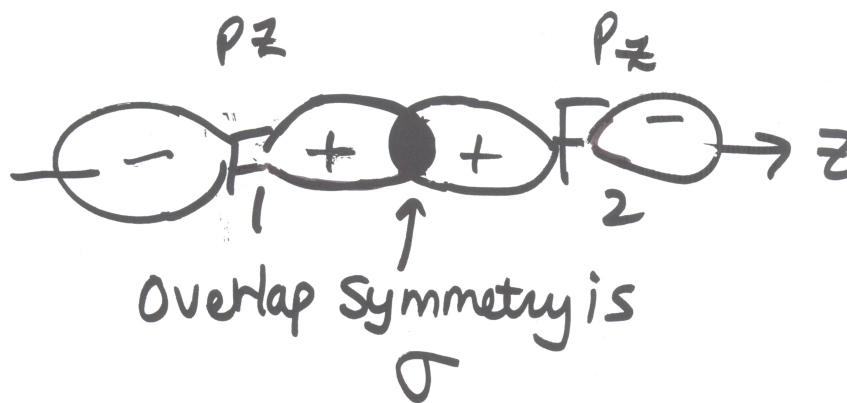Fill the diagram with the 14 valence electrons (7 from each F)

F_2

<u>Electronic Configuration</u> is :
$\sigma_1{}^2\ \sigma_2{}^{*2}\ \sigma_3{}^2\ \pi_1{}^4\ \pi_2{}^{*4}$ (σ levels are non degenerate)
   (π levels are doubly degenerate)

<u>Net bonding</u> is:
$\sigma_1{}^2\ \sigma_2{}^{*2}\ \sigma_3{}^2\ \pi_1{}^4\ \pi_2{}^{*4}$
one σ bond based on the $2p_z \ldots . 2p_z$ overlap
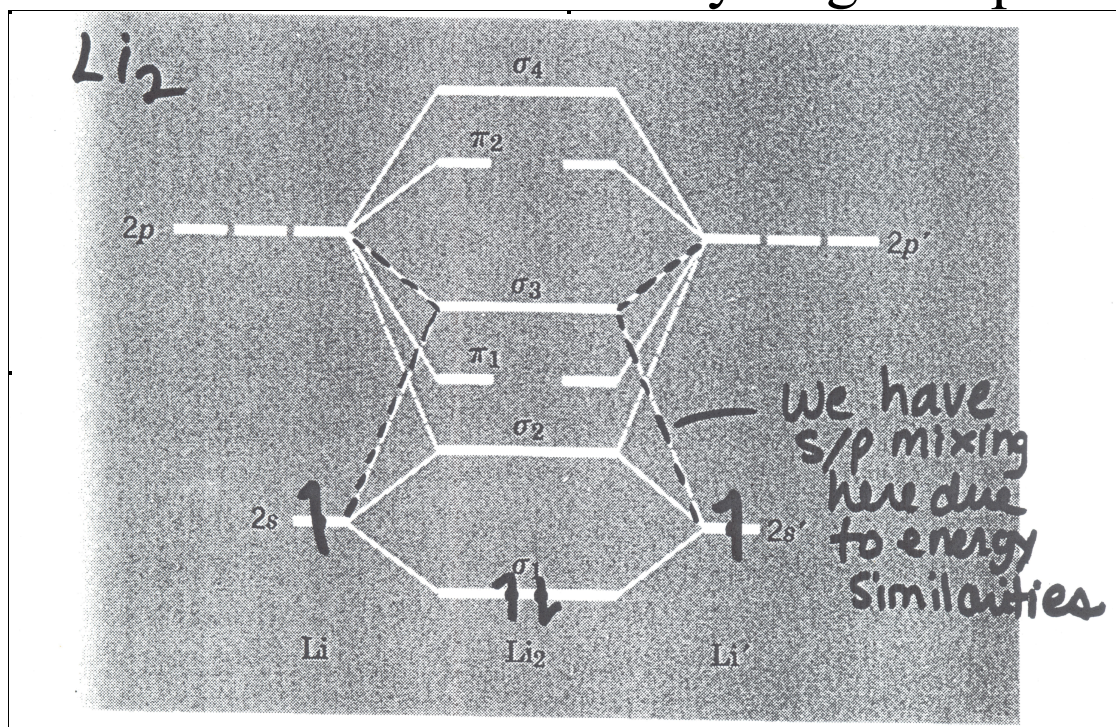
Bond order in MO theory is:
(#of bonding electrons - # of antibonding electrons)/2 ←

                  2e⁻ per bond

Example 2 Li_2

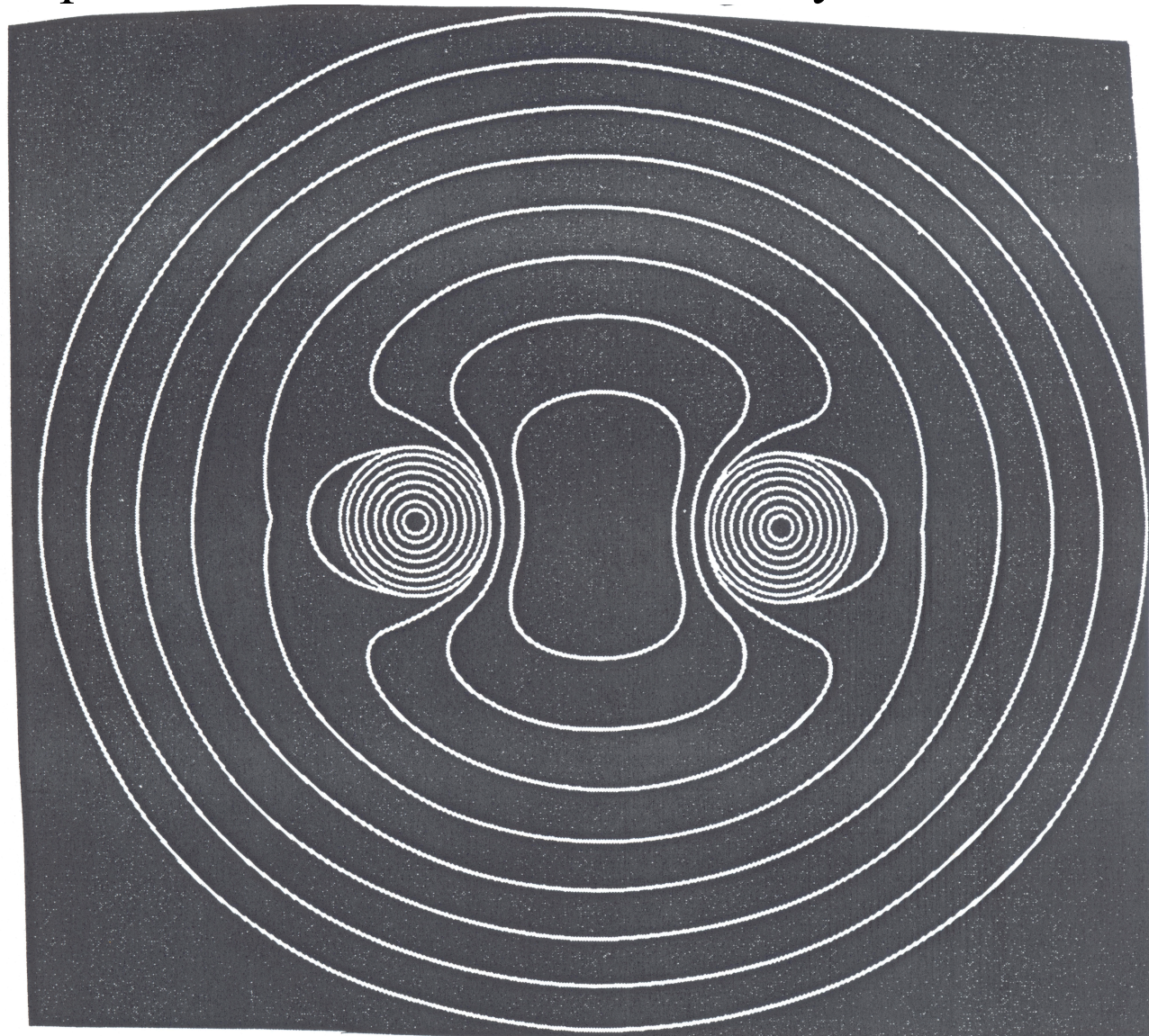Main difference between Li_2 and F_2 is that the 2s and 2p separation is much less in Li_2

Li $1s^2 2s^1 2p^0$
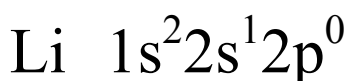
        Need to understand why σ^3 goes up

The electronic configuration is $\sigma_1{}^2$ based only on s…s overlap.
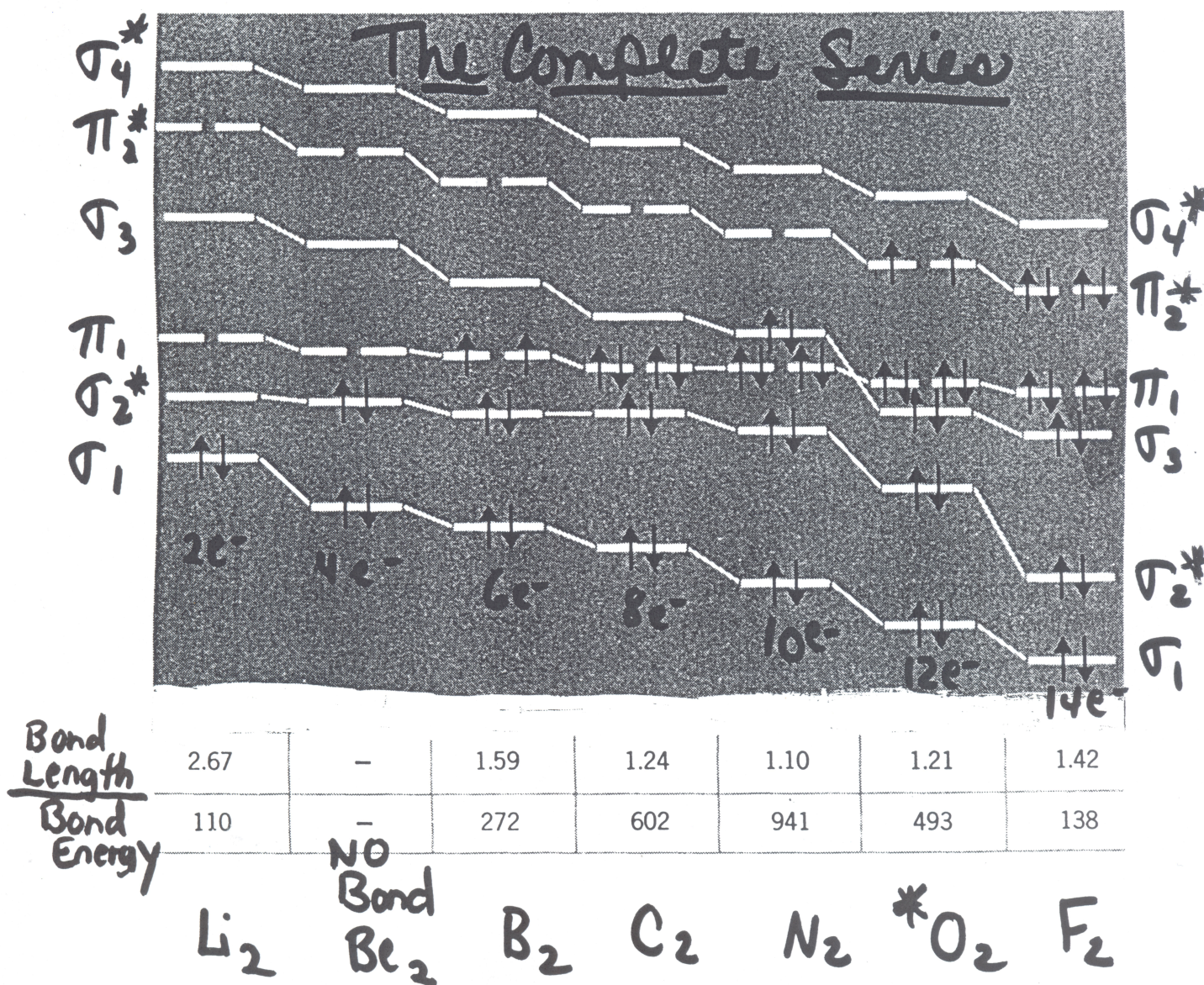
Li$_2$ (σ)

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

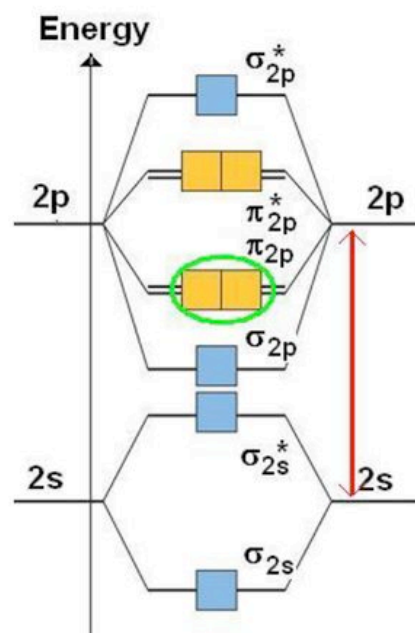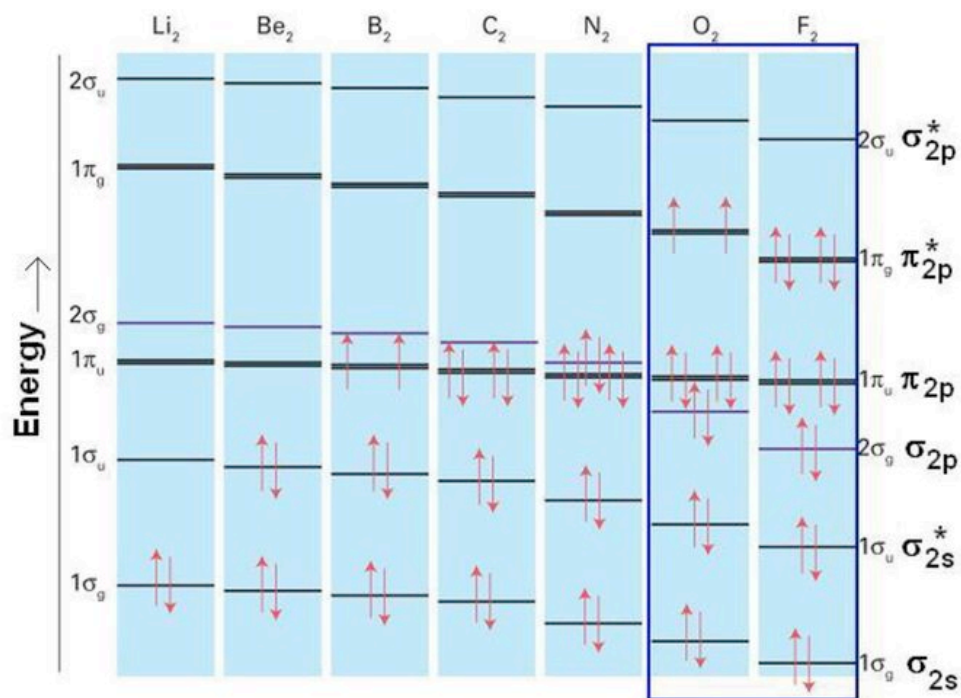Note: this bond doesn't depend on any of the higher energy M.O.'s

The difference in the separation of 2s and 2p leads to different energy orderings for $Li_2 \to F_2$
*Crossing of π, and σ_3 occurs at O_2 when mixing becomes unimportant.

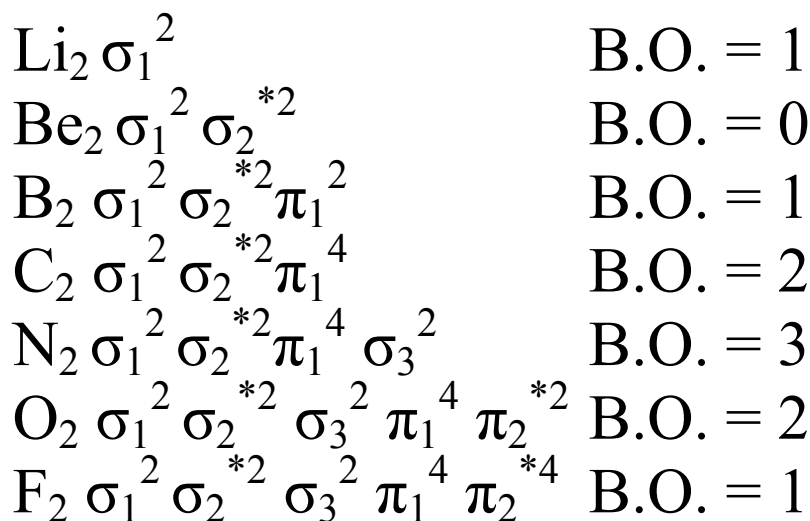|	Li₂	Be₂	B₂	C₂	N₂	*O₂	F₂
Bond Length	2.67	—	1.59	1.24	1.10	1.21	1.42
Bond Energy	110	— NO Bond	272	602	941	493	138

the separation of 2s and 2p leads to different energy orderings for $Li_2 \to F_2$

-For O_2 and F_2, the energy levels of 2s and 2p are well-separated: there is no participation of 2s AO in forming σ_{2p} orbital. There is no mixing of . σ_{2s}^* and σ_{2p}


from Shriver

KAIST
CHEMISTRY

What are the bond orders for the series?

Li_2 $\sigma_1{}^2$ B.O. = 1

Be_2 $\sigma_1{}^2 \sigma_2{}^{*2}$ B.O. = 0

B_2 $\sigma_1{}^2 \sigma_2{}^{*2} \pi_1{}^2$ B.O. = 1

C_2 $\sigma_1{}^2 \sigma_2{}^{*2} \pi_1{}^4$ B.O. = 2

N_2 $\sigma_1{}^2 \sigma_2{}^{*2} \pi_1{}^4 \sigma_3{}^2$ B.O. = 3

O_2 $\sigma_1{}^2 \sigma_2{}^{*2} \sigma_3{}^2 \pi_1{}^4 \pi_2{}^{*2}$ B.O. = 2

F_2 $\sigma_1{}^2 \sigma_2{}^{*2} \sigma_3{}^2 \pi_1{}^4 \pi_2{}^{*4}$ B.O. = 1

- N_2 has highest bond order (:N≡N:), the shortest, and the strongest bond
- O_2 is a double bond and is a paramagnetic molecule because the last two electrons go in the π set unpaired. It is called "triplet" oxygen.

* O_2 Lewis Structure is correct, but it <u>does</u> <u>not</u> predict two unpaired electrons.

Q. What about Ne_2?

A. This is an unstable molecule:
$\sigma_1{}^2 \sigma_2{}^{*2} \sigma_3{}^2 \pi_1{}^4 \pi_2{}^{*4} \pi_4{}^{*2}$
16 valence electrons (B.O. =0)
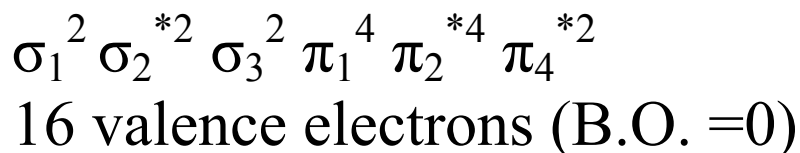
Heteronuclear Diatomic Molecules
AB rather than A_2 means that the atomic orbitals no longer begin at the same energies.

Carbon Monoxide, CO

How do we create an MO energy level diagram for a heteronuclear diatomic species in which both atoms have valence s and p orbitals?

Step #1: We need to figure out the relative energies of the valence orbitals.

- We know that O is more electronegative than C, therefore the orbitals of O should be lower in energy than that of C.
- We know that the energy gap between the $2s$ and $2p$ orbitals increases across the period...so a larger separation in O than in C.
- If we have IP values for the valence orbitals, we use these. If not, we use the above knowledge to estimate the relative atomic orbital energy and plot them.

Step #2: We need to figure out which orbitals are of the correct symmetry to mix with each other. ₘAs always, the *z*-axis is the bond axis.

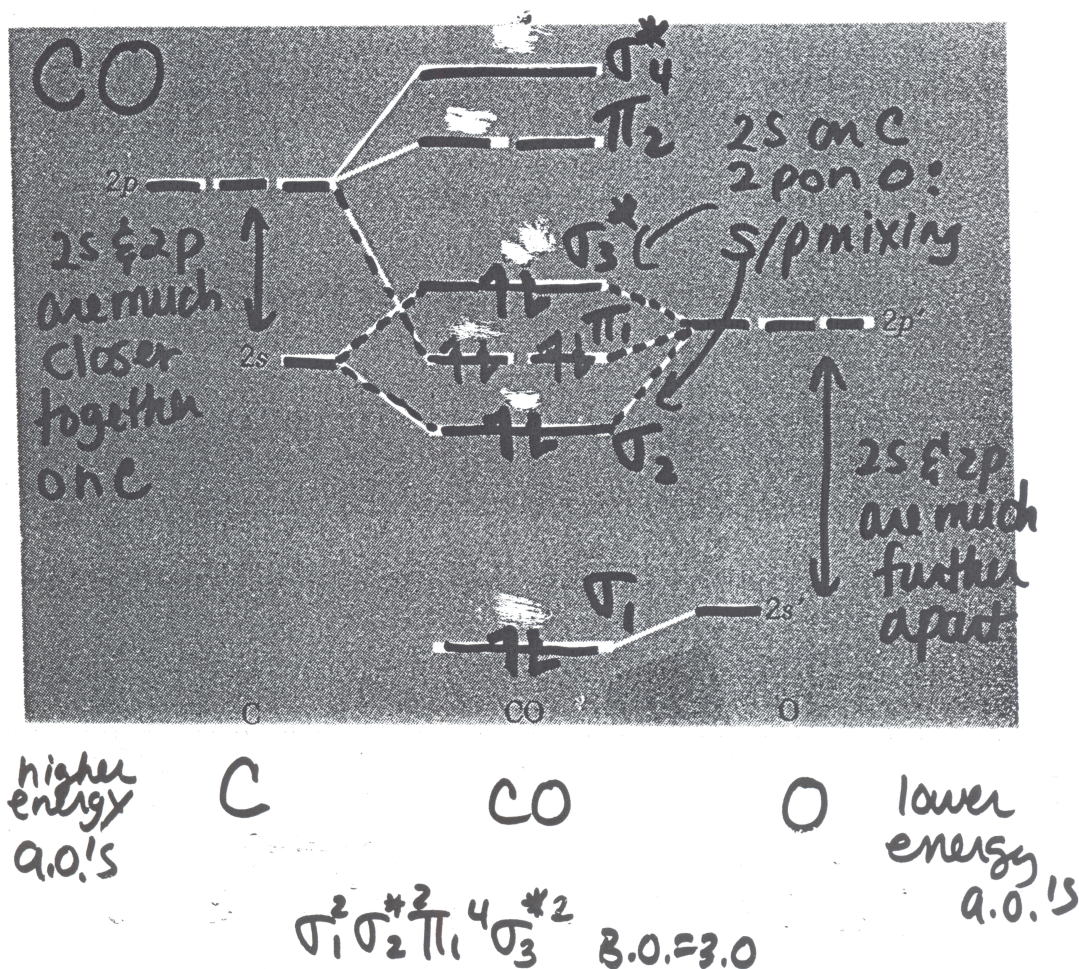The *s* orbitals and *p* orbitals of both atoms are the correct symmetry to form σ interactions.

   MIX 4 ATOMIC ORBITALS (σ) ⇒ GET 4 MOs (σ)

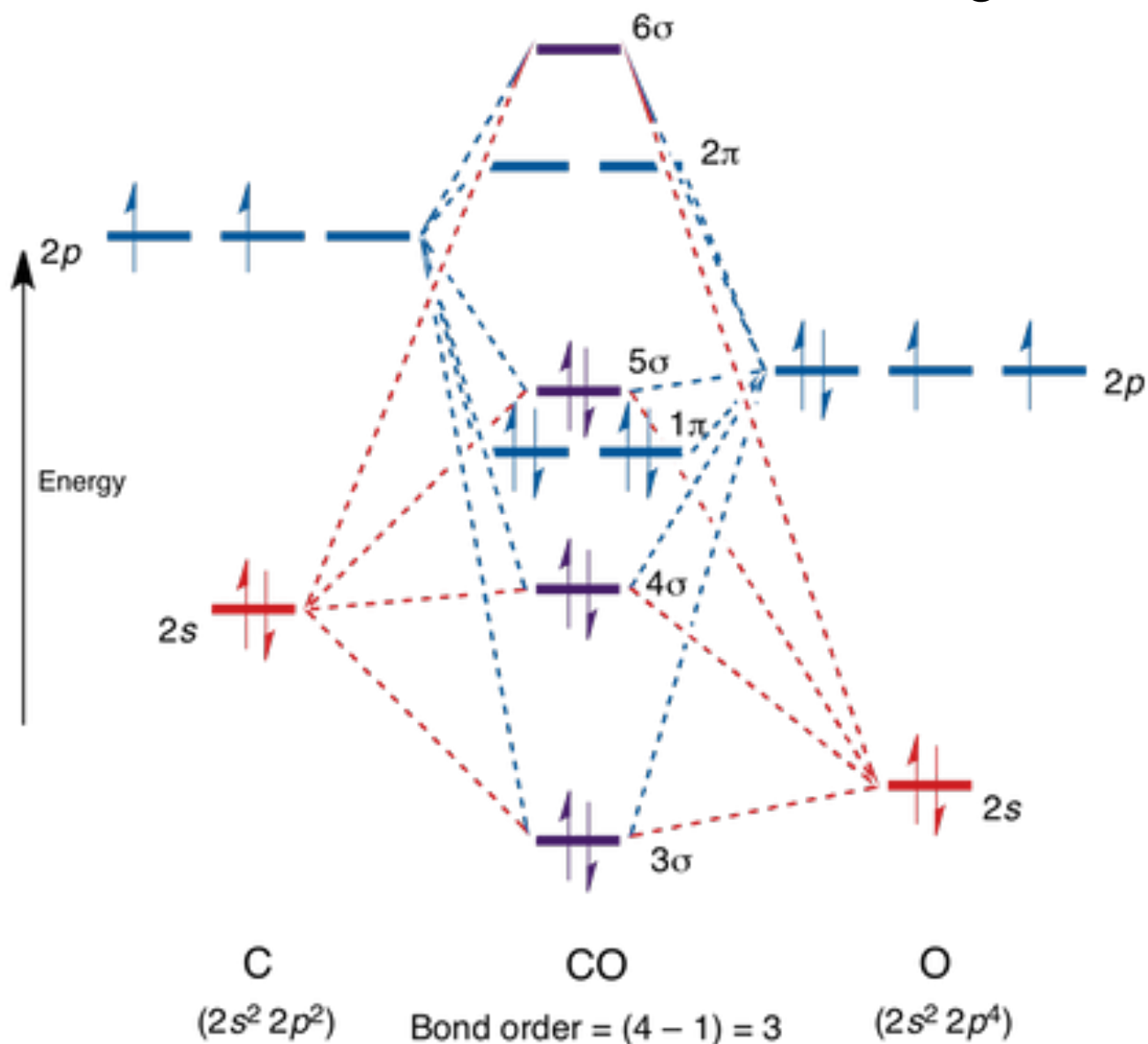The *p* orbitals of each atom are π symmetry along *x*.

   MIX 2 ATOMIC ORBITALS (π in *x*) ⇒ GET 2 MOs (π in *x*)

The *p* orbitals of each atom are π symmetry along *y*.

   MIX 2 ATOMIC ORBITALS (π in *y*) ⇒ GET 2 MOs (π in *y*)

$\sigma_1^2 \sigma_2^{*2} \pi_1^4 \sigma_3^{*2}$ B.O.=3.0

ANOTHER VIEW OF THE CO M.O. Diagram

LUMO = lowest unoccupied molecular orbital.

$\Rightarrow 2\pi^*$ is largely C character

HOMO = highest occupied molecular orbital.

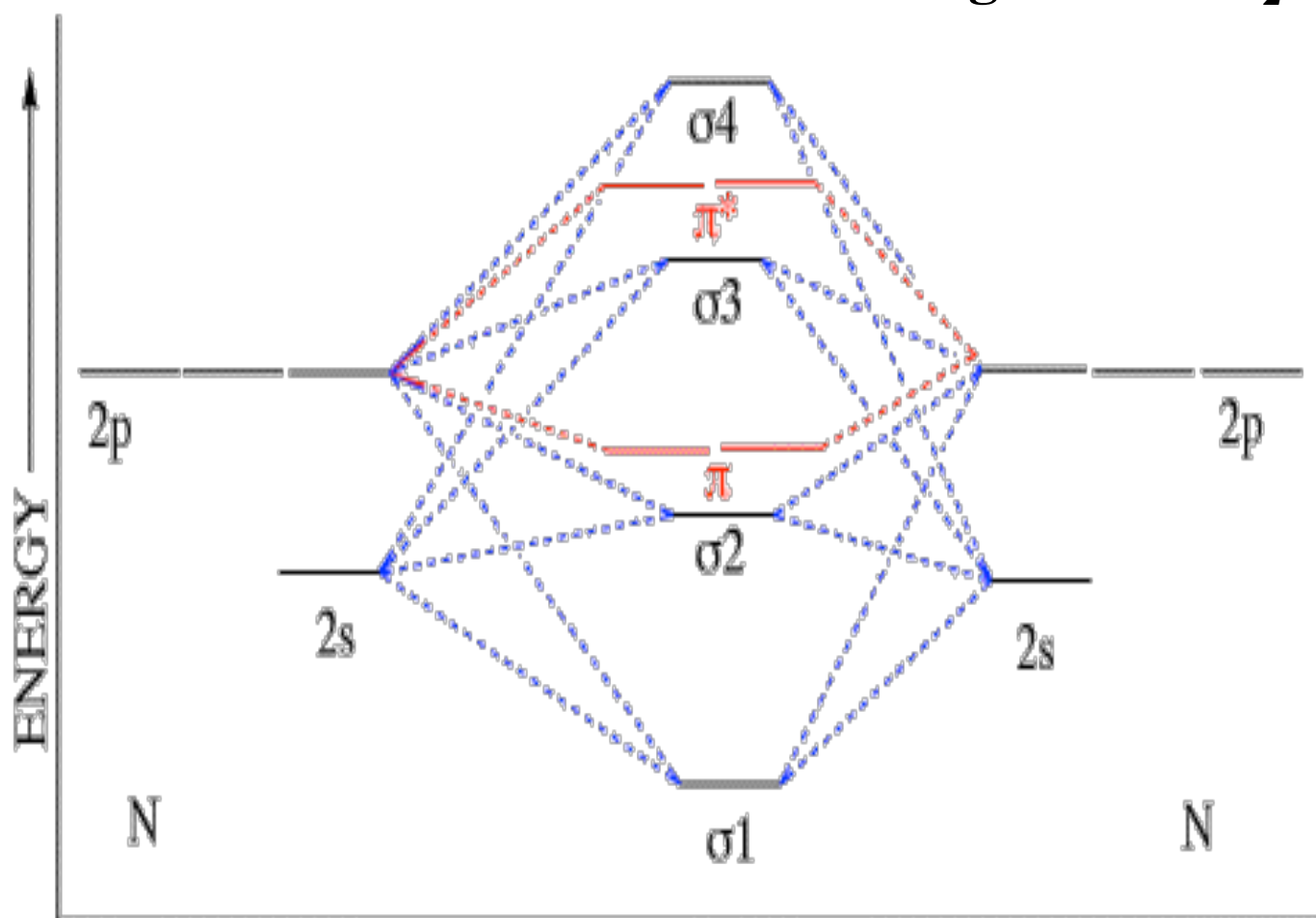$\Rightarrow 5\sigma$ is largely C character (actually non-bonding...C lone pair)

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

M.O. Diagram for Carbon monoxide CO
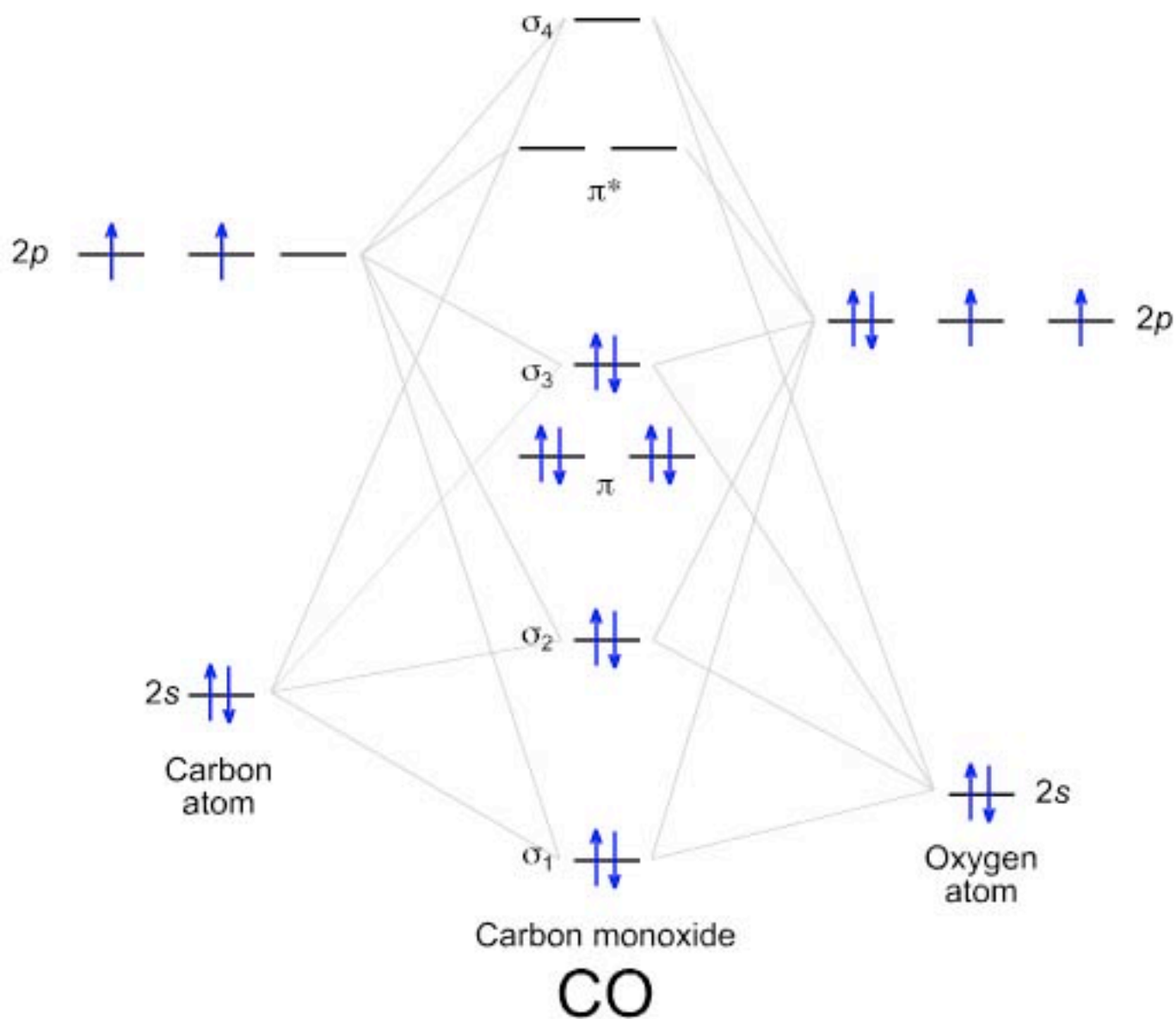
Contrast M.O. Diagram for CO with N_2:

Here is the full molecular orbital diagram for N_2.

Now we add the 10 electrons, 5 from each nitrogen atom. Note that the bottom sigma symmetry orbital is strongly bonding, the top one is strongly antibonding, and the 2 in the middle are only weakly bonding and antibonding, respectively. The 2 and 3 orbitals correspond to the non-bonding electron pairs in the Lewis structure. There is one sigma bond and 2 pi bonds when the 10 electrons are added to the lowest energy molecular orbitals.