Molecular Orbital (MO) Theory

Lewis dot, VESPR & Valence Bond (VB) theories all do a good job at predicting the shapes and bonding in covalent molecules.

Chemists however sometimes require another theory of bonding that explains phenomenon such as ***paramagnetism*** in covalent molecules or why certain species form unstable compounds while others don't.

To address such issues, we can describe bonding from a perspective of ***Molecular Orbitals***. In MO theory, the ***atomic orbitals*** on individual atoms combine (*constructively and destructively*) to produce new ***molecular orbitals*** that give rise to bonding and anti-bonding orbitals that exist between nuclei.

Molecular Orbital Theory has several advantages and differences over VESPR & VB theory:

- MO does a good job of predicting electronic spectra and paramagnetism, when VSEPR and the VB theories don't.

- The MO theory like VB theory, predicts the bond order of molecules, however it does not need resonance structures to describe molecules

- MO theory treats molecular bonds as a sharing of electrons between nuclei. Unlike the VB theory, which treats the electrons as *localized hybrid orbitals* of electron density.

- MO theory says that the electrons are *delocalized*. That means that they are spread out over the entire molecule.

The main drawback to our discussion of MO theory is that we are limited to talking about *diatomic molecules* (molecules that have only two atoms bonded together), or the theory gets very complex.

MO Theory:

When two atoms come together, their atomic orbitals interact to form two possible molecular orbitals, (1) the lower energy "***bonding***" MO and (2) the higher energy "***anti-bonding***" MO.

Recall that the atomic orbitals on an atom are described by ***Wave Functions*** (**Ψ**), i.e. the mathematical representations of the probability of space in which an electron resides.

Considered a molecule A-B

When two wave functions (orbitals) on different atoms add constructively they produce a new MO that promotes boding given by:
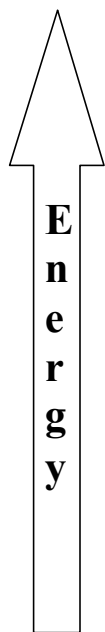
(1) $$\Psi_A \ + \ \Psi_B \ \rightarrow \ \Omega_{AB}$$

When two wave functions (orbitals) on different atoms add destructively (subtract) they produce a new MO that promotes anti-bonding boding given by:
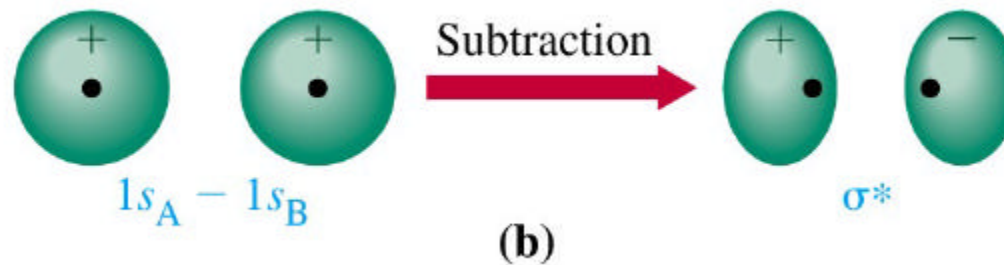
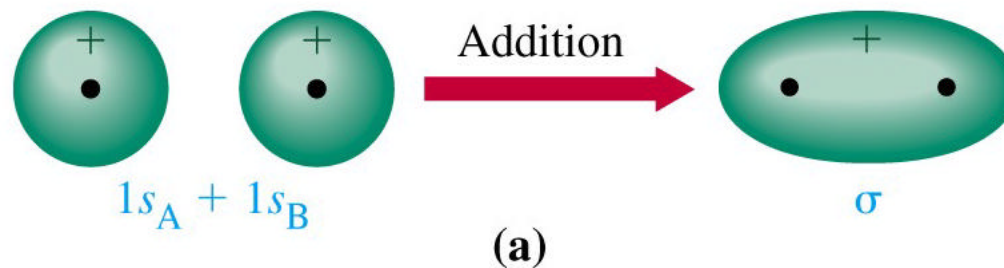(2) $$\Psi_A \ - \ \Psi_B \ \rightarrow \ \Omega^*_{AB}$$

MO Theory:

- The lower energy bonding molecular orbital (1) stabilizes the molecule is.

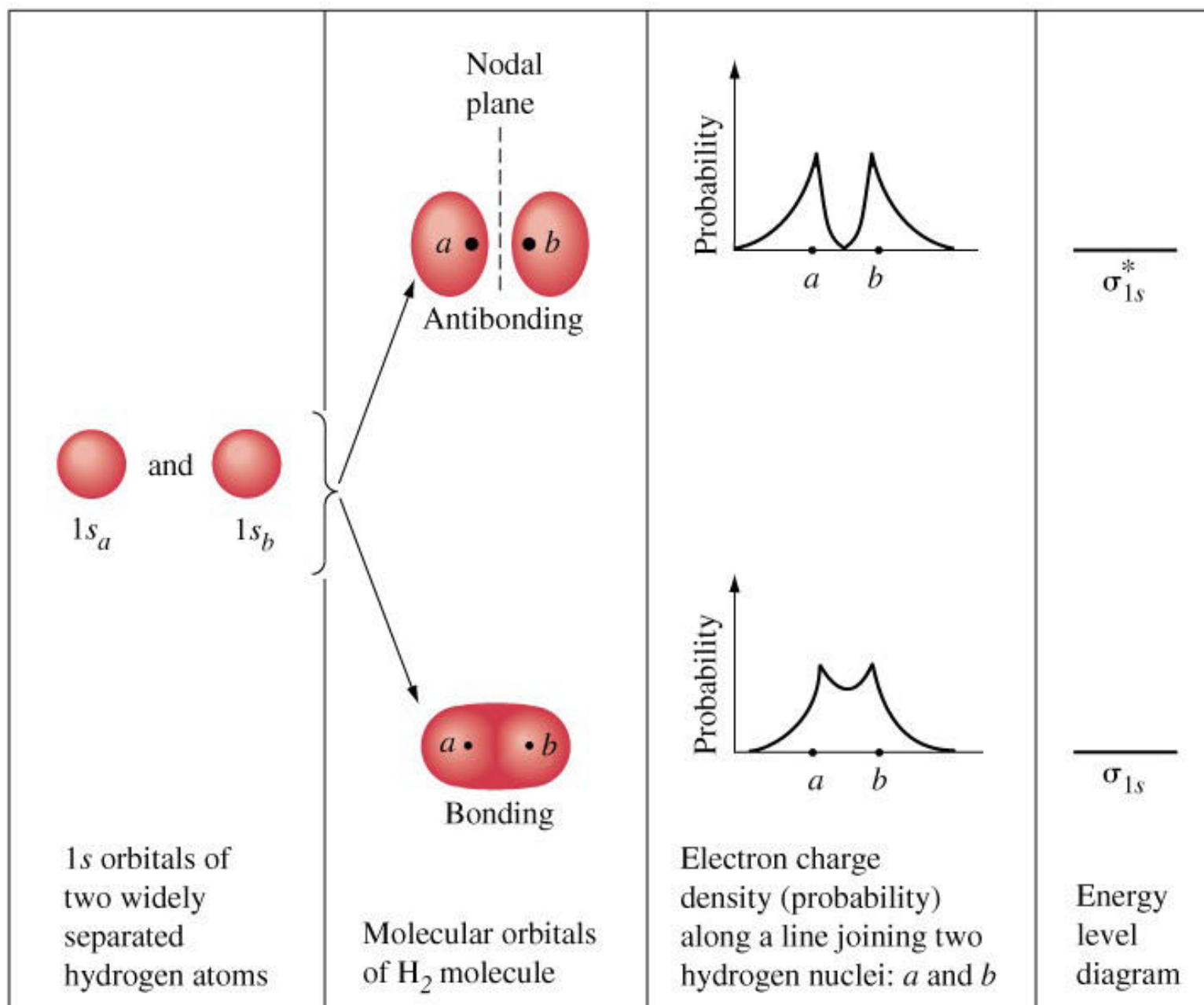- The higher energy anti-bonding orbital (2) destabilizes the molecule.

Consider H_2

When the 1s orbitals of each H-atom subtract, an anti-bonding orbital forms.

$1s_A - 1s_B$

Subtraction

$\sigma*$

(b)

When the 1s orbitals of each H-atom add, a bonding orbital forms.

$1s_A + 1s_B$

Addition

σ

(a)

Nodal plane

a b

Antibonding

a b

Bonding

Probability

a b

Probability

a b

σ_{1s}^{*}

σ_{1s}

$1s_a$ $1s_b$

and

1s orbitals of two widely separated hydrogen atoms

Molecular orbitals of H_2 molecule

Electron charge density (probability) along a line joining two hydrogen nuclei: a and b

Energy level diagram

Terminology in MO theory:

- ***s*-bonding orbital**: stabilizing MO that exists between nuclei.

- ***s**-anti-bonding orbital**: destabilizing MO that exists between nuclei.

- ***p*-bonding orbital**: stabilizing MO that exists above and below the inter nuclear axis.

- ***p**-anti-bonding orbital**: destabilizing MO that exists above and below the inter nuclear axis.

- ***node***:   region of zero probability

- ***ground state***: lowest energy configuration of electrons in a molecule

- ***excited state***: electron(s) moved to higher energy MO's

- ***Bond Order***: $BO = \dfrac{\text{\# of bonding electrons in MO's - \# of anti - bonding electrons in MO's}}{2}$

- ***LUMO***: lowest energy occupied MO

- ***HOMO***: highest energy occupied MO

MO Diagrams:

Once again we consider the simplest molecule, H_2.

When two hydrogen atoms combine the 1s orbitals on each can add or subtract to form a $\sigma(1s)$ bonding or $\sigma*(1s)$ anti-bonding orbital.

H   H

$\sigma*(1s)$

1s   1s

$\sigma(1s)$

Each H-atom has one 1s electron that can contribute to the MO bonding and anti-bonding MO's.

Just as in the electron configurations of atoms, the electron fill from the lowest energy MO first (**Aufbau principle**) only pairing when forced to (**Hund's rule**). Each MO can only hold two electrons of opposite spin (**Pauli priciple**)

H   H

$\sigma*(1s)$

↑   ↑

1s   1s

↑↓

$\sigma(1s)$
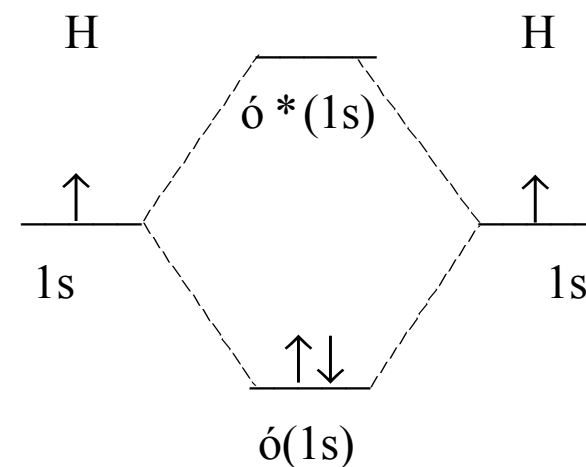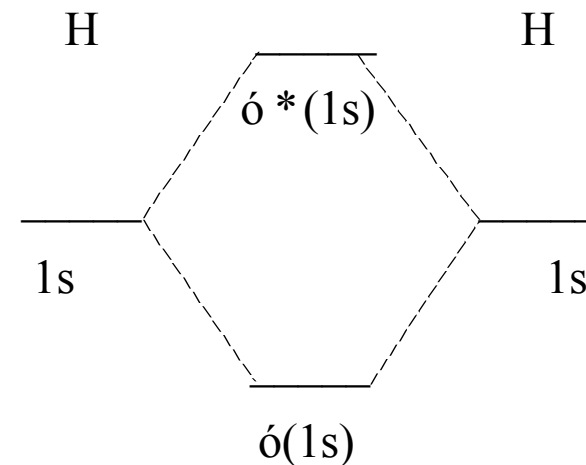
MO Diagrams:

From this we find that the bonding in H$_2$ is described by:

Bond Order = 1 (single bond)

$$BO = \frac{\text{\# of bonding electrons in MO's - \# of anti - bonding electrons in MO's}}{2} = \frac{2 - 0}{2} = 1$$

MO electron configuration of: σ_{1s}^2

And we conclude that the molecule (H$_2$) is ***diamagnetic*** (no unpaired electrons)
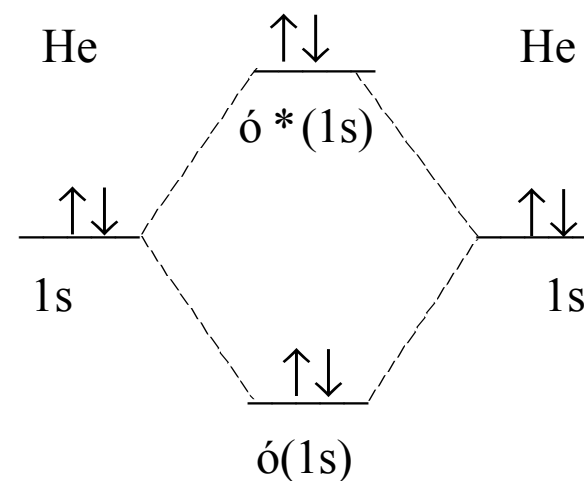
MO Diagrams: He$_2$

H$_2$, O$_2$, N$_2$ and the halogens all exist in nature as stable diatomic molecules.

Why is it then that He is a monatomic species?

Let's use MO theory to explain:

- Each He-atom has two 1s electron that can contribute to the MO bonding and anti-bonding MO's.

- To determine whether He$_2$ is a stable molecule, we fill the MO diagram for the 1s system just like H$_2$.

$$BO = \frac{2-2}{2} = 0$$

He   ↑↓   He

ó * (1s)

↑↓   ↑↓

1s   1s

↑↓

ó(1s)

From this we see that He$_2$ is an unstable molecule. The bond order is *zero*!

MO Diagrams: Li$_2$

- Since lithium is in the second period, the MO diagram must involve the formation of MO's from the interaction of the 1s & 2s orbitals. The 1s orbitals and the 2s orbitals don not mix due to the significant energy difference.

- The result is a MO diagram that forms a σ(1s) and σ(2s) system of bonds and anti-bonds

- Each Li-atom has three electrons; two 1s electron & 1 2s electron that contribute to the MO bonding and anti-bonding MO's.

- Upon filling the MO diagram, we find…

$$BO = \frac{4-2}{2} = 1$$

The molecule is predicted to be stable!

Li _____ _____ Li

ó * (2s)

↑ 2s   ↑ 2s

↑↓
ó(2s)

↑↓
ó * (1s)

↑↓ 1s   ↑↓ 1s

↑↓
ó(1s)
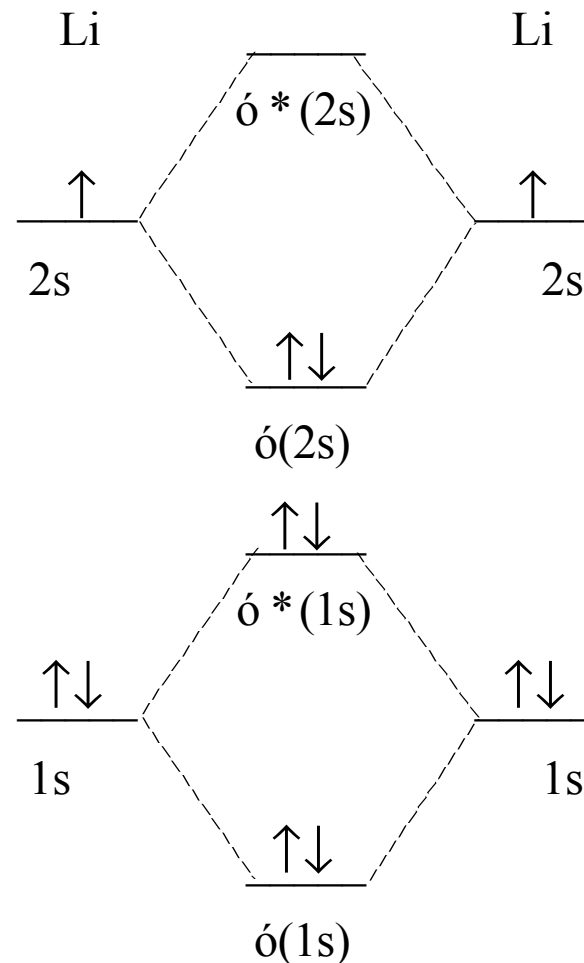
MO theory recap:

1. The number of *molecular orbitals* (MO's) formed is equal to the number of *atomic orbitals* (AO's) that combine.

2. When AO's combine they *add* (constructive) and *subtract* (destructive) to form bonding and anti-bonding MO's respectively

3. The bonding MO's are always at a lower state of energy than the anti-bonding MO's.

4. The maximum number of electrons in any MO is two.

5. The electrons from each atom that form the MO's fill from the lowest energy states first, pairing only when forced to. This is the *ground state*.

6. When electrons in the ground state are promoted to higher energy MO's, an *excited state* results.

Molecular Orbitals and the p Atomic Orbitals

Recall that the p-orbitals of an atom are oriented along the axes of a Cartesian set of coordinates. Each lobe is orthogonal to one another (90°).
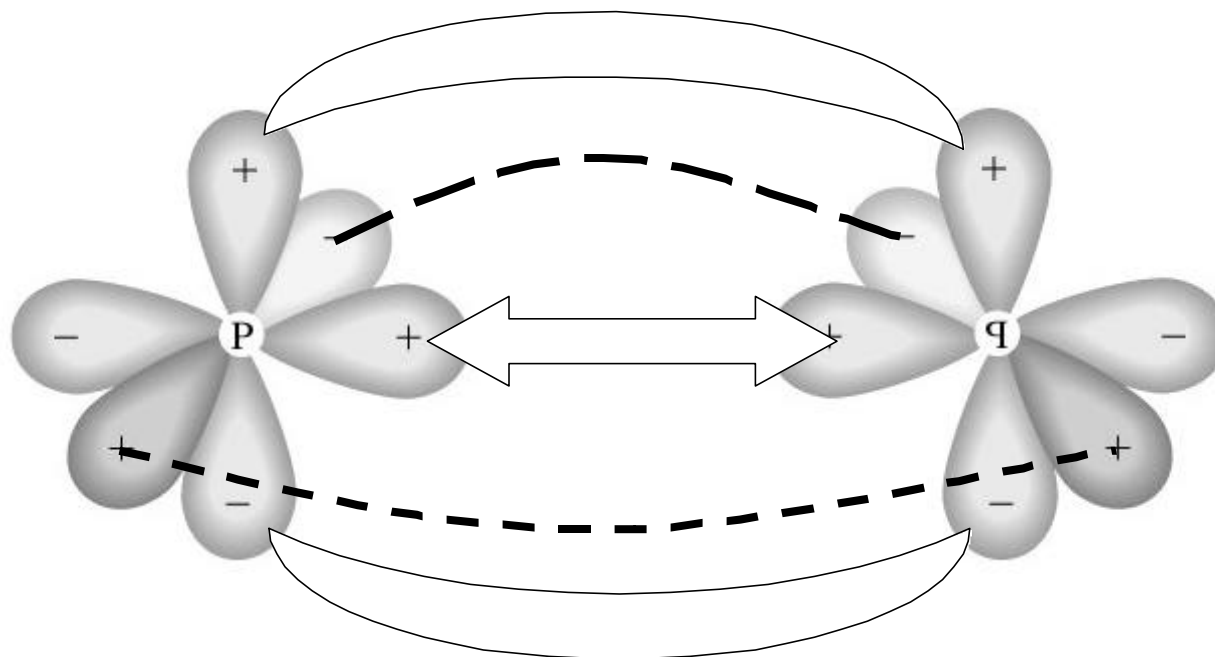
- When the lobes add and subtract, three sets of bonding and three sets of anti-bonding MO's result.

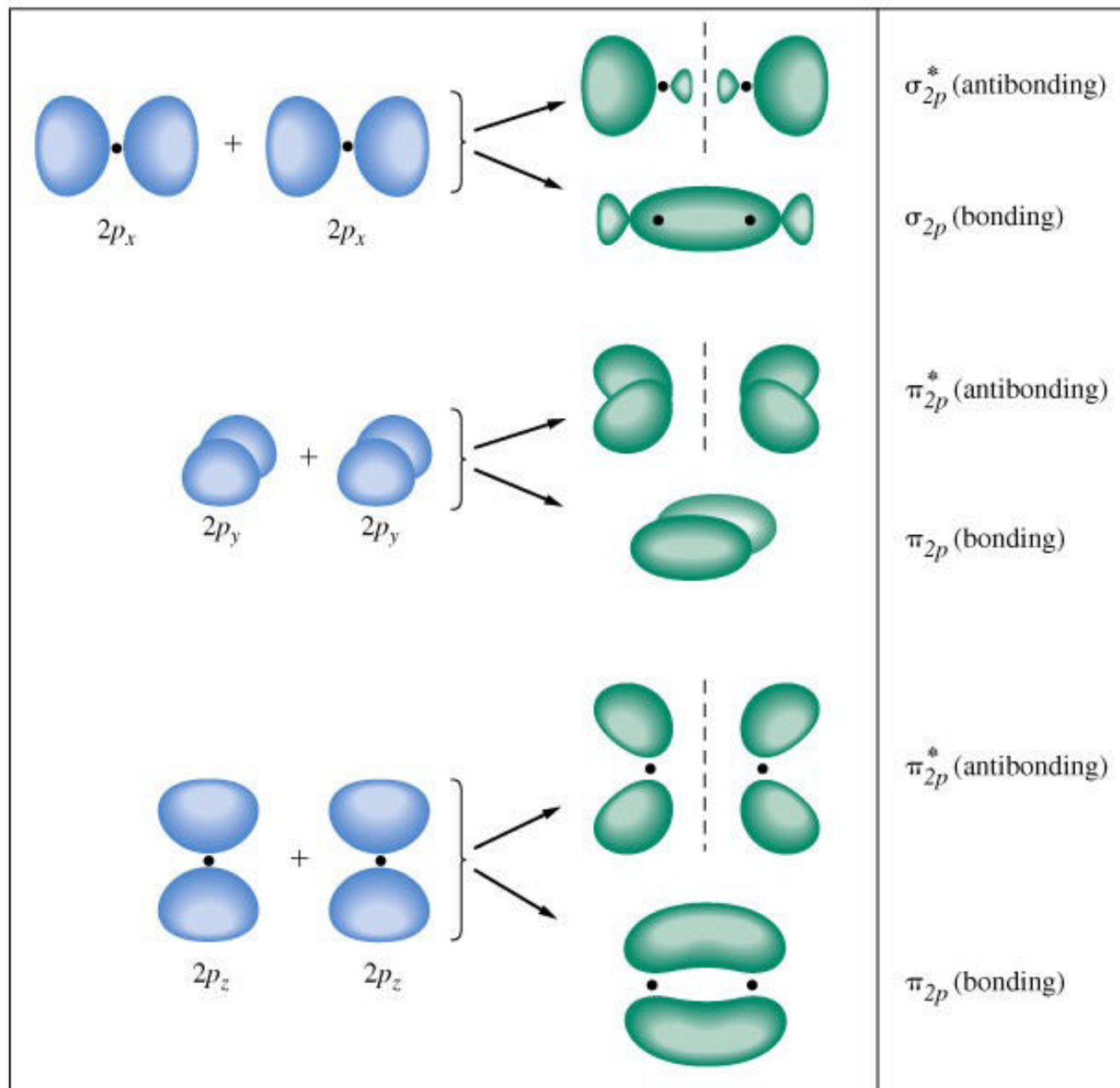- One has sigma character (σ) and two have pi (π) character.

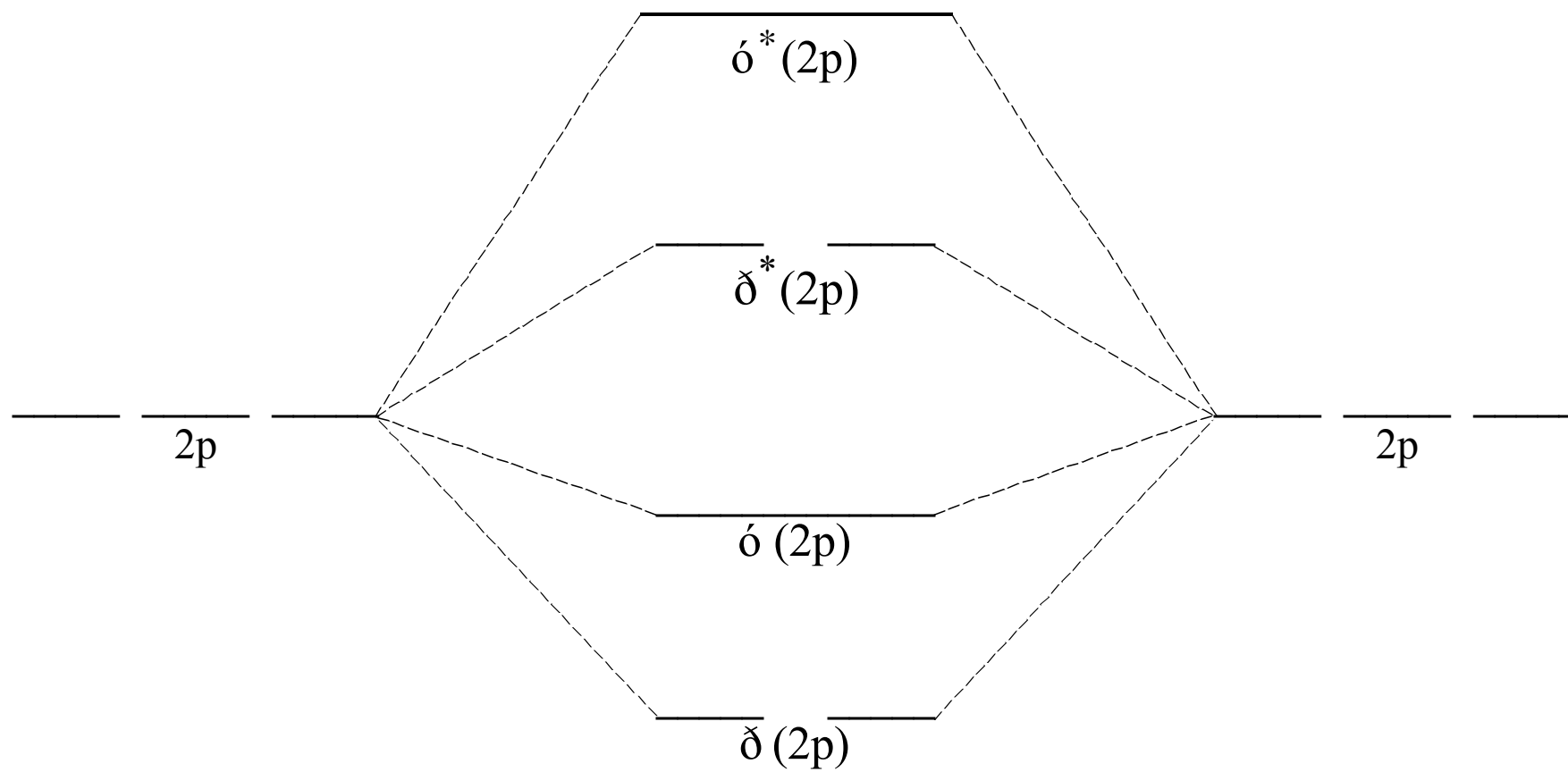One addition/subtraction results in (a) & (b), $\sigma(2p)$ and $\sigma^*(2p)$
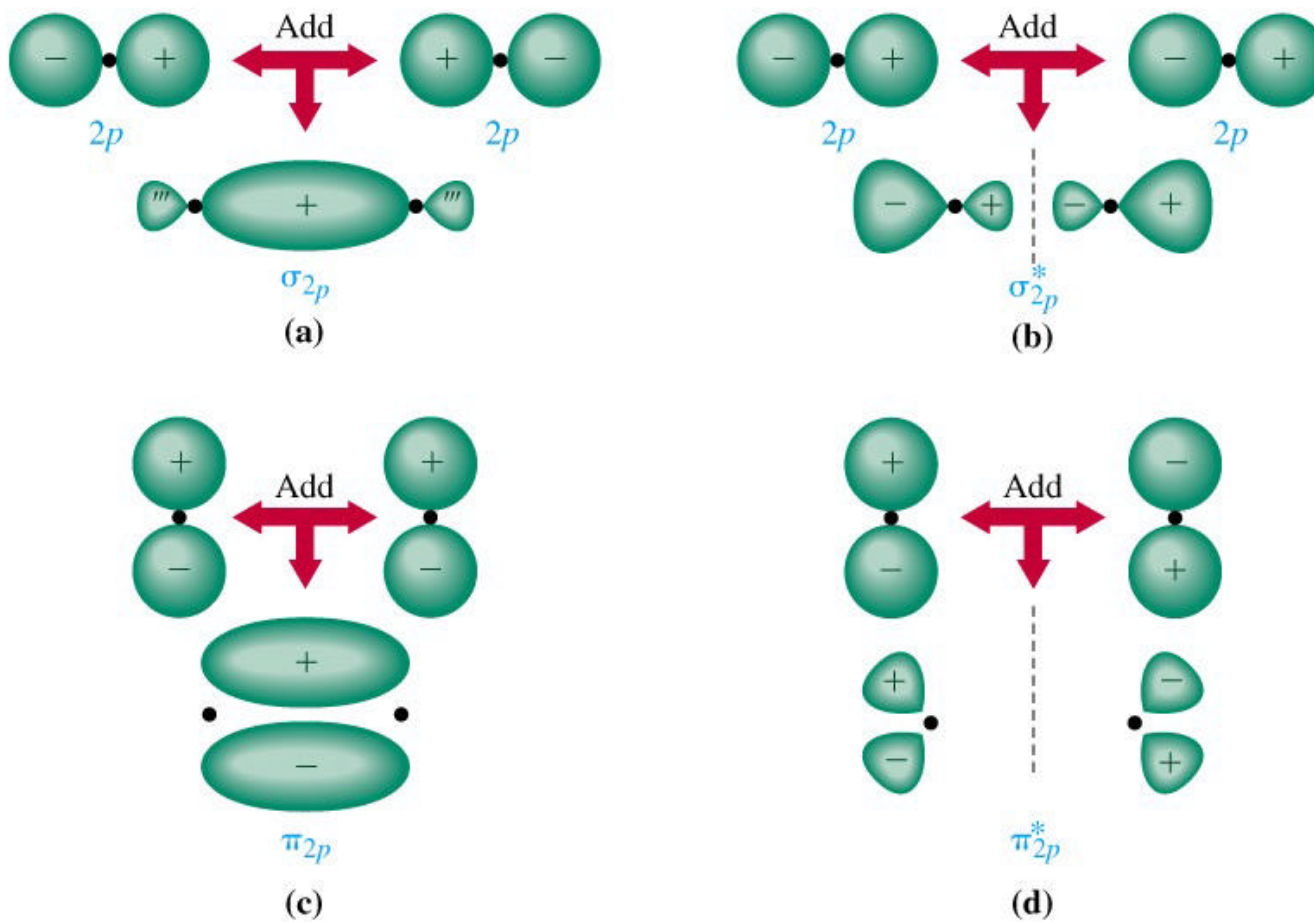
The other results in two degenerate $\pi(2p)$ and $\pi^*(2p)$ MO's.

End on produces the sigma system.

Above and below produced the two pi systems.

$2p_x$ $+$ $2p_x$ → σ_{2p}^{*} (antibonding)

σ_{2p} (bonding)

$2p_y$ $+$ $2p_y$ → π_{2p}^{*} (antibonding)

π_{2p} (bonding)

$2p_z$ $+$ $2p_z$ → π_{2p}^{*} (antibonding)

π_{2p} (bonding)

The π(2p) System (Z 7):

The π(2p) System (Z≥8):