Molecular Orbital Theory of Diatomic Molecules

L   MO theory seeks to formulate orbitals that extend over the entire molecule as linear combinations of atomic orbitals (LCAOs) on the individual atoms.

L   For diatomic molecules the MOs are positive and negative combinations of the wave functions for pairs of atomic orbitals (AOs) on the two atoms, A and B:

$$\Psi^+ = a\psi_A + b\psi_B$$

$$\Psi^- = a\psi_A - b\psi_B = a\psi_A + (-b\psi_B)$$

where a and b are mixing constants, which indicate the degree of overlap of the two orbitals.

MOs from 1s Orbitals
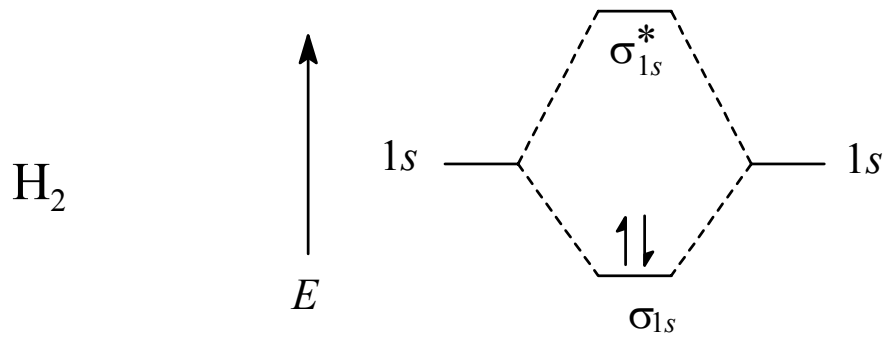# Homonuclear Diatomic Molecules

σ bonding MO
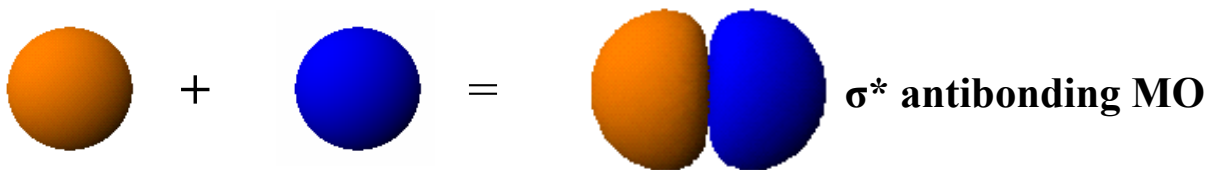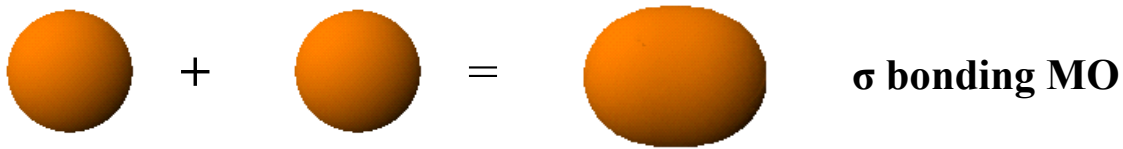
σ* antibonding MO

L   Positive combination causes a build-up of electron density between the nuclei, resulting in a **sigma bonding MO (σ)**.

L   Negative combination results in a nodal plane between the nuclei, which works against bonding, resulting in a **sigma antibonding MO (σ*)**.

L   In general, number of MOs formed as LCAOs equals number of AOs used.

MO Energy Level Scheme
First Period Homonuclear Diatomic Cases
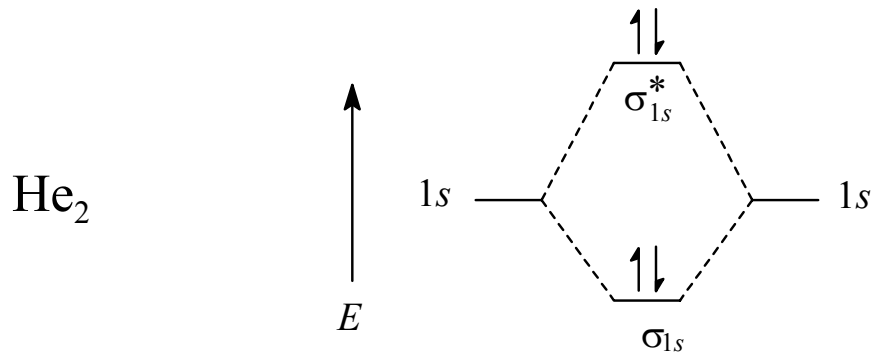
$$1s \quad \sigma_{1s}^* \quad 1s$$

$$\sigma_{1s}$$
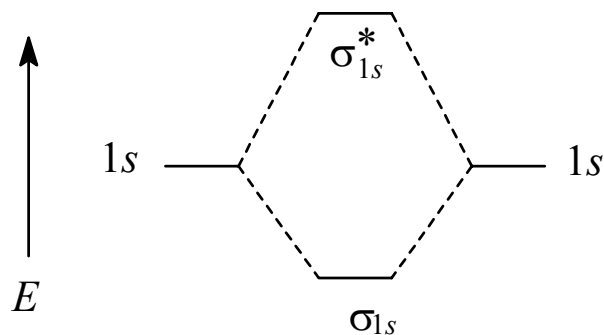
L   Scheme is filled in the usual aufbau manner, following the Pauli exclusion principle and Hund's rule of maximum multiplicity (for the ground state).

L   Bond order is defined as follows:

bond order = ½ (bonding e's – antibonding e's)

H₂ and He₂

H₂

$$\sigma_{1s}^*$$

$1s$ ——   —— $1s$

$$\sigma_{1s}$$

E

bond order = ½(2 − 0) = 1

He₂

$$\sigma_{1s}^*$$

$1s$ ——   —— $1s$

$$\sigma_{1s}$$

E

bond order = ½(2 − 2) = 0

(He₂ does not exist.)

H_2^+ and He_2^+ Ions

H_2^+

E

$$\sigma_{1s}^*$$

$1s \quad\quad\quad\quad 1s$

σ_{1s}

bond order $= \frac{1}{2}(1 - 0) = \frac{1}{2}$

He_2^+

E

$$\sigma_{1s}^*$$

$1s \quad\quad\quad\quad 1s$

σ_{1s}
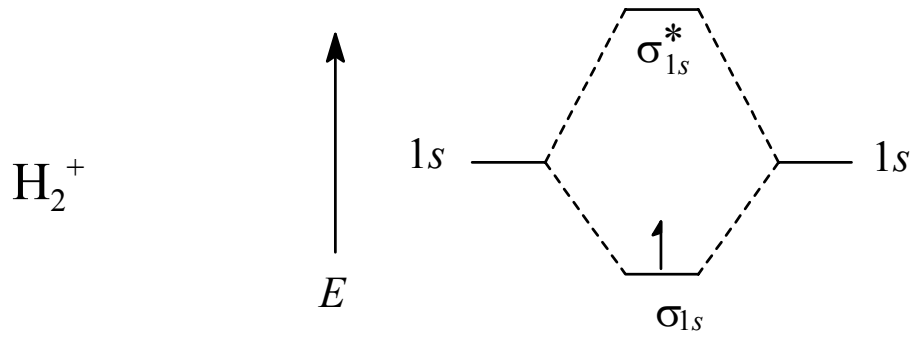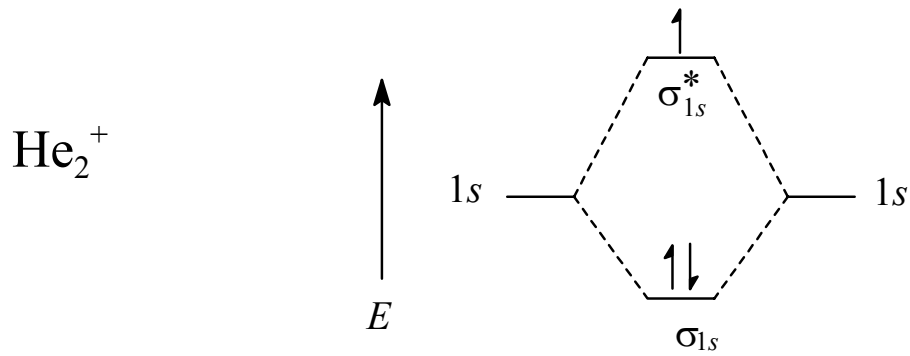
bond order $= \frac{1}{2}(2 - 1) = \frac{1}{2}$

MOs for Second Period
Homonuclear Diatomic Molecules

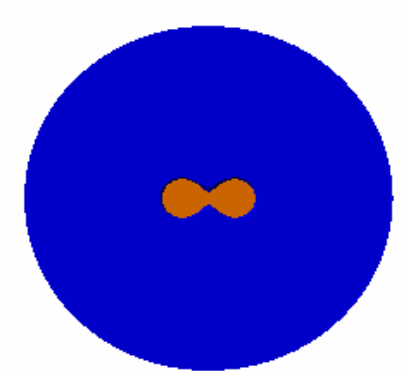L   In general, atomic orbitals that are most similar in energy interact most effectively in forming MOs.

L   MOs for second period diatomic molecules are combinations of the type $2s \pm 2s$ and $2p \pm 2p$.

Sigma MOs from 2*s* ± 2*s*
(cutaway views)

σ_{2s}
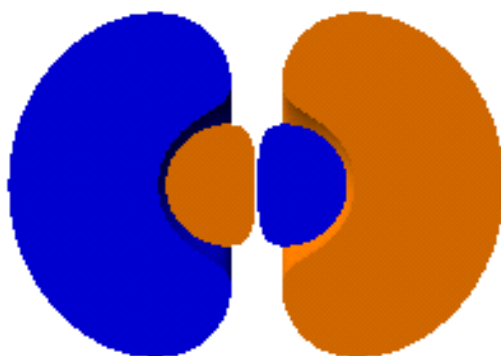
σ^*_{2s}

MO Energy Level Scheme
Li$_2$, Be$_2$, and Related Ions

$$\sigma_{2s}^*$$

$2s$ — — $2s$

σ_{2s}

$$\sigma_{1s}^*$$

$1s$ — — $1s$

E

σ_{1s}

Configurations of Li₂ and Be₂

$$\text{Configurations of Li}_2 \text{ and Be}_2$$

Li₂

Be₂

$2s$ ———— ———— $2s$

σ^*_{2s}

σ_{2s}

$1s$ ———— ———— $1s$

σ^*_{1s}

σ_{1s}

E

bond order = 1

$2s$ ———— ———— $2s$

σ^*_{2s}

σ_{2s}

$1s$ ———— ———— $1s$

σ^*_{1s}

σ_{1s}

E
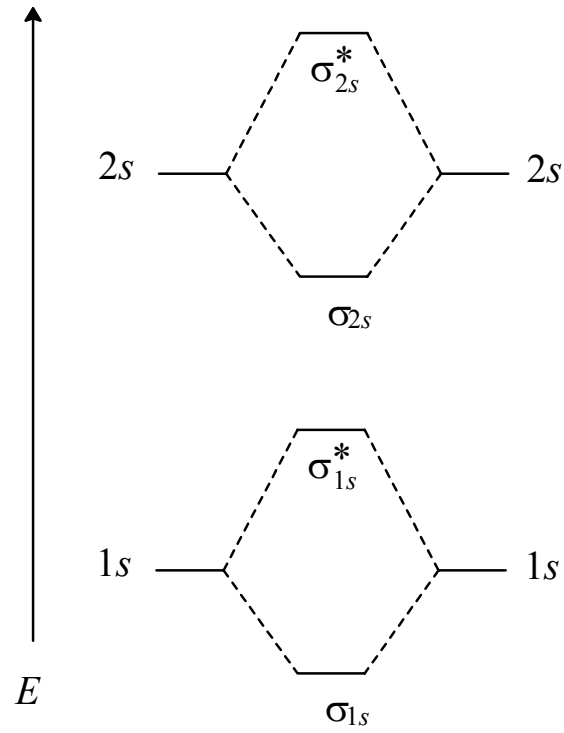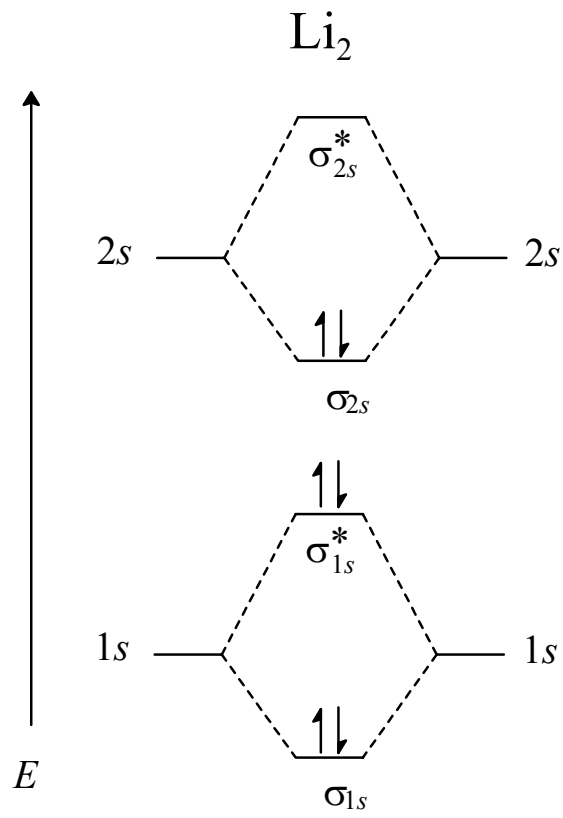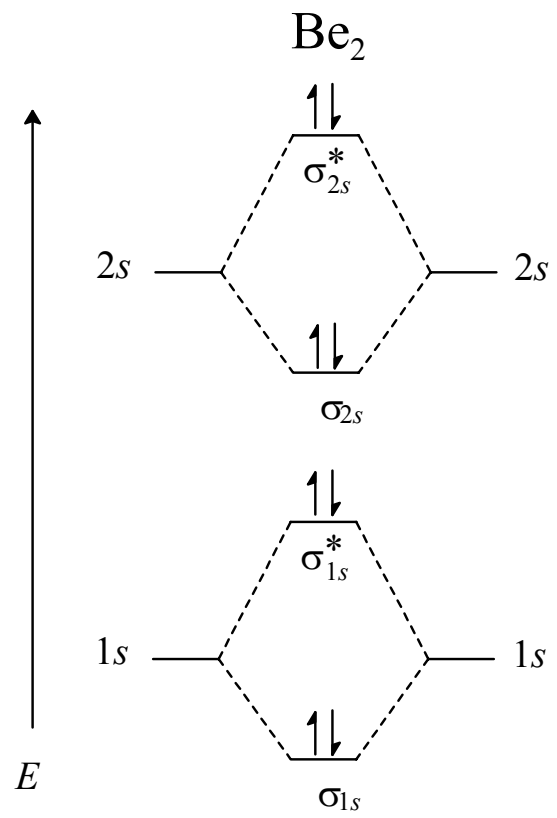
bond order = 0

Sigma Orbitals from $2p \pm 2p$

σ_{2p}

σ^*_{2p}
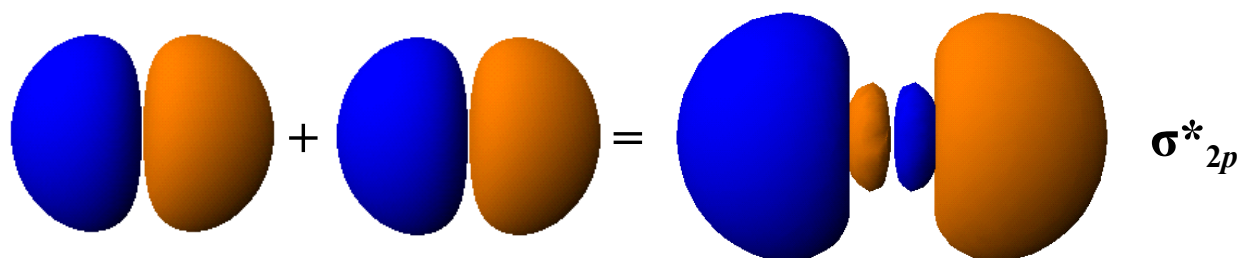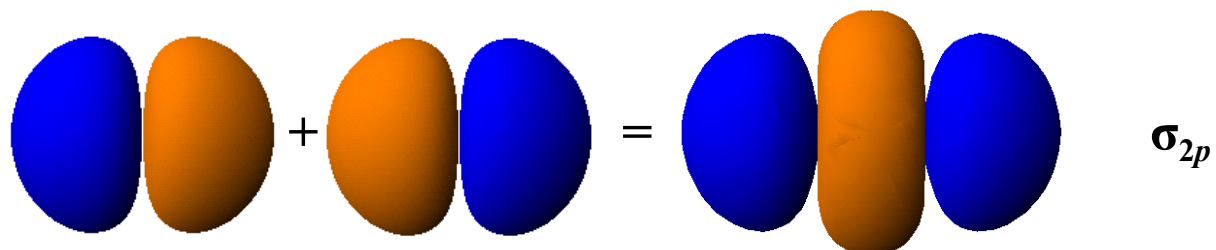
Pi MOs from $2p \pm 2p$

L Two degenerate π_{2p} bonding MOs, one from $2p_x + 2p_x$ and one from $2p_y + 2p_y$.

L Two degenerate π^*_{2p} antibonding MOs, one from $2p_x - 2p_x$ and one from $2p_y - 2p_y$.

$2p_y \pm 2p_y$ Combinations

π_{2p}

π^*_{2p}
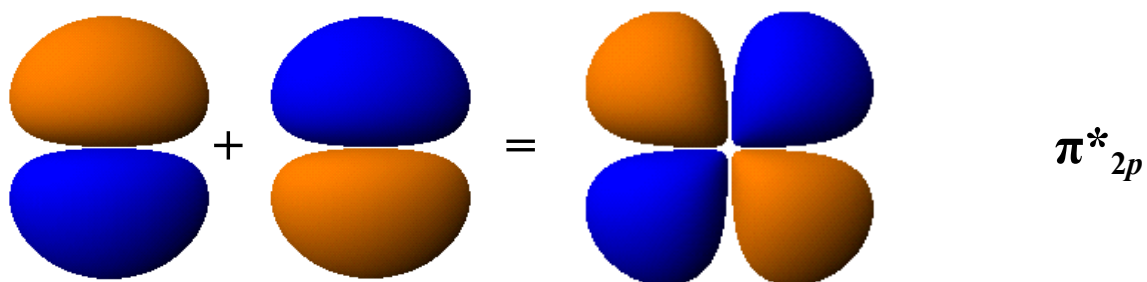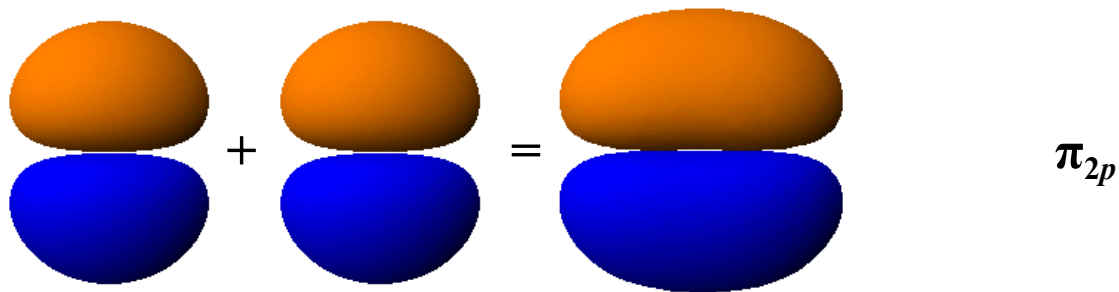
MO Scheme for O_2 through Ne_2 and Related Ions

L   The core configuration levels σ_{1s} and σ^*_{1s} are omitted.

$$\sigma^*_{2p}$$

$$\pi^*_{2p}$$

$2p\,[\,\equiv\,]$

$[\,\equiv\,]\,2p$

$$\pi_{2p}$$

$$\sigma_{2p}$$

$$\sigma^*_{2s}$$

$2s$

$2s$

$$\sigma_{2s}$$

E
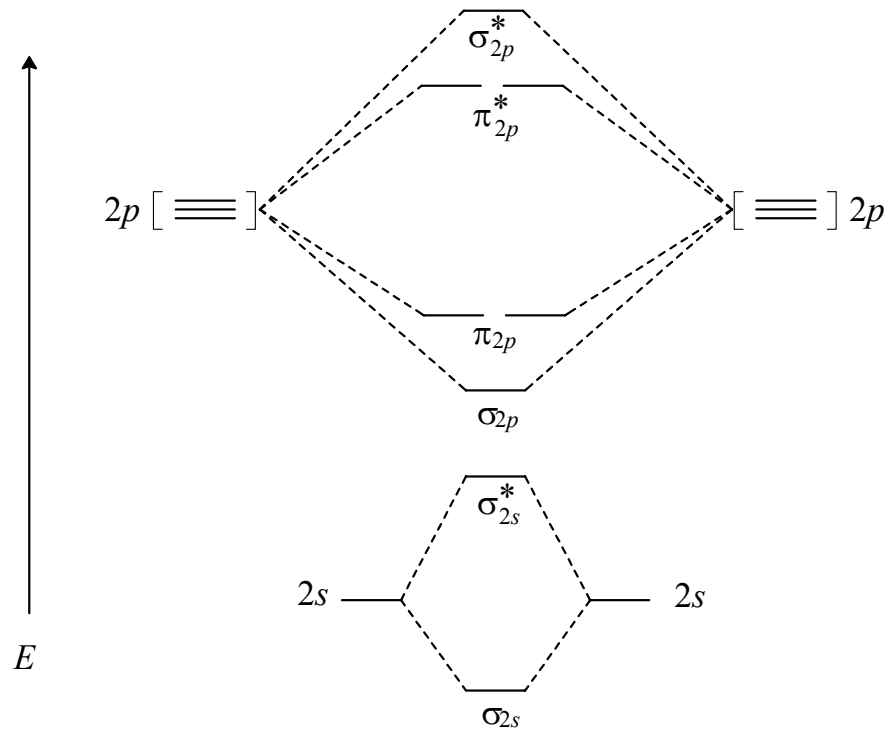
MO Scheme for B_2 through N_2 and Related Ions

L   In diatomic molecules of the lighter elements B_2, C_2, and N_2, mixing between sigma-type MOs causes the σ^*_{2s} level to move down and the σ_{2p} level to move up in energy.

L   The σ_{2p} level rises above that of π_{2p}.

L   This results in the following scheme, in which the relative ordering $\pi_{2p} < \sigma_{2p}$ occurs:
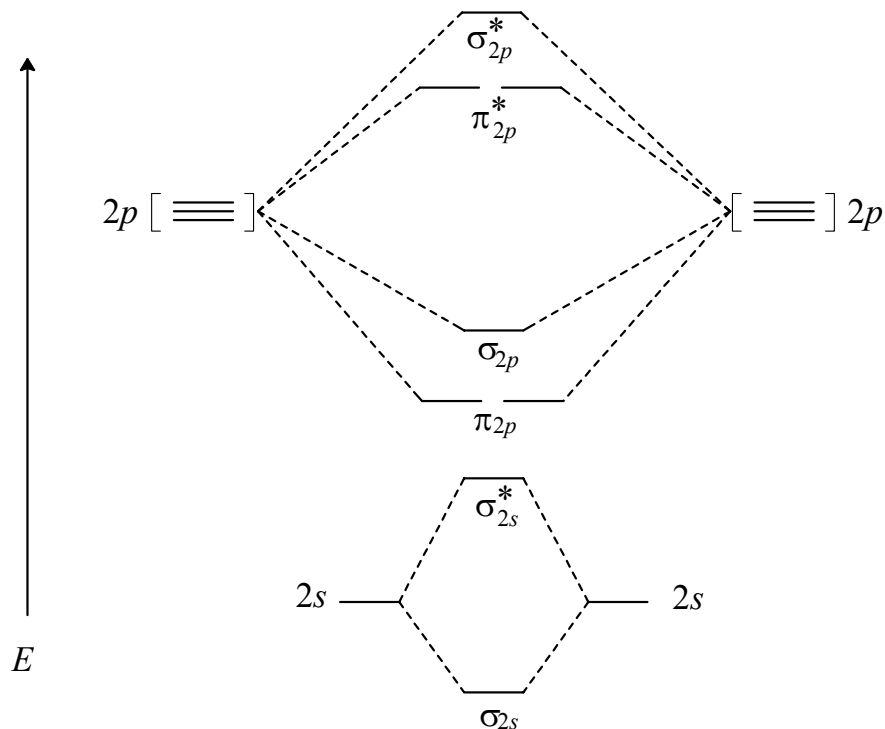
Configurations of Second Period Homonuclear Diatomic Molecules

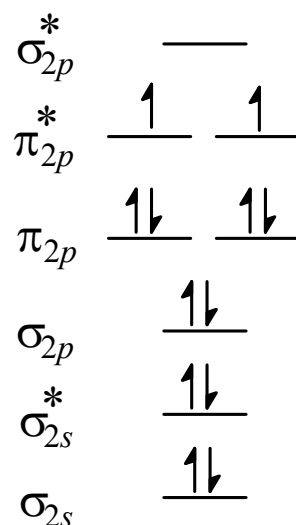| X_2	Configuration	Bond Order	$D(X_2)$ kJ/mol	$d(X–X)$ pm	Magnetic Property
Li_2	$(\sigma_{2s})^2$	1	101	267.3	dia
Be_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	n/a	n/a	n/a
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2$	1	291	159	para
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	599	124.3	dia
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	942	109.77	dia
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	155	141	dia
Ne_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4(\sigma^*_{2p})^2$	0	n/a	n/a	n/a

MO Description of O$_2$ and Its Ions

$$\sigma^*_{2p} \quad \underline{}$$

$$\pi^*_{2p} \quad \underline{\uparrow} \quad \underline{\uparrow}$$

$$\pi_{2p} \quad \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow}$$

$$\sigma_{2p} \quad \underline{\uparrow\downarrow}$$

$$\sigma^*_{2s} \quad \underline{\uparrow\downarrow}$$

$$\sigma_{2s} \quad \underline{\uparrow\downarrow}$$

L   MO model predicts the observed paramagnetism, which VB theory cannot explain easily.

Formula	Configuration	Bond Order	$D(X_2)$ kJ/mol	d(X–X) pm	Magnetic Property
O$_2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
O$_2^-$	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$	1.5	395	135	para
O$_2^{2-}$	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	126	149	dia
O$_2^+$	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$	2.5	643	111.6	para

Second Period Heteronuclear Diatomic Molecules

L   MO scheme for homonuclear diatomic molecules can be adapted to describe bonding in heteronuclear diatomic molecules.

L   The two atoms do not contribute equally to each MO.

       ● More electronegative element has lower energy AOs and makes a greater contribution to bonding MOs.

       ● Less electronegative atom makes a greater contribution to antibonding MOs.

L   Ordering of MOs energies in heteronuclear cases tends to be like lighter homonuclear cases: i.e., $\pi_{2p} < \sigma_{2p}$
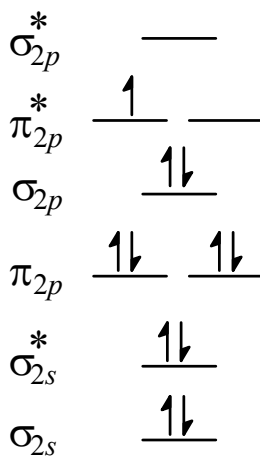
Heteronuclear Diatomic Molecules
Examples

CO, CN^-, NO^+ (10 valence electrons, like N_2)

σ_{2p}^*	—	
π_{2p}^*	—	—
σ_{2p}	↑↓	
π_{2p}	↑↓	↑↓
σ_{2s}^*	↑↓	
σ_{2s}	↑↓	
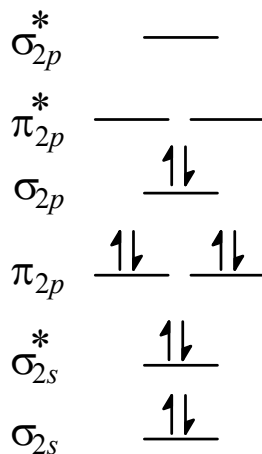
bond order = 3

NO (11-electron free radical, like O_2^+)

σ_{2p}^*	—	
π_{2p}^*	↑	—
σ_{2p}	↑↓	
π_{2p}	↑↓	↑↓
σ_{2s}^*	↑↓	
σ_{2s}	↑↓	

bond order = 2.5