Quantum Mechanical Approaches to Molecular Bonding

☺   In principle, it is possible to construct a Schrödinger equation, $\mathcal{H}\Psi = E\Psi$, to describe the electronic structure of a molecule.

☹   In practice, seeking exact solutions to the Schrödinger equation for molecules is an insurmountable mathematical problem.

☞   Two principal approaches have been taken to construct approximate wave functions for molecules, starting with the atomic orbitals of the atoms comprising the molecules.

   1.   Valence Bond (VB) theory - developed by Linus Pauling and co-workers, essentially puts the Lewis notion of electron pairs on a quantum mechanical footing, in which each shared or lone pair of electrons about an atom occupies a localized orbital.

   2.   Molecular orbital (MO) theory, developed by Robert S. Mulliken and co-workers, constructs new orbitals that are *delocalized* (i.e., "spread out") across the molecule.

☞   VB and MO theories take different mathematical approaches to constructing wave functions for the molecule, but their results are often equivalent.

Molecular Orbital Theory of Diatomic Molecules

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

☞ 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 1*s* Orbitals
Homonuclear Diatomic Molecules

σ bonding MO
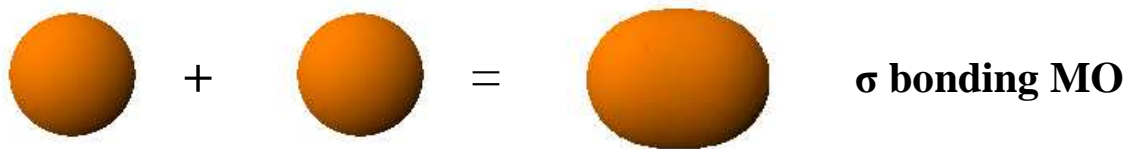
σ* antibonding MO

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

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

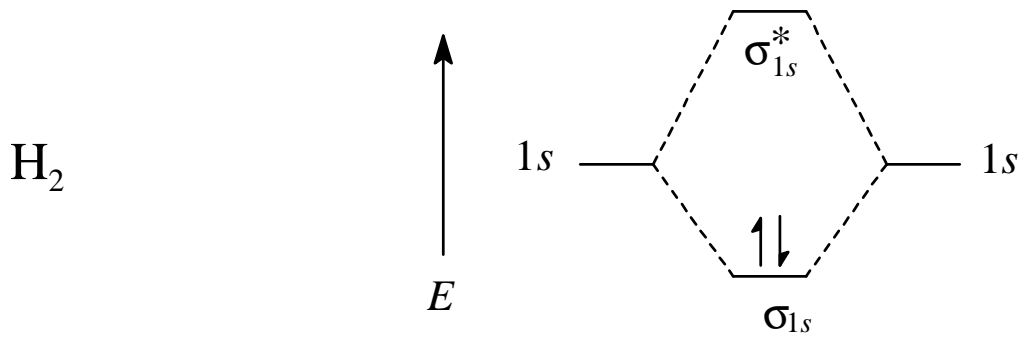☞ In general, number of MOs formed as LCAOs equals number of AOs used.

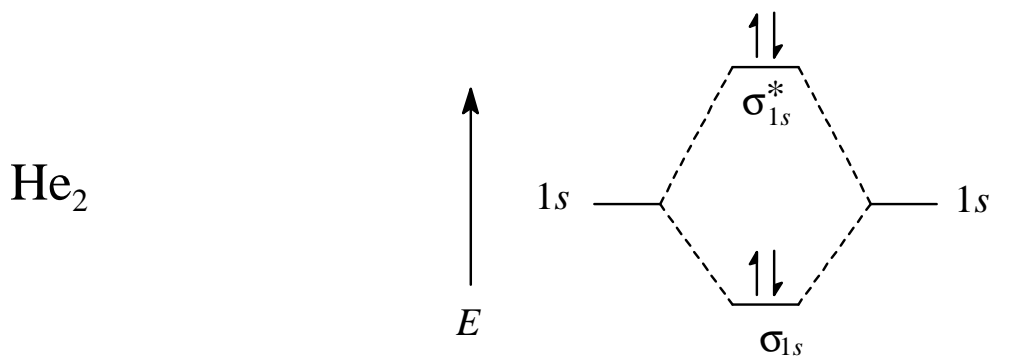# MO Energy Level Scheme
First Period Homonuclear Diatomic Cases
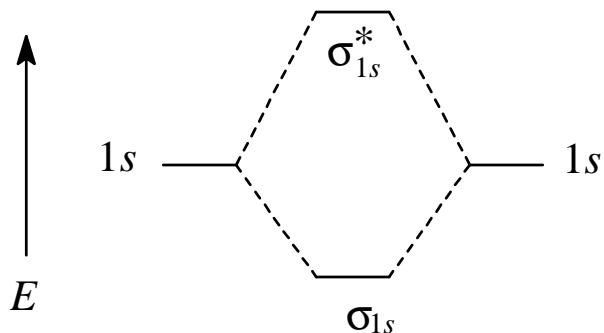
☞ Scheme is filled in the usual aufbau manner, following the Pauli exclusion principle and Hund's rule of maximum multiplicity (for the ground state).

☞ Bond order is defined as follows:

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

H$_2$ and He$_2$

H$_2$

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

$1s$ —————— $1s$

$\uparrow\downarrow$

σ_{1s}

E

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

He$_2$

$\uparrow\downarrow$

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

$1s$ —————— $1s$

$\uparrow\downarrow$

σ_{1s}

E

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

(He$_2$ does not exist.)

H$_2^+$ and He$_2^+$ Ions

H$_2^+$

E

$1s$ σ_{1s}^* $1s$

σ_{1s}

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

He$_2^+$

E

$1s$ σ_{1s}^* $1s$

σ_{1s}
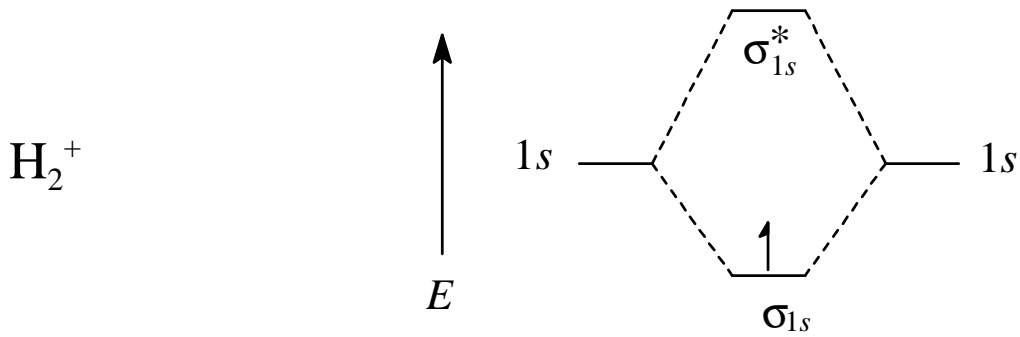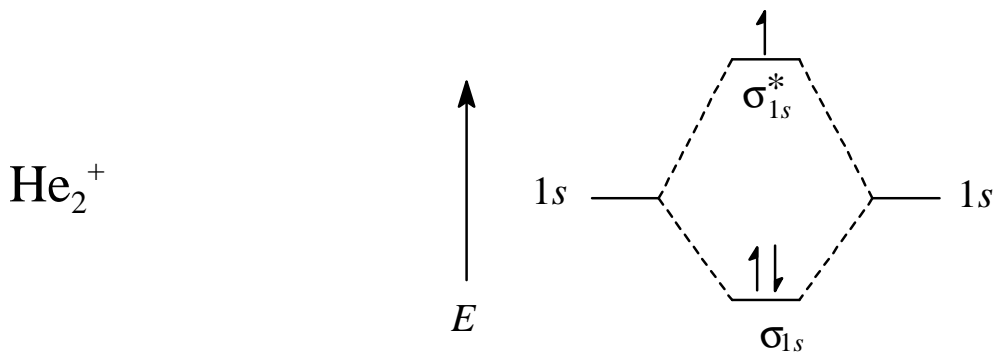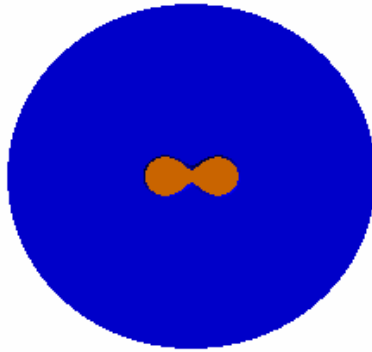
bond order $= \frac{1}{2}(2 - 1) = \frac{1}{2}$
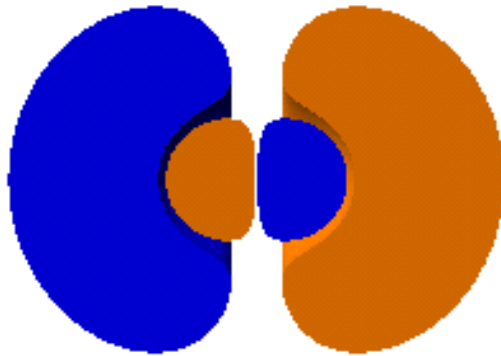
MOs for Second Period
Homonuclear Diatomic Molecules

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

☞ 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

$$E$$

σ^*_{2s}

$2s$ —— —— $2s$

σ_{2s}

σ^*_{1s}

$1s$ —— —— $1s$

σ_{1s}
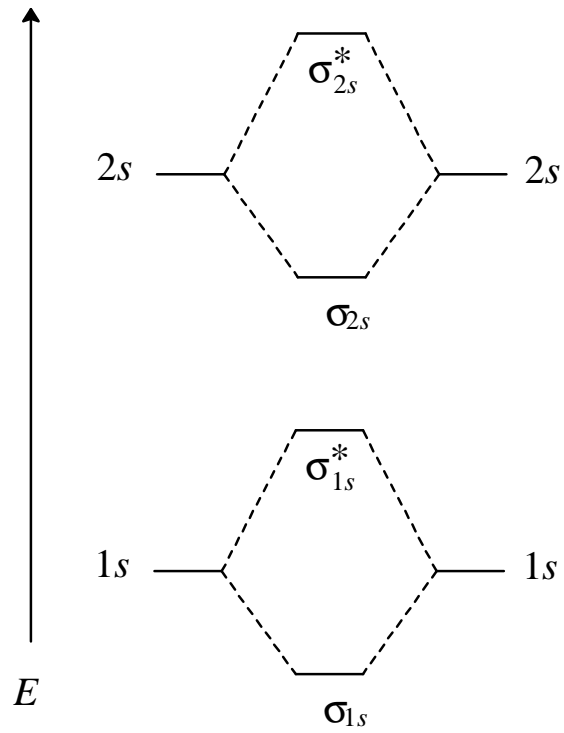
Configurations of Li$_2$ and Be$_2$

Li$_2$

σ^*_{2s}

2s — — 2s

σ_{2s}

σ^*_{1s}

1s — — 1s

σ_{1s}

E

bond order = 1

Be$_2$

σ^*_{2s}

2s — — 2s

σ_{2s}

σ^*_{1s}

1s — — 1s

σ_{1s}

E
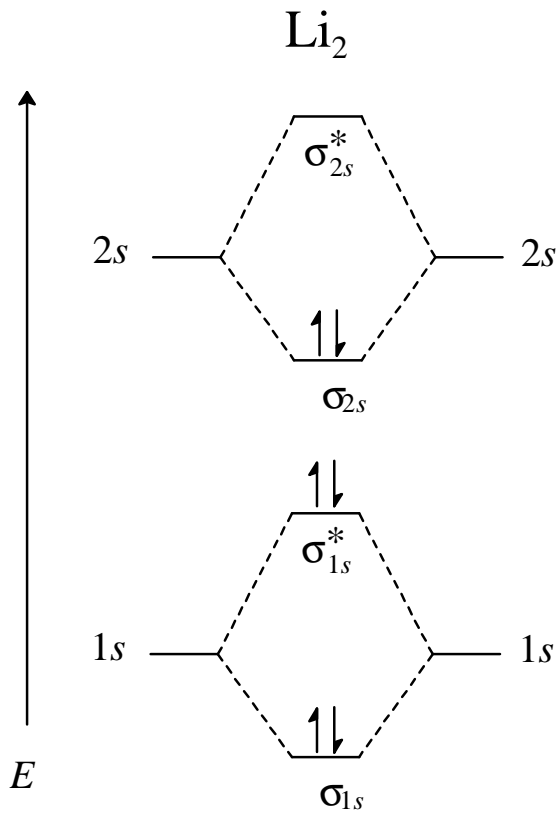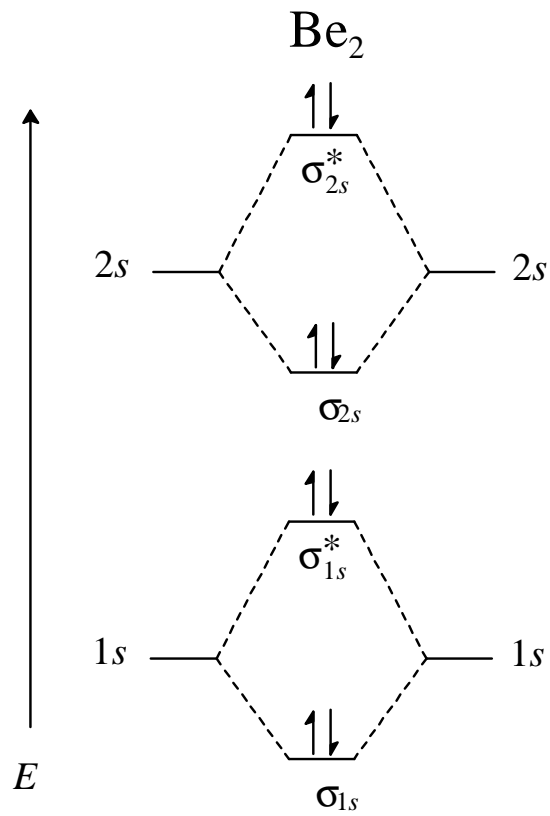
bond order = 0

Sigma Orbitals from 2*p* ± 2*p*
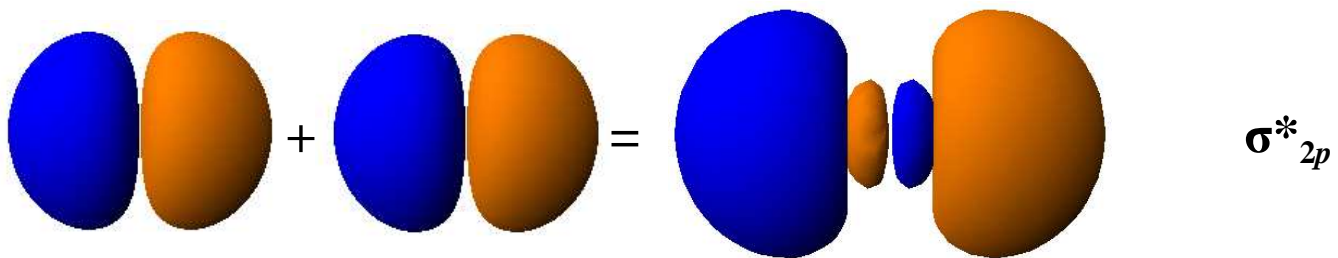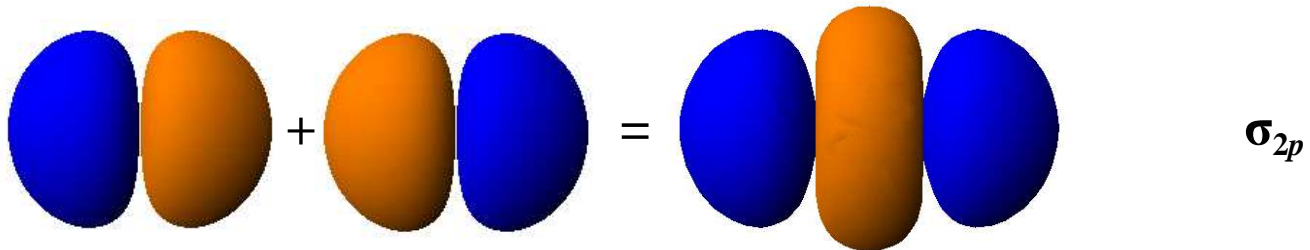
σ_{2p}

$\sigma*_{2p}$

- For homonuclear diatomic molecules ($D_{\infty h}$) σ MOs, whether formed from *s* or *p* AOs, have Σ_g^+ symmetry, and σ* MOs have Σ_u^+ symmetry.

- For heteronuclear diatomic molecules ($C_{\infty v}$) σ and σ* MOs, whether formed from *s* or *p* AOs, have Σ^+ symmetry.

Pi MOs from $2p \pm 2p$

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

☞ 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
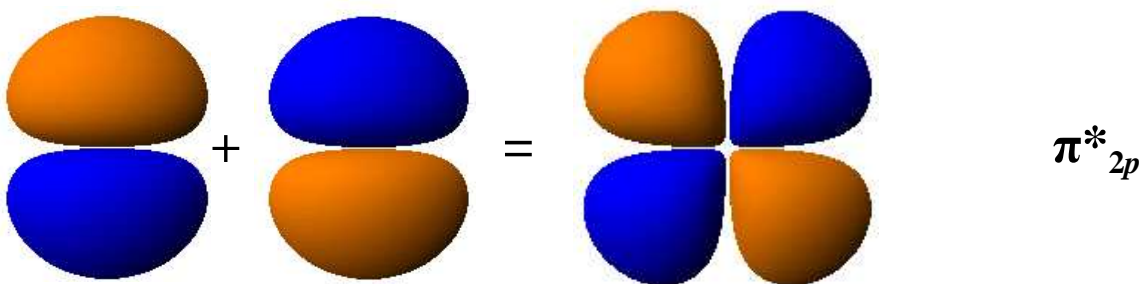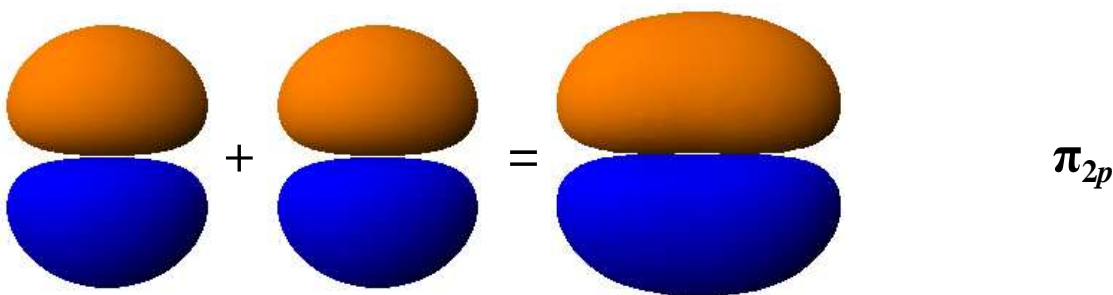
- For homonuclear diatomic molecules ($D_{\infty h}$) π MOs have Π_u symmetry, and π^* have Π_g symmetry.

- For heteronuclear diatomic molecules ($C_{\infty v}$) π and π^* MOs have Π symmetry.

MO Scheme for O_2 through Ne_2
and Related Ions

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

$$E$$

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

σ^*_{2p}

π^*_{2p}

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

π_{2p}

σ_{2p}

σ^*_{2s}

$2s$ ——— ——— $2s$

σ_{2s}
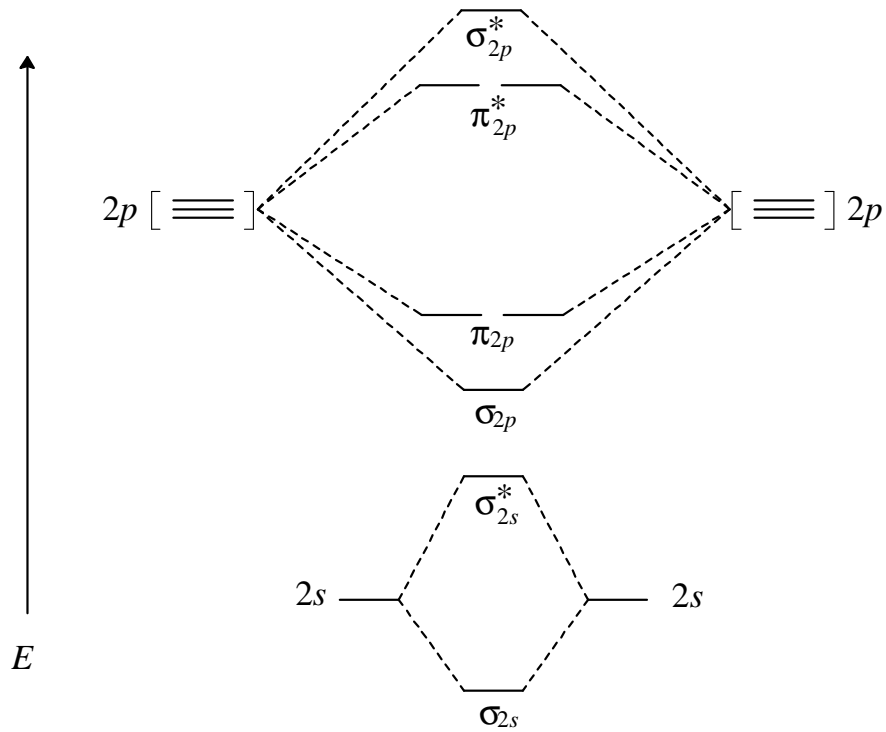
MO Scheme for B_2 through N_2 and Related Ions

☞ 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.

$$\pi_{2p} \qquad \sigma_{2p} \qquad \sigma^*_{2s} \qquad \sigma_{2s}$$

$$\sigma_{2p} \qquad \pi_{2p} \qquad \sigma^*_{2s} \qquad \sigma_{2s}$$

s-p mixing ⟶
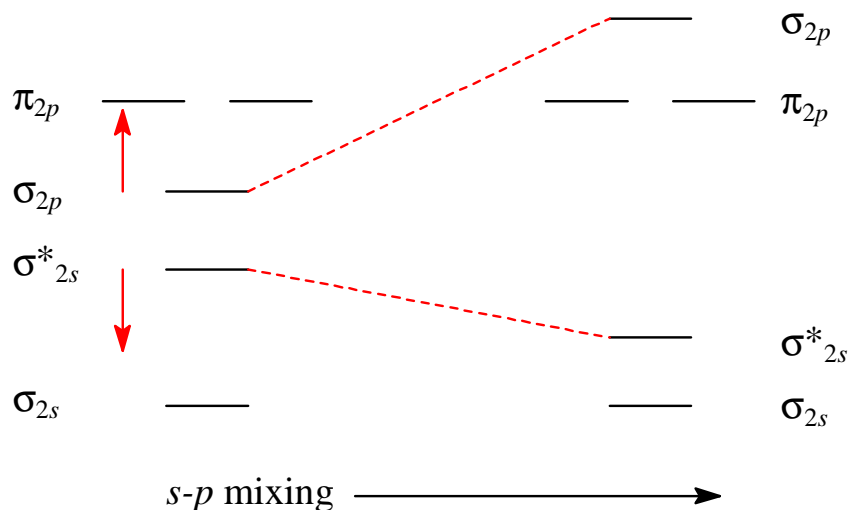
☞ The σ_{2p} level rises above that of π_{2p}.

☞ This results in the following scheme, in which the relative ordering $\pi_{2p} < \sigma_{2p}$ occurs:

MO Scheme for B_2 through N_2 and Related Ions

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

$$\pi_{2p}^*$$

$2p\ [\equiv]$

$[\equiv]\ 2p$

$$\sigma_{2p}$$

$$\pi_{2p}$$

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

$2s$

$2s$

$$\sigma_{2s}$$

E
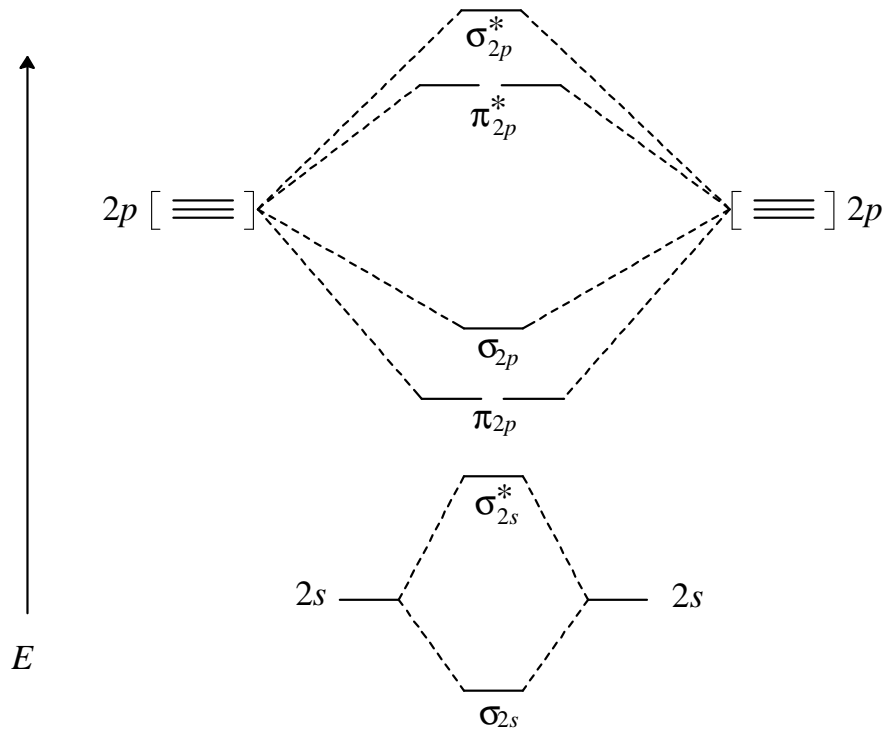
Configurations of Second Period Homonuclear Diatomic Molecules

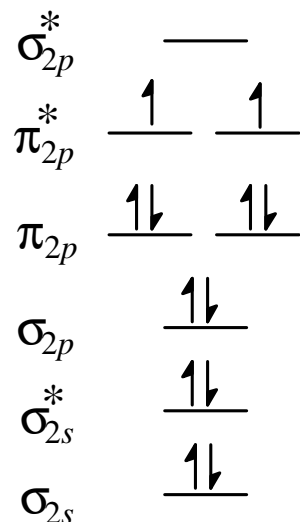| X_2	Configuration	Bond Order	$D(X_2)$ kJ/mol	d(X–X) pm	Magnetic Property
Li_2	$(\sigma_{2s})^2$	1	101	267.3	dia
Be_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	n/a	n/a	n/a
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2$	1	291	159	para
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	599	124.3	dia
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

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

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

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

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

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

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

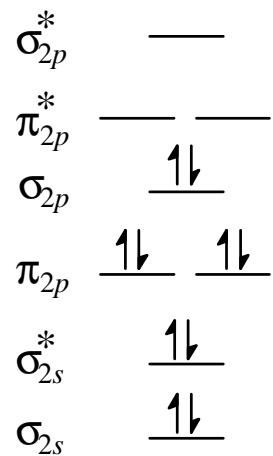☞   MO model predicts the observed paramagnetism, which VB theory cannot explain easily.

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

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

☞ 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.

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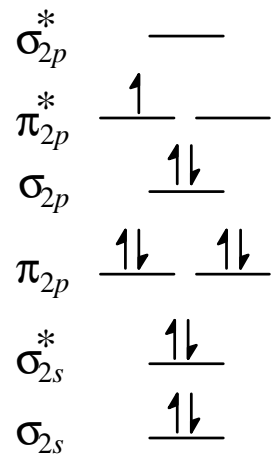
Heteronuclear Diatomic Molecules
Examples

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

$$
\begin{array}{ll}
\sigma_{2p}^* & \underline{\quad} \\[6pt]
\pi_{2p}^* & \underline{\quad} \quad \underline{\quad} \\[6pt]
\sigma_{2p} & \underline{\uparrow\downarrow} \\[6pt]
\pi_{2p} & \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow} \\[6pt]
\sigma_{2s}^* & \underline{\uparrow\downarrow} \\[6pt]
\sigma_{2s} & \underline{\uparrow\downarrow}
\end{array}
$$

bond order = 3

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

$$
\begin{array}{ll}
\sigma_{2p}^* & \underline{\quad} \\[6pt]
\pi_{2p}^* & \underline{\uparrow} \quad \underline{\quad} \\[6pt]
\sigma_{2p} & \underline{\uparrow\downarrow} \\[6pt]
\pi_{2p} & \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow} \\[6pt]
\sigma_{2s}^* & \underline{\uparrow\downarrow} \\[6pt]
\sigma_{2s} & \underline{\uparrow\downarrow}
\end{array}
$$

bond order = 2.5