

Molecular Orbital Theory of H₂⁺

$$E_1 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J + K]}{[1 + S]}$$

$$E_2 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J - K]}{[1 - S]}$$

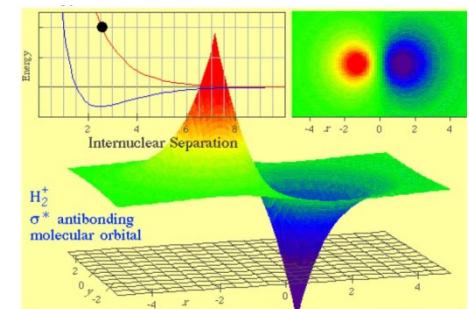
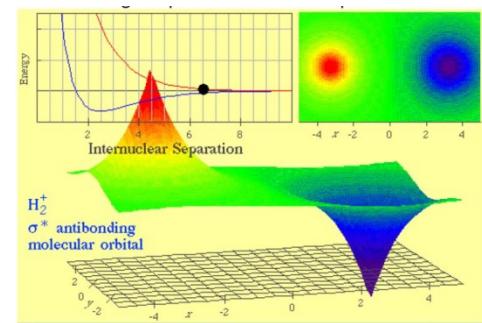
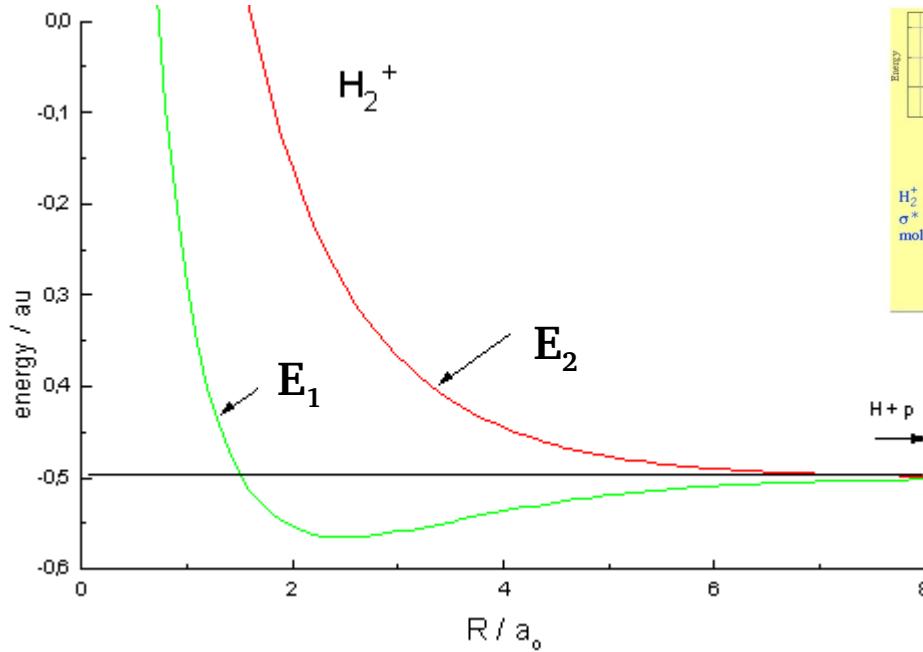
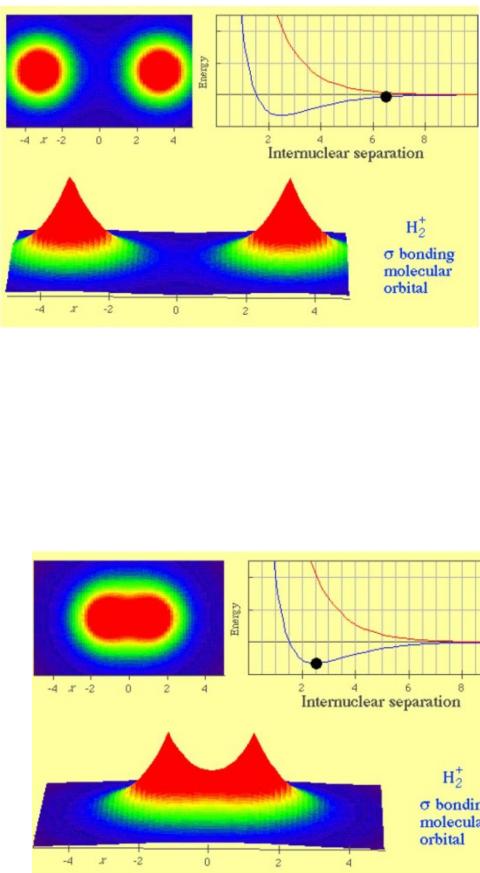
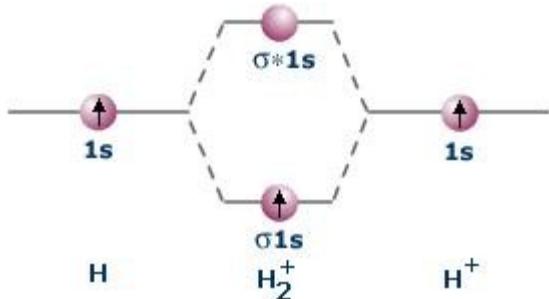
$$0 \leq |S| \leq 1; J < 0 \text{ & } K < 0$$

J - Coulomb integral - interaction of electron in 1s orbital around A with a nucleus at B

K - Exchange integral – exchange (resonance) of electron between the two nuclei.

Destabilization of Anti-bonding orbital is more than Stabilization of Bonding orbital

Molecular Orbital Theory of H_2^+



Molecular Orbital Theory of H₂

$$H(H_2) = -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 - \frac{\hbar^2}{2m_e} \nabla_{e1}^2 - \frac{\hbar^2}{2m_e} \nabla_{e2}^2$$

$$-Q \frac{e^2}{r_{1A}} - Q \frac{e^2}{r_{1B}} - Q \frac{e^2}{r_{2A}} - Q \frac{e^2}{r_{2B}} + Q \frac{e^2}{r_{12}} + Q \frac{e^2}{R}$$

$$H(H_2) = -\frac{\hbar^2}{2m_e} \nabla_{e1}^2 - \frac{\hbar^2}{2m_e} \nabla_{e2}^2 - Q \frac{e^2}{r_{1A}} - Q \frac{e^2}{r_{1B}} - Q \frac{e^2}{r_{2A}} - Q \frac{e^2}{r_{2B}} + Q \frac{e^2}{r_{12}} + Q \frac{e^2}{R}$$

$$H(H_2) = -\left[\frac{\hbar^2}{2m_e} \nabla_{e1}^2 + Q \frac{e^2}{r_{1A}} \right] - \left[\frac{\hbar^2}{2m_e} \nabla_{e2}^2 + Q \frac{e^2}{r_{2B}} \right] - Q \frac{e^2}{r_{1B}} - Q \frac{e^2}{r_{2A}} + Q \frac{e^2}{r_{12}} + Q \frac{e^2}{R}$$

$$H(H_2) = H(H_{1e}) + H(H_{2e}) - Q \frac{e^2}{r_{1B}} - Q \frac{e^2}{r_{2A}} + Q \frac{e^2}{r_{12}} + Q \frac{e^2}{R}$$

Cannot be Solved

Molecular Orbital Theory of H₂

For H₂⁺

$$\psi_{bonding} = \psi_1 = \frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A} + \phi_{1s_B})$$

Place the second electron in the bonding orbital to get H₂

$$\psi_{bonding}(H_2) = \psi_1 \times \psi_2$$

$$= \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^1 + \phi_{1s_B}^1) \right] \times \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^2 + \phi_{1s_B}^2) \right] \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right]$$

Molecular Orbital Theory of H₂

$$\psi_{bonding}(H_2)$$

$$= \frac{1}{2[1+S]} \left[\left(\phi_{1s_A}^1 + \phi_{1s_B}^1 \right) \right] \times \left[\left(\phi_{1s_A}^2 + \phi_{1s_B}^2 \right) \right] \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right]$$

Spatial Part

$$\psi_{bonding} = \frac{1}{2[1+S]} \left[\phi_{1s_A}^1 \phi_{1s_A}^2 + \phi_{1s_B}^1 \phi_{1s_B}^2 + \phi_{1s_A}^1 \phi_{1s_B}^2 + \phi_{1s_B}^1 \phi_{1s_A}^2 \right]$$

$$\frac{1}{2[1+S]} [1s_A(1) \times 1s_A(2) + 1s_B(1) \times 1s_B(2) + 1s_A(1) \times 1s_B(2) + 1s_B(1) \times 1s_A(2)]$$

Molecular Orbital Theory of H₂

$\psi_{anti-bonding}(H_2)$

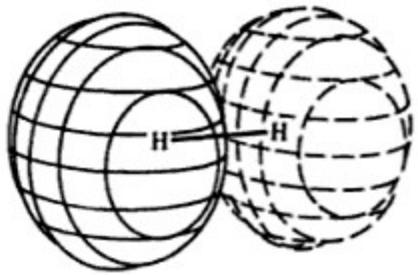
$$= \frac{1}{2[1-S]} \left[\left(\phi_{1s_A}^1 - \phi_{1s_B}^1 \right) \right] \times \left[\left(\phi_{1s_A}^2 - \phi_{1s_B}^2 \right) \right] \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right]$$

Spatial Part

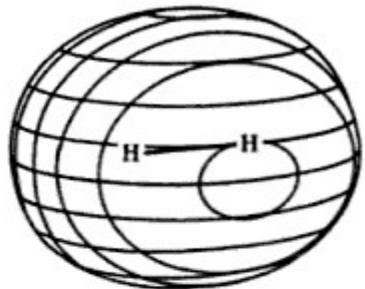
$$\psi_{anti-bonding} = \frac{1}{2[1-S]} \left[\phi_{1s_A}^1 \phi_{1s_A}^2 + \phi_{1s_B}^1 \phi_{1s_B}^2 - \phi_{1s_A}^1 \phi_{1s_B}^2 - \phi_{1s_B}^1 \phi_{1s_A}^2 \right]$$

$$\frac{1}{2[1-S]} [1s_A(1) \times 1s_A(2) + 1s_B(1) \times 1s_B(2) - 1s_A(1) \times 1s_B(2) - 1s_B(1) \times 1s_A(2)]$$

Molecular Orbital Theory of H₂

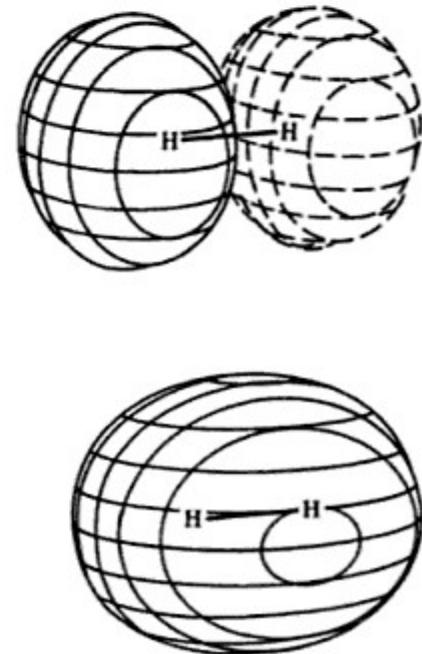
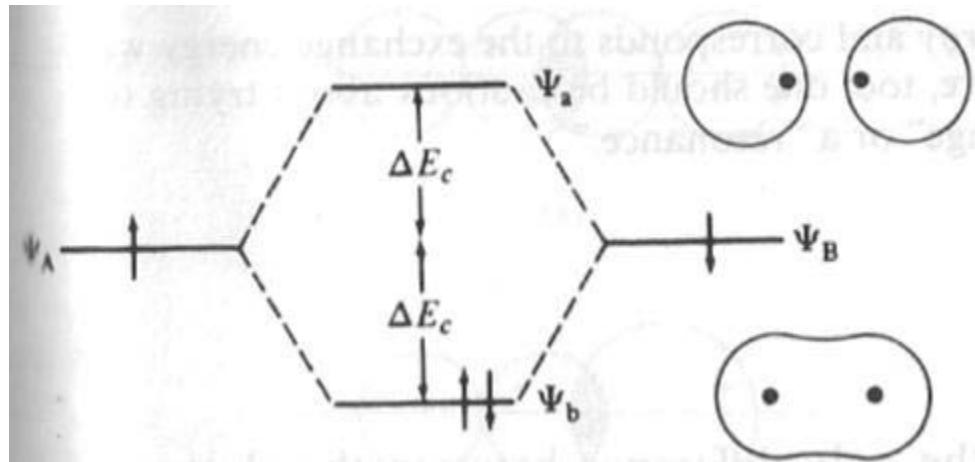


$$\psi_{anti-bonding} = \frac{1}{2[1-S]} [\phi_{1s_A}^1 \phi_{1s_A}^2 + \phi_{1s_B}^1 \phi_{1s_B}^2 - \phi_{1s_A}^1 \phi_{1s_B}^2 - \phi_{1s_B}^1 \phi_{1s_A}^2]$$
$$\frac{1}{2[1-S]} [1s_A(1) \otimes 1s_A(2) + 1s_B(1) \otimes 1s_B(2) - 1s_A(1) \otimes 1s_B(2) - 1s_B(1) \otimes 1s_A(2)]$$



$$\psi_{bonding} = \frac{1}{2[1+S]} [\phi_{1s_A}^1 \phi_{1s_A}^2 + \phi_{1s_B}^1 \phi_{1s_B}^2 + \phi_{1s_A}^1 \phi_{1s_B}^2 + \phi_{1s_B}^1 \phi_{1s_A}^2]$$
$$\frac{1}{2[1+S]} [1s_A(1) \otimes 1s_A(2) + 1s_B(1) \otimes 1s_B(2) + 1s_A(1) \otimes 1s_B(2) + 1s_B(1) \otimes 1s_A(2)]$$

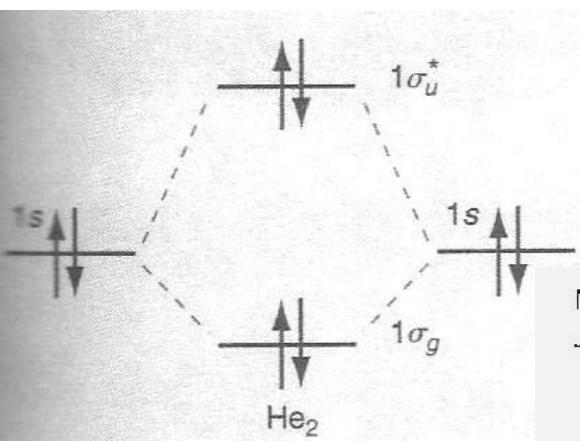
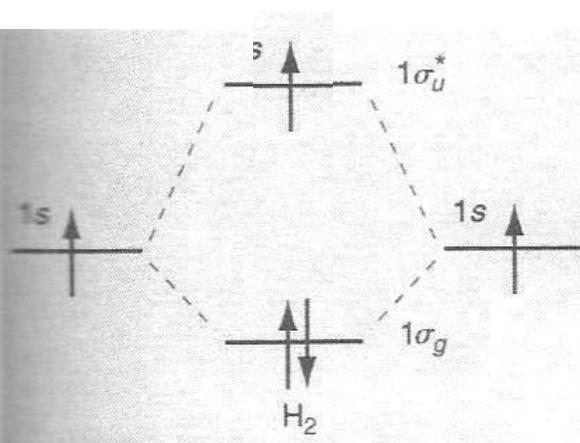
Molecular Orbital Theory of H₂



Effective nuclear charge changes the absolute energy
Levels and the size of orbitals!

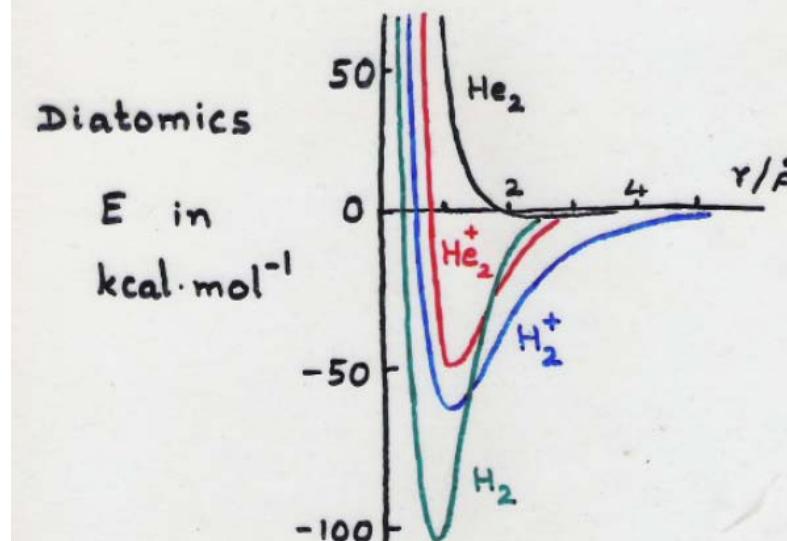
Matching of energies of AOs important for LCAO-MO
If energies are not close to each other, they would
Not interact to form MOs.

Diatoms of First Row: H_2^+ , H_2 , He_2 , He_2^+



Potential Energy as a function of r

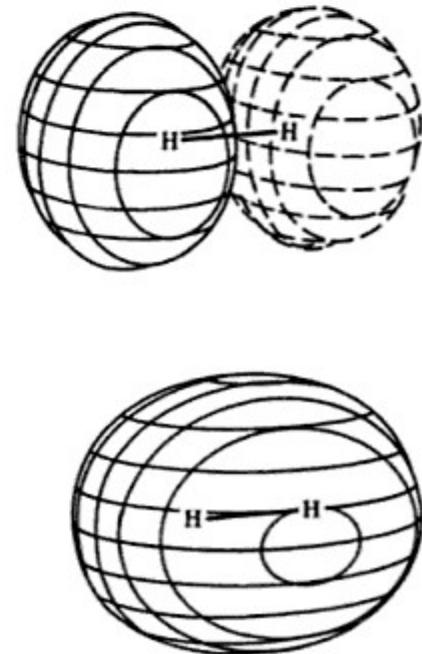
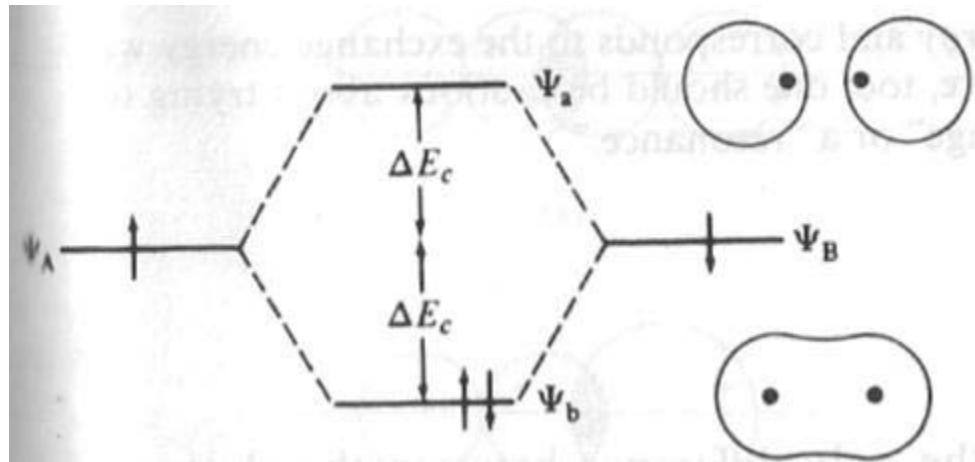
72



Molecular properties of H_2^+ , H_2 , He_2^+ , and He_2 .

Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Binding energy/ $\text{kJ} \cdot \text{mol}^{-1}$
H_2^+	1	$(\sigma_g 1s)^1$	1/2	106	268
H_2	2	$(\sigma_g 1s)^2$	1	74	457
He_2^+	3	$(\sigma_g 1s)^2 (\sigma_u 1s)^1$	1/2	108	241
He_2	4	$(\sigma_g 1s)^2 (\sigma_u 1s)^2$	0	≈ 6000	$\ll 1$

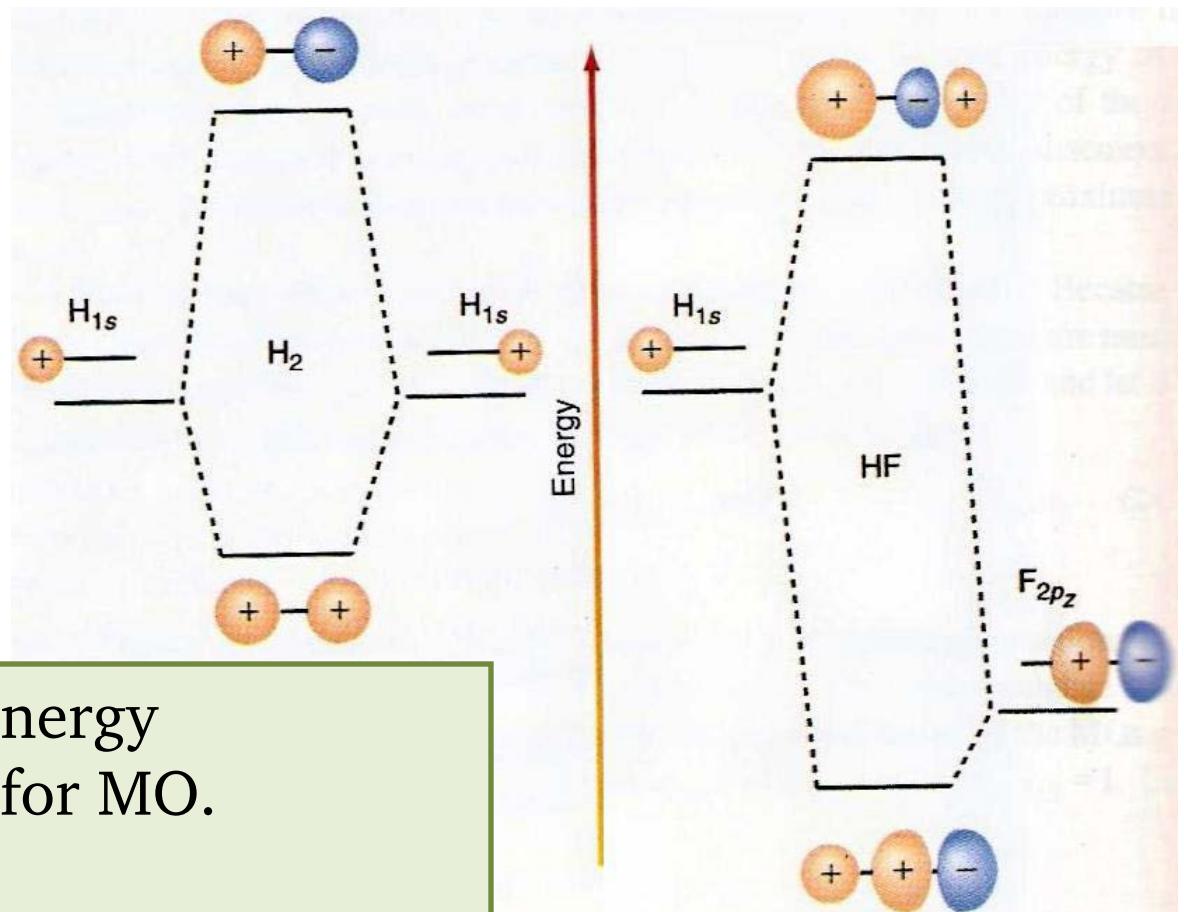
Molecular Orbital Theory of H₂



Effective nuclear charge changes the absolute energy levels and the size of orbitals!

Matching of energies of AOs important for LCAO-MO, if the energies of two AOs are not close they will not interact to form MOs.

Matching of AO energies for MO



Both symmetry and energy
Matching is required for MO.

Valence electrons are most important

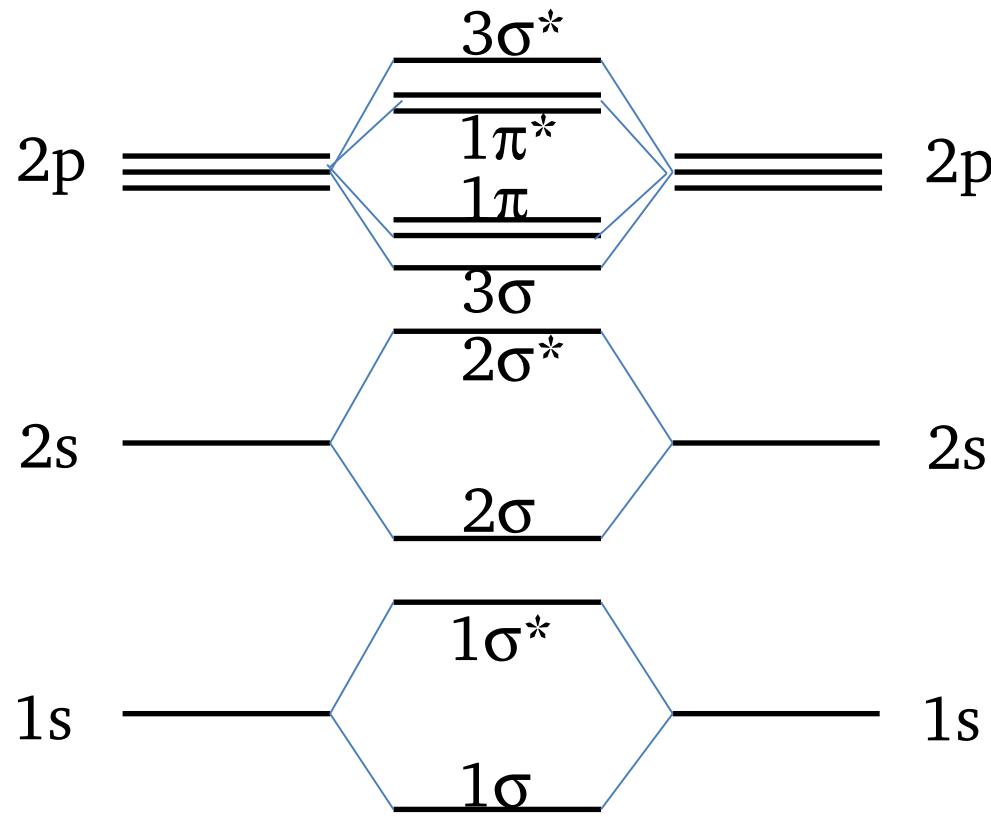
Due to large difference in energy of 1s(H) and 1s(F),
LCAO-MO for both 1S is not feasible in HF.
Rather, 2p_z(F) and 1s(H) form a sigma bond.

Bonding in First-Row Homo-Diatomic Molecules



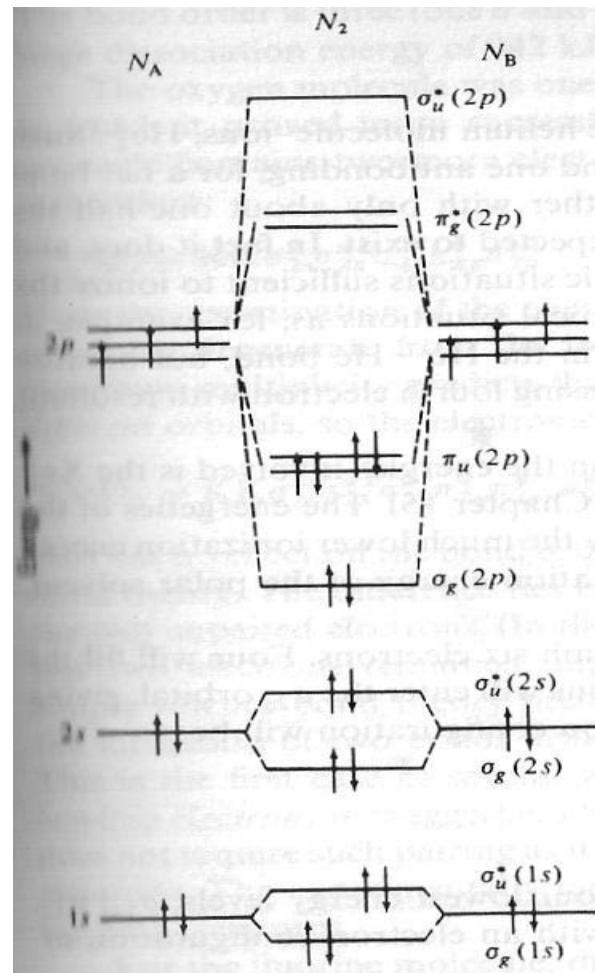
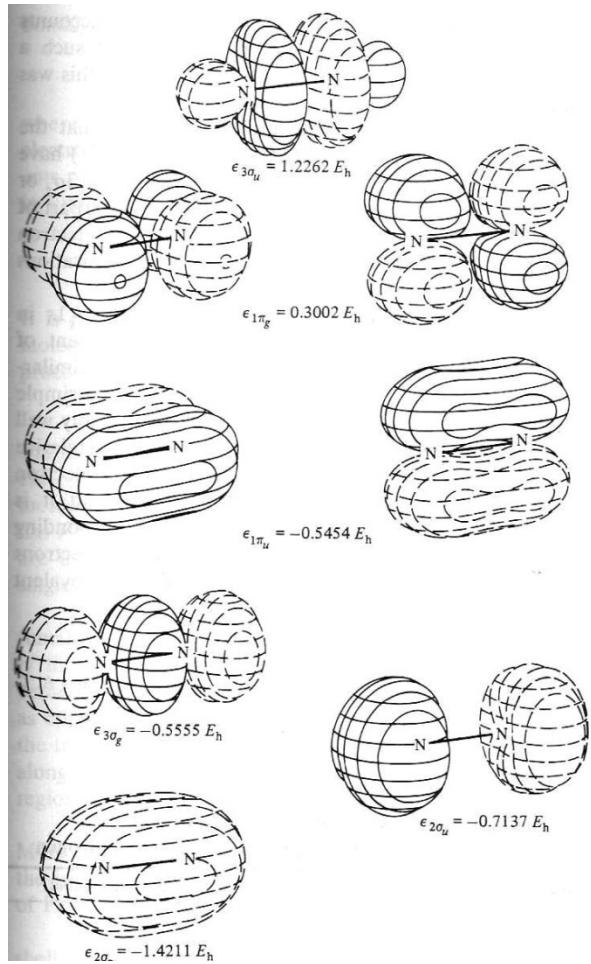
The orbital energies of the two approaching atoms are identical before they start interacting to form a BOND

Bonding in First-Row Homo-Diatomic Molecules



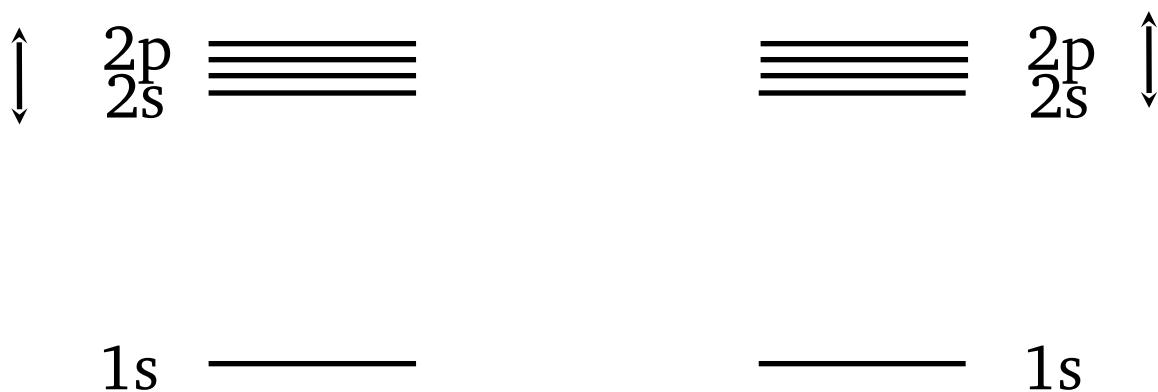
The interaction between the energy and symmetry matched orbitals leads to various types of BONDS

MO Energies of Dinitrogen



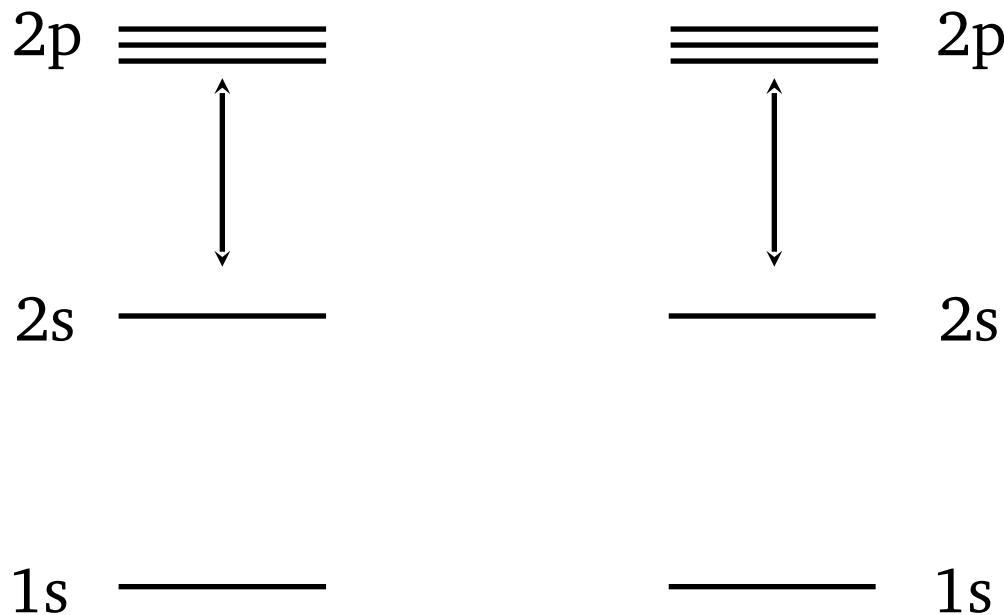
Experiments tell us this picture is incorrect!

Bonding in First-Row Homo-Diatomic Molecules



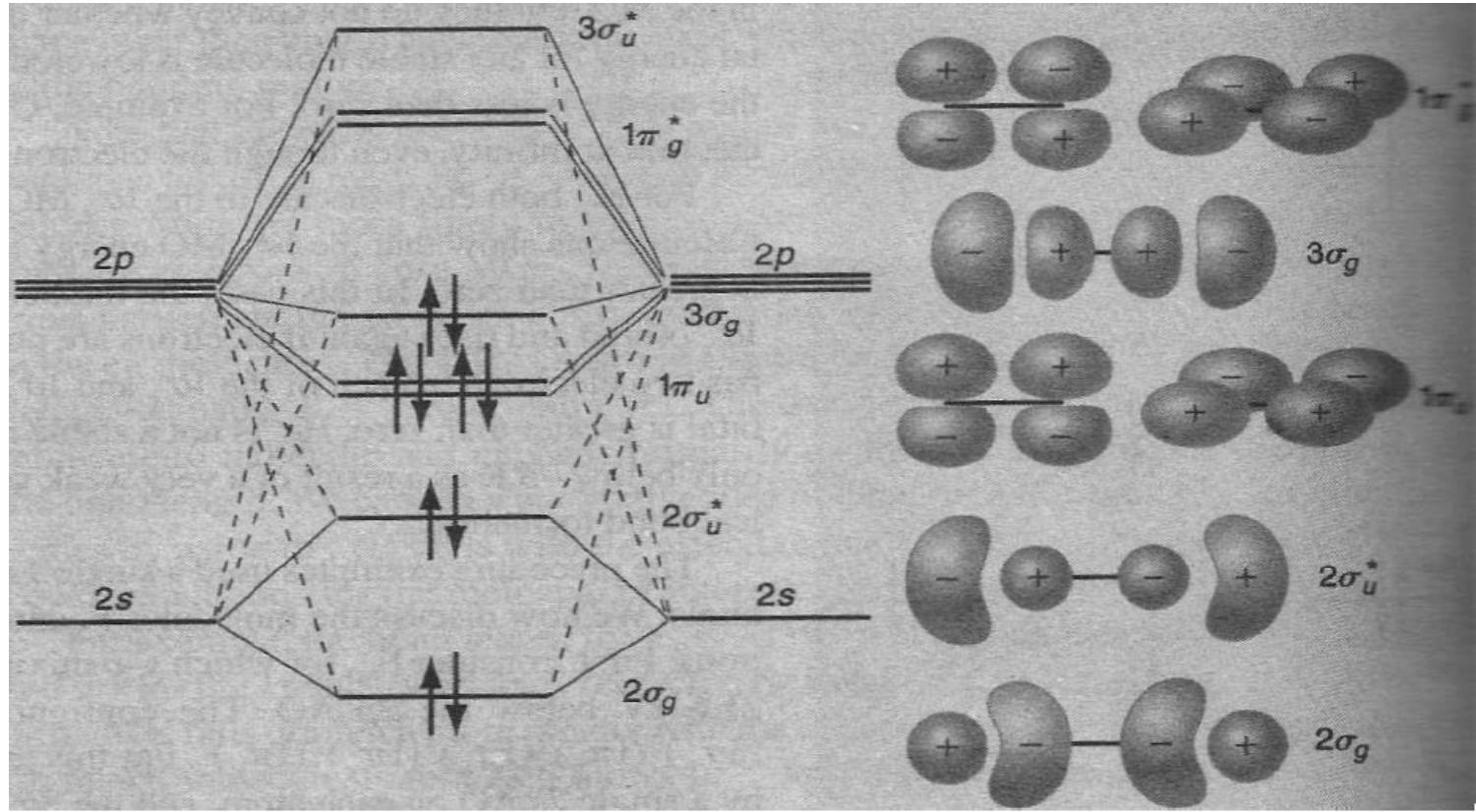
The 2s and 2p orbitals are degenerate in Hydrogen. However in the many electron atoms these two sets of orbitals are no longer degenerate.

Bonding in First-Row Homo-Diatomic Molecules



The difference in the energies of the $2s$ and $2p$ orbitals increases along the period. Its is minimum for Li and maximum for Ne

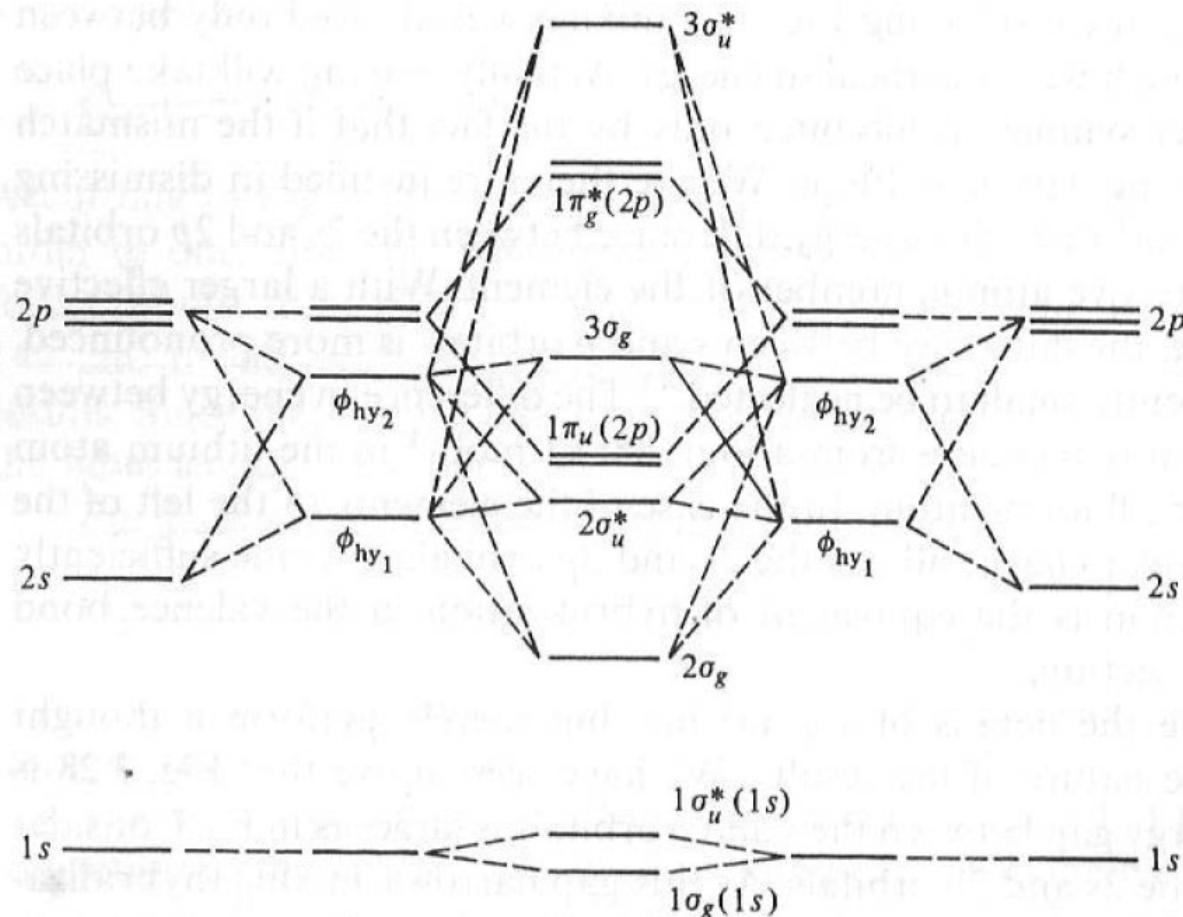
MO Energies of Dinitrogen



Mixing of 2s and 2p orbital occur because of small energy gap between them
2s and 2p electrons feels not so different nuclear charge.

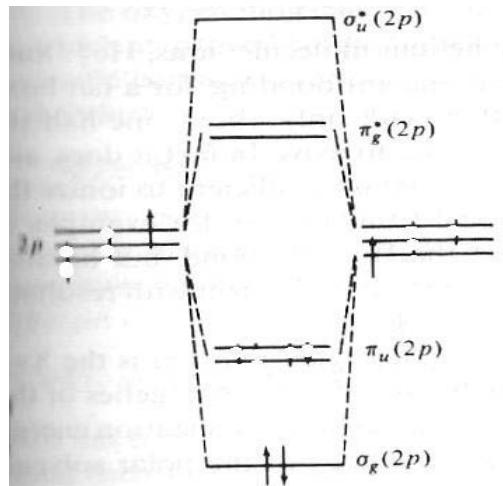
Note how the MO of $2s \rightarrow \sigma$ have p-type looks, while π -levels are clean

s-p Mixing: Hybridization of MO

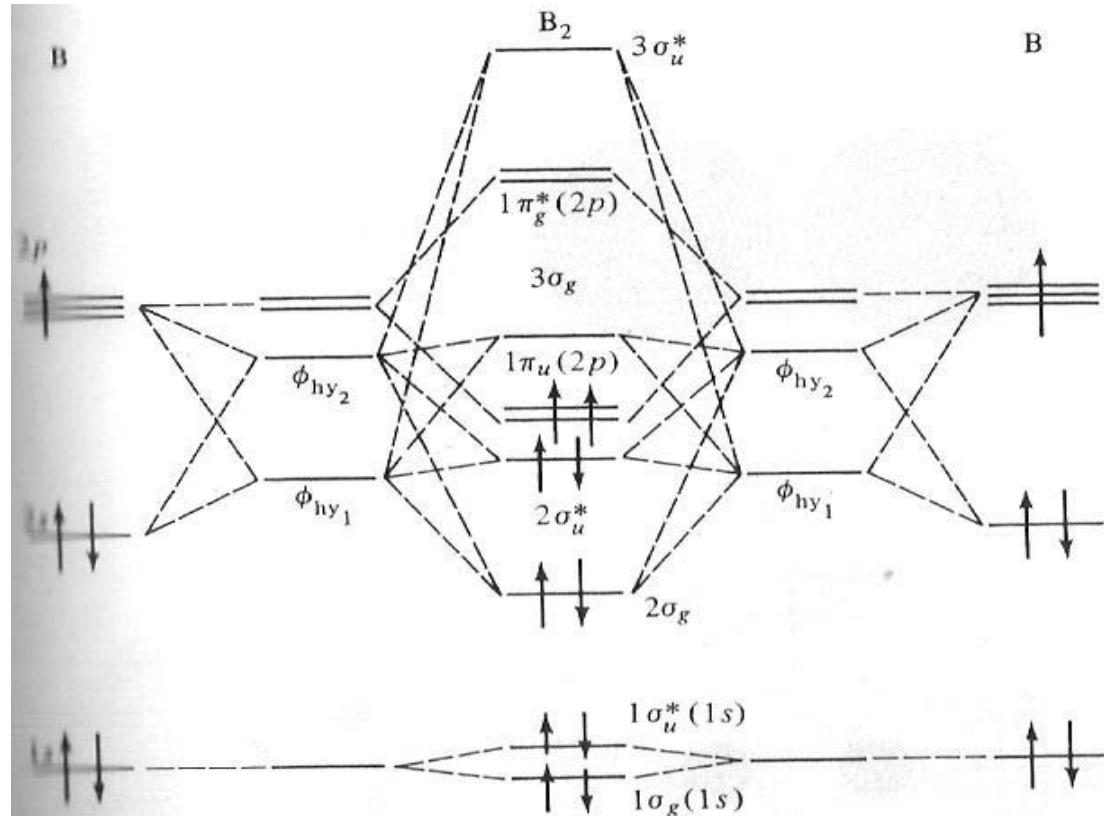
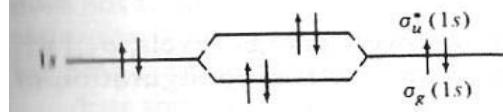
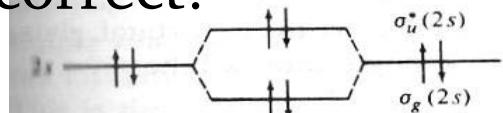


Mixing of $2s$ and $2p$ orbital occur because of small energy gap between them $2s$ and $2p$ electrons feels not so different nuclear charge

s-p Mixing: Hybridization of MO

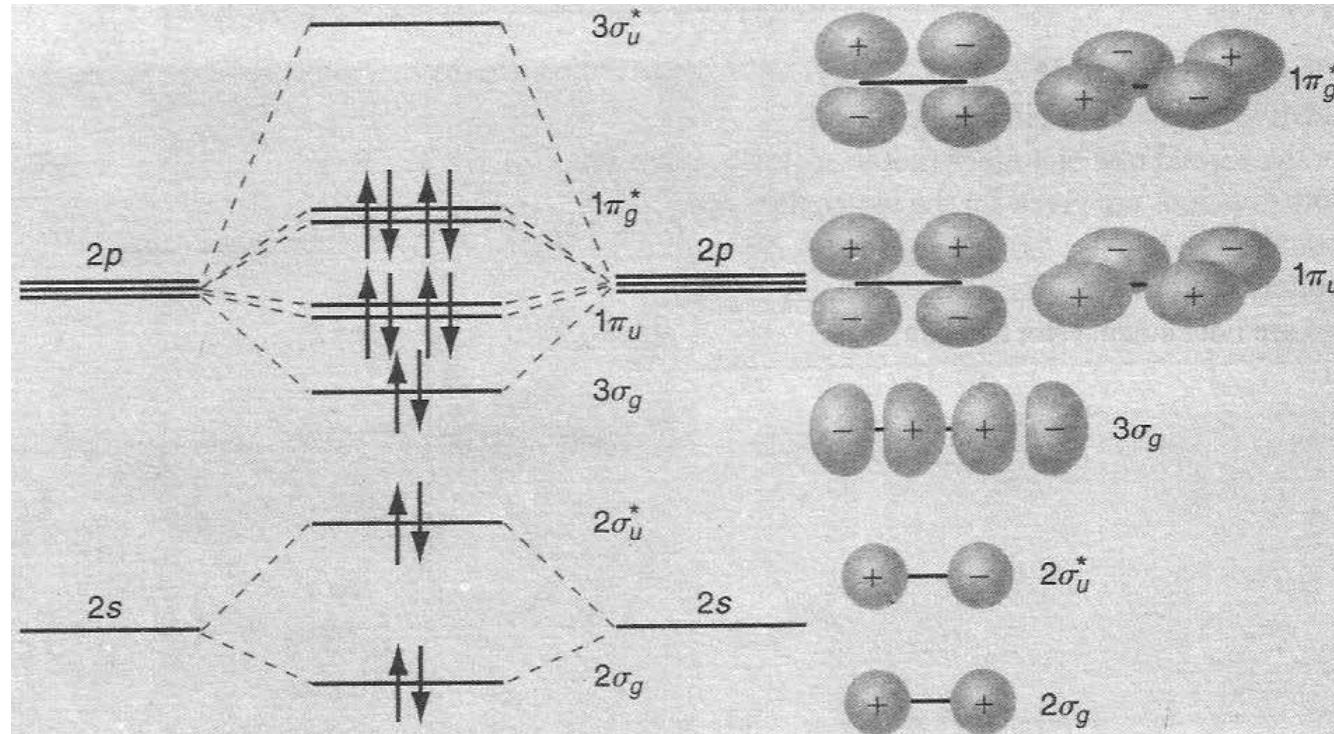


Incorrect!



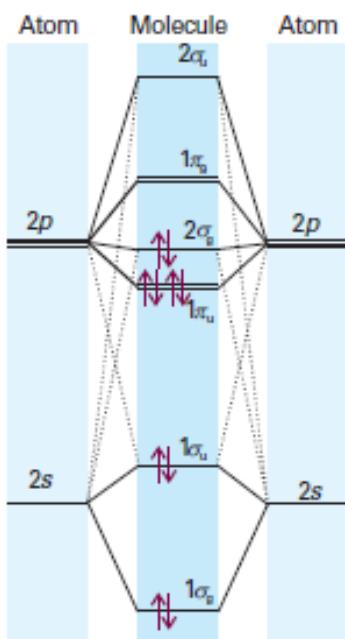
B_2 is paramagnetic. This can only happen if the two electrons with parallel spin are placed in the degenerate π -orbitals and if π orbitals are energetically lower than the σ orbital

MO diagram of F₂: No s-p Mixing

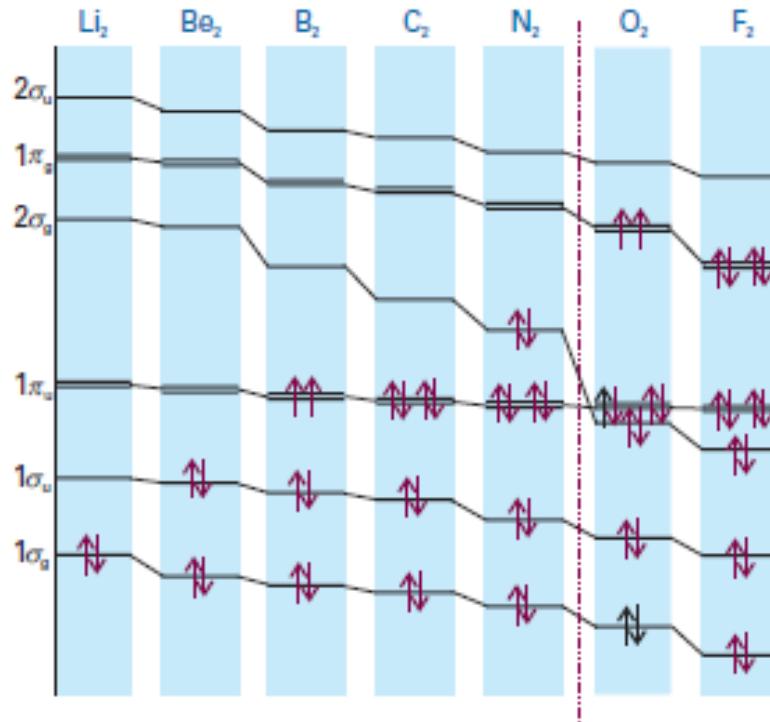


No Mixing of **s** and **p** orbital because of higher energy
Gap between **2s** and **2p** levels in Oxygen and Fluorine!
2s and **2p** electrons feels very different nuclear charge

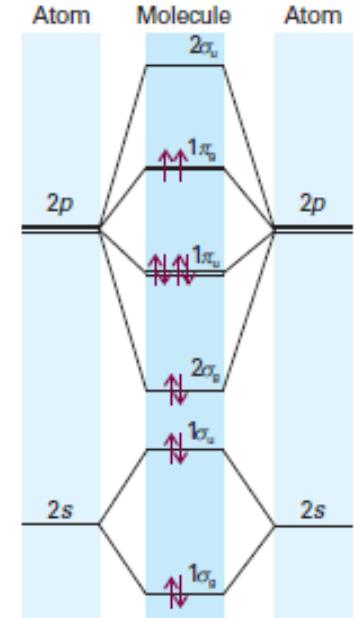
MO Energy Level Diagram for Homo-Diatomics



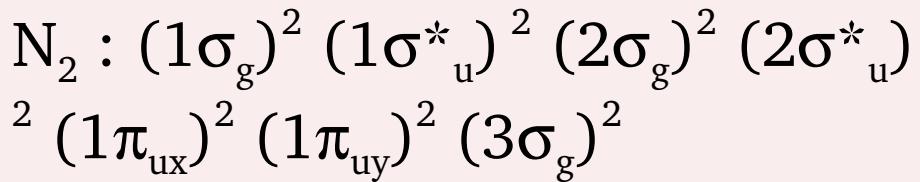
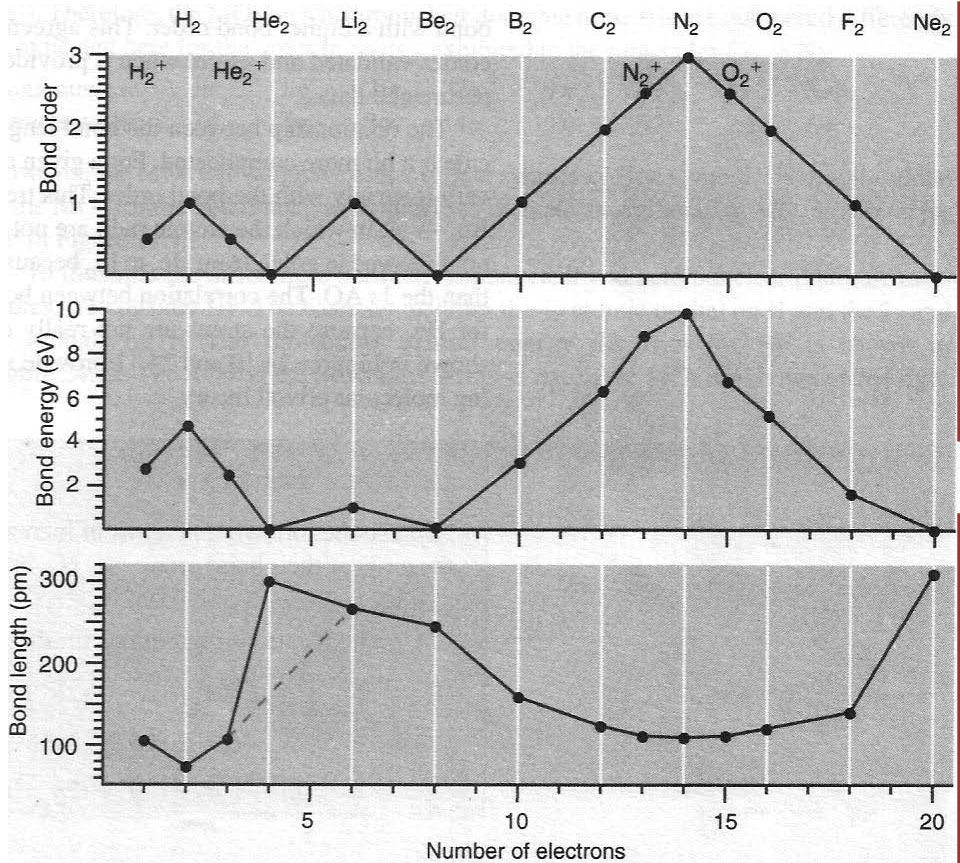
Upto N₂



Beyond N₂

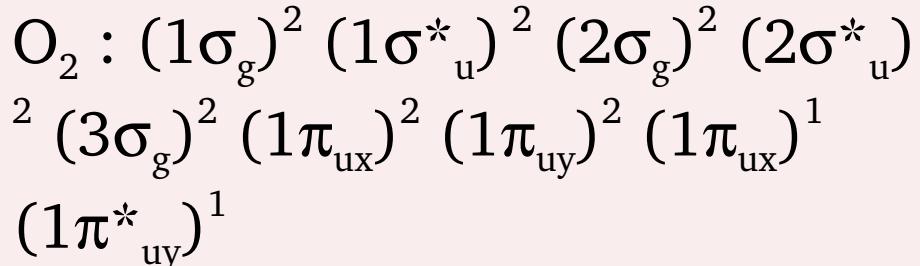


Bond-Order and Other Properties



$$BO = 3$$

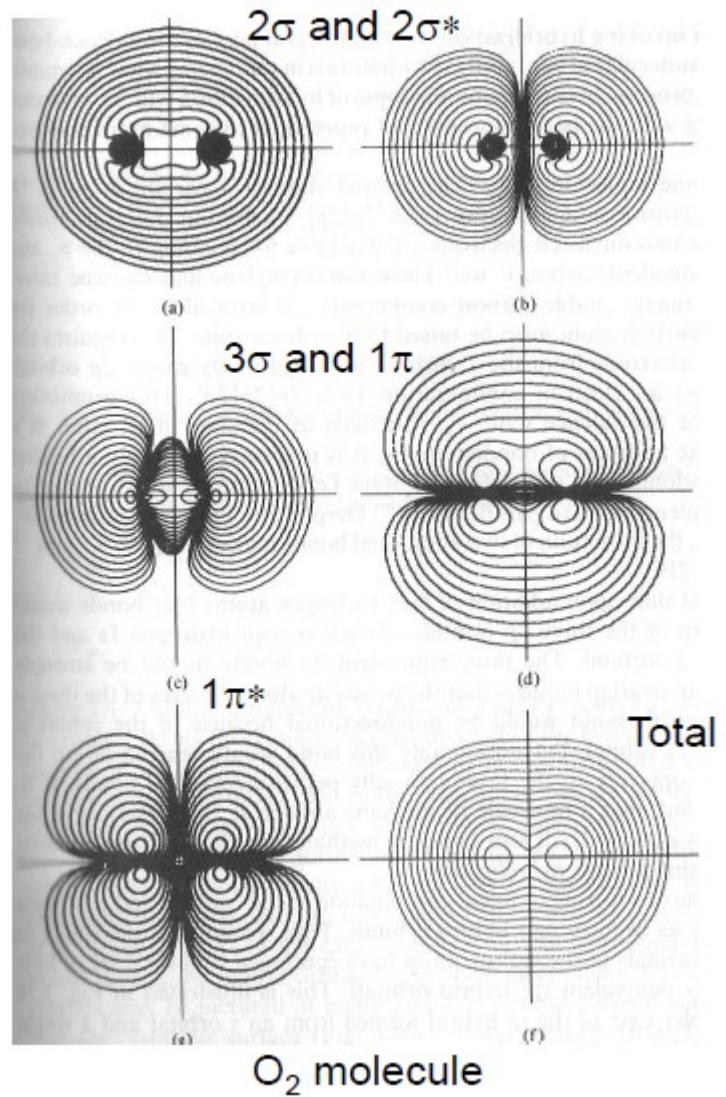
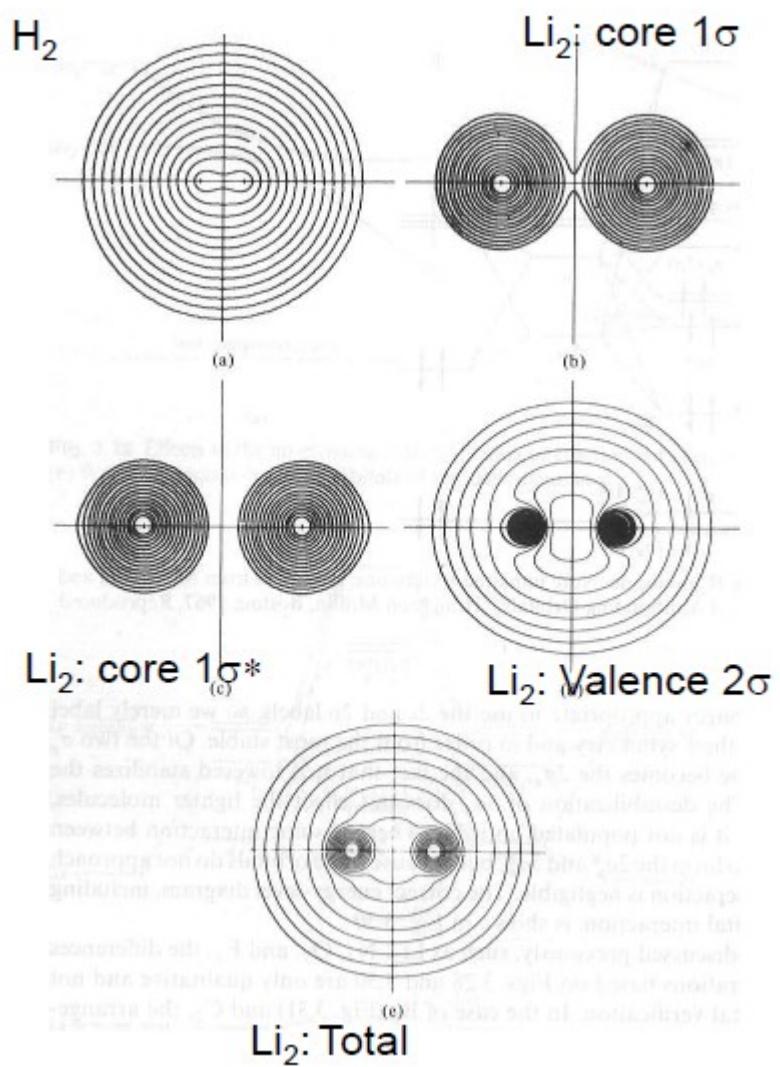
All spins paired: diamagnetic



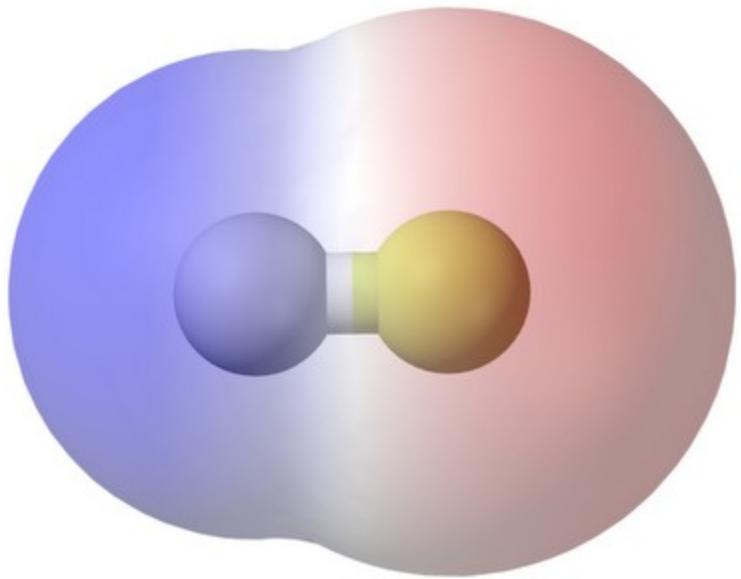
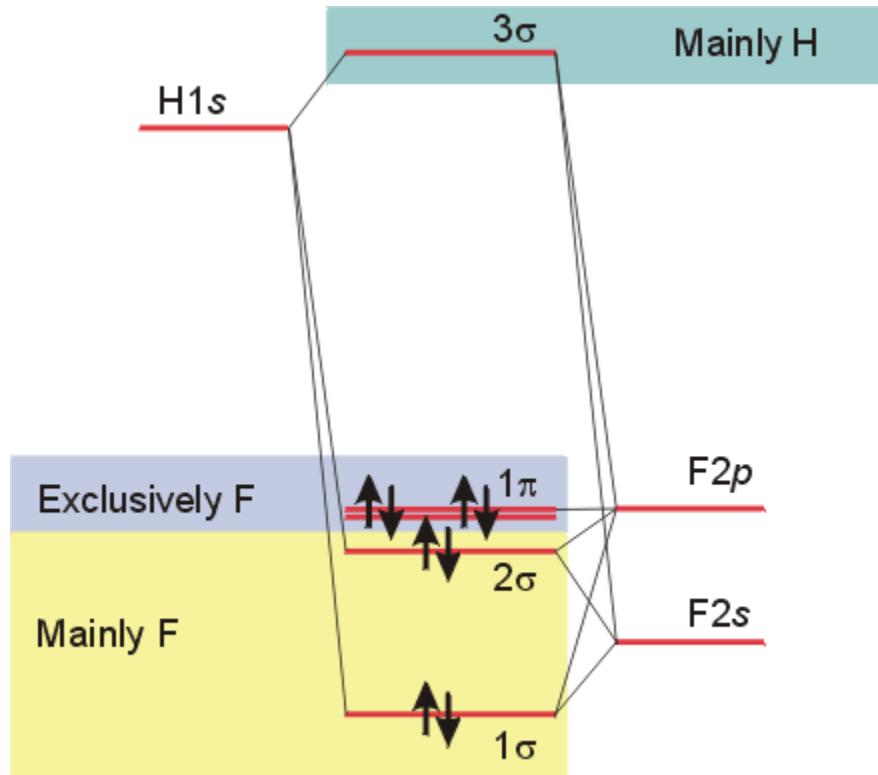
$$BO = 2$$

2 spins unpaired: paramagnetic

MO Contours and Electron Density

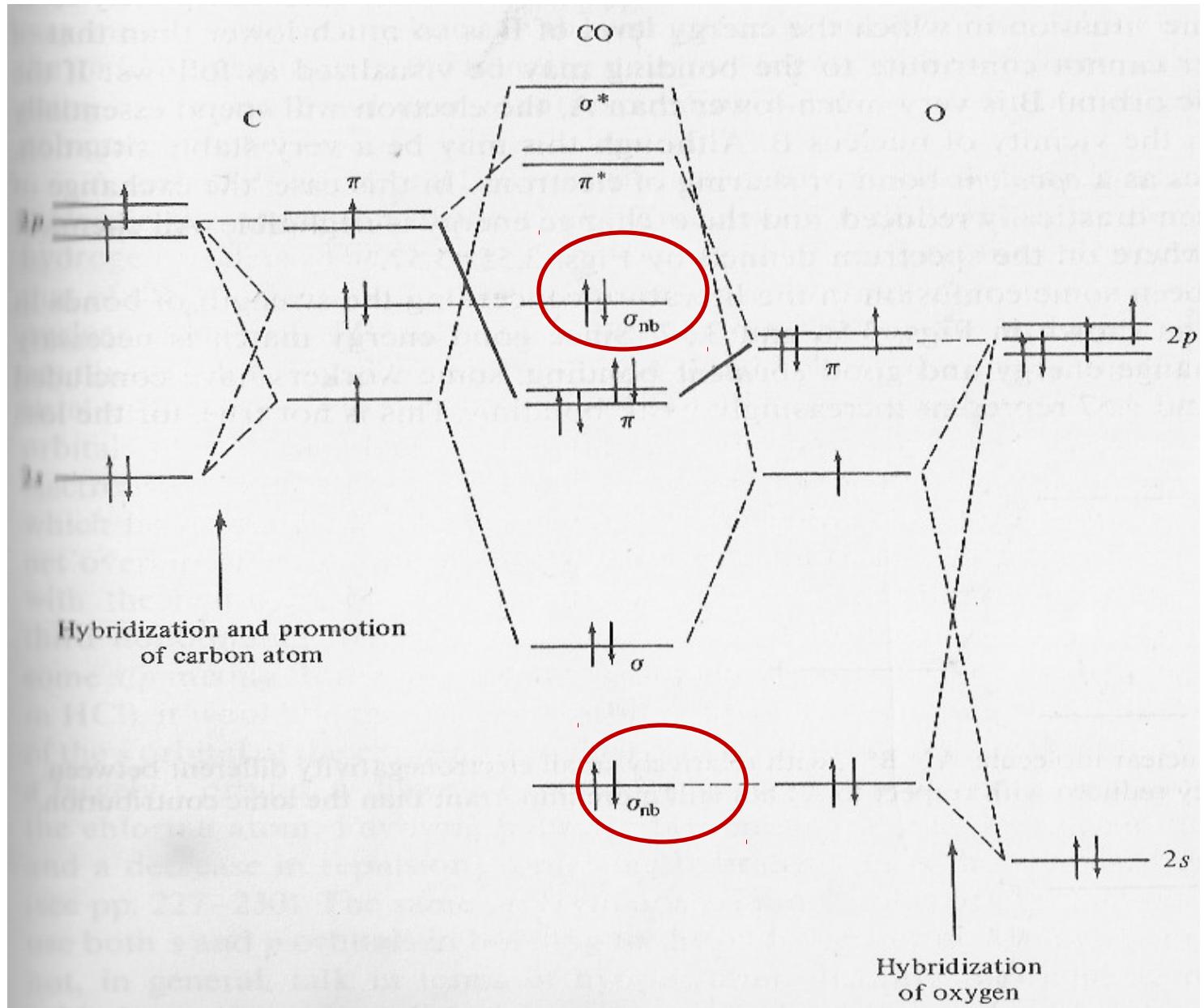


Hetero-Diatomics: HF

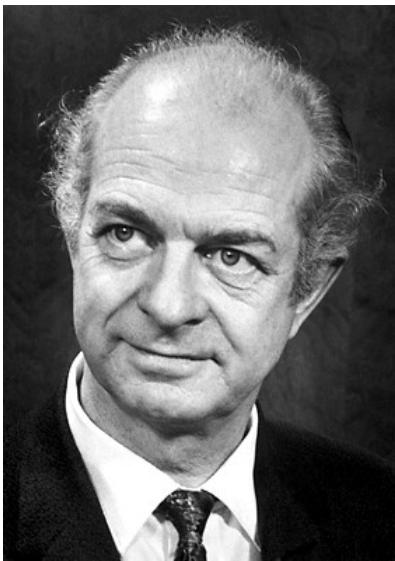


Due to higher electronegativity of F than H, the electron distribution is lopsided

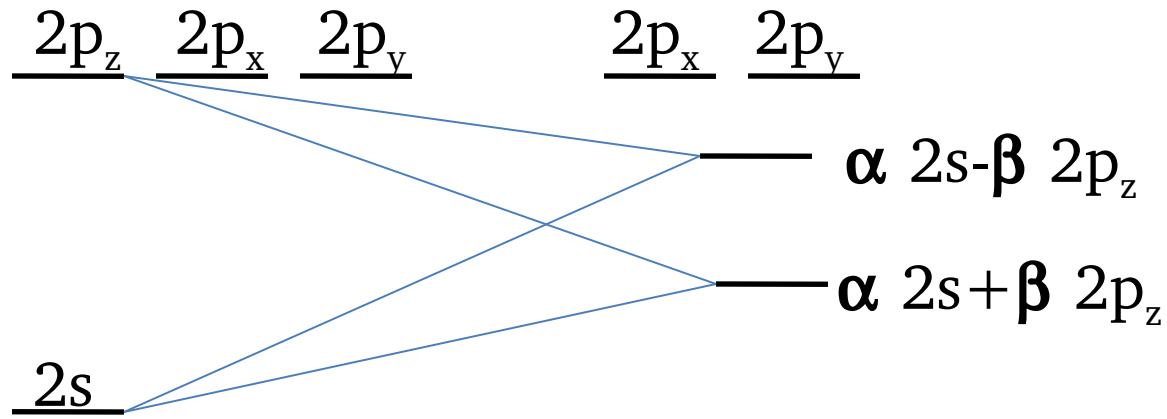
Hetero-Diatomics: CO



Hybridization



Linear combination of atomic orbitals within an atom leading to more effective bonding



The coefficients α and β depend on field strength

Hybridization is close to VBT approach. Use of experimental information
All hybridized orbitals are equivalent and are ortho-normal to each other