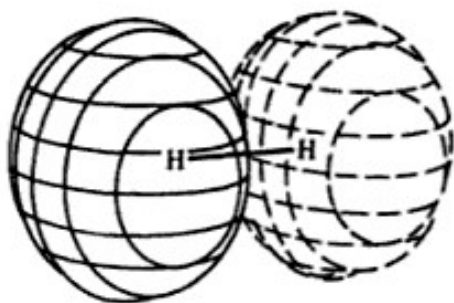
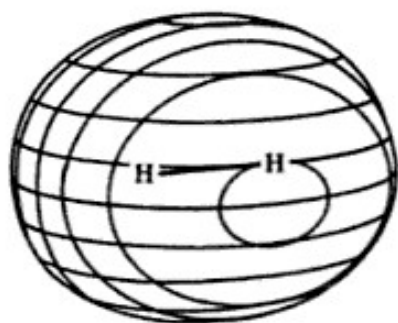


Molecular Orbital Theory of H₂



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

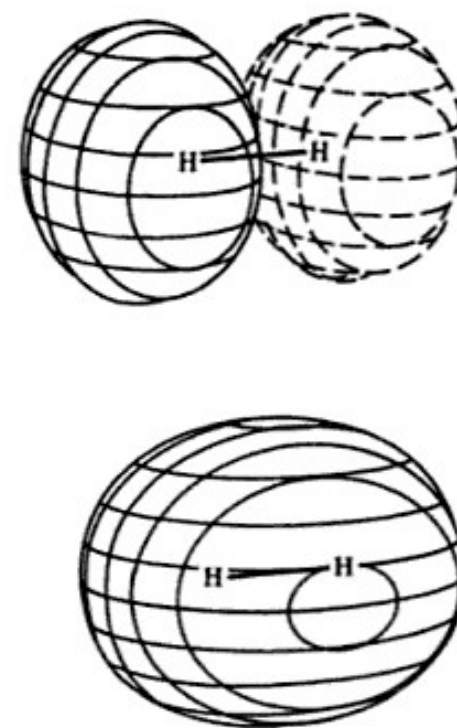
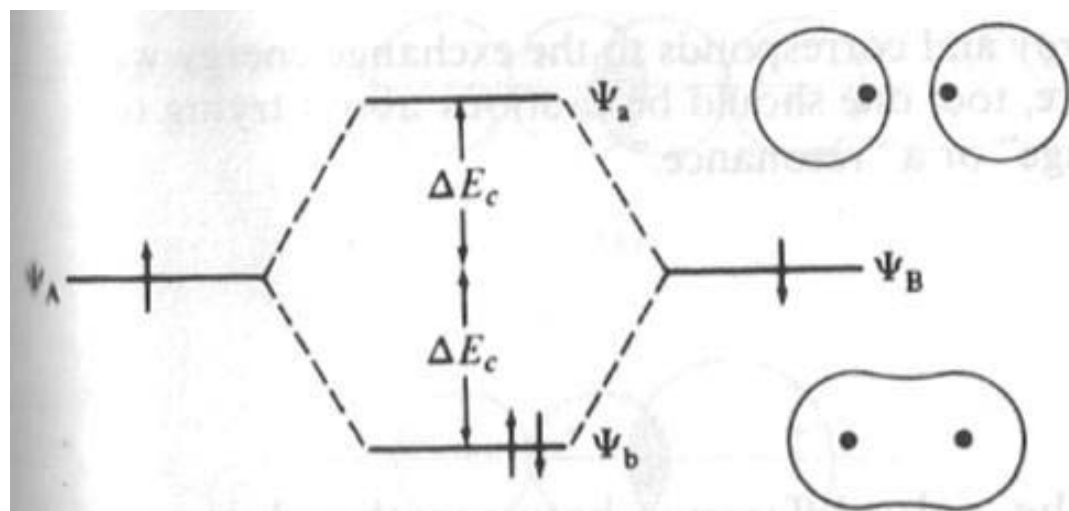
$$\frac{1}{2[1-S]} \left[1s_A(1) \cdot 1s_A(2) + 1s_B(1) \cdot 1s_B(2) - 1s_A(1) \cdot 1s_B(2) - 1s_B(1) \cdot 1s_A(2) \right]$$



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

$$\frac{1}{2[1+S]} \left[1s_A(1) \cdot 1s_A(2) + 1s_B(1) \cdot 1s_B(2) + 1s_A(1) \cdot 1s_B(2) + 1s_B(1) \cdot 1s_A(2) \right]$$

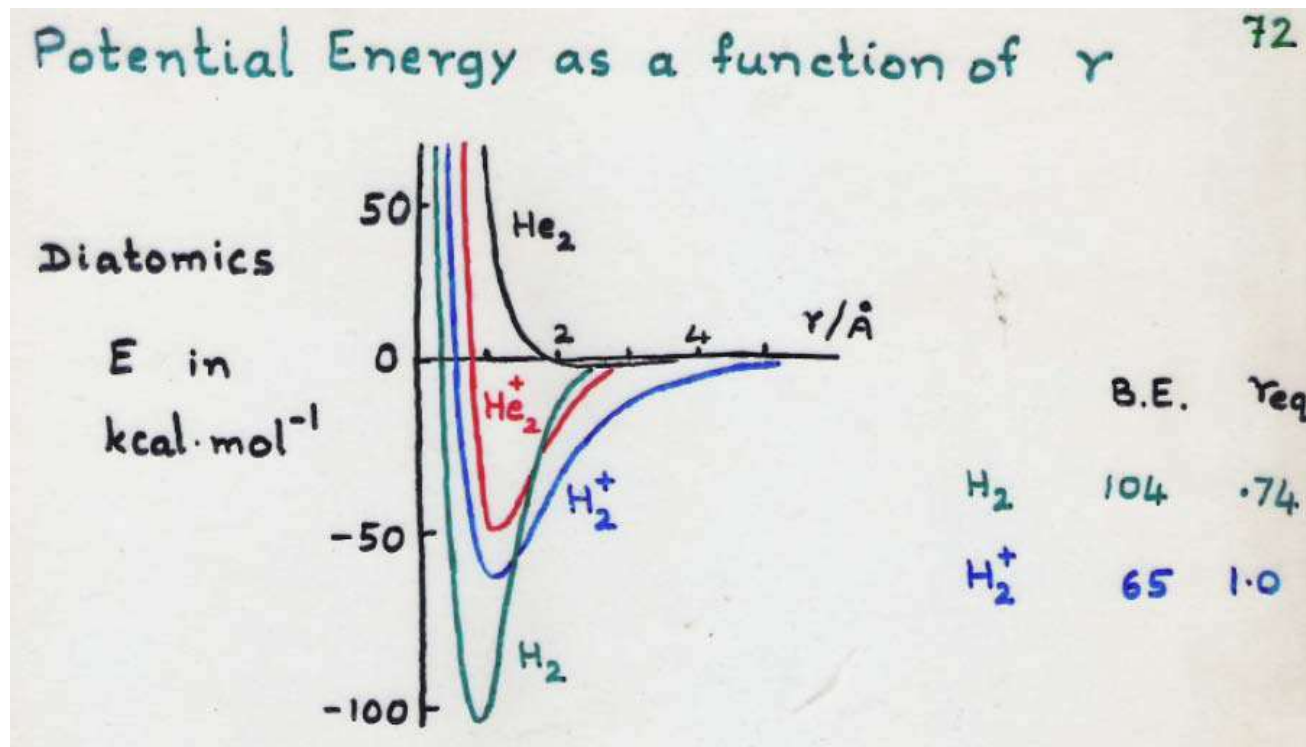
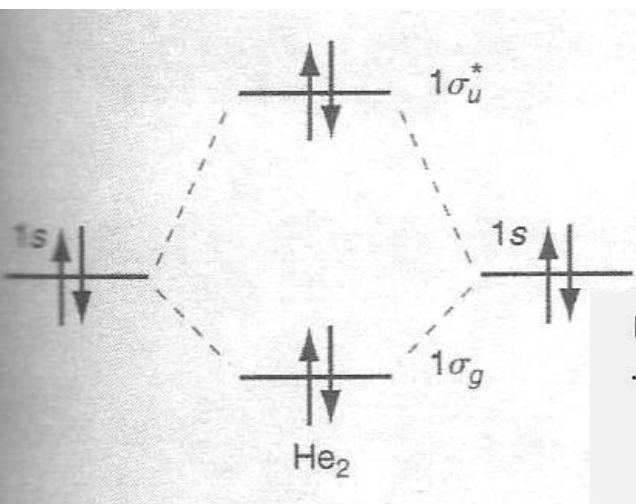
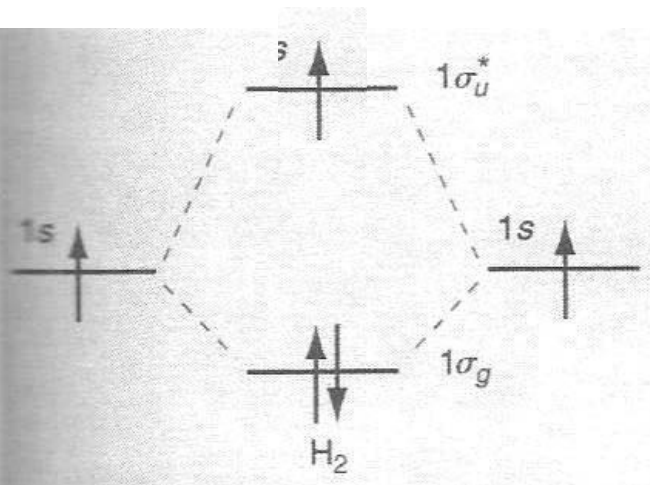
Molecular Orbital Theory of H₂



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.

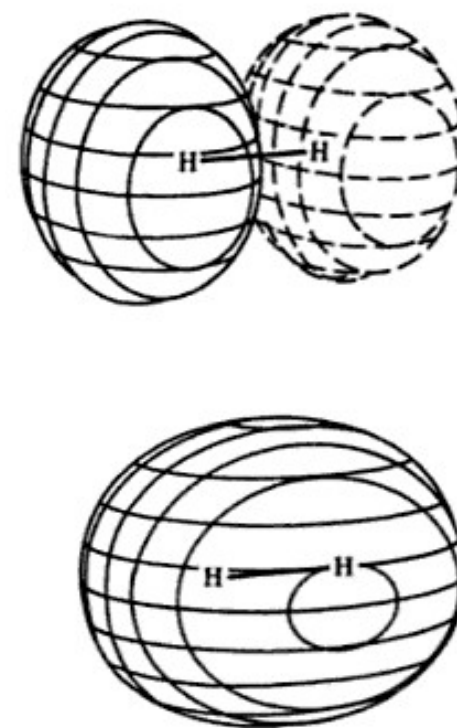
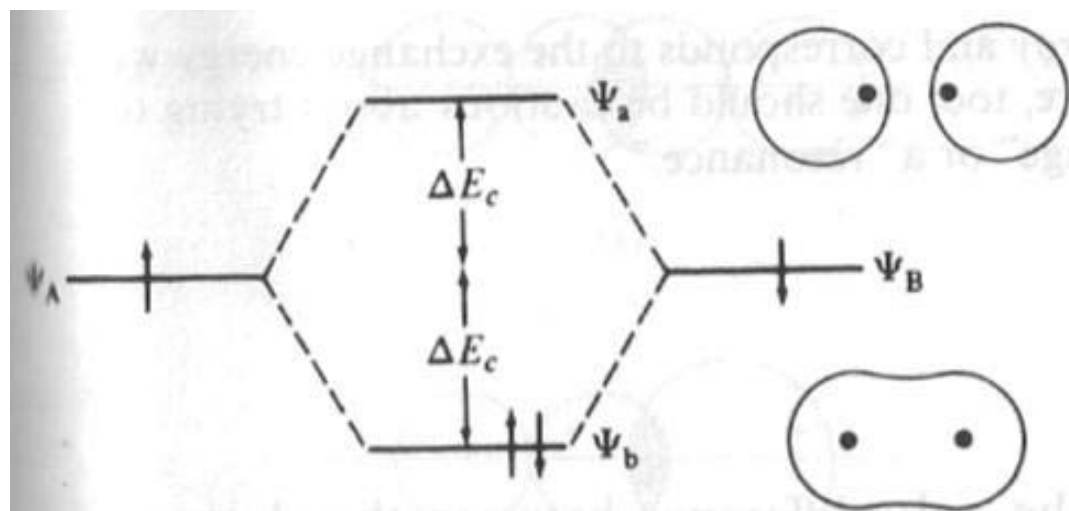
Diatoms of First Row: H_2^+ , H_2 , He_2 , He_2^+



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	$\ll 1$

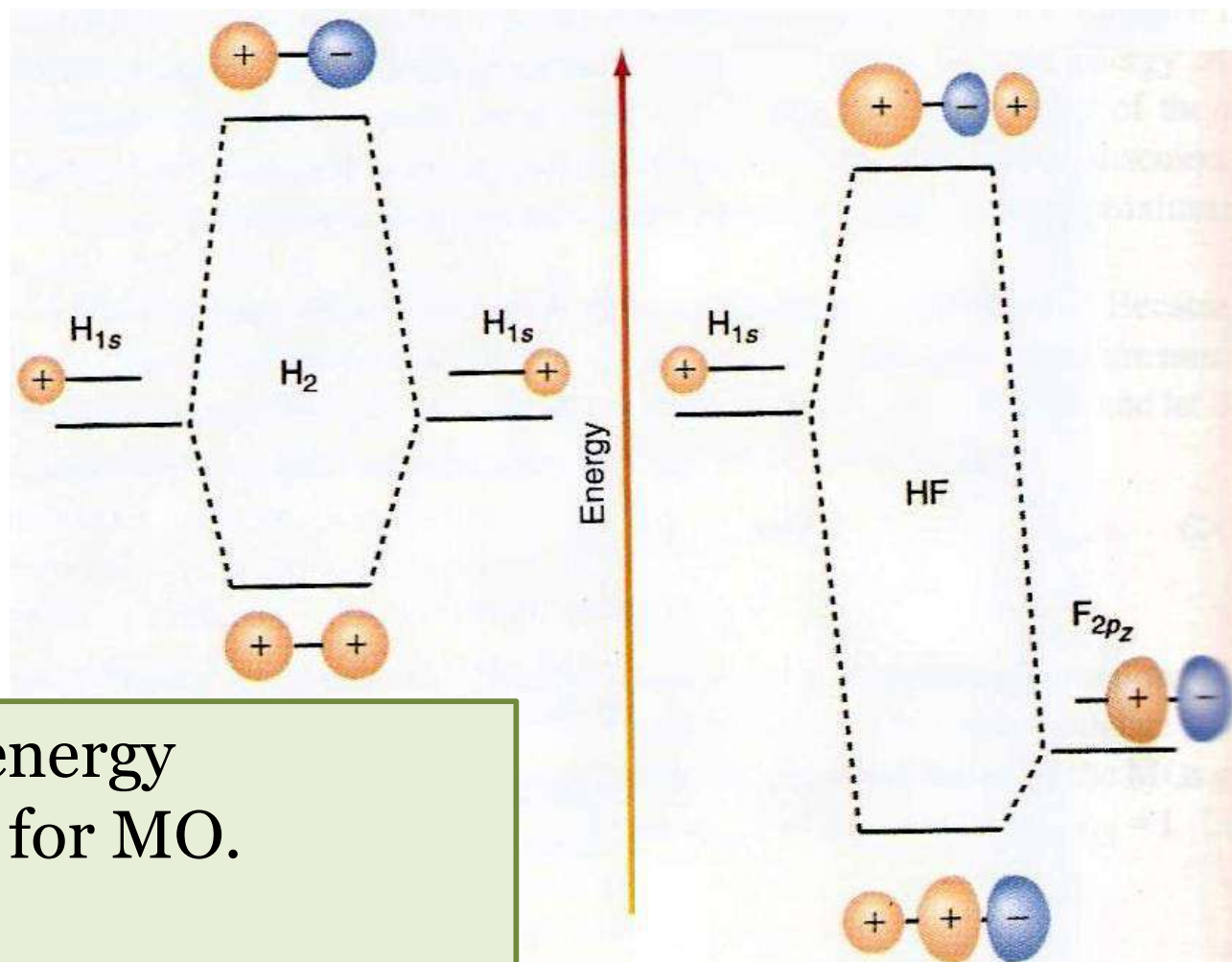
Molecular Orbital Theory of H_2



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

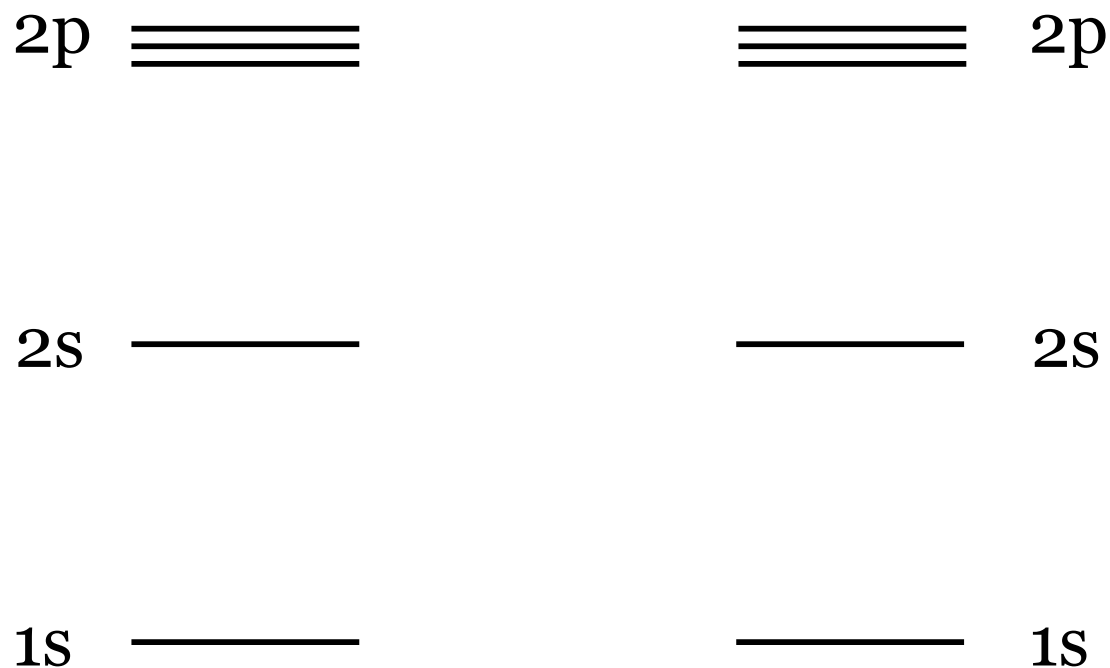


Both symmetry and energy
Matching is required for MO.

Valence electrons are most important

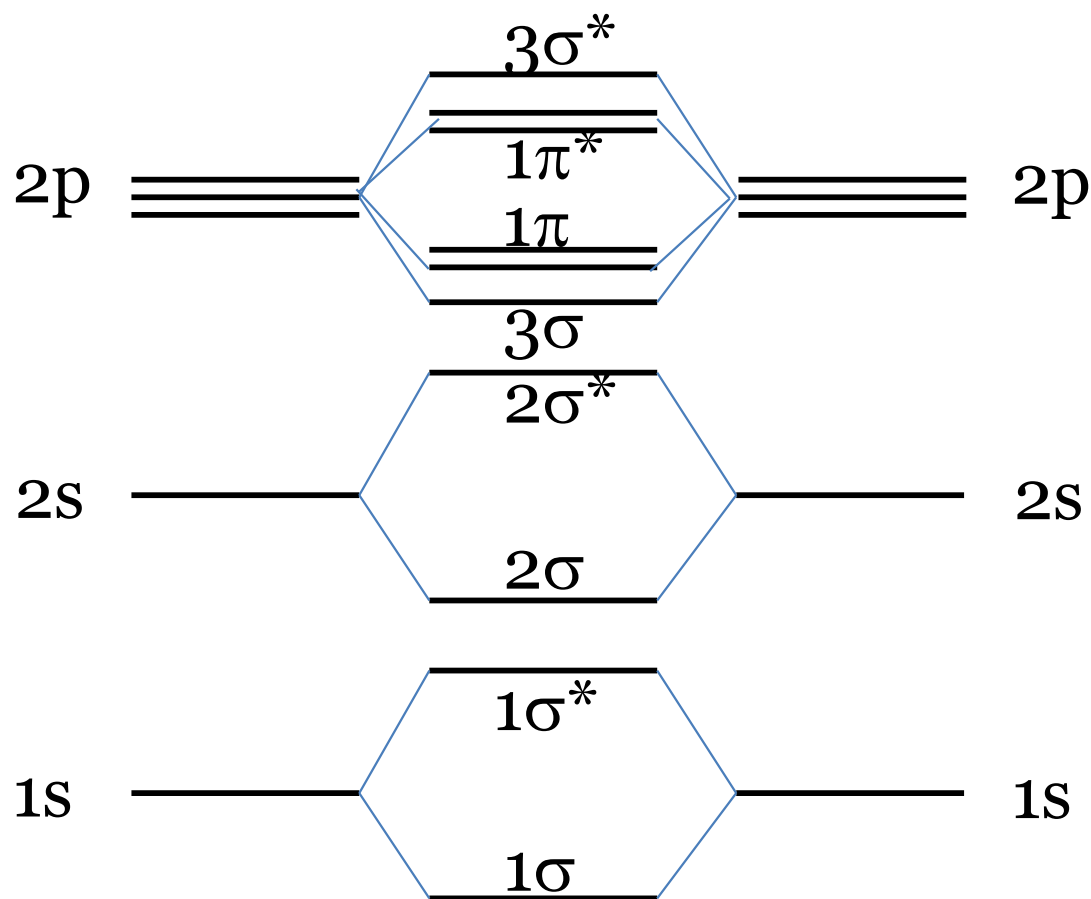
Due to large difference in energy of $1s(H)$ and $1s(F)$,
LCAO-MO for both $1s$ is not feasible in HF .
Rather, $2p_z(F)$ and $1s(H)$ form a sigma bond.

Bonding in First-Row Homo-Diatomic Molecules



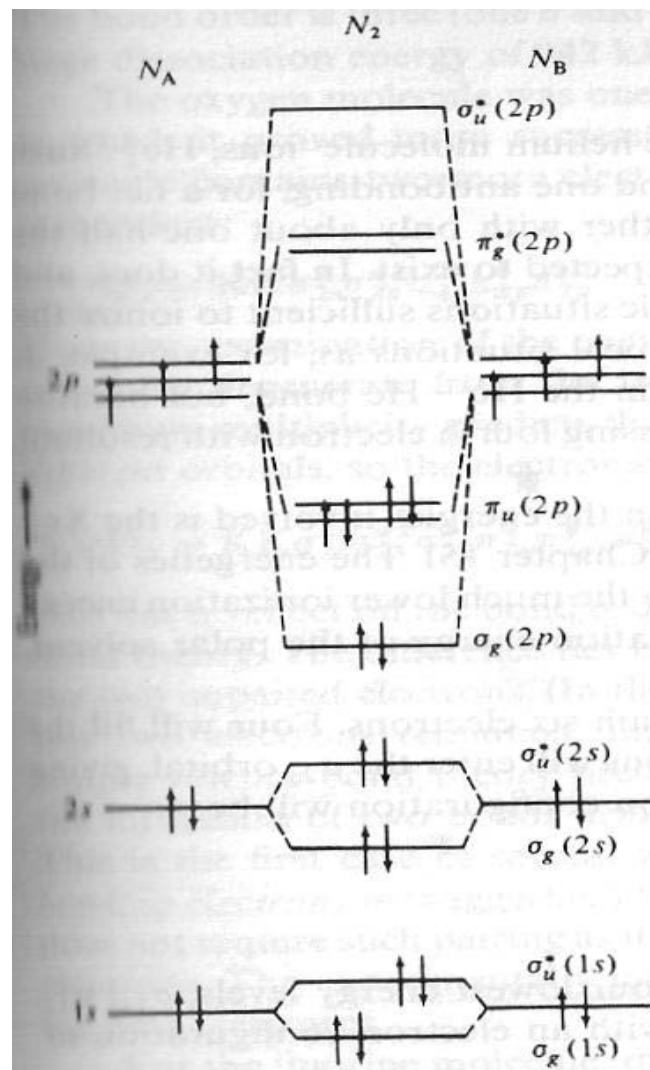
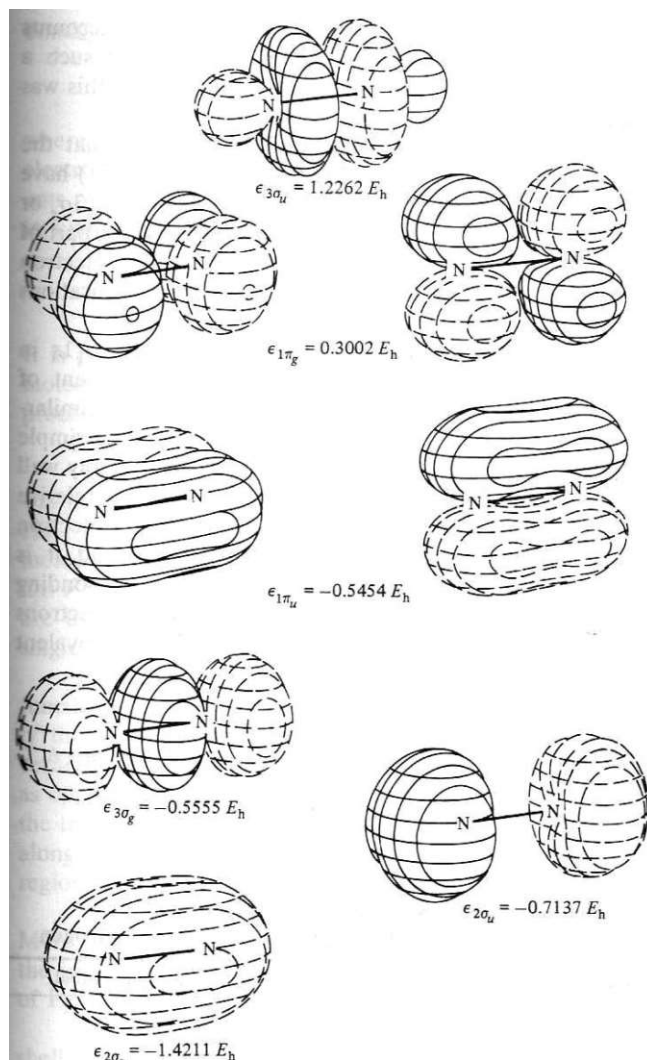
The orbital energies of the two approaching atoms are identical before they start interacting to form a BOND

Bonding in First-Row Homo-Diatomic Molecules



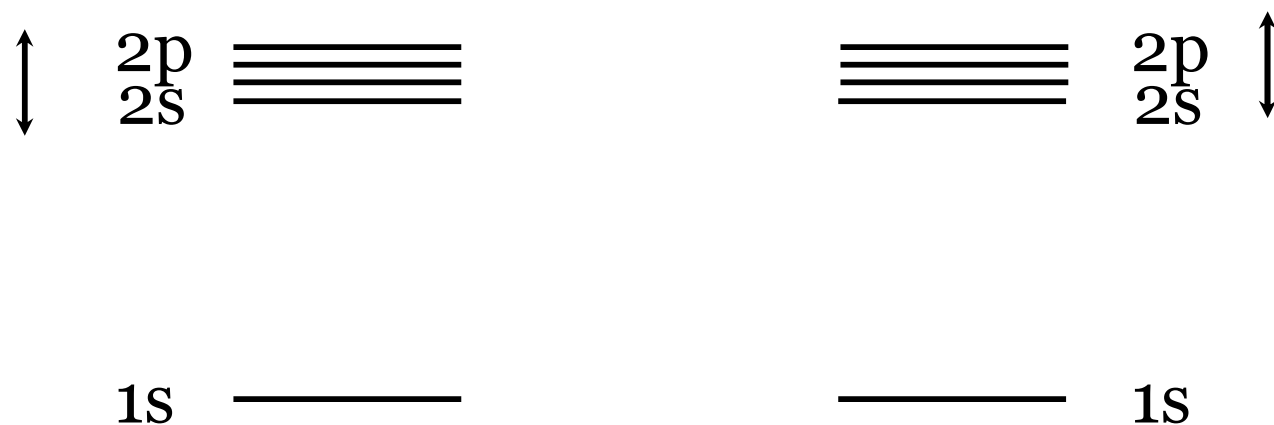
The interaction between the energy and symmetry matched orbitals leads to various types of BONDS

MO Energies of Dinitrogen



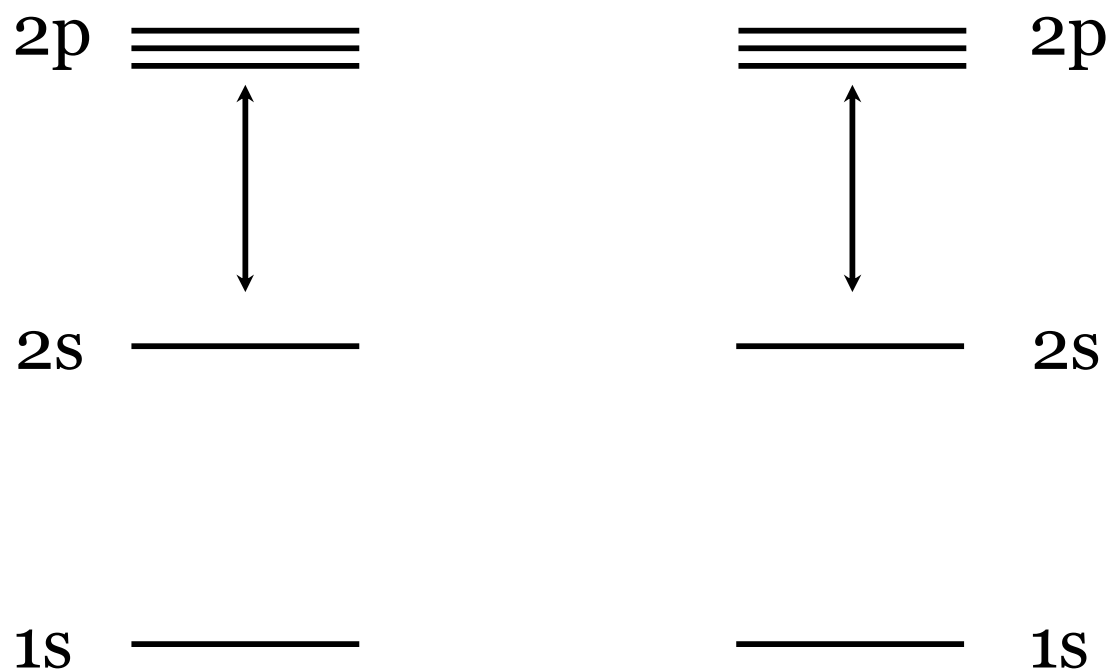
Experiments tell us this picture is incorrect!

Bonding in First-Row Homo-Diatomic Molecules



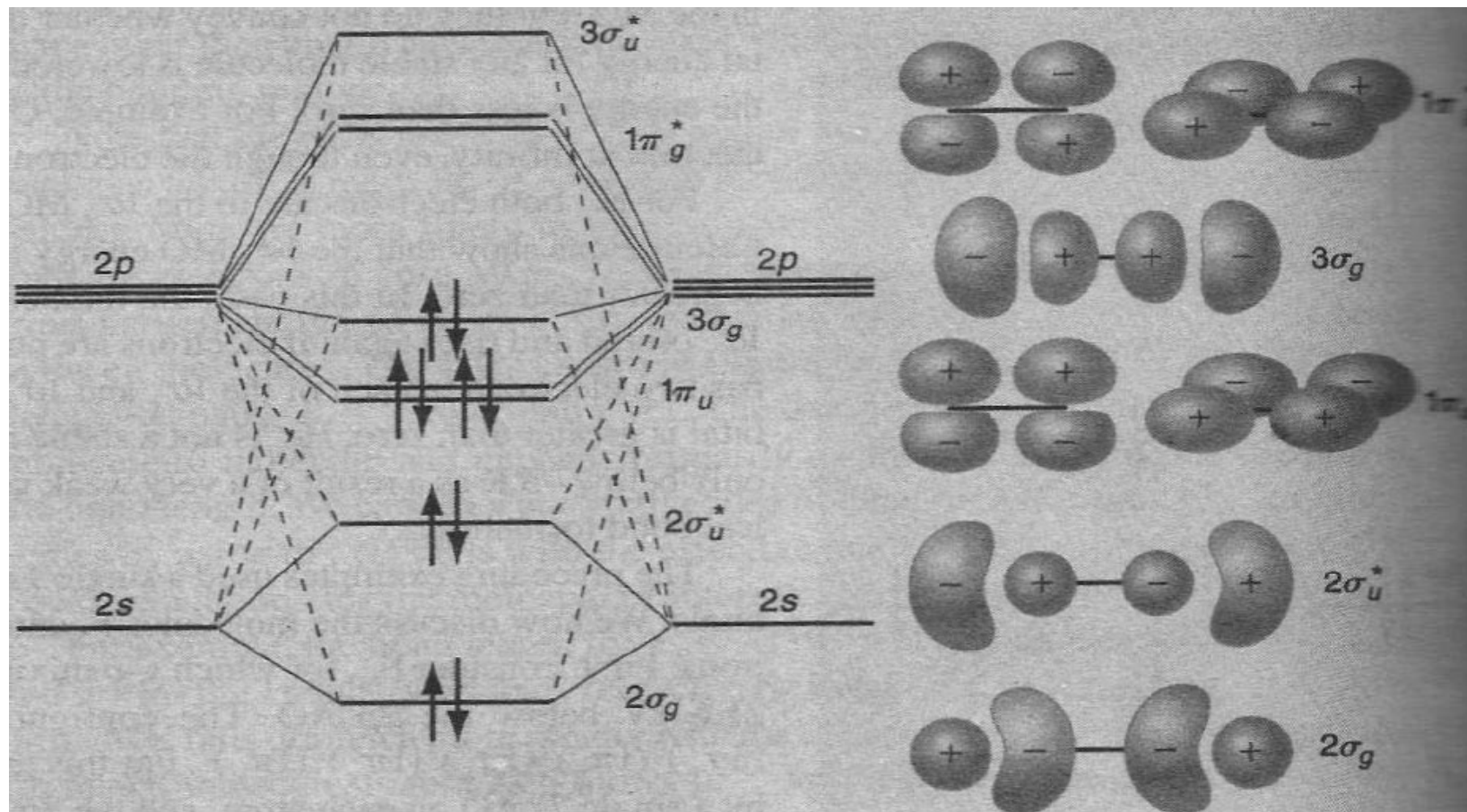
The 2s and 2p orbitals are degenerate in Hydrogen. However in the many electron atoms these two sets of orbitals are no longer degenerate.

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

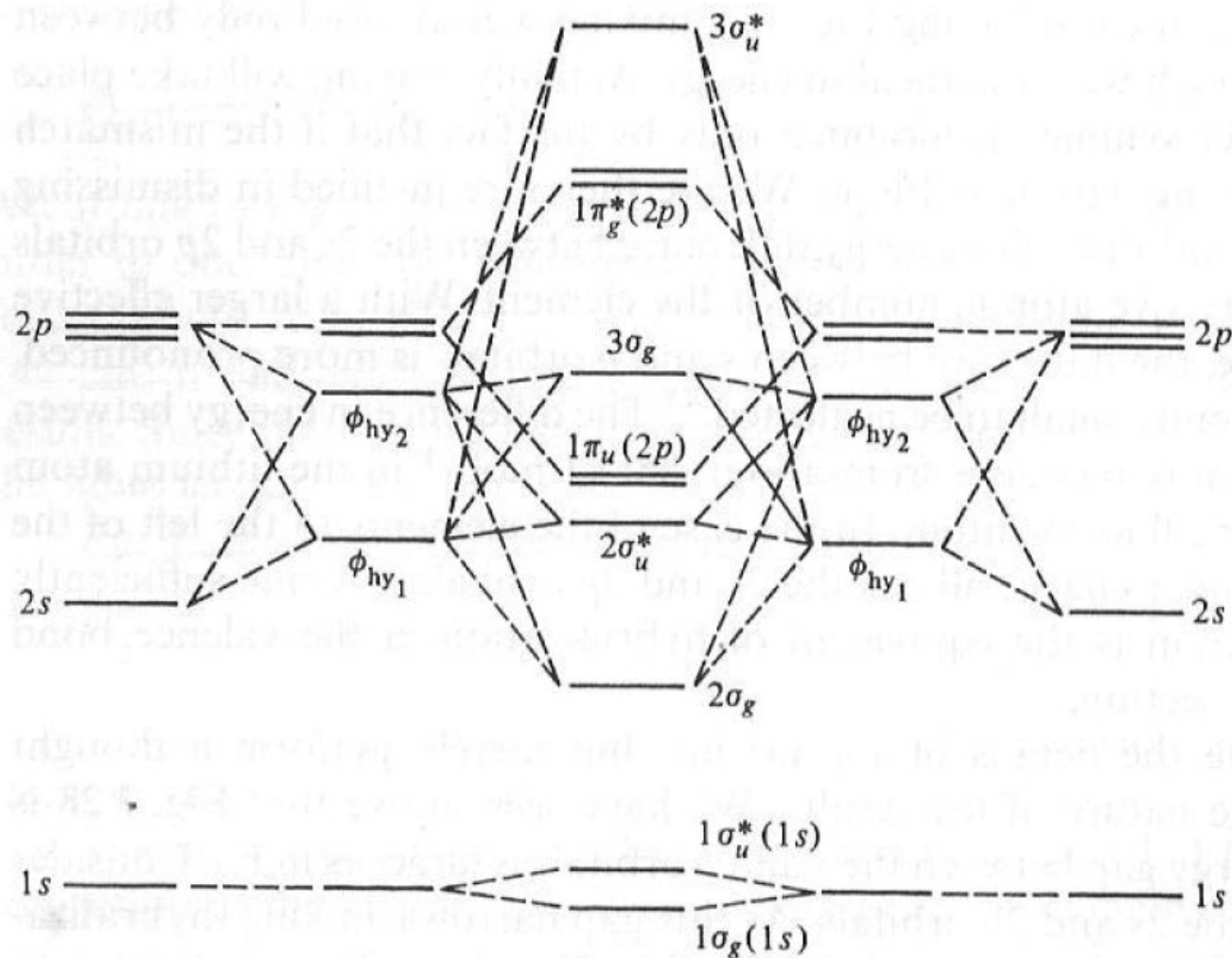
MO Energies of Dinitrogen



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

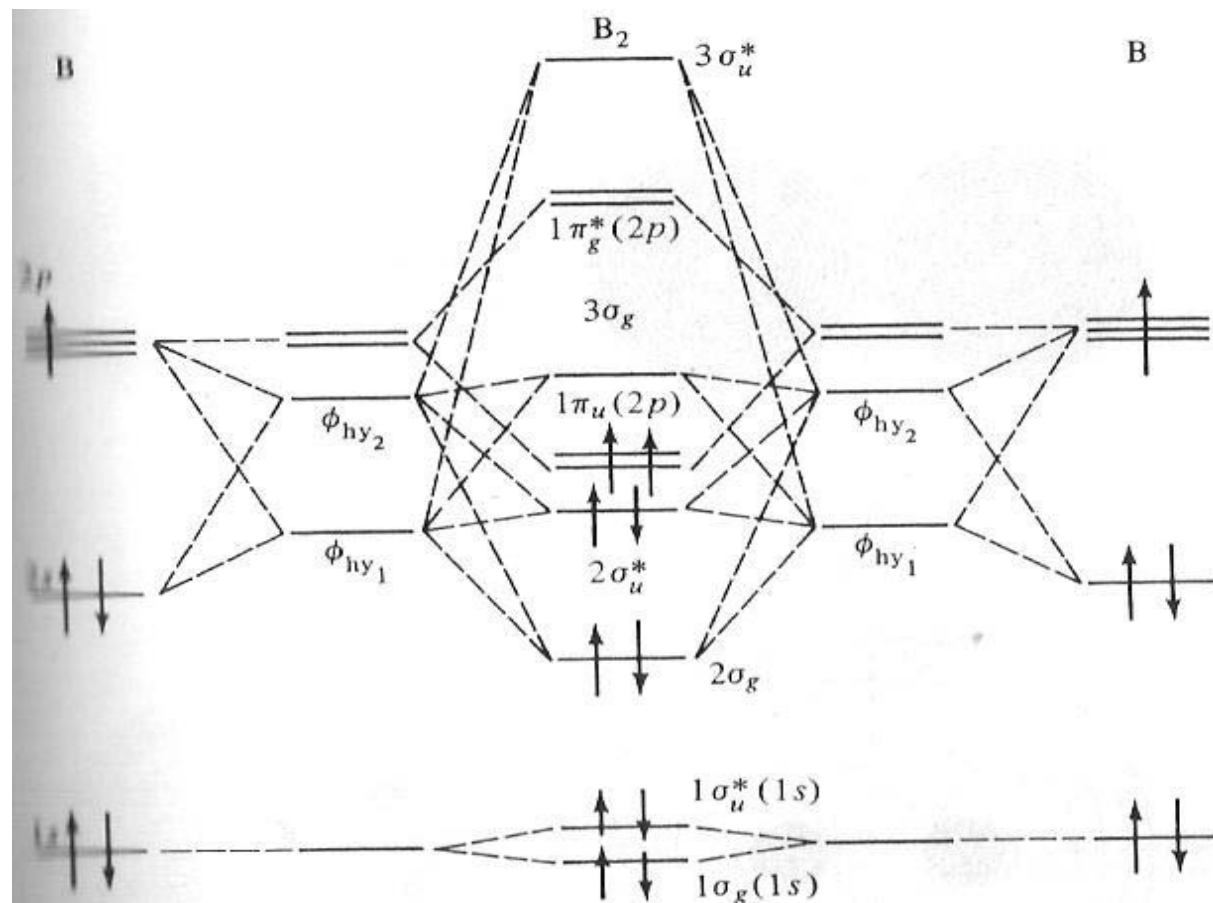
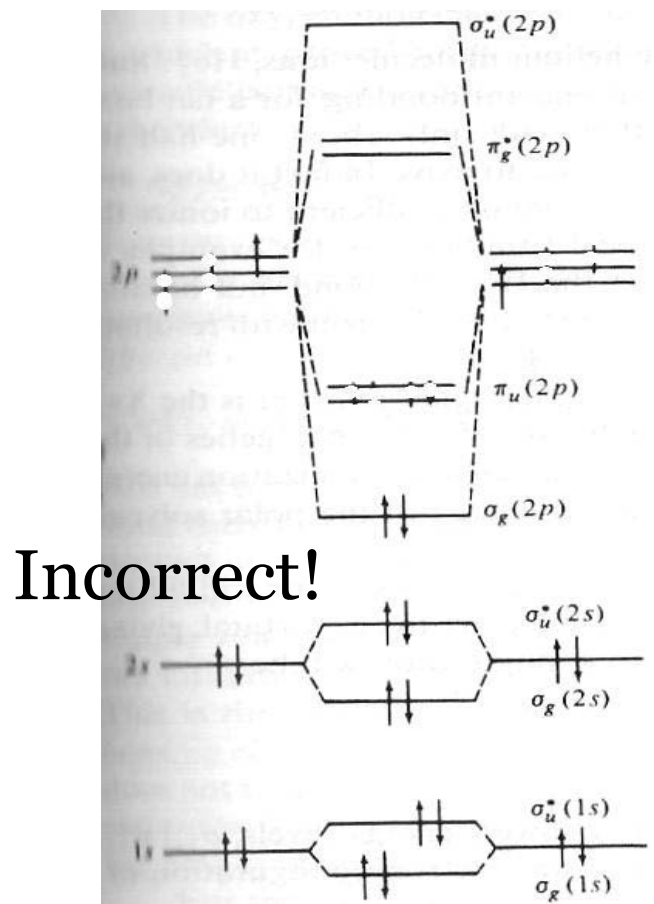
Note how the MO of $2s \rightarrow \sigma$ have p-type looks, while π -levels are clean

s-p Mixing: Hybridization of MO



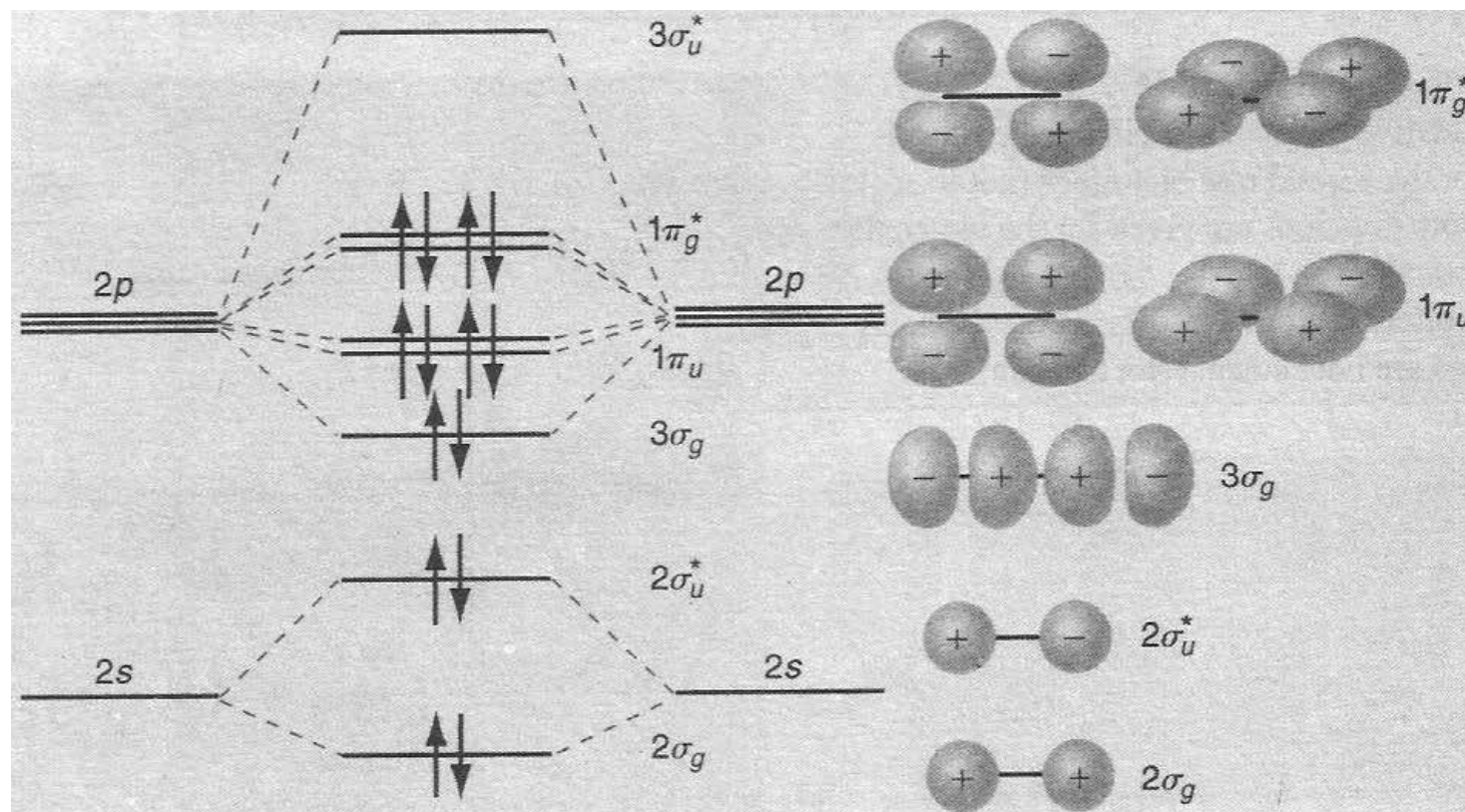
Mixing of $2s$ and $2p$ orbital occur because of small energy gap between them $2s$ and $2p$ electrons feels not so different nuclear charge

s-p Mixing: Hybridization of MO



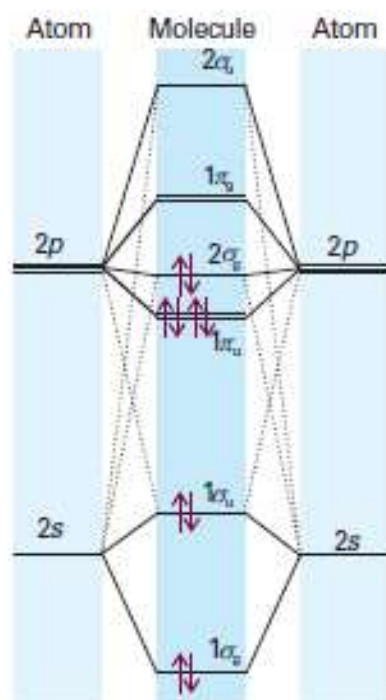
B_2 is paramagnetic. This can only happen if the two electrons with parallel spin are placed in the degenerate π -orbitals and if π orbitals are energetically lower than the σ orbital

MO diagram of F₂: No s-p Mixing

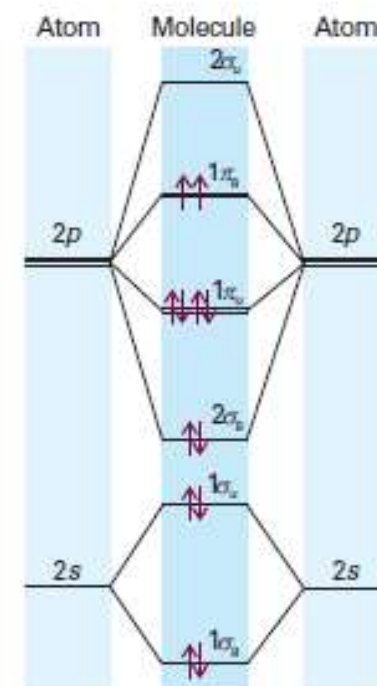
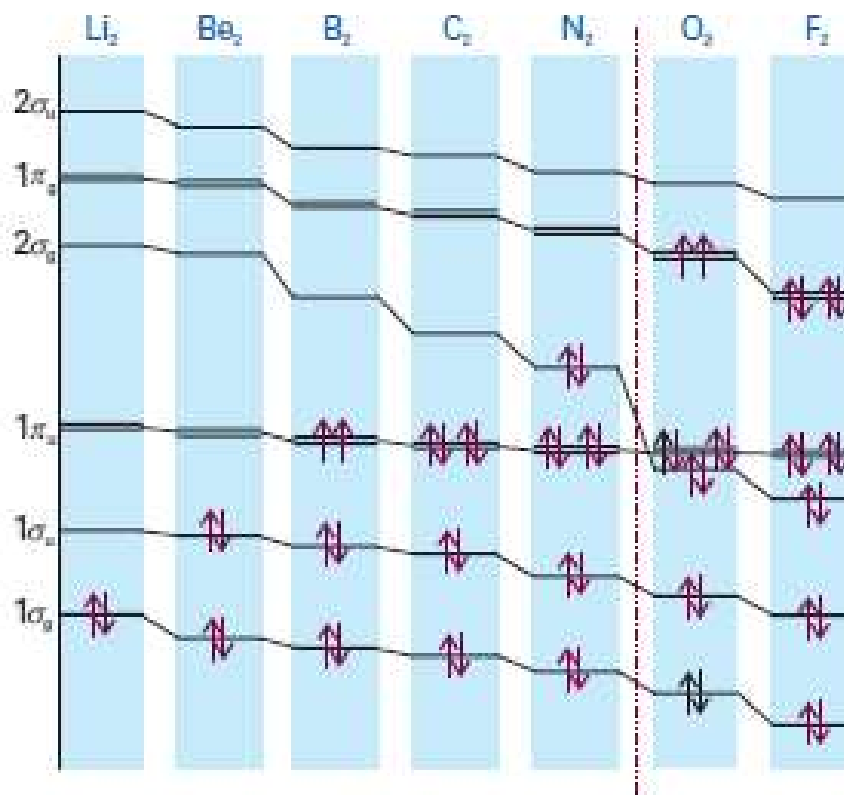


No Mixing of **s** and **p** orbital because of higher energy Gap between **2s** and **2p** levels in Oxygen and Fluorine! **2s** and **2p** electrons feels very different nuclear charge

MO Energy Level Diagram for Homo-Diatomics

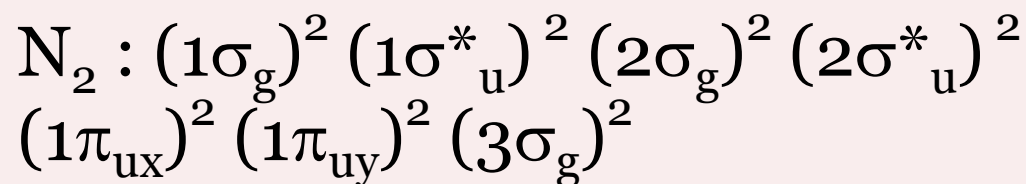
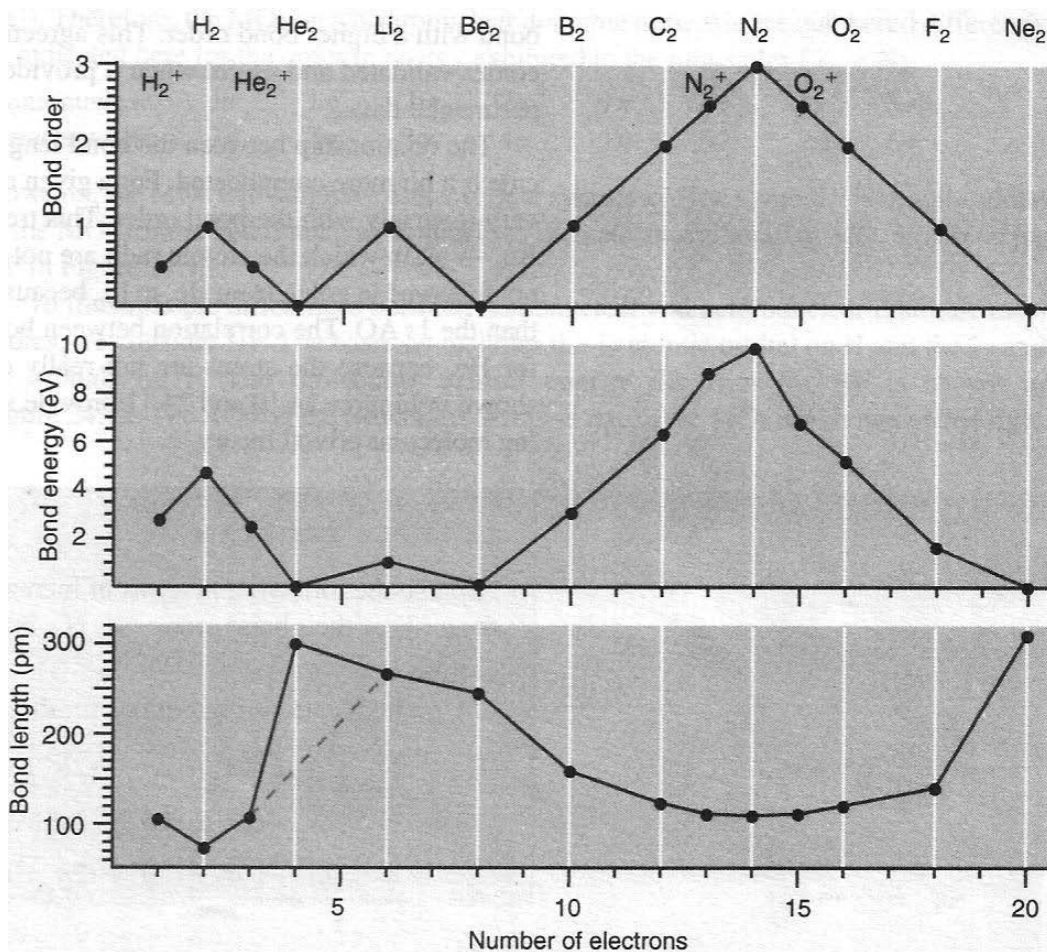


Upto N_2



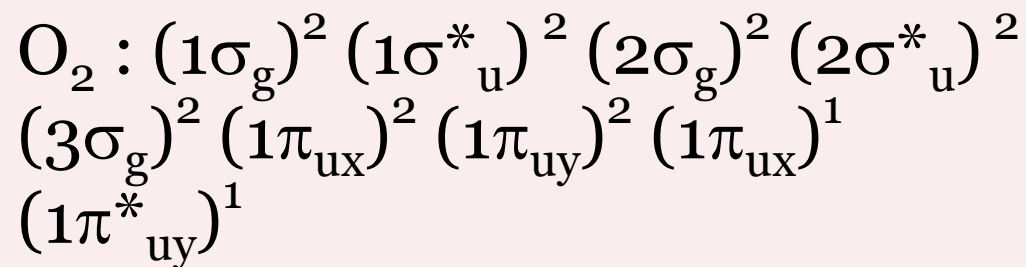
Beyond N_2

Bond-Order and Other Properties



$$\text{BO} = 3$$

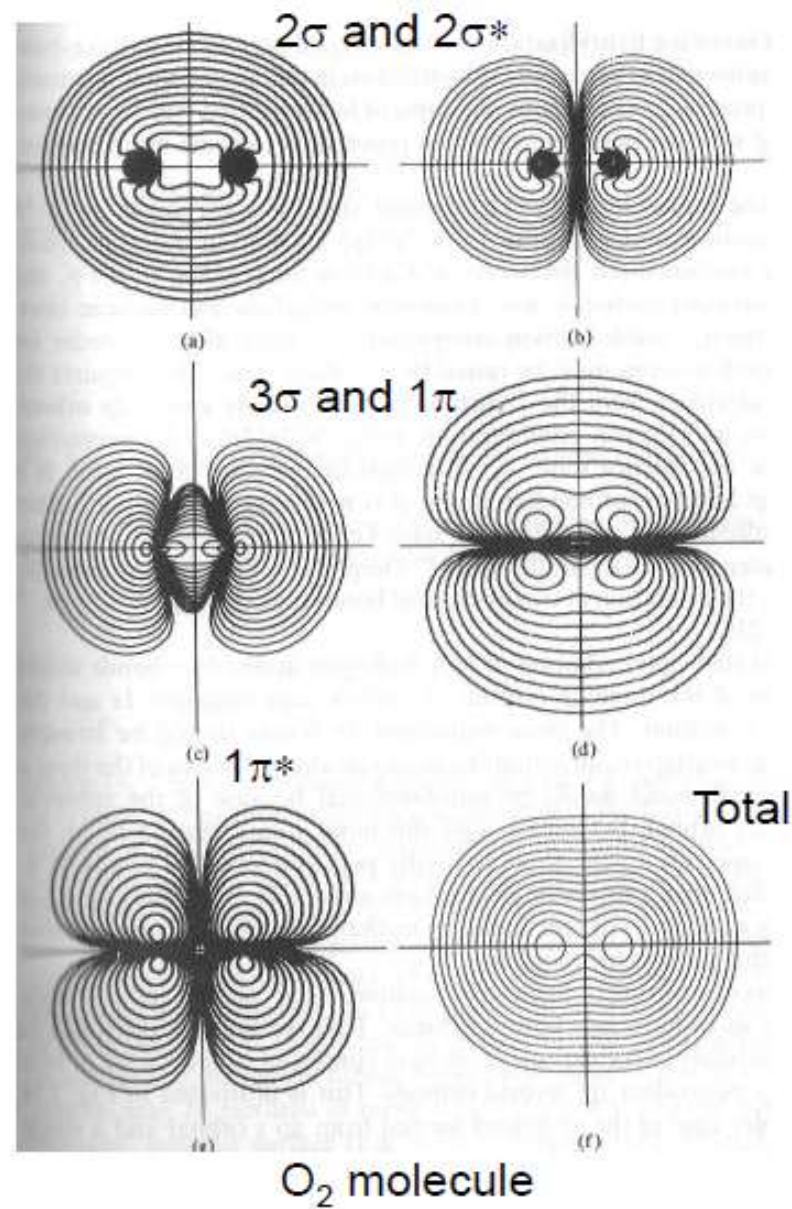
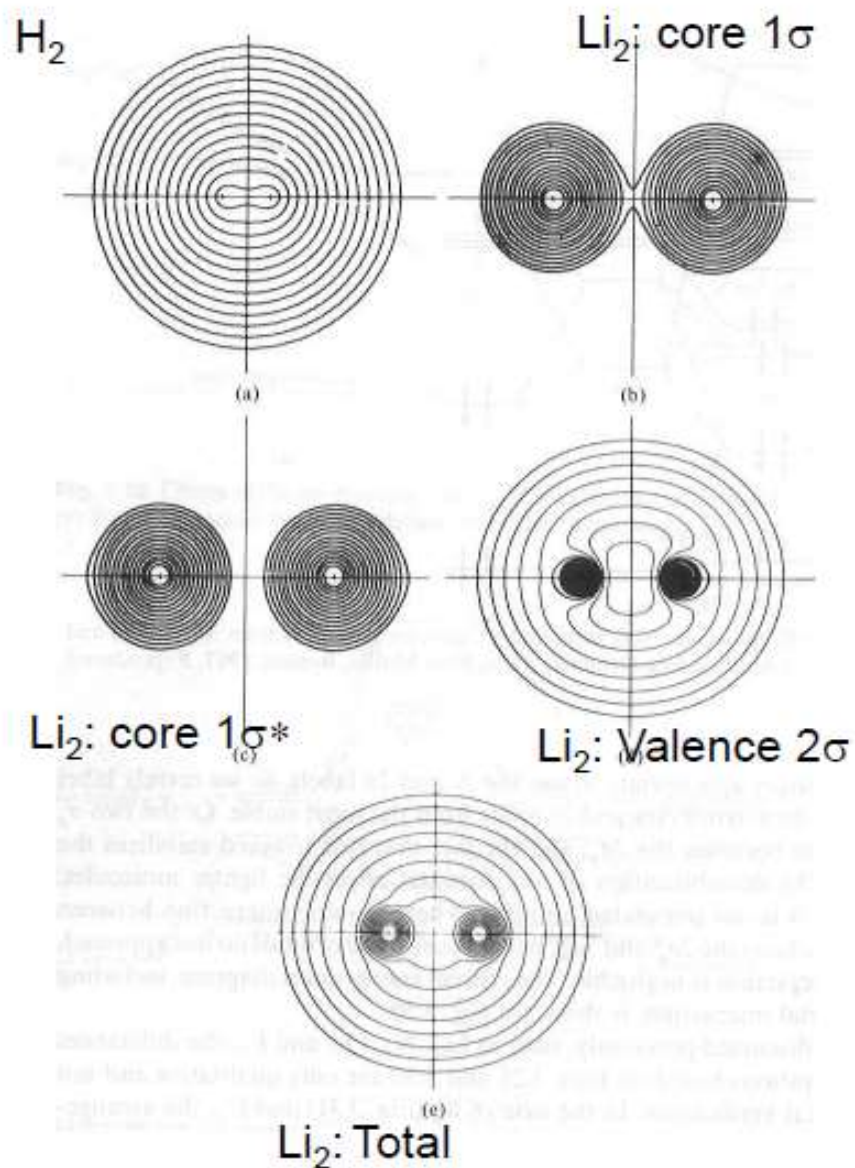
All spins paired: diamagnetic



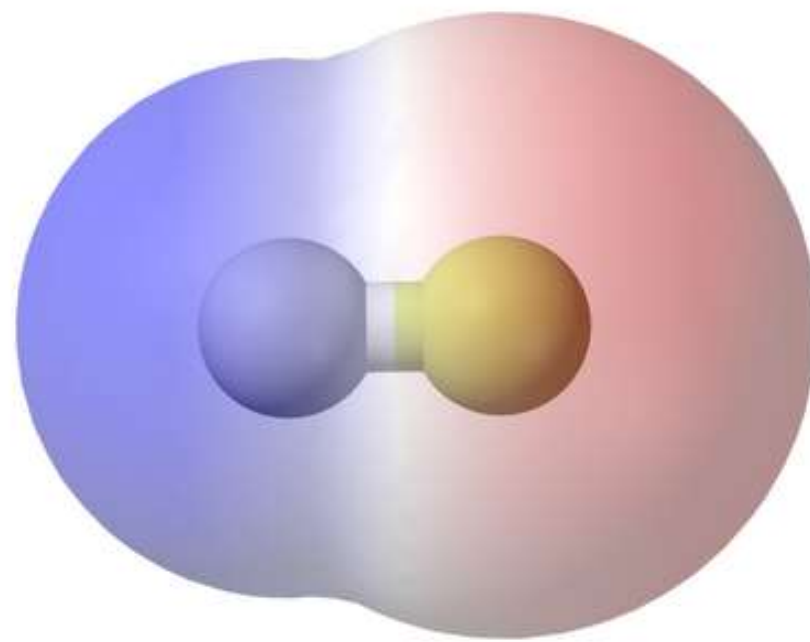
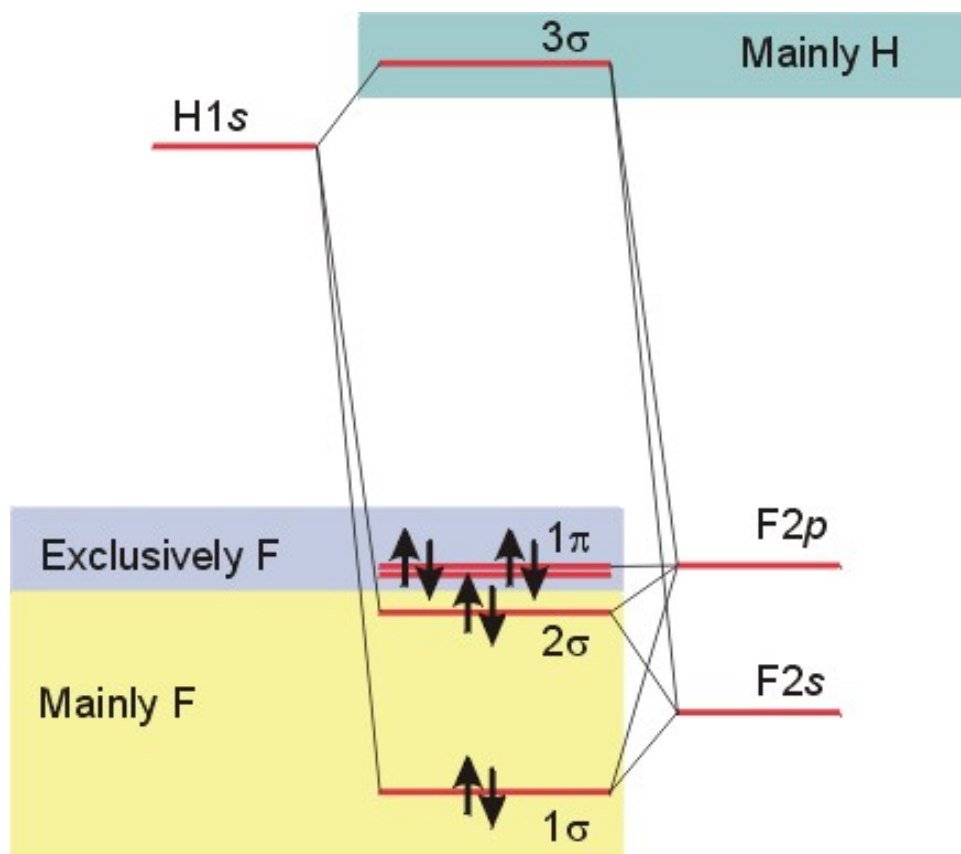
$$\text{BO} = 2$$

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: HCl

For Cl **3p** states close in energy to the **1s** of H

