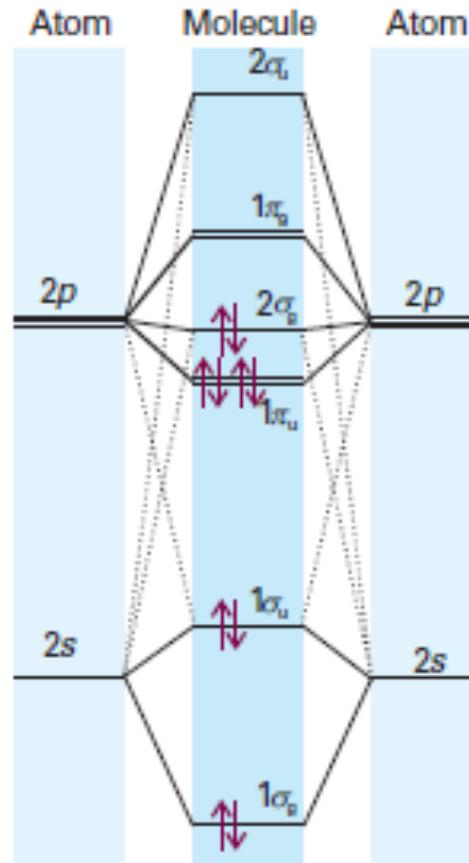


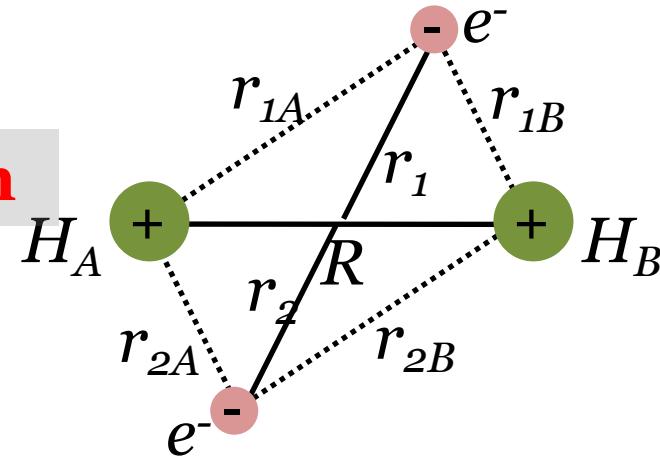
Molecular orbital theory for homonuclear diatomic molecules



Atkins' Physical Chemistry

Bonding: H₂ molecule

Born – Oppenheimer Approximation



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

$$\hat{H}(H_2) \cdot \psi(r, R) = E(R) \cdot \psi(r, R)$$

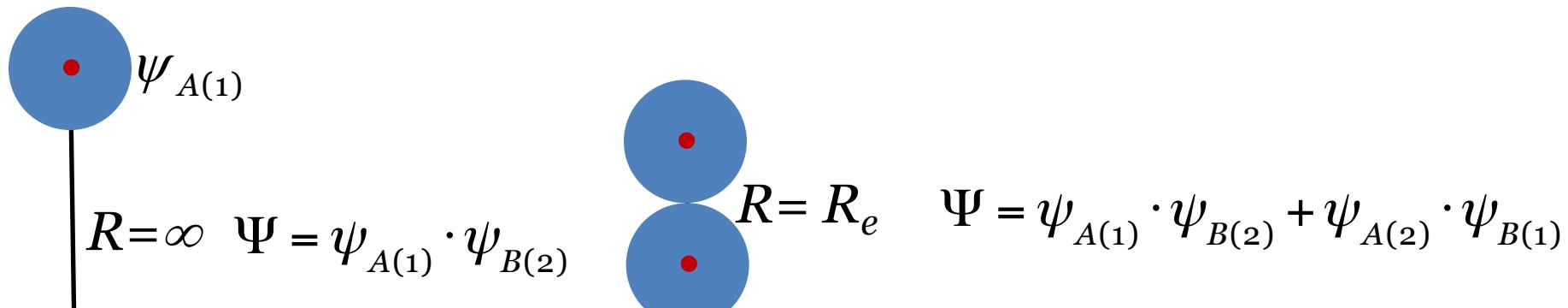
NOT a constant

CANNOT be Solved

For all the molecules except the simplest molecule H₂⁺ the Schrodinger equation cannot be solved.

We need methods to find approximate solutions

Valence Bond Theory



Resonance

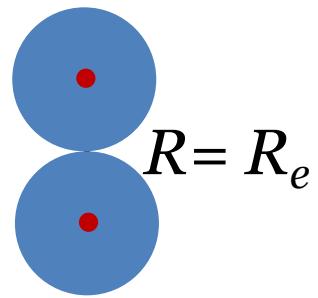


Inclusion of Ionic terms

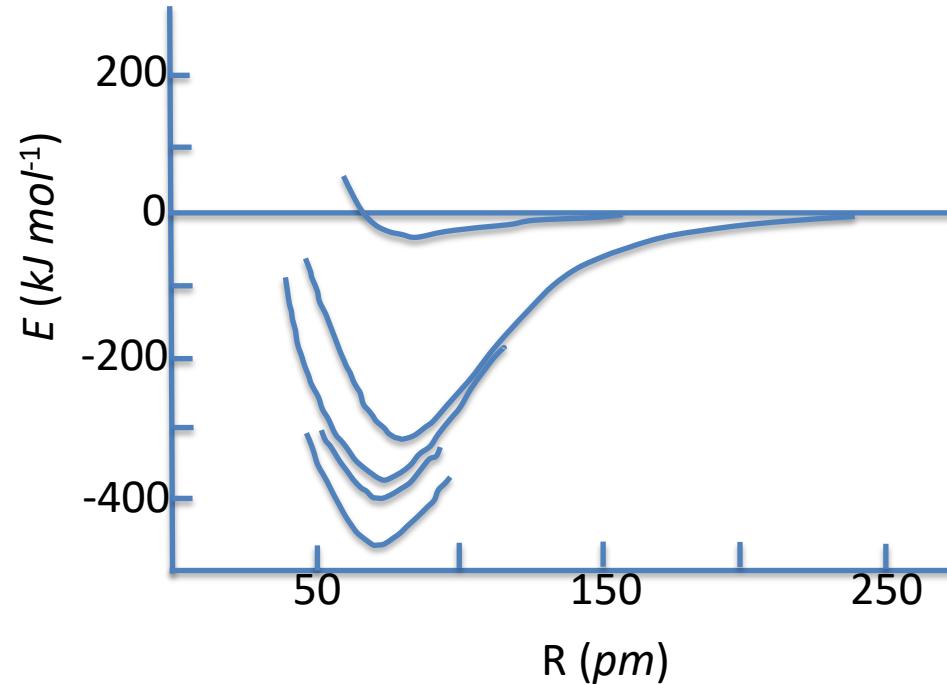
$$\Psi = \psi_{A(1)} \cdot \psi_{B(2)} + \psi_{A(2)} \cdot \psi_{B(1)} + \lambda(\psi_{A(1)} \cdot \psi_{A(2)}) + \lambda(\psi_{B(1)} \cdot \psi_{B(2)})$$

$$\Psi = \Psi_{\text{cov}} + \lambda\Psi_{H^+H^-} + \lambda\Psi_{H^-H^+}$$

Valence Bond Theory



$$\Psi = \Psi_{\text{cov}} + \lambda \Psi_{H^+H^-} + \lambda \Psi_{H^-H^+}$$



Type of wavefunction	$E (\text{kJ mol}^{-1})$	$R (\text{pm})$
Uncorrected $\Psi = \Psi_A \Psi_B$	24	90.0
Heitler London	303	86.9
Addition of shielding	365	74.3
Addition of Ionic contributions	388	74.9
Experimental values	458	74.1

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 (ground state)

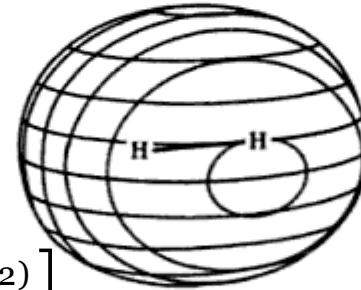
$$\begin{aligned}\psi_{bonding}(H_2) &= \psi_{bonding}(1) \cdot \psi_{bonding}(2) \\ &= \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(1)} + \phi_{1s_B}^{(1)}) \right] \cdot \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(2)}) \right] \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right]\end{aligned}$$

Molecular Orbital Theory of H₂

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

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

Spatial Part

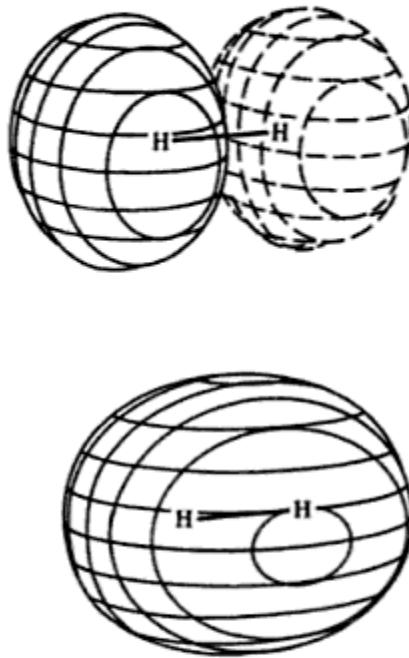
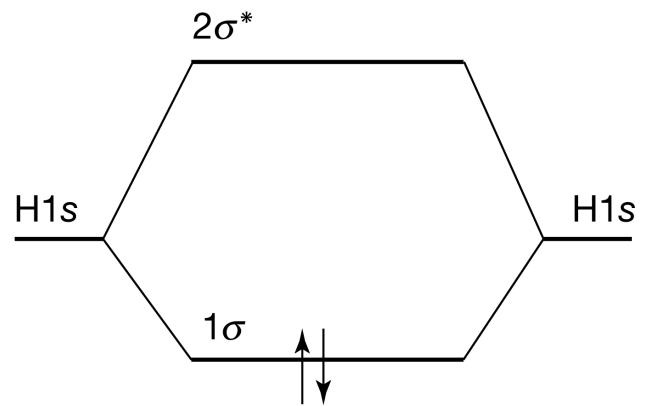


$$\psi_{bonding} = \frac{1}{2[1+S]} \left[\phi_{1s_A}^{(1)} \phi_{1s_A}^{(2)} + \phi_{1s_B}^{(1)} \phi_{1s_B}^{(2)} + \phi_{1s_A}^{(1)} \phi_{1s_B}^{(2)} + \phi_{1s_B}^{(1)} \phi_{1s_A}^{(2)} \right]$$

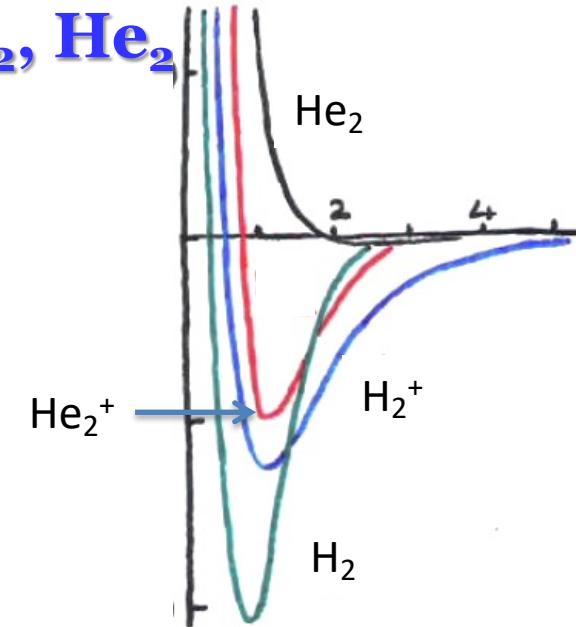
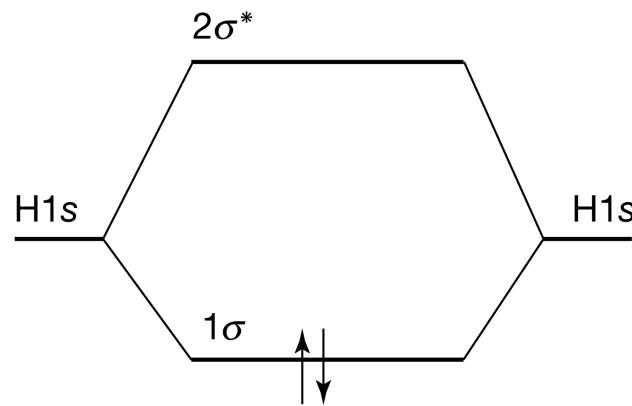
$$= \frac{1}{2[1+S]} \left[1s_A(1) \cdot 1s_A(2) + 1s_B(1) \cdot 1s_B(2) + 1s_A(1) \cdot 1s_B(2) + 1s_B(1) \cdot 1s_A(2) \right]$$

Ionic terms: overemphasized

Molecular Orbital Theory of H₂

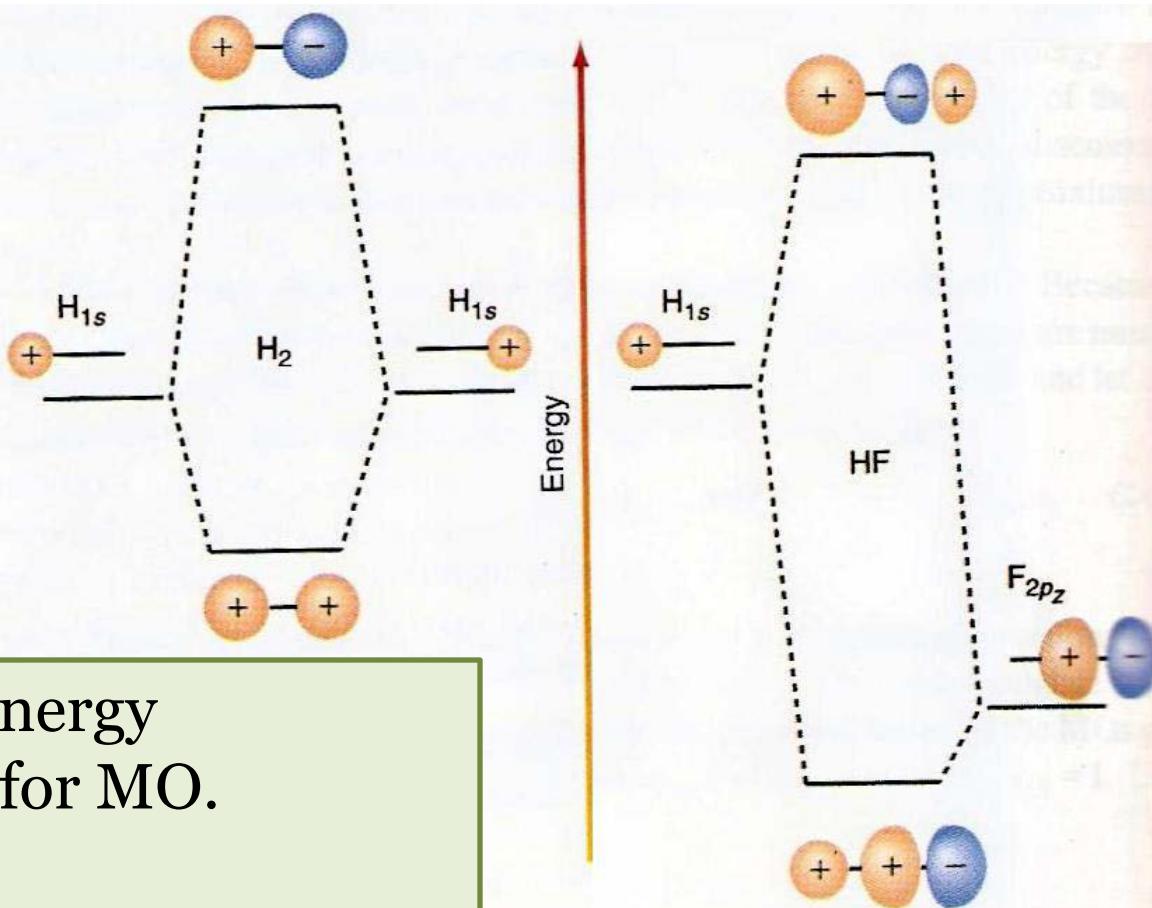


Diatoms of First Row: H_2^+ , H_2 , He_2 , He_2^+



Species	No. of electrons	Electron config.	Bond order	Bond length (pm)	Binding energy (kJ mol ⁻¹)
H_2^+	1	$(1\sigma)^1$	0.5	106	268
H_2	2	$(1\sigma)^2$	1	74	457
He_2^+	3	$(1\sigma)^2(1\sigma^*)^1$	0.5	108	241
He_2	4	$(1\sigma)^2(1\sigma^*)^2$	0	6000	<<1

Matching of AO energies for MO

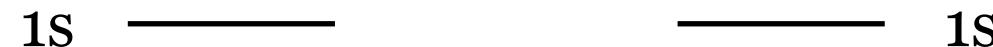


Both symmetry and energy
Matching is required for MO.

Valence electrons are most important

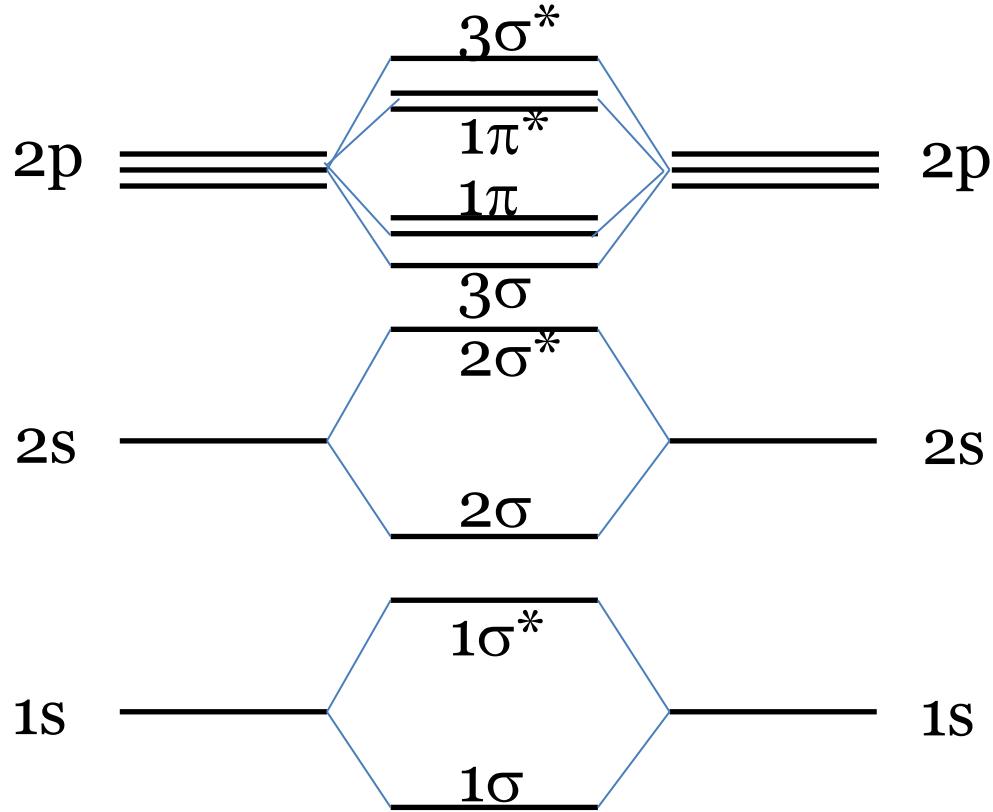
Due to large difference in energy of **1s**(H) and **1s**(F),
LCAO-MO for both **1s** is not feasible in HF.
Rather, **2p_z**(F) and **1s**(H) form a sigma bond.

Bonding in 2nd Row Homo-Diatomic Molecules



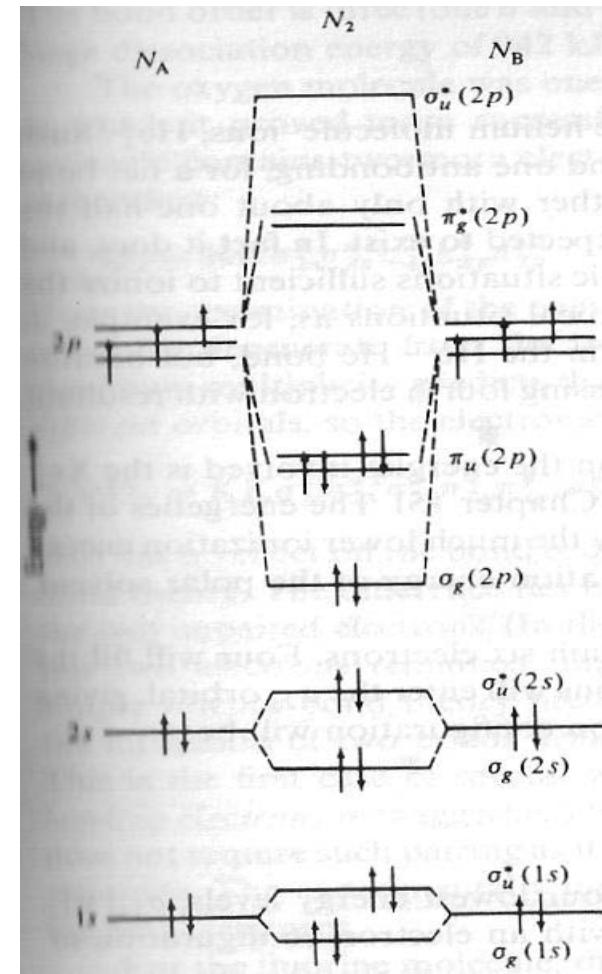
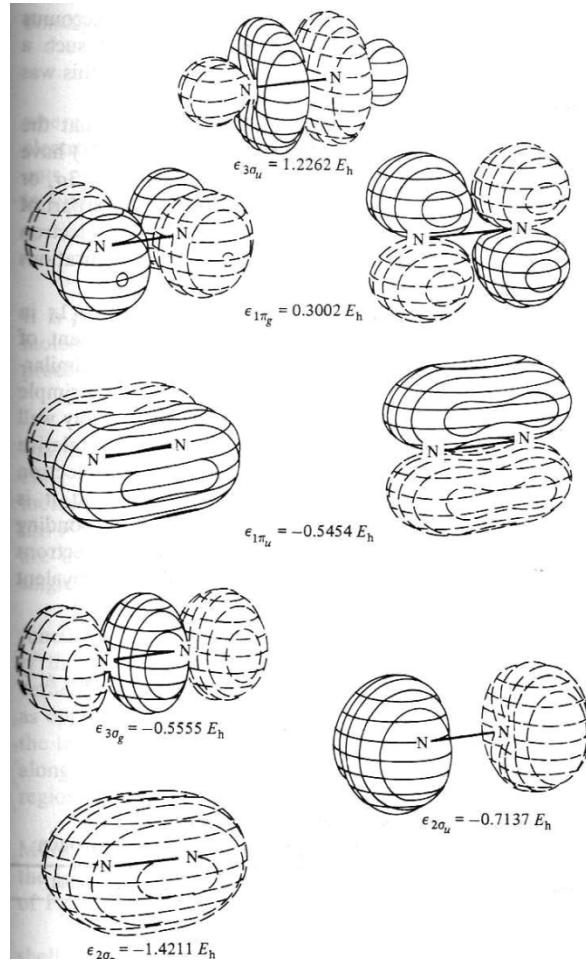
The orbital energies of the two approaching atoms are identical before they start interacting to form a BOND

Bonding in First-Row Homo-Diatomic Molecules



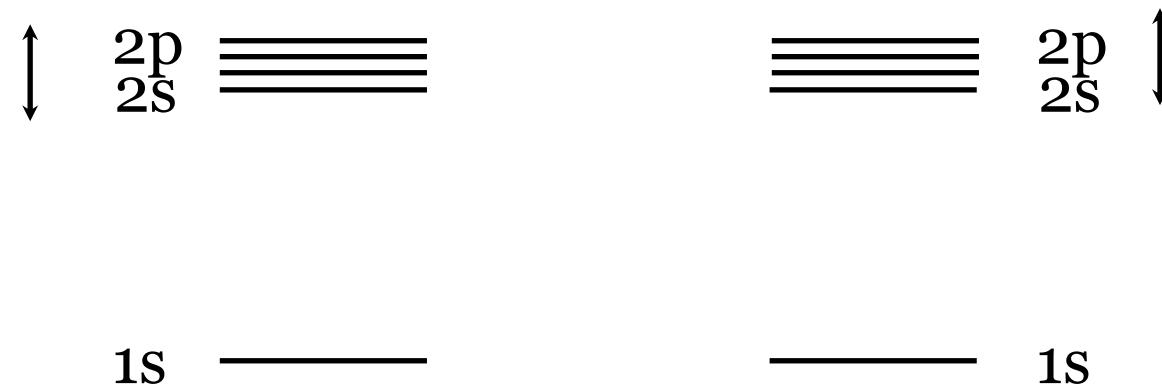
The interaction between the energy and symmetry matched orbitals leads to various types of BONDS

MO Energies of Dinitrogen



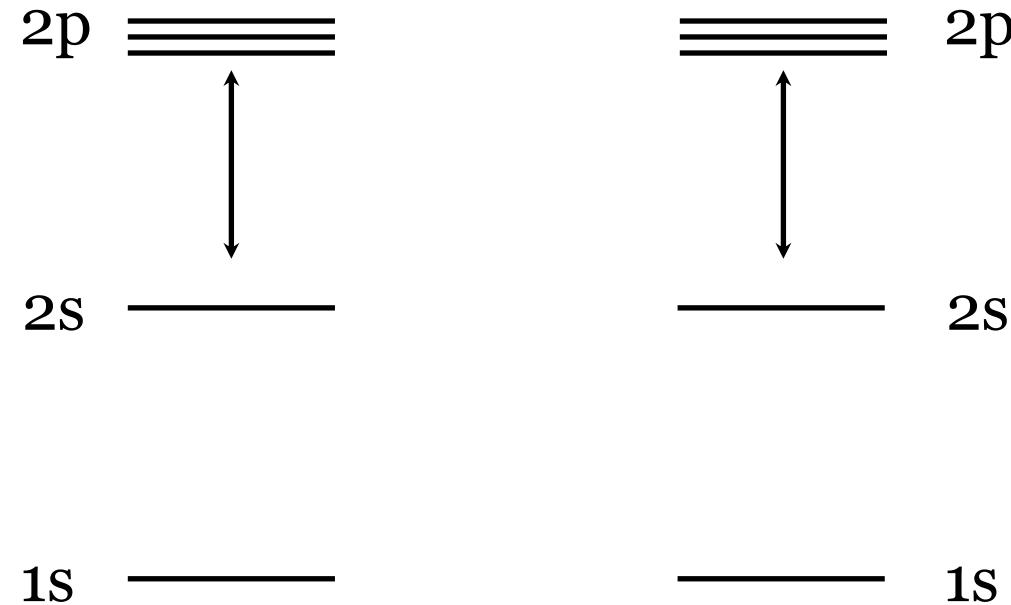
Experiments tell us this picture is incorrect!

Bonding in 2nd Row Homo-Diatomic Molecules



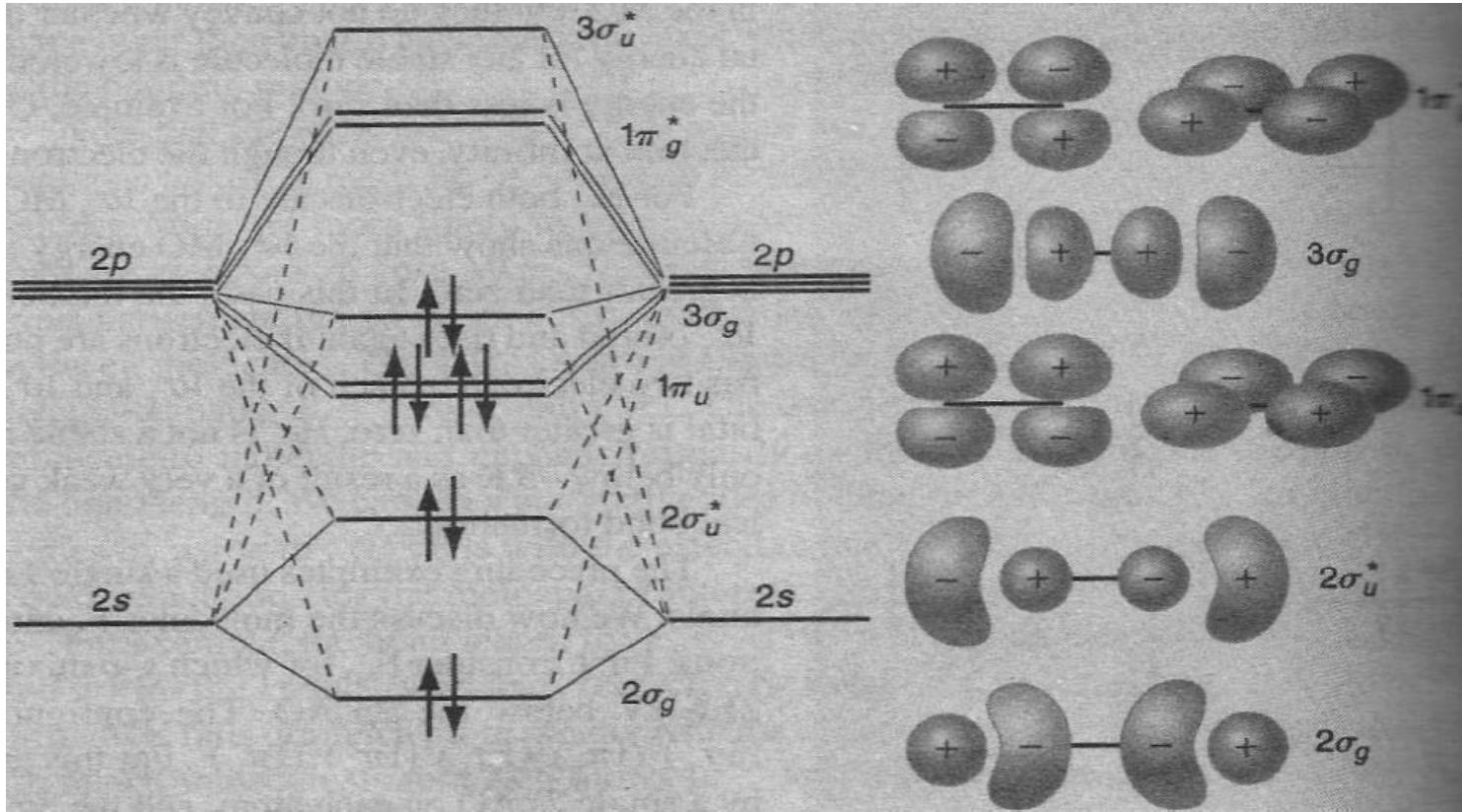
The 2s and 2p orbitals are degenerate in Hydrogen.
However in the many electron atoms these two sets of orbitals are no longer degenerate.

Bonding in 2nd Row Homo-Diatomic Molecules



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

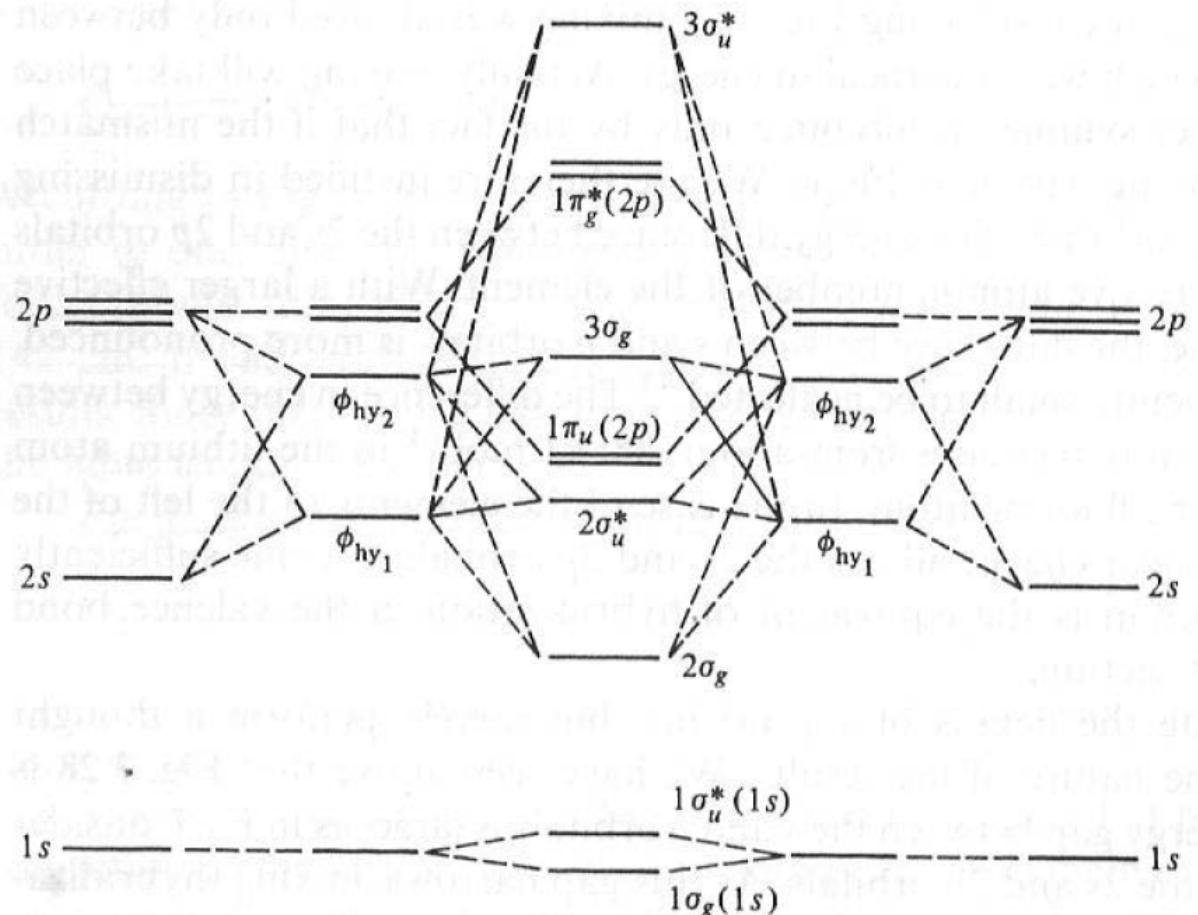
MO Energies of Dinitrogen



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

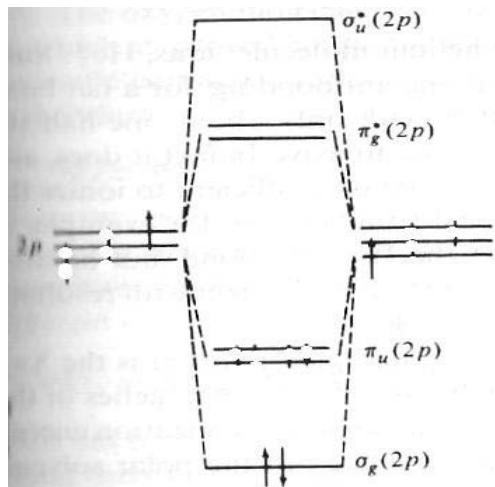
Note how the MO of $2s \rightarrow \sigma$ have p-type looks, while π -levels are clean

s-p Mixing: Hybridization of MO

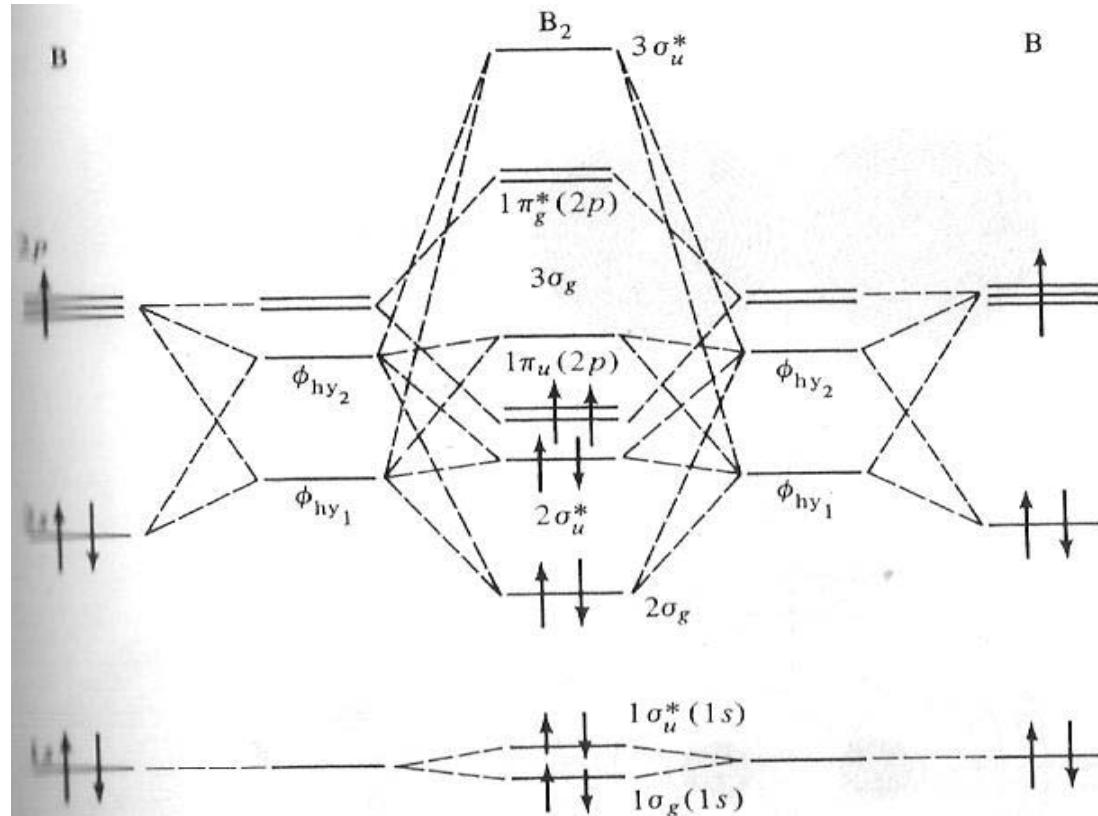
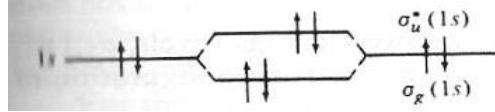
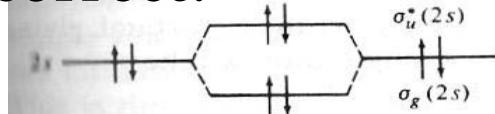


Mixing of $2s$ and $2p$ orbital occur because of small energy gap between them $2s$ and $2p$ electrons feels not so different nuclear charge

s-p Mixing: Hybridization of MO

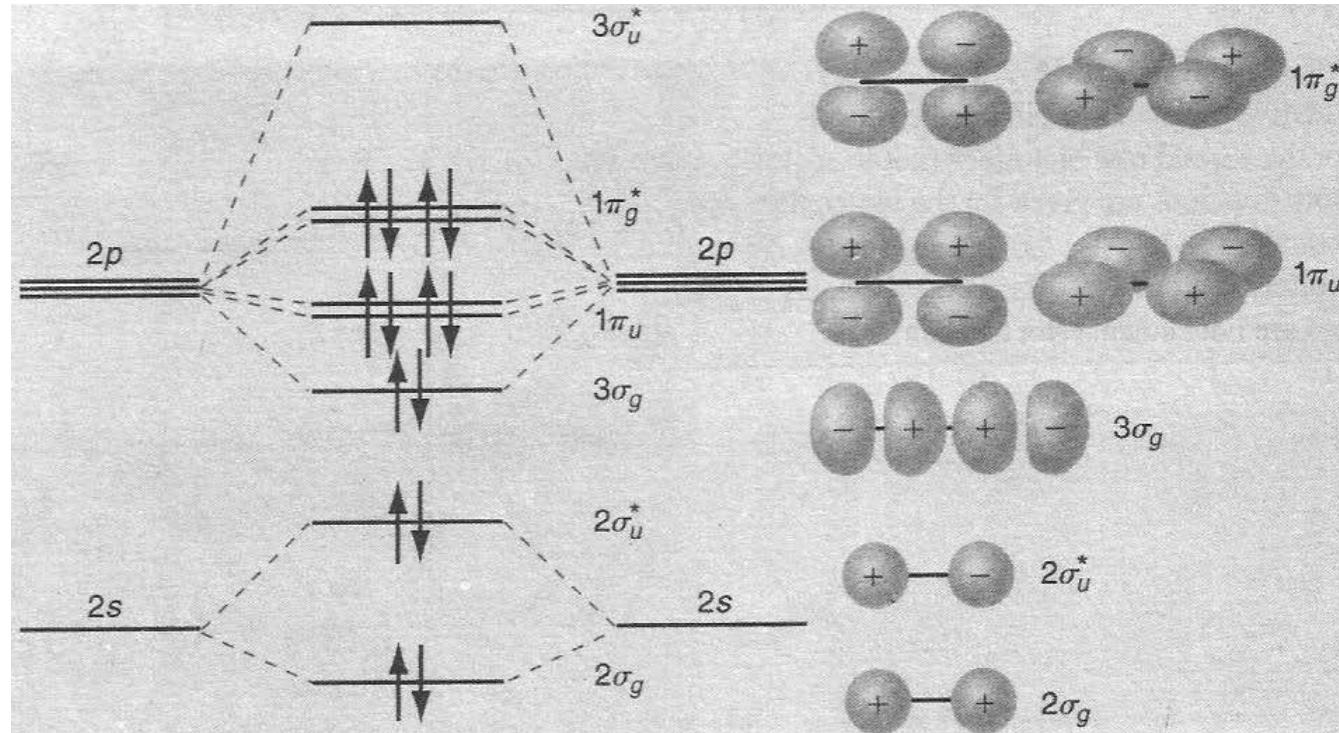


Incorrect!



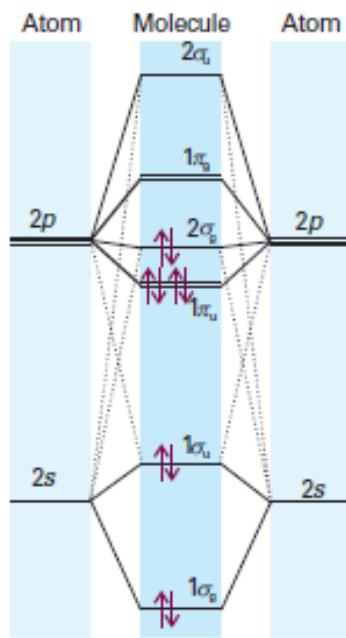
B_2 is paramagnetic. This can only happen if the two electrons with parallel spin are placed in the degenerate π -orbitals and if π orbitals are energetically lower than the σ orbital

MO diagram of F₂: No s-p Mixing

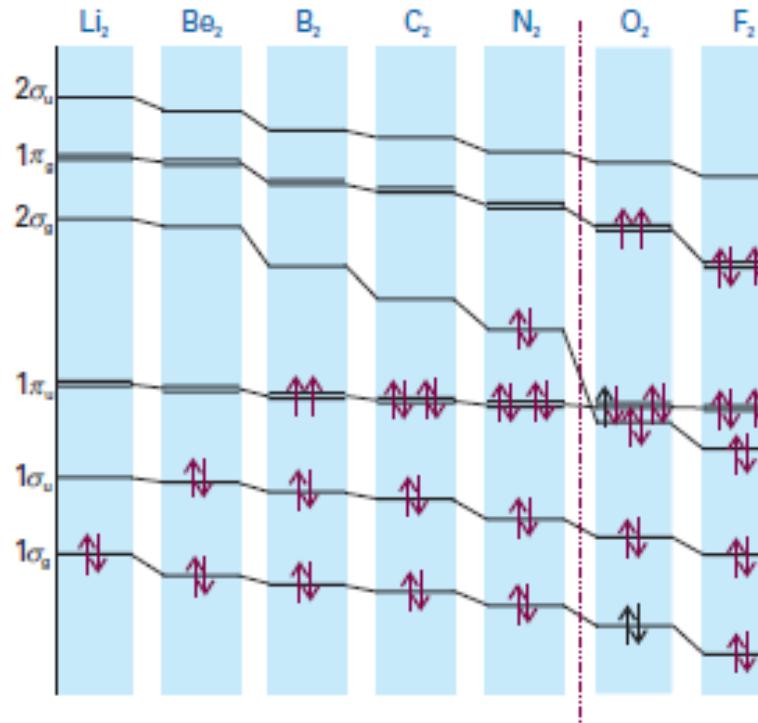


No Mixing of **s** and **p** orbital because of higher energy
Gap between **2s** and **2p** levels in Oxygen and Fluorine!
2s and **2p** electrons feels very different nuclear charge

MO Energy Level Diagram for Homo-Diatomics



Upto N_2



Beyond N_2

