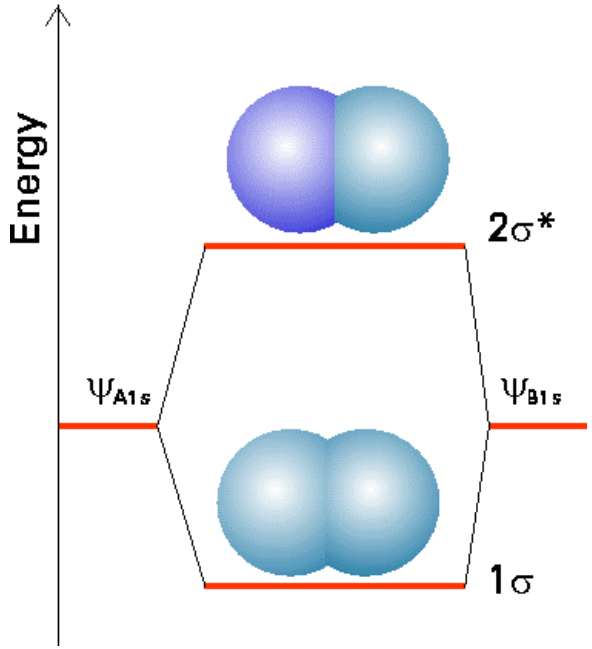
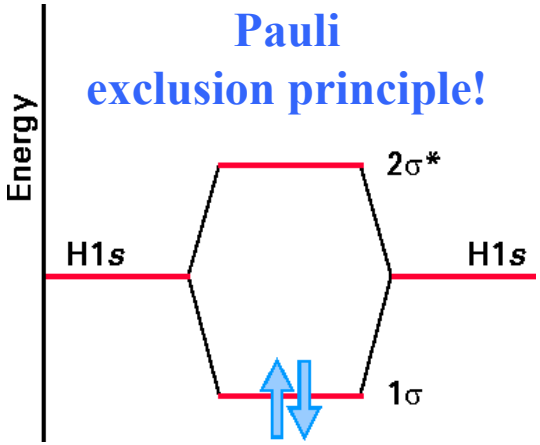
Building up Many-Electron Diatomic Molecules



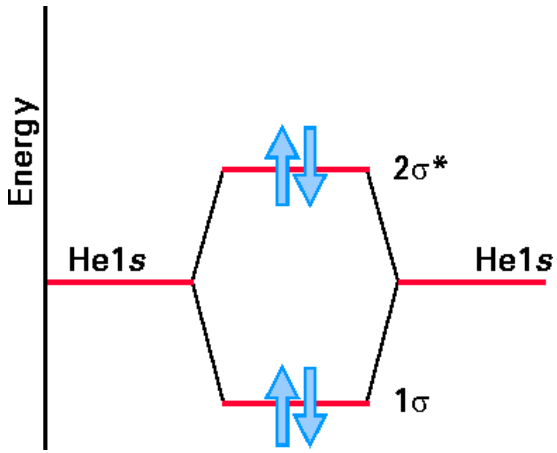
MO energy level diagram built from two 1s orbitals

Pauli exclusion principle!



H_2: $1\sigma^2$

More strongly and closely bonded than H_2^+



"He_2": $1\sigma^2 2\sigma^{*2}$

More antibonding than bonding

$\Rightarrow$ does not exist

"Aufbau" rules:

1.) Construct N MOs from N atomic orbitals

2.) Fill in electrons to achieve lowest overall energy; observe the **Pauli exclusion principle**

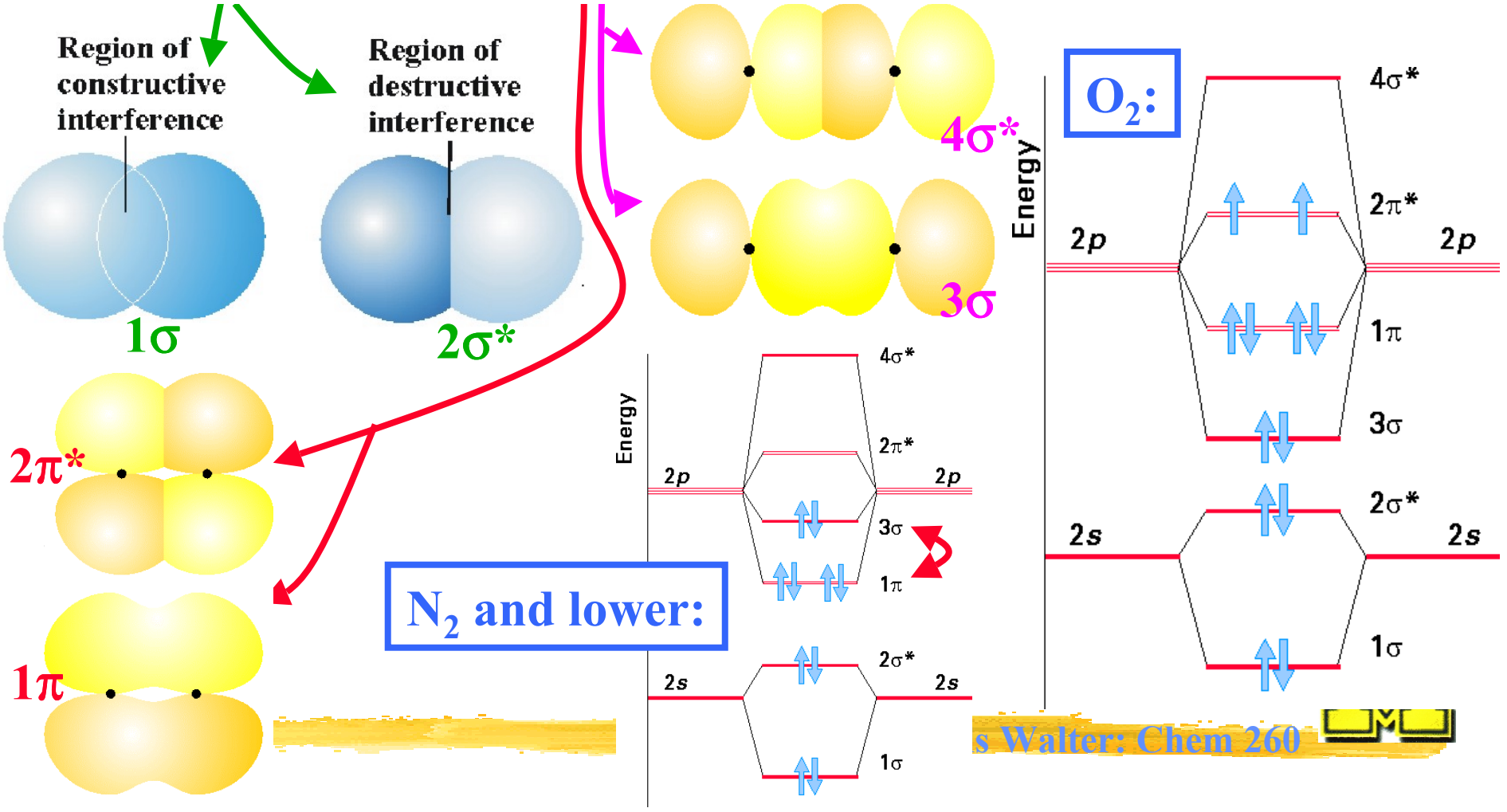
3.) Electrons occupy different degenerate MOs before doubly occupying any one of them

4.) Observe **Hund's rule:** If electrons occupy different degenerate MOs, then they do so with parallel spins

Period 2 Homonuclear Diatomic Molecules

E.g., O_2: $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$ and $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$

Simplify by only linearly combining orbitals of similar geometry

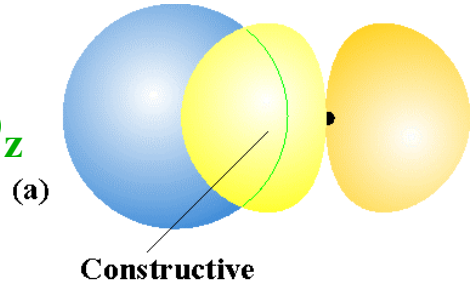


How Does it Work Again?

Simplify by only linearly combining orbitals of similar geometry

WHY?

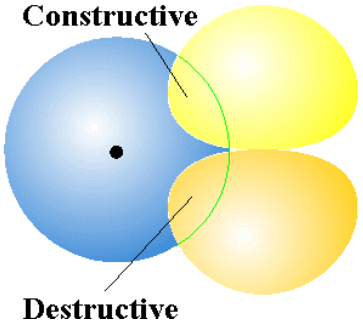
s and p_z



s and p_x

$\Rightarrow$

overlap integral



$$S = \int \Psi_A \Psi_B dx dy dz = 0$$

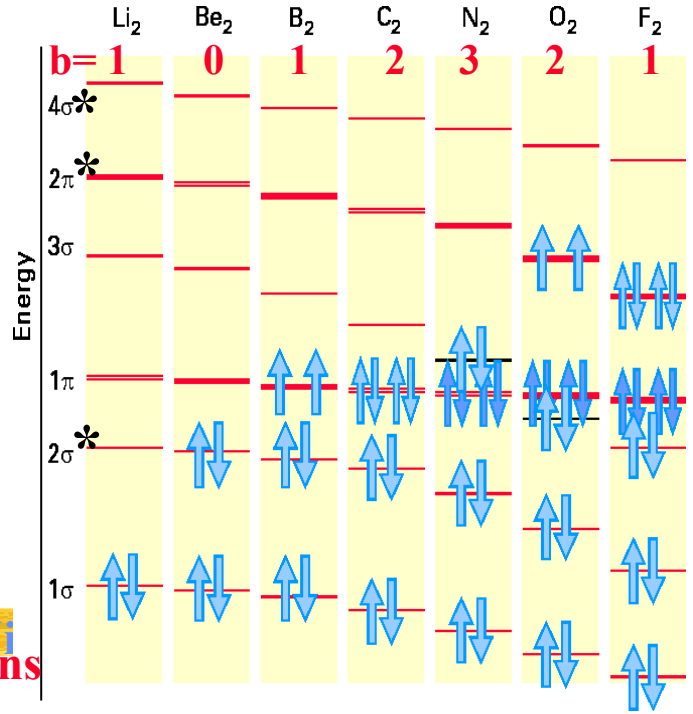
Rules for building molecular orbitals:

1.) Use all available valence orbitals from all atoms

2.) Classify the orbitals as having σ and π symmetry with respect to the internuclear axis

3.) From N_σ atomic orbitals of σ symmetry N_σ MOs with progressively higher energy can be built

4.) From N_π atomic orbitals of π symmetry N_π MOs with progressively higher energy can be built; π orbitals are doubly degenerate



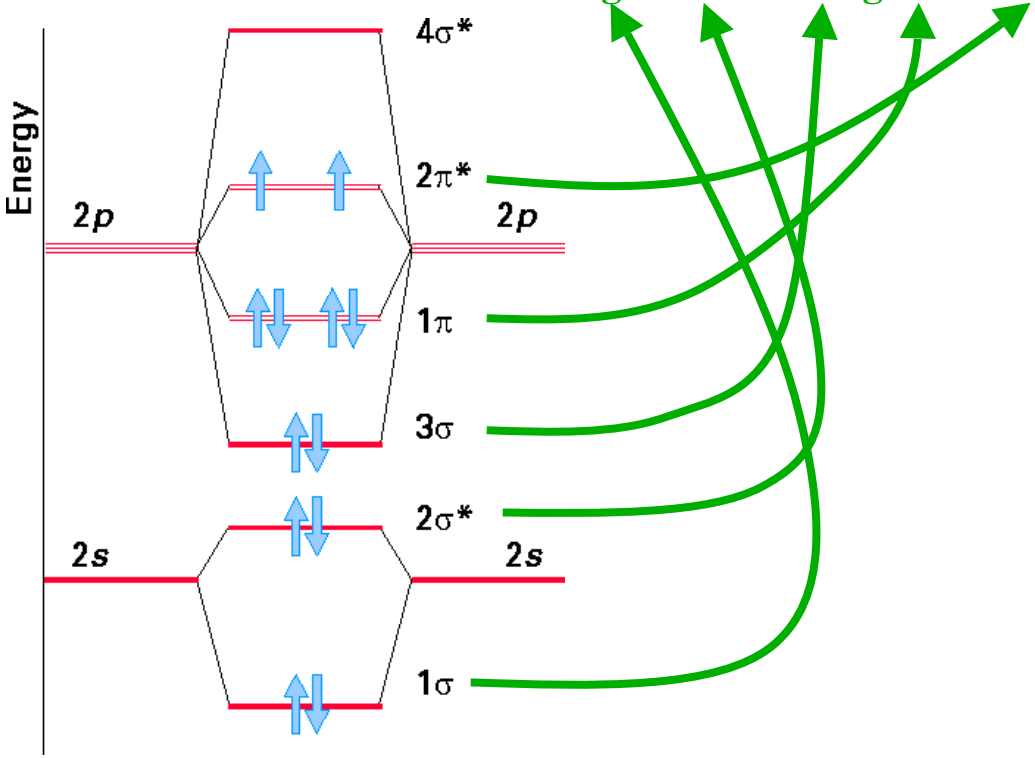
Bond order? $b = \frac{1}{2}(n - n^*)$

bonding electrons ← → **antibonding electrons**

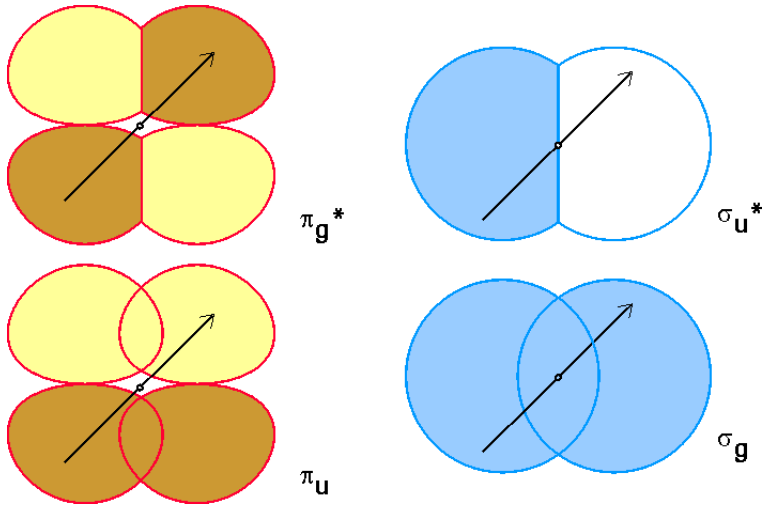
Ni

The Electronic Configuration of a Diatomic Molecule

Example: $O_2 = 1\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 2\pi_g^{*2}$



Further classification of MOs: Parity (= behavior under inversion)



Quantum mechanics for a σ^2 MO: $\Psi = \sigma(1)\sigma(2)$ **(normalized)**

$$\Psi = (1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2))$$

$$\Psi = (1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)) + (1s_A(1)1s_A(2) + 1s_B(1)1s_B(2))$$

= VB theory, covalent **ionic bond contribution**