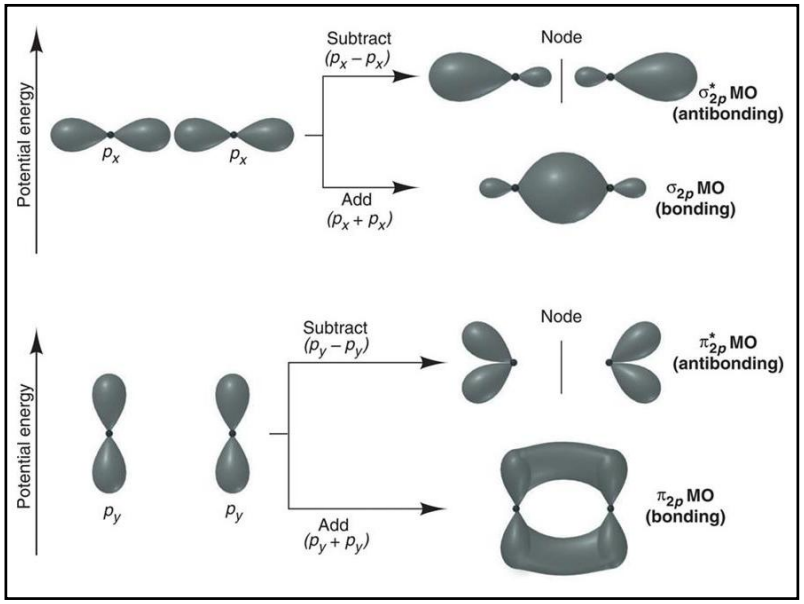
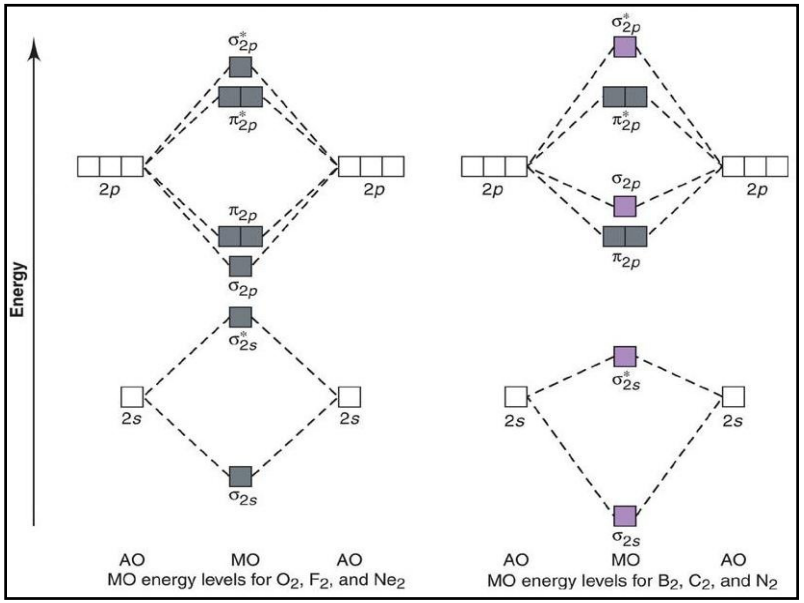
MOs for Period 2 Homonuclear Diatomic Molecules

- Only the valence **AO**s are considered – **one 2*s*** orbital and **three 2*p*** orbitals for each atom
- When two atoms approach each other:
  - The **2*s*** orbitals overlap to form two **σ MO**s, bonding (σ_{2s}) and antibonding (σ_{2s}*) (as in H_2)
  - The **2*p*** orbitals directed along the internuclear axis overlap to form **two σ MO**s, bonding (σ_{2p}) and antibonding (σ_{2p}*)
  - The **2*p*** orbitals perpendicular to the internuclear axis (2 from each atom) overlap to form **four π MO**s, **two** bonding (π_{2p}) and **two** antibonding (π_{2p}*)





Example: N_2

Total # of valence **e**⁻s

→ **5+5=10**

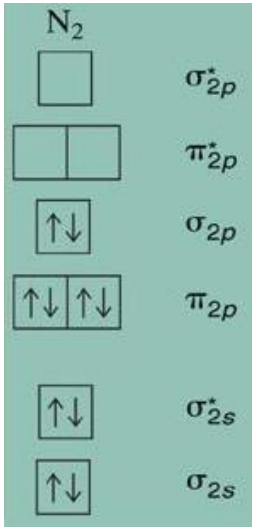
→ place **10 e**⁻s on the lowest energy **MO**s

Electron configuration →

N_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$

BO = (8 - 2)/2 = 3

→ Consistent with the Lewis structure **(:N≡N:)**



Example: O_2

Total # of valence **e**$^-$s → **6+6=12**

→ **12 e**$^-$s on the lowest energy **MO**s

Electron configuration →

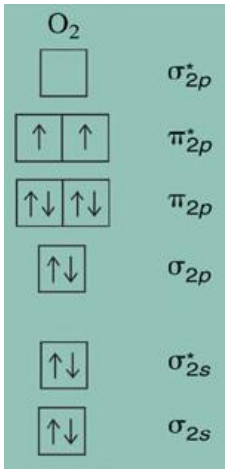
O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^{*2})$

BO = (8 - 4)/2 = 2

→The electron configuration of **O_2** contains **two unpaired** electrons on the **π_{2p}^* MOs** (Hund's rule)

– Inconsistent with the Lewis structure (:O=O:)

→Explains the **paramagnetic properties** of **O_2**



Example: Be_2

Total # of valence **e**$^-$s → **2+2=4**

⇒ place **4 e**$^-$s on the lowest energy **MO**s

Electron configuration → $(\sigma_{2s})^2(\sigma_{2s}^*)^2$

BO = (2 - 2)/2 = 0 → (the molecule is unstable)

Example: Ne_2

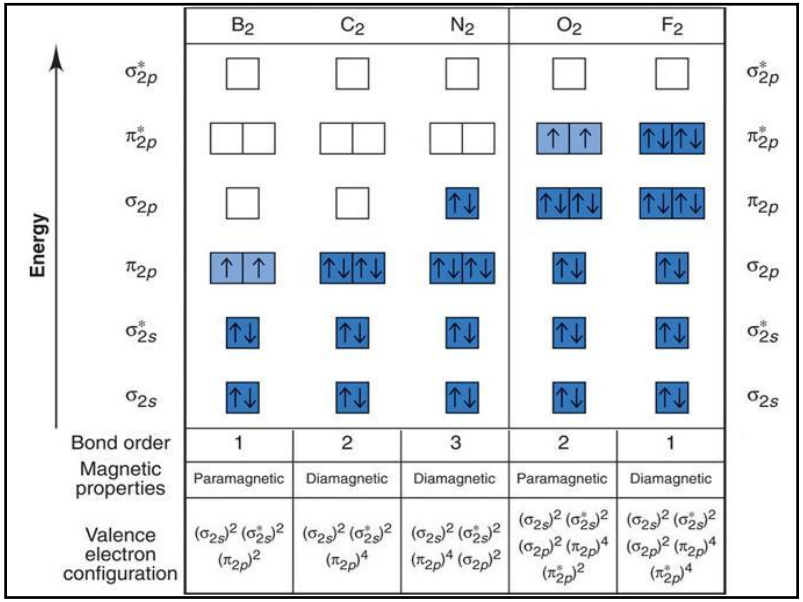
Total # of valence **e**$^-$s → **8+8=16**

⇒ place **16 e**$^-$s on the lowest energy **MO**s

Electron configuration →

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$

BO = (8 - 8)/2 = 0 → (the molecule is unstable)



Example:

Predict the electron configuration, BO and bond strength of the N_2^- ion

Total # of valence **e**$^-$s → **5+5+1=11**

⇒ place **11 e**$^-$s on the lowest energy **MO**s

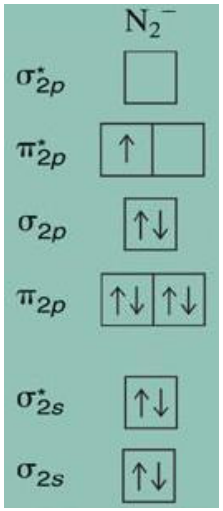
Electron configuration →

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1$

BO = (8 - 3)/2 = 2.5

→The ion exists (BO > 0)

→The bond is weaker than that in **N_2** (lower bond order 2.5<3)



MOs for Heteronuclear Diatomic Molecules

- Diagrams are asymmetric since the **AO**s of the two atoms have different energies

Example: NO

Total # of valence **e**$^-$s → **5+6=11**

⇒ place **11 e**$^-$s on the lowest energy **MO**s

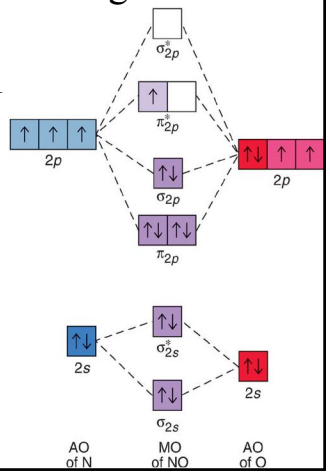
Electron configuration →

$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1$

BO = (8 - 3)/2 = 2.5

→Contains **one unpaired e**$^-$

→Explains the existence of **odd electron molecules** (radicals)

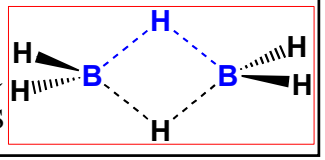


MOs in Polyatomic Species

- The general approach is similar
- The **MO**s are build by more than two **AO**s
  - Linear Combinations of Atomic Orbitals (**LCAO**)
- The **MO**s are spread over the entire molecule
  - **Delocalization** of electrons
  - Explains the existence of **electron deficient molecules** (on average less than two electrons may be binding two atoms → multi-center bonds)

Example: B_2H_6

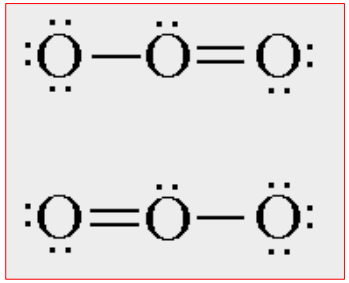
The **H**-bridges are based on a three-center **MO** holding 2**e**$^-$s



- **Delocalization** and **multi-center bonds** eliminate the need of resonance structures used by the Lewis's and VB models

Example: O_3

Resonance structures:



Lowest energy **π-MO**: