9.15 Molecular Orbitals in Hydrogen

- As two **H** atoms (*A* and *B*) approach each other, their **1s** orbitals (ψ_A and ψ_B) overlap and interfere with each other
- The interference yields two **molecular orbitals**
  - constructive interference (the amplitudes of the wavefunctions add together) → **bonding orbital** (σ_{1s})

  $$\psi_{bonding} = \psi_A + \psi_B$$
  - destructive interference (the amplitudes of the wavefunctions subtract from each other) → **antibonding orbital** (σ_{1s}*)

  $$\psi_{antibonding} = \psi_A - \psi_B$$

- The bonding **MO** (molecular orbital) is enhanced between the nuclei
  - increased electron density between the nuclei
  - e⁻s on σ_{1s} have lower energy than in the isolated **H**s
- The antibonding **MO** has a nodal plane between the nuclei
  - reduced electron density between the nuclei
  - e⁻s on σ_{1s}* have higher energy than in the isolated **H**s
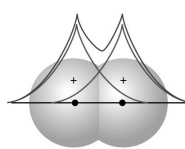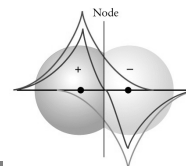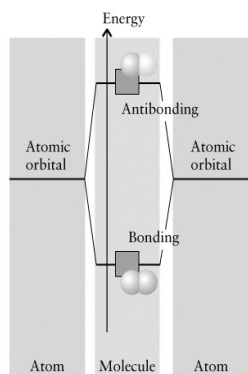

Fig. 9.51 Fig. 9.52

Fig. 9.53

- **MO** energy level diagrams
  - e⁻s occupy first the lowest energy **MO**s
  - each **MO** can accommodate up to two e⁻s with opposite spins (Pauli)
  - e⁻s enter degenerate **MO**s singly adopting parallel spins (Hund)
- **MO**s formed by the overlap of **AO**s along the internuclear axis are labeled as σ (σ-bonding)
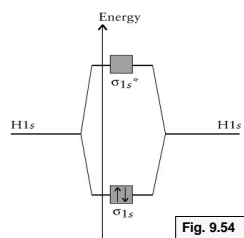

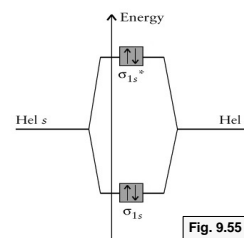Fig. 9.54 Fig. 9.55

- For **H₂**, the two e⁻s enter σ_{1s} – the energy of the molecule is lower than that of the free atoms
- For **He₂**, the four e⁻s fill both σ_{1s} and σ_{1s}* – no lowering of the energy (the bonding effects of σ_{1s} and σ_{1s}* cancel and the molecule is not stable)

9.16 Molecular Orbitals in Period 2 Diatomic Molecules

- Only the valence **AO**s are considered – **one 2s** orbital and **three 2p** orbitals for each atom
- When two atoms approach each other:
  - the **2s** orbitals overlap to form two σ **MO**s, bonding (σ_{2s}) and antibonding (σ_{2s}*)
  - the **2p** orbitals directed along the internuclear axis overlap to form **two** σ **MO**s, bonding (σ_{2p}) and antibonding (σ_{2p}*)
  - the **2p** 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}*)
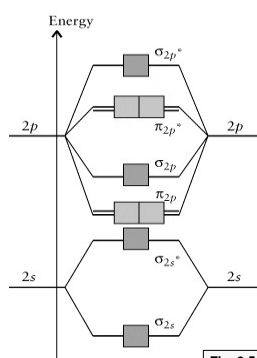
For Li₂ through N₂   For O₂ and F₂
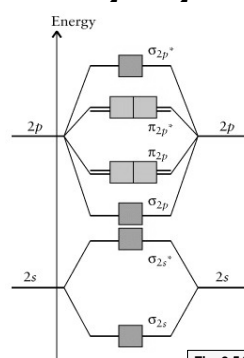
Fig. 9.54 Fig. 9.54

- Bond order (**BO**)

  BO = (B - A)/2

  B - # **e⁻**s on bonding **MO**s

  A - # **e⁻**s on antibonding **MO**s

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

σ_{2p}

π_{2p}

σ_{2s}^*

σ_{2s}
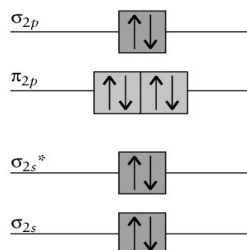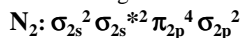
52   Nitrogen, N_2

BO = (8 - 2)/2 = 3 → consistent with the Lewis structure (**:N≡N:**)

Example: Be_2

Total # of valence **e⁻**s → **2+2=4**

⇒ place **4 e⁻**s on the lowest energy **MO**s

Electron configuration → Be_2: $\sigma_{2s}^2 \sigma_{2s}^{*2}$

BO = (2 - 2)/2 = 0 → (the molecule is unstable)
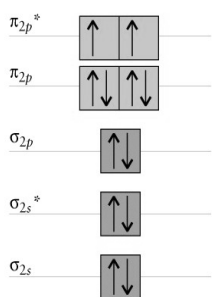
Example: O_2

Total # of valence **e⁻**s → **6+6=12**

⇒ place **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 → consistent with the Lewis structure (**:Ö=Ö:**)

π_{2p}^*

π_{2p}

σ_{2p}

σ_{2s}^*

σ_{2s}

54   Oxygen, O_2

- The electron configuration of O_2 contains two unpaired electrons on the π_{2p}^* **MO**s (Hund's rule)
  - inconsistent with the Lewis structure
  - explains the paramagnetic properties of O_2

9.17 Orbitals in Polyatomic Molecules

- 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)   **Ex: B_2H_6**
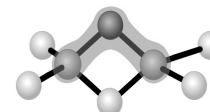
55   Three-center bond

Assignments

- **Homework:** Chpt. 9/ 1, 5, 7, 9, 11, 19, 23, 25, 27, 31, 33, 35, 37, **39, 43, 47, 49, 51, 53, 55, 79**

- **Student Companion:** 9.1, 9.2, **9.4, 9.5**