Chemical Bonding

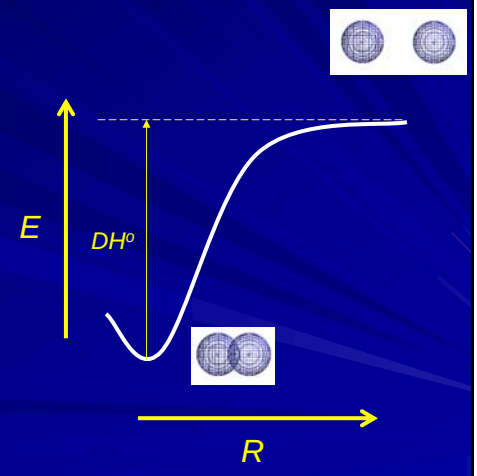
Revisited

Valence Bond

- Bond (attraction) exists if
  - AO overlap *AND*
  - 1 electron per AO → 2 electron bond
    - 1 electron bond possible (weaker)
    - 3 electron bond possible (weaker)
- No bond (repulsion) if
  - 2 electron per AO

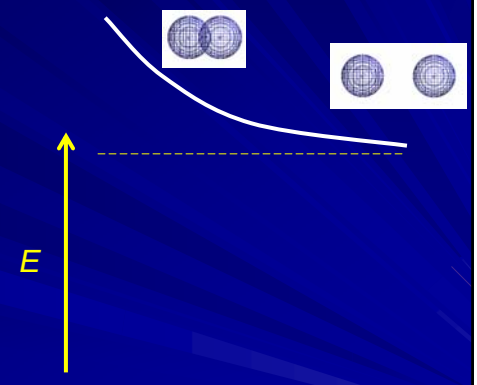
Bond (attraction) → H-H

- 2 electrons *AND*
- Geometry
  - large *R* → no overlap → no bond
  - small *R* → AO overlap → bond



No Bond (repulsion) → He He

- 4 electrons *AND*
- Geometry
  - large *R* → no overlap → no bond
  - small *R* → AO overlap → Pauli repulsion



Valence Bond - Summary

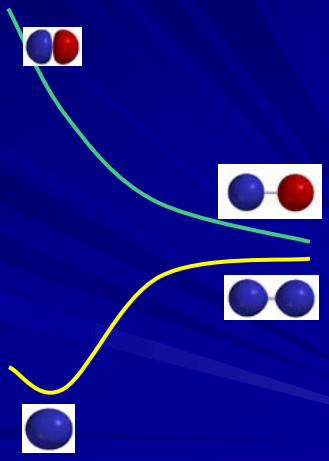
- Geometry & Energy
  - large *R* → $E_{total} = E_{atom\ 1} + E_{atom\ 2}$
  - small *R* → E_{total} rises or falls
- Energy *CHANGE* correlated w/
  - orbital overlap
  - # electrons
    - 2 sharing (nice, but why?)
    - 4 sharing + Pauli repulsion (bad, but why?)

Molecular Orbital

- Construct MO (*new* orbitals) from AO
- MO energy depends on geometry
  - Track MO energy as atoms approach
    - Energy falls → "bonding MO"
    - Energy rises → "antibonding MO"
- $E_{total} \approx$ sum $E_{MO\ occupied}$
  - E_{total} falls → bond (attraction)
  - E_{total} rises → no bond (repulsion)

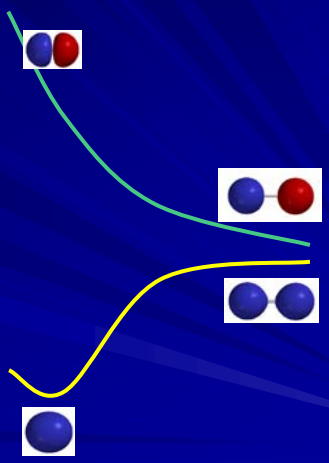
Bond (attraction) → H-H

- Two *1s* combine
  - MO no node
  - MO node
- Geometry
  - large *R* → ~ same E
  - small *R* →
    - no node MO falls → σ
    - node MO rises → σ*
- $E_{total} \approx 2\ E_{\sigma}$



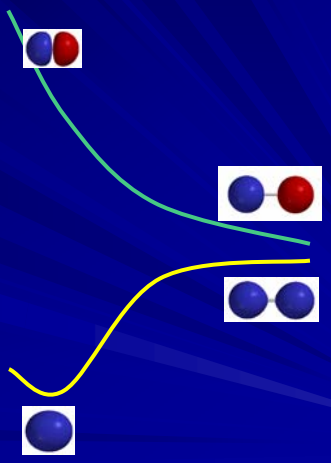
Bond (repulsion) → He He

- Two *1s* combine
  - MO no node
  - MO node
- Geometry
  - large *R* → ~ same E
  - small *R* →
    - no node MO falls → σ
    - node MO rises → σ*
- $E_{total} \approx 2\ E_{\sigma} + 2\ E_{\sigma^*}$



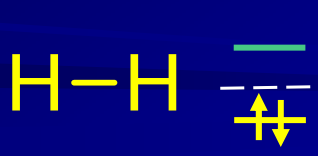
What Controls E_{MO}?

- Electron location
  - attraction to nuclei
  - repulsion from other electrons
- Electron motion
  - low kinetic E better
- Correlates w/
  - # nodes
  - "AO overlap"
    - visualize AO pieces



VB vs. MO

- Valence Bond
  - No new orbitals
  - Overlap (geometry)
  - # electrons
    - 2 e → nice
    - 4 e → bad (Pauli rep)
- Molecular Orbital
  - New orbitals
    - Overlap (geometry)
    - Nodes
  - # electrons
    - # occupied MO
    - $E_{total} \approx$ sum ($E_{MO\ occupied}$)

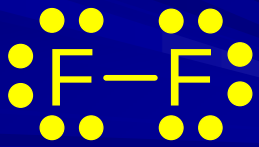


H-H (strong) vs. F-F (weak)

- Valence Bond
  - balance the 'nice' and the 'bad'
    - ☺ 2 electrons in overlapping AO
    - ☹ 4 electrons in overlapping AO
      - Pauli repulsion

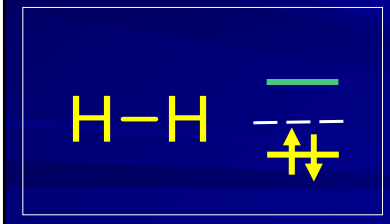
	H_2	F_2
☺	+	+
☹		++

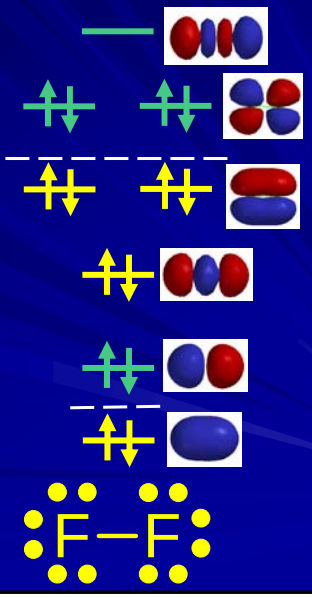
H–H



H-H (strong) vs. F-F (weak)

- Molecular Orbital
  - sum $E_{MO\ occupied}$
    - Antibonding is bad
      - 4electrons are destabilizing





2 lone pair ≈ bond + bond*