Molecular Orbital (MO) Theory

Robert Mulliken (1896 - 1987)

Friedrich Hund (1896 - 1997)

Nobel Prize, Chemistry, 1966
"For his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"
The Bases of MO Theory

In VB theory, each electron is attached to a specific atomic orbital centered on one atom; these orbitals are then allowed to interact to form bonds.

In MO theory, we still use the idea of overlapping atomic orbitals, but we do not put the electrons right away in the atomic orbitals. Instead, we form new orbitals (the molecular orbitals) by combining all the atomic orbitals together, then we add the electrons in these new orbitals. This approach to MO theory (not the only one, but by far the most commonly used one) is called:

**LCAO-MO**

*Linear Combination of Atomic Orbitals (to form) Molecular Orbitals*
Energy dependence on inter-atomic distance

\[ E \]

\[ r \]

region where nuclei repel

most likely distance for a bond (lowest energy point)

electrons start being pulled to the other atom’s nucleus

at \( r = \infty, E = 0 \); the atoms don’t interact

\[ E = 0 \]

indicates the direction of dominating forces
An antibonding MO changes its phase when you go from one atom to the other atom.

A bonding MO has no change of phase as you go from one atom to the other atom.

\[ \psi(\sigma^*) = 1s_A - 1s_B \]

\[ \psi(\sigma) = 1s_A + 1s_B \]
Another Perspective on the $\sigma_s$ MO

• The 1s atomic orbitals are symmetric about the bond axis.

• The overlap of the atomic orbitals is also symmetric about the bond axis.

• Therefore, the complete molecular orbital is symmetric around the bond axis.
Definitions:

\[ \text{Bond Order} \equiv \frac{(\# \text{ of } e^- \text{ in } \sigma_b) - (\# \text{ of } e^- \text{ in } \sigma^*)}{2} \]

\text{e.g.} \quad \text{Bond Order for } H_2 = \frac{2 - 0}{2} = 1 \quad \Rightarrow \text{single bond}

Note: Bond lengths are related to bond order:
    larger bond order \Rightarrow shorter bond length

Magnetic Properties:

\textbf{Paramagnetic} - there are unpaired electrons

\textbf{Diamagnetic} - no unpaired electrons

\text{e.g.} \quad H_2 \text{ is diamagnetic}
Two Important Ideas in Chemical Bonding

1) **Overlap** between orbitals (larger the better)

- no overlap
- small overlap
- large overlap

2) **Energy Difference** between orbitals (smaller the better)

- no energy difference
- large energy difference
The Symmetry of MOs: The Sigma orbitals

$\sigma$-MO and $\sigma^*$-MO formed by combining $p_z$ orbitals
The Symmetry of MOs: The Pi orbitals

A MO has π-symmetry if a 180° rotation around the internuclear axis changes the phase of the MO.

π-MO and π*-MO formed by combining pₓ or pᵧ orbitals
Homonuclear problem: $\text{O}_2$

B.O. = ?

Agrees with $\text{O} = \text{O}$

Liquid oxygen
The s-p Mixing Effect

[Graph showing the change in atomic orbital energy per mole (kJ/mol) with atomic number for elements Li through F.]
The s-p Mixing Effect