Chapter 9: Molecular Orbitals

Valence bond theory: bonds result from the sharing of electrons in overlapping orbitals of different atoms. These can be pure atomic orbitals or hybridized atomic orbitals of individual atoms.

Molecular Orbital Theory: postulates that atomic orbitals of different atoms combine to form molecular orbitals. The electrons in them belong to the molecule as a whole. A molecular orbital can be located over the entire molecule.

(Show picture of overlapping orbitals in H₂)

The two theories work in conjunction: VB theory is easily visualized and MO theory explains some aspects that VB theory cannot. eg. the fact that O₂ is paramagnetic (recall demonstration.) We have been discussing electrons as being wave-like. Recall that the electron waves that describe atomic orbitals are mathematical descriptions similar to sine waves:
  • have positive and negative phases
  • can interact in phase and out of phase

IN PHASE \[ \left\{ \begin{array}{c}
+ \\
- 
\end{array} \right\} + \left\{ \begin{array}{c}
+ \\
- 
\end{array} \right\} \rightarrow \left\{ \begin{array}{c}
+ \\
- 
\end{array} \right\} \]

when 2 atomic orbitals overlap in phase \(\rightarrow\) bonding orbital

OUT OF PHASE \[ \left\{ \begin{array}{c}
+ \\
- 
\end{array} \right\} + \left\{ \begin{array}{c}
+ \\
- 
\end{array} \right\} \rightarrow \left\{ \begin{array}{c}
- \\
+ 
\end{array} \right\} \]

when 2 atomic orbitals overlap out of phase \(\rightarrow\) anti-bonding orbital

The anti-bonding orbital has higher energy - it is "against" bonding and wants to destabilize the system.
Consider the combination of 2 1s orbitals to give 2 molecular orbitals. (Figure 9-2)

\[ \begin{array}{ccc}
\text{Atomic Orbital} & \text{Molecular Orbital} & \text{Atomic Orbital} \\
\uparrow & \sigma^* & \uparrow \\
1s & \downarrow \downarrow & 1s
\end{array} \]

For example: \( \text{H}_2 \) has 2 electrons in bonding \( \sigma_{1s} \) molecular orbital and no electrons in antibonding \( \sigma^*_{1s} \).

Note that electrons go into lower energy orbitals first and Hund's Rule and Pauli Exclusion principle hold. (diatomic \( \text{H}_2 \) has 2 e\(^{-}\): one from 1\( ^1 \) atom and another electron from the other 1\( ^1 \) atom).

Consider the combination of p orbitals (Figs 9-3 and 9-4)

- head-on overlap of \( 2p_x \) atomic orbitals \( \rightarrow \) two \( \sigma \) molecular orbitals \( \sigma^* \)
- side-on overlap of two \( 2p_y \) atomic orbitals \( \rightarrow \) two \( \pi \) molecular orbitals \( \pi^* \)
- side-on overlap of two \( 2p_z \) atomic orbitals \( \rightarrow \) two \( \pi' \) molecular orbitals \( \pi'^* \)

(Molecular Orbital Energy-Level Diagrams for diatomic homonuclear species with atoms with atomic numbers 1 \rightarrow 10. (Fig 9-5)

Remember that one diagram is used for \( \text{H}_2, \text{He}_2, \text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2 \) and their ions.

Another diagram is used for \( \text{O}_2, \text{F}_2, \text{Ne}_2 \) and their ions.

The order of filling the orbitals is very similar to filling atomic orbitals.
Energy Level Diagram for $\text{H}_2 \quad \text{He}_2 \quad \text{Li}_2 \quad \text{Be}_2 \quad \text{B}_2 \quad \text{C}_2 \quad \text{N}_2$ + ions

Energy Level Diagram for $\text{O}_2 \quad \text{F}_2 \quad \text{Ne}_2$ + their ions

Atomic Orbitals  Molecular Orbitals  Atomic Orbitals

$2p$  $\sigma_{2p}$  $\pi_{2p}$

$\pi_{2p}$  $\pi_{2p}$

$2s$  $\sigma_{2s}$

$\sigma_{1s}$  $\sigma_{1s}$
Recall: A molecule is paramagnetic if there are unpaired electrons present.
Therefore, B₂ and O₂ are paramagnetic.

**Shorthand Notation**

The shorthand notation for the electrons in these diatomic molecules is very similar to the notation for atomic orbital electrons.

**Examples:**

\[
\text{Li}_2 (6e^-) \quad 6s^2 \quad \sigma_{1s}^2 \quad \sigma_{1s}^* \quad \sigma_{2s}^2 \\
\text{O}_2 (16e^-) \quad 6s^2 \quad \sigma_{1s}^* \quad \sigma_{1s}^2 \quad \sigma_{2s}^2 \quad \sigma_{2p}^2 \quad \pi_{2p_y}^2 \quad \pi_{2p_z}^2 \quad \pi_{2p_x}^* \quad \pi_{2p_x}^*
\]

**Bond Order**

After the energy level diagram has been filled appropriately, the stability of the molecule can be judged by bond order:

\[
\text{bond order} = \frac{\text{number of electrons in bonding orbitals} - \text{number of electrons in nonbonding orbitals}}{2}
\]
In general, the bond order = number of bonds in the molecule as set by the Lewis dot structure in Valence Bond Theory.

And so, bond order of 3 = triple bond
bond order of 2 = double bond
bond order of 1 = single bond
bond order of 0 = no bond and the molecule does not exist

Note: there are also fractional bond orders: \( \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \), which have intermediate characteristics.

Example: for \( \text{O}_2 \)

\[
\text{bond order} = \frac{(10 \text{ e}^- \text{ in bonding orbitals}) - (6 \text{ e}^- \text{ in antibonding orbitals})}{2} = \frac{4}{2} = 2.
\]

According to V.B. theory, we have \( \overset{\cdot}{\text{O}} : \overset{\cdot}{\text{O}} \) or \( \overset{\cdot}{\text{O}} = \overset{\cdot}{\text{O}} \) a double bond Voila!

Note: V.B. theory, however, shows \( \text{O}_2 \) to be diamagnetic. It is paramagnetic.

There are the following relationships involving bonds and bond order:

as the bond order increases, stability of the bond increases
bond energy (strength) increases
bond length decreases.

Consider 4 species of diatomic oxygen:

\[
\begin{array}{ccc}
\text{Species} & \text{Bond Order} & \text{Bond Length} \\
\text{O}_2^+ (15 \text{ e}^-) & 2 \frac{1}{2} & 1.1227 \text{ Å} \\
\text{O}_2 (16 \text{ e}^-) & 2 & 1.20741 \text{ Å} \\
\text{O}_2^- (17 \text{ e}^-) & 1 \frac{1}{2} & 1.26 \text{ Å} \\
\text{O}_2^{2-} (18 \text{ e}^-) & 1 & 1.49 \text{ Å}
\end{array}
\]
Questions that can be answered using this brief introduction to MO theory

(1) What is shorthand notation?
(2) Is the species paramagnetic or diamagnetic?
(3) What is the bond order?
(4) Is the molecule stable? If bond order > 0, molecule is stable. If bond order = 0, molecule is not stable.

Examples

$N_2^+$ has total of $(7+7-1)$ electrons to put in molecular orbitals

\[ \begin{align*}
\phi_1^2 & \ 0_1s^2 \ 0_2s^2 \ 0_2s^2 \ 1\pi^2 \ 1\pi^2 \ 2\pi \ 2\pi \ 0_1p^1 \\
\text{paramagnetic} \\
\text{bond order} = \frac{9-4}{2} = 2.5 \\
molecule \ is \ stable.
\end{align*} \]

$Be_2$ has total of $(4+4)$ electrons to put in molecular orbitals

\[ \begin{align*}
\phi_1^2 & \ 0_1s^2 \ 0_2s^2 \ 0_2s^2 \\
\text{diamagnetic} \\
\text{bond order} = \frac{4-4}{2} = 0 \\
molecule \ is \ not \ stable \ - \ would \ not \ exist.
\end{align*} \]

Molecular Orbital theory gives a better explanation of molecules with delocalized electrons than does valence bond theory.

(See next pages).
Examples:

Carbonate ion

$\text{CO}_3^{2-}$

FIGURE 8-9 Representations of the bonding in the carbonate ion, $\text{CO}_3^{2-}$: (a) Valence bond representations of the three resonance structures. Each of the resonance forms has one double bond. (b) Overlap of $p$-orbitals to form the $\pi$ components of the (hypothetical) double bonds in the resonance forms. Each $O$ atom has two additional $sp^2$ orbitals (not shown) in the plane of the nuclei. These additional $sp^2$ orbitals each contain an oxygen lone pair. (c) In the MO description, the electrons in the $\pi$-bonded region are spread out, or delocalized, over all four atoms of the $\text{CO}_3^{2-}$ ion.

Benzene

$\text{C}_6\text{H}_6$

FIGURE 8-10 Representations of the bonding in the benzene molecule, $\text{C}_6\text{H}_6$: (a) The valence bond resonance structures. (b) The six $p$ orbitals of the benzene ring, shown overlapping to form the (hypothetical) double bond of the two resonance forms. (c) In the MO description, the six electrons in the $\pi$-bonded region are delocalized, occupying an extended $\pi$-bonding region above and below the plane of the six $\text{C}$ atoms.