The molecular orbital (MO) theory is a powerful and extensive approach which describes electrons as delocalized moieties over adjacent atoms. The applications of the MO theory extend beyond the limitations of the Valence Shell Electron Pair Repulsion (VSEPR) model and the Valence Bond theory. These previous theories provide substantial information on predicting the structure and bonding properties of a molecule by portraying electrons as localized “balloons” of high density.

Introduction

Although VSEPR and the Valence Bond theory accurately predict bond properties, they fail to fully explain some molecules. The MO theory incorporates the wave character of electrons in developing MO diagrams. MO diagrams predict physical and chemical properties of a molecule such as shape, bond energy, bond length and bond angle. They also provide information in predicting a molecule’s electronic spectra and paramagnetism. The objective of this wiki is to provide readers with the fundamental steps in constructing simple homonuclear and heteronuclear diatomic molecular orbital diagrams. These steps may then be extrapolated to construct more difficult polyatomic diagrams.

Molecular Orbitals
The region an electron is most likely to be found in a molecule. A MO is defined as the combination of atomic orbitals.

Homonuclear Diatomics
Molecules consisting of two identical atoms are said to be homonuclear diatomic, such as: H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, and F\textsubscript{2}.

Heteronuclear Diatomics
Molecules consisting of two non-identical atoms are said to be heteronuclear diatomic, such as: CO, NO, HF, and LiF.

Bonding and Antibonding Orbitals
Orbitals that are out-of-phase with one of another are "antibonding" orbitals because regions with dense electron probabilities do not merge which destabilizes the molecule. "Bonding" orbitals are less energetic than antibonding atomic orbitals and are in-phase, as depicted in the figure below. Note how the bonding orbitals come together constructively, while the antibonding orbitals do not.
Phases and nodes
Phases are designated either (+) or (-) relative to their wave "up" or wave "down" displacements. A node occurs if the phase signs change from (+) to (-) or vice versa. It is important to notice that the phase signs do NOT symbolize charges. Nodes are regions where the probability of finding an electron is ZERO.

Sigma and Pi Bonds
A sigma-bond is an "end-to-end" bond formed from symmetric atomic orbitals. A pi-bond is formed from a "sideways" overlap.

General Notes on Molecular Orbital Diagrams

1. The Y-axis of a MO diagram represents the total energy (not potential nor Gibbs Energy) of the orbitals.
2. Individual atomic orbitals (AO) are arranged on the far left and far right of the diagram.
3. Overlapping atomic orbitals produce molecular orbitals located in the middle of the diagram. These MO overlap with either a sigma or pi bond and are designated in bonding, nonbonding, or antibonding orbitals with respect to their phases.
4. Electrons from the atomic orbitals are assigned molecular orbitals in accordance with the Pauli Exclusion Principle. Lower energy MOs are filled first, followed by consecutively increasing orbitals.

FUNDAMENTAL STEPS IN DERIVING MO DIAGRAMS

There are several steps common in all MO diagrams. Understanding these basic steps to derive simple homonuclear and heteronuclear MOs will enable us to construct more complicated, polyatomic diagrams.

STEP 1

Find the valence electron configuration of each atom in the molecule. The valence electrons will be placed on the atomic
orbital for that atom. Do this for each atom. Ex) Boron (B) = (He)2s² 2p¹ = 3 valence electrons

STEP 2

Decide if the molecule is homonuclear of heteronuclear. If the molecule is homonuclear, the AOs will be symmetric. Heteronuclear AOs will be slightly different because the more electronegative atom will be placed lower on the diagram. This is due to lone pairs of electrons being more stable on more electronegative elements leading them to be lower in energy. Ex) HF = “F” will be placed lower in the diagram than “H”.

STEP 3

Fill molecular orbitals using energy and bonding properties of the overlapping atomic orbitals. Keep in mind the energy of the atomic orbitals and molecular orbitals! The following factors contribute to the position of one MO with respect to other MOs.

- More nodes = more energetic = higher MOs
- Sigma orbitals are stronger than pi bonds
- Antibonding MOs are higher in energy than bonding MOs
- Constructive overlap = fewer nodes = more stable (less energetic)
- Destructive overlap = more nodes = less stable (more energetic)

STEP 4

Use the diagram to predict properties of the molecule. Remember: the number of individual atomic orbitals should equal the number of MOs! Ex) Bond order, bond angle, paramagnetism, etc.

Building Molecular Orbital Diagrams for Homonuclear and Heteronuclear Diatomic Molecules

Due to symmetry of the molecule, homonuclear MO’s are less difficult to derive than heteronuclear molecules and polyatomic molecules. (Such as H₂O, NH₃, and CH₄.) However, notice the difference between orbitals of homonuclear diatomics for elements with an atomic number less than or equal to 7 versus more than 7. In general, B₂, C₂, and N₂ have the MO diagram depicted on the left. O₂ and F₂ have the MO on the right. Why does this difference exist?
Constructing MO diagrams for heteronuclear molecules require the same 4 steps as above. However, recall that the more electronegative atom will be lower on the diagram. The best way to learn how to draw MO diagrams is to work on practice problems. Try the following MO's on your own, and then check with the answers provided.

**Question 1:** Draw the MO diagram for N2:
**Question 2:** Draw the MO for O2:
**Question 3:** Draw the MO diagram for HF:

**Answers:**

**Question 1:**

**STEP 1:** N\textsubscript{2} = (He) 2s\textsuperscript{2} 2p\textsuperscript{3} (5 valence electrons for each atom)

**STEP 2:** Homonuclear molecule; each "N" AO will be equivalent in energy.

**STEP 3:** Fill the MOs with electrons:
**STEP 4:** Check. Do the number of AO’s = number of MO’s? If so, good! You can now calculate the bond order.

**BOND ORDER:** \( \frac{1}{2} (\text{#Bonding orbitals} - \text{#Antibonding orbitals}) \)

\[=\frac{1}{2}(8-4) = 3. \text{ What is the significance of the bond order? Think about it, then click here.2} \]

**Question 2:**

**STEP 1:** \( \text{O}_2 = (\text{He}) \, 2s^2 \, 2p^4 \) (6 valence electrons for each atom)

**STEP 2:** Homonuclear molecule; each “O” AO will be equivalent in energy.

**STEP 3:** Fill the MOs with electrons:

**STEP 4:** Check. Do the number of AO’s = number of MO’s? If so, calculate the bond order.

**BOND ORDER:** \( \frac{1}{2} (\text{#Bonding orbitals} - \text{#Antibonding orbitals}) \)

\[=\frac{1}{2}(8-4) = 2. \text{ Consistent with Oxygen's double bond.} \]

**Question 3:**

**STEP 1:** \( \text{H} = 1s^1 \) (1 valence electron) \( \text{F} = (\text{He}) \, 2s^2 \, 2p^5 \) (7 valence electrons)

**STEP 2:** Heteronuclear molecule; “F” will be lower on the diagram.

**STEP 3:** Fill the MOs with electrons:
**STEP 4:** Check; Do the number of AO’s = number of MO’s?

Now more difficult MO diagrams can be derived using the four simple step above. Keep the energies of atomic/molecular orbitals when arranging the diagram!

**References**

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