Activity 201 – 9
Molecular Orbital Theory

Directions: This Guided Learning Activity (GLA) discusses the Molecular Orbital Theory and its application to homonuclear diatomic molecules. Part A describes the basics of linear combination of orbitals, Part B describes how the bond order for a molecule is determined, and Part C describes s-p mixing and how the magnetic properties of a substance can be determined. This worksheet is accompanied by an in-depth key. See http://www.canyons.edu/Departments/CHEM/GLA for additional materials.

Part A – Molecular Orbitals for Diatomic Molecules

Molecular Orbital (MO) Theory helps us to explain and understand certain characteristics of molecules – specifically things that are not well explained by Valence Bond Theory. Like Valence Bond Theory, MO Theory is based on the linear combination of atomic orbitals (LCAO). But MO theory differs from Valence Bond Theory because it allows the combination of orbitals from different atoms. According to the theory, molecular orbitals extend over all of the atoms within a molecule – a property that helps to provide physical meaning to resonant Lewis structures.

Keep in mind that the atomic orbitals described in Chapter 6 (s, p, d and f orbitals) are mathematical probability functions. Like all mathematical functions, these can be added and subtracted to yield new functions that represent the same total distribution. When atomic orbitals are mathematically combined to form new molecular orbitals, we simplify the possible molecular orbitals by limiting ourselves to combinations of the same orbital from each atom. In other words, we combine the s orbital from one atom with the s orbital from another atom, and the px orbital from one atom with the px orbital from another, and so forth. Each combination of orbitals results in a lower energy bonding orbital and a higher energy antibonding orbital.

Since the molecular orbitals are linear combinations of atomic orbitals, you can imagine that that molecular orbital shape will resemble the shapes of the combined orbitals. For example, when the s-orbitals from two atoms are combined to form a molecular orbital, the bonding and antibonding orbitals are shown below.

![Bonding and Antibonding Orbitals](Source: Chemistry, published by Openstax College, 2016)

Notice that the bonding orbital lies along the internuclear axis, and is therefore called $\sigma_s$, to indicate if forms a $\sigma$-bond and is created by the combination of the s-orbitals. (Refer to GLA 201-8 Hybrid Atomic Orbitals for a review of $\sigma$- and $\pi$-bonds.) The antibonding orbital forms a $\sigma$-bond, as well, but is denoted with an asterisk, $\sigma^{*}_s$. When a bond forms, it is more favorable for an electron to occupy the bonding orbital, $\sigma_s$, than it is for the electron to occupy the original atomic s-orbital. Therefore occupying a bonding orbital favors bond formation. Conversely, it is less favorable for the electron to occupy the anti-
bonding, or $\sigma^*$ orbital, meaning that when electrons occupy antibonding orbitals, the bonding interaction is weakened.

The $p$-orbitals can also overlap to form molecular orbitals. However, because the $p$-orbitals have different orientations, we must distinguish between them. We define the $x$-axis as the internuclear axis. When the $p_x$-orbitals from two atoms overlap, the bonding and antibonding orbitals lie along the internuclear axis, and so are called the $\sigma_{px}$ and the $\sigma_{px}^*$ orbitals, respectively. The figure below represents the molecular orbitals formed from the $p_x$-orbitals.

![Molecular orbitals formed from $p_x$-orbitals](image)

(Source: Chemistry, published by Openstax College, 2016)

When the $p_y$-orbitals from two separate atoms overlap, the overlap occurs outside of the internuclear space. The bonding and antibonding orbitals are called $\pi_{py}$ and $\pi_{py}^*$, respectively.

![Molecular orbitals formed from $p_y$-orbitals](image)

(Source: Chemistry, published by Openstax College, 2016)

The molecular orbitals formed by the overlap of the $p_z$-orbitals are identical to those formed by the $p_y$-orbitals, but are rotated by 90° (into and out of this page). This equivalency also results in the orbitals being degenerate, meaning they are energetically equivalent. (You are familiar with degenerate orbitals – all $p$-orbitals that occur in the same energy level of an atom are degenerate).

**Example #1**
Which of the molecular orbitals discussed above is likely the most energetically favorable? Which is least favorable? Why?
Part B – Molecular Orbital Energy Diagrams & Bond Order

As mentioned above, each combination of two atomic orbitals results in one bonding orbital with a lower energy, and one antibonding orbital with higher energy. We can use energy diagrams to predict how electrons will occupy molecular orbitals. The energy diagram for O$_2$ is shown below.

![Molecular Orbital Diagram for O$_2$]

When drawing molecular orbital diagrams, generally the valence atomic orbitals and how they are occupied by electrons are shown on the outside and the molecular orbitals are shown in the middle. When the molecule forms, the electrons are transferred into the molecular orbitals. For clarity the electrons are usually shown in both the atomic orbitals (outside) and the molecular orbitals (inside). For example, in the diagram, there are 6 valence electrons shown in the atomic orbitals for each oxygen. The same 12 electrons ($2 \times 6$ electrons) are shown in the molecular orbitals.

Just as in individual atoms, electrons in molecules occupy the lowest energy orbitals first. When two molecular orbitals are degenerate (such as $\pi_{2p}$ and $\pi_{2p'}$), the electrons occupy the orbitals singly first.

Recall that bonding orbitals enhance the interaction between atoms and antibonding orbitals disrupt the interaction between atoms. In MO Theory, the strength of the interaction between atoms is called the bond order. You can think of the bond order as being equivalent to the number of bonds formed between two atoms. The bond order for a molecule is calculated by:

$$ Bond \ Order = \frac{(# \ electrons \ in \ bonding \ orbitals - # \ electrons \ in \ antibonding \ orbitals)}{2} $$

A molecule with a predicted bond order of 0 will not form. Using the molecular orbital diagram, we can calculate the bond order for oxygen.

$$ Bond \ Order = \frac{(8 - 4)}{2} = 2 $$
Practice
Draw the MO energy diagram for F$_2^+$ ion and determine the ion’s bond order.

The F$_2^+$ ion has 13 valence electrons:
2 F atoms x 7/atom – 1 (charge). We show seven valence electrons in one atom (left side), and six in the other (right side).

\[
\text{Bond Order} = \frac{(8-5)}{2} = 1.5
\]

Because the bond order is 1.5, we expect the bond will be stronger than a single bond and weaker than a double bond.

Example #2
Draw the MO energy diagram for peroxide (O$_2^{2-}$) and calculate the bond order. Based on this, do you expect the O-O bond in peroxide to be longer or shorter than in oxygen gas (O$_2$)?

Part C – Magnetic Properties of Homonuclear Diatoms
As discussed in part A, MO Theory combines atomic orbitals to form bonding and antibonding molecular orbitals. We have limited ourselves to considering the molecular orbitals that will result from the overlap of like atomic orbitals (e.g. $2s + 2s$, or $2p_x + 2p_y$). Because the $p$-orbitals are all perpendicular to each
other, this approach is valid for these orbitals. (Little to no overlap occurs between orbitals that are oriented in different directions.) However, the $\sigma_s$ and the $\sigma_{2p_x}$ orbitals overlap in space. Because of this overlap, we observe that the four atomic orbitals ($2s$ and $2p_x$ from each of the two atoms) hybridize to form two bonding orbitals and two antibonding orbitals. This combination of the $s$ and the $p_x$ orbitals is termed $s$-$p_x$ mixing. $s$-$p_x$ mixing results in the $\sigma_{2s}$ orbital becoming lower in energy, and more favorable to occupy, and the $\sigma_{2p_x}$ orbital becoming higher in energy, and less favorable to occupy.

The figure shows that the $\sigma_s$ orbital becomes more favorable to occupy at the expense of the $\sigma_{2p_x}$ orbital.

The magnitude of the change in energy depends on the atoms that are involved in the bond. In Period 2, B$_2$, C$_2$, and N$_2$ all show significant mixing and result in the $\sigma_{2p_x}$ orbital becoming less favorable to occupy than the $\pi_{2p_y}$ and $\pi_{2p_z}$ orbitals. In contrast, O$_2$, F$_2$, and Ne$_2$ display limited mixing and therefore the $\sigma_{2p_x}$ orbital remains more favorable to occupy than the $\pi_{2p_y}$ and $\pi_{2p_z}$ orbitals.
Another property that MO Theory can predict is the magnetism of compounds. Compounds are classified as diamagnetic or paramagnetic based on their electronic properties.

- **Diamagnetic** compounds are slightly repulsed by a magnetic field. They contain no unpaired electrons.
- **Paramagnetic** compounds are slightly attracted to a magnetic field. They contain at least one unpaired electron.

MO energy diagrams are used to predict the bond order of a homonuclear molecule, but also its magnetic properties.

**Practice**

What is the bond order for N₂? Is it diamagnetic or paramagnetic?

![MO diagram for N₂](image)

The bond order for N₂ is:

\[
\text{Bond Order} = \frac{(8 - 2)}{2} = 3
\]

N₂ is diamagnetic since it contains no unpaired electrons.

**Example #3**

H₂, N₂, O₂ and F₂ are all gases under standard conditions. Which of these gases are paramagnetic? Which do you expect will have the strongest bond?
Part D – Extra Practice

1. Draw the molecular orbital energy diagram for Be$_2^+$ and Be$_2^{2-}$ and determine the bond order. Do these ions exist?

2. Is C$_2$ paramagnetic or diamagnetic? How do you know?

3. What is the bond order for the disulfide ion (S$_2^{2-}$)? Do you expect the ion to be paramagnetic or diamagnetic?

4. Determine whether B$_2$ is diamagnetic or paramagnetic. Explain.

5. Sketch the molecular orbitals present in the H$_2^-$ ion. Then draw the energy diagram and determine the bond order. Why does the Lewis model fail to describe this ion accurately?

6. Draw the bonding orbitals produced by the combination of the $p_x$-orbitals and the bonding orbital produced by the combination of the $p_y$-orbitals. Explain why the $p_x$-orbital combination results in a $\sigma$ molecular orbital, while the $p_y$-orbital combination results in a $\pi$ molecular orbital.

7. What does it mean for two orbitals to be degenerate? Which molecular orbitals in diatomic molecules are expected to be degenerate?

8. Explain why the antibonding $\sigma_{2s}^*$ orbital will fill before the bonding $\sigma_{2p}$ orbital.

Challenge. Determine whether each of the following ions or molecules is diamagnetic or paramagnetic: CO, CN$, OF$. 