9.2 - 9.3 - The Molecular Orbital Model

Molecular Orbital (MO) Theory

We've seen how the localized electron model is great for interpreting structure and bonding of molecules.

Another model often used to describe bonding is the molecular orbital model, which attempts to address bonding between atoms in terms of relative energy.

Just as atomic orbitals are the solutions to the quantum mechanical treatment of atoms, so too does MO theory present solutions to molecules.

Introductory Terms in MO

Atoms will join together if the resulting energy of their joining is lower than if they were separate.

Two types of orbitals arise, depending on where the electons are likely to be found around in a molecule:

Bonding MO: lower in energy than the atomic orbitals of which it is composed. These electrons will be between atoms, or in parallel as pi bonds.

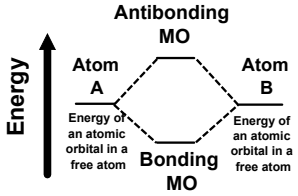
Antibonding MO: higher in energy than the atomic orbitals than the original. These are often denoted with an asterisk (*) in MO diagrams.

Degenerate orbitals: orbitals of a sublevel with the same energy.

Introductory Terms in MO

MO diagrams are used to show relative placements of electrons in bonding atoms.

The rough structure is as follows:

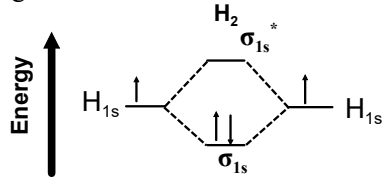


To indicate bond strength, we calculate the Bond Order: the different between the number of bonding and antibonding electrons divided by two:

$$Bond\ Order = \frac{bonding\ e^- - antibonding\ e^-}{2}$$

Hydrogen Example

Consider the diatomic hydrogen molecule: each atom contributes one electron to the bond, so the MO diagram is as follows:



The bond order equals: $Bond\ Order = \frac{2e^- - 0e^-}{2} = 1$

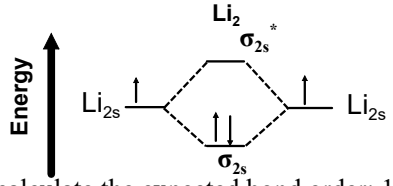
A valence **molecular electron configuration** can be made as well, for H_2 it is: σ_{1s}^2.

Bonding in Homonuclear Diatomic Orbitals

When it is possible for two atoms of the same element (homonuclear) to join, MO theory can be applied as a first check on the viability of such a grouping.

1. Lithium Example

Use MO theory to predict the Li_2 molecule.
Start by making a MO diagram for lithium:

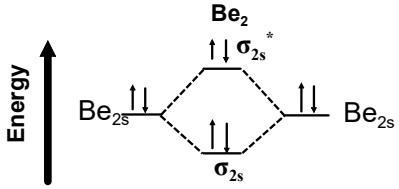


Then calculate the expected bond order: 1.
Valence electron configuration: σ_{2s}^2.

By all this, it would appear that the Li_2 molecule is stable.
Indeed it is (under the right conditions)!
However, it is not the most stable form of lithium metal at normal temperature and pressure, showing how simple models do not always reflect realities.

2. Beryllium Example

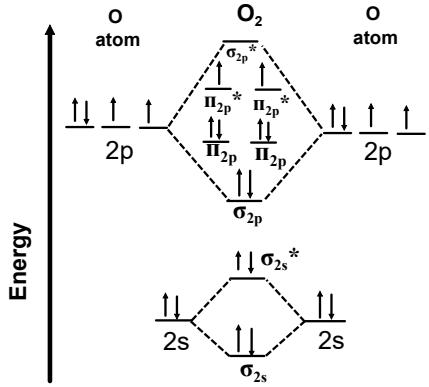
Use MO theory to predict the viability of the Be_2 molecule.
Start by making a MO diagram for beryllium:



Here, there are two antibonding electrons which counteract the bonding electrons, resulting in a bond order of zero.
Diatomic beryllium will not form.

More Complex MO Molecules

As we get into the p sublevel, more parts need to appear in the MO diagram.
Consider oxygen: its MO diagram, showing all valence electrons, and degenerate orbitals is:



Magnetic Properties of Molecules

Depending on how electrons are paired or one, magnetic properties of atoms and molecules emerge. Most substances are not magnetic until they are placed in a magnetic field. The magnetic field aligns their electrons, causing them to be attracted or repelled depending on what's going on.

Paramagnetism: property of matter in which a substance is attracted to an external magnetic field. It is associated with unpaired electrons in the MO diagram.

Diamagnetism: Property of matter in which a substance is repelled by a magnetic field. it is associated with paired electrons in the MO diagram.

3. Magnetism Example

Would O_2 be expected to be paramagnetic or diamagnetic?

Looking at the MO diagram, it would be expected to be paramagnetic: there are two lone electrons in the 2 π* orbital.

Homework

Preview 9.4 - 9.6

9.2 - 9.3 Problems in your Booklet
Due: Next Class