CHEM1101 Worksheet 5: Molecular Orbitals, Bonding and Atomic Spectroscopy

Model 1: Molecular Orbitals

Molecular orbitals are formed from combinations of atomic orbitals. When orbitals are combined, they can either add in phase (same sign) or out of phase (opposite signs). This gives rise to two molecular orbitals. The bonding molecular orbital results from addition of lobes with the same phase, while the antibonding molecular orbital results from addition of lobes with opposite phase. The latter will have a node between the nuclei.

For example, two 1s orbitals can combine to give rise to a bonding and an antibonding orbital in the following way:

In the same way, p atomic orbitals can combine to give molecular orbitals. The shape of the orbitals will depend on the orientation of the interaction. p orbitals can either combine in a head-on fashion, or a side-on fashion.

1. Draw the molecular orbital results from interaction of the following p orbitals.

   head-on interactions

   ![Diagram showing head-on interactions](image)

   side-on interactions

   ![Diagram showing side-on interactions](image)
2. Indicate whether the molecular orbitals that you have drawn in question 1 are bonding or antibonding orbitals.

**Model 2: σ, σ*, π, and π* Orbitals**

Molecular orbitals describe the properties of electrons in molecules and a knowledge of them gives insight into the reactivity and stability of compounds. Commonly, molecular orbitals are described as being σ (pronounced ‘sigma’) or π (pronounced ‘pi’). The pictures below show two examples of σ orbitals and one example of a π orbital in a diatomic molecule. The black dots (●) show the position of the nuclei.

σ orbitals are symmetric around a line joining the two nuclei. π orbitals have a node along this line: they are zero along the horizontal dotted line shown above.

When electrons occupy a **bonding orbital**, they strengthen the bond. When electrons occupy an **antibonding orbital**, they weaken the bond.

Anti-bonding orbitals, such as the one drawn opposite, have a nodal plane between the nuclei: they are zero along the vertical dotted line shown.

An asterisk ("*"") is added to the σ or π label to show this.
Critical thinking questions

3. Label the orbitals below as σ, σ*, π, or π*.

4. For the orbitals that you drew in question 1, assign labels of σ, σ*, π, or π*.

Model 3: Molecular Orbital Diagrams

The figure opposite is a molecular orbital diagram, or MO diagram, for a diatomic molecule made of second row elements. Each orbital is represented by a line, showing its energy, and may hold a maximum of 2 electrons.

Note that there are 2 π orbitals and 2 π* orbitals and this is represented by 2 lines in each case.

The valence electrons of the two elements are placed in these orbitals, starting from the lowest energy orbitals at the bottom.

For example, as a B atom has 3 valence electrons, the diatomic molecule B₂ has 6 valence electrons. These are placed as shown on the diagram. 2 electrons occupy σ, 2 electrons occupy σ* and 2 electrons occupy the π orbitals.

The last 2 electrons occupy one π orbital each as this keeps the electrons further away from each other. The completed MO diagram correctly predicts that the B₂ molecule has 2 unpaired electrons and is, as a result, paramagnetic.

Once the electrons have been added to the diagram, the bond order can be worked out by first counting up the number of bonding and anti-bonding electrons and then calculating:

\[
\text{bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of anti-bonding electrons})
\]

For B₂, there are 4 bonding electrons (2 in σ and 2 in π) and 2 anti-bonding electrons (in σ*) and so:

\[
\text{bond order} = \frac{1}{2} (4 - 2) = 1
\]
**Critical thinking questions**

5. Using the labels as a guide, sketch the remaining orbitals from Model 1 on the diagram above.

6. Add electrons to the diagram on the next page so that it shows the occupation for N\textsubscript{2}. Calculate its bond order.

7. Add electrons to the diagram below so that it shows the occupation for O\textsubscript{2}. Calculate its bond order.

8. What combinations of bonds (\sigma and/or \pi) make up double and triple bonds?

9. What is the bond order of nitric oxide (NO)?

\[ \begin{array}{ccc}
\sigma^* & \sigma^* & \sigma^* \\
\pi^* & \pi^* & \pi^* \\
\sigma & \sigma & \sigma \\
\pi & \pi & \pi \\
\sigma^* & \sigma^* & \sigma^* \\
\sigma & \sigma & \sigma \\
\hline
\text{N}_2 & \text{O}_2 & \text{NO} \\
\end{array} \]