CHEM1901/3 Worksheet 5: Molecular Orbitals and Bonding

Model 1: Single, Double and Triple Bonds

The table below shows structures and bond multiplicities and energies for selected molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>Bond</th>
<th>Bond Multiplicity</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td><img src="image" alt="H2O structure" /></td>
<td>O-H</td>
<td>1</td>
<td>498</td>
</tr>
<tr>
<td>ethane</td>
<td><img src="image" alt="Ethane structure" /></td>
<td>C-C, C-H</td>
<td>1, 1</td>
<td>376, 420</td>
</tr>
<tr>
<td>ethylene</td>
<td><img src="image" alt="Ethylene structure" /></td>
<td>C-C, C-H</td>
<td>2, 1</td>
<td>720, 444</td>
</tr>
<tr>
<td>acetylene</td>
<td><img src="image" alt="Acetylene structure" /></td>
<td>C-C, C-H</td>
<td>3, 1</td>
<td>962, 552</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td><img src="image" alt="Carbon Dioxide structure" /></td>
<td>C-O</td>
<td>2</td>
<td>804</td>
</tr>
<tr>
<td>formaldehyde</td>
<td><img src="image" alt="Formaldehyde structure" /></td>
<td>C-O, C-H</td>
<td>2, 1</td>
<td>782, 364</td>
</tr>
<tr>
<td>oxygen</td>
<td><img src="image" alt="Oxygen structure" /></td>
<td>O-O</td>
<td>2</td>
<td>498</td>
</tr>
<tr>
<td>nitrogen</td>
<td><img src="image" alt="Nitrogen structure" /></td>
<td>N-N</td>
<td>3</td>
<td>945</td>
</tr>
</tbody>
</table>

Critical thinking questions

1. The title of Model 1 identifies 3 types of bonds. Give an example of each type of bond from the molecules in the table.

2. What is the relationship between the bond multiplicity of a bond and the designation single, double and triple bonds?

3. Rank the three types of bonds in Model 1 in order of increasing strength.
Model 2: Molecular Orbitals

**σ 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.

![](image1.png)

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.

**Critical thinking questions**

1. Label the orbitals below as σ or π.

![](image2.png)

2. Identify the anti-bonding orbitals on this page and add an asterisk to their σ or π labels.

![](image3.png)

**Bonding and Anti-Bonding Molecular Orbitals**

When electrons occupy a bonding orbital, they strengthen the bond. When electrons occupy an anti-bonding 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.

2. Identify the anti-bonding orbitals on this page and add an asterisk to their σ or π labels.
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 \( \pi \) orbitals and 2 \( \pi^* \) 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 \( \text{B}_2 \) has 6 valence electrons. These are placed as shown on the diagram. 2 electrons occupy \( \sigma \), 2 electrons occupy \( \sigma^* \) and 2 electrons occupy the \( \pi \) orbitals.

The last 2 electrons occupy one \( \pi \) orbital each as this keeps the electrons further away from each other. The completed MO diagram correctly predicts that the \( \text{B}_2 \) 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 \( \text{B}_2 \), there are 4 bonding electrons (2 in \( \sigma \) and 2 in \( \pi \)) and 2 anti-bonding electrons (in \( \sigma^* \)) and so:

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

**Critical thinking questions**

1. Using the labels as a guide, sketch the remaining orbitals from Model 2 on the diagram.

2. Add electrons to the diagram so that it shows the occupation for \( \text{N}_2 \). Calculate its bond order.

3. Add electrons to the diagram so that it shows the occupation for \( \text{O}_2 \). Calculate its bond order.

5. What would be the bond order in nitric oxide, \( \text{NO} \)?

6. Use your knowledge of atomic orbitals to explain why, given that there are three degenerate \( p \) orbitals in an atom, there only two degenerate \( \pi \) orbitals in a diatomic molecule.
The “Great Comet of 1881” was discovered by Tebbutt from his observatory at Windsor, NSW. Observations by Huggins of the comet’s emission spectrum (pictured) revealed the presence of what was later determined to be the CN radical.

This emission system of CN is known as the “violet system”, and results from a radical returning to the ground state as an electron makes a transition from a \( \sigma \) orbital to a \( \sigma^* \) orbital. The “red system” of CN results from a radical returning to the ground state as an electron makes a transition from a \( \sigma \) orbital to a \( \pi \) orbital.

(a) On the diagram below, indicate the orbital occupancy, using arrow notation, of the upper electronic states of the “violet” and “red” systems of CN. Also indicate how the excited electron relaxes when the radical emits light (use a curved arrow).

(b) Explain in terms of bond order why the upper state of the violet system exhibits a shorter bond length (1.15\( \text{Å} \)) than the ground state (1.17\( \text{Å} \)).

(c) The Fraunhofer feature labelled ‘h’ is due to atomic hydrogen. What is the electronic transition responsible for this absorption feature? (Hint: one of the energy levels involved is \( n = 2 \).)