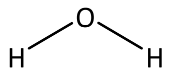
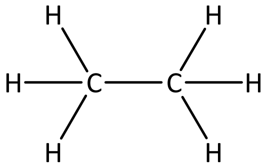
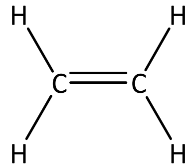
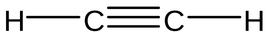
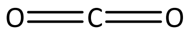
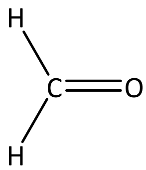
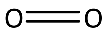
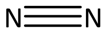
MOLECULAR ORBITALS AND BONDING

Model 1: Single, Double and Triple Bonds

The table below lists Lewis structures and bond orders and energies for selected molecules.

Molecule	Structure	Bond	Bond Order	Bond Energy (kJ mol^{-1})
H_2O		O-H	1	498
ethane		C-C C-H	1 1	376 420
ethene		C-C C-H	2 1	720 444
ethyne		C-C C-H	3 1	962 552
carbon dioxide		C-O	2	804
methanal (formaldehyde)		C-O C-H	2 1	782 364
oxygen		O-O	2	498
nitrogen		N-N	3	945

Critical thinking questions

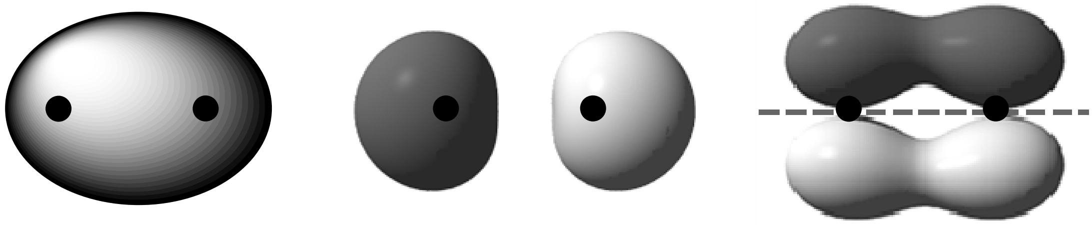
1. The title of Model 1 identifies 3 types of bonds. Give an example of each type of bond from the molecules in the table.

2. What is the relationship between the *bond order* 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: σ and π Molecular 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.

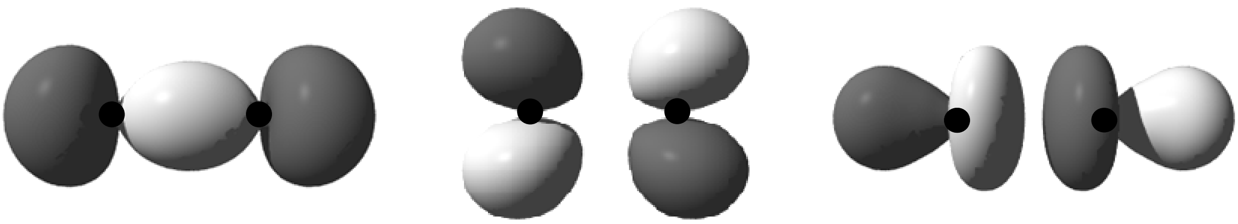


σ σ π

- 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

4. Label the orbitals below as σ or π.

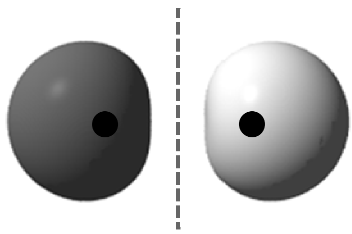


Model 3: Bonding and Anti-Bonding Molecular Orbitals

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.



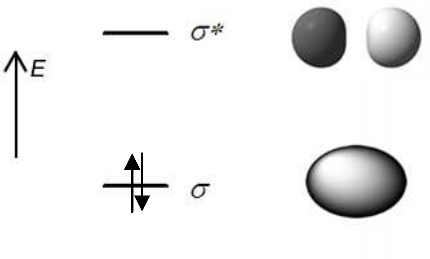
σ*

Critical thinking questions

5. Identify the anti-bonding orbitals in Model 2 and add an asterisk to their σ or π labels.

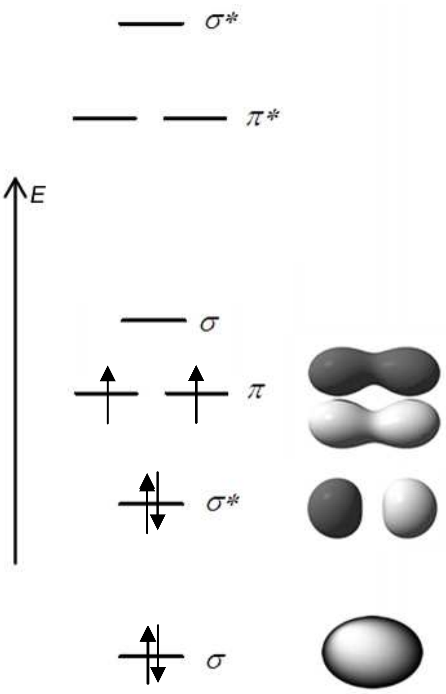
Model 4: Molecular Orbital Diagrams

The figures opposite show two *molecular orbital diagrams*, or MO diagrams. The top one is for H_2. The bottom one is for a diatomic molecule made of second row elements such as N_2. 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 H has 1 valence electron, the molecule H_2 has 2. These are placed as shown on the top diagram with the electrons in the σ orbital.

- As B has 3 valence electrons, the diatomic molecule B_2 has 6. These are placed as shown on the bottom diagram. 2 electrons in σ, 2 electrons in σ* and 2 electrons in 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 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:

bond order = ½ (number of bonding electrons – number of anti-bonding electrons)

For H_2, there are 2 bonding electrons (2 in σ) and no anti-bonding electrons and so:

bond order = ½ (2 – 0) = 1

For B_2, there are 4 bonding electrons (2 in σ and 2 in π) and 2 anti-bonding electrons (in σ*) and so:

bond order = ½ (4 – 2) = 1

Critical thinking questions

6. Using the labels as a guide, sketch the remaining orbitals from Model 2 on the bottom diagram.
7. Add electrons to the diagram so that it shows the occupation for N_2. Calculate its bond order.

8. Add electrons to the diagram so that it shows the occupation for O_2. Calculate its bond order.

9. How do the bond orders you calculated in Q7 and Q8 compare to those in the table in Model 1?

10. What would be the bond order in nitric oxide, NO?