Chem Factsheet

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Bonding and Anti-Bonding Molecular Orbitals

To succeed in this topic you need to:-
- Be familiar with basic ideas about atomic orbitals
- Be familiar with the Pauli Exclusion principle (in the form "the maximum number of electrons in each orbital is two" – a more sophisticated statement is "no two electrons can have the same four Principal Quantum Numbers").
- Know Hund's Rule of Maximum Multiplicity (if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs)

After working through this Factsheet you will:-
- be familiar with the concept of Molecular Orbital Theory
- be able to apply the LCAO approximation to generate some simple molecular orbital diagrams
- be able to draw conclusions from molecular orbital diagrams regarding the likely stability of some simple diatomic molecules

Introduction

The aim of molecular orbital theory is to describe molecules in a similar way to that in which we describe atoms, which is in terms of orbitals, orbital diagrams, and electron configurations.

Atomic Orbital Diagram for an oxygen atom, O

2p ↑↓ ↑ ↑
2s ↑↓
1s ↑↓

Each line in a molecular orbital diagram represents a molecular orbital, which is the volume within which a high percentage of the negative charge generated by the electron is to be found. We assume that the electrons would fill the molecular orbitals of molecules in the same way as electrons fill atomic orbitals in atoms.
- The molecular orbitals are filled in a way that yields the lowest potential energy for the molecule.
- The maximum number of electrons in each molecular orbital is two. (i.e. the Pauli Exclusion Principle.)
- Orbitals of equal energy are half filled with parallel spin before they begin to pair up. (i.e. Hund's Rule.)

Drawing Molecular Orbital Diagrams for Simple Diatomic Molecules

The concept of bonding and anti-bonding molecular orbitals is most easily approached by analogy with the interaction of light waves, which means that we need to remember that an electron can be considered to behave as a wave as well as a particle.

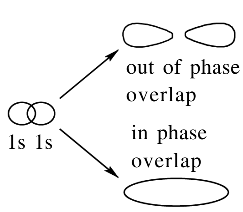
Light waves can interact in-phase, which leads to an increase in the intensity of the light (brighter) and out-of-phase, which leads to a decrease in the intensity of the light (less bright). Electron waves can also interact in-phase and out-of-phase.

In-phase interaction leads to an increase in the intensity of the negative charge between the bonded nuclei, which therefore increases the electrostatic attraction between the electrons and the nuclei of the bonded atoms. As the attraction is stronger, the potential energy is lower so energy would therefore be needed to move the electrons back into the separate atomic orbitals. This therefore holds the atoms together. Hence, this type of overlap is called a *bonding molecular orbital.*

Out-of-phase interaction leads to a decrease in the intensity of the negative charge between the nuclei and thus a decrease in the electrostatic attraction between the electrons and the nuclei of the bonded atoms. This weaker attraction results in a higher potential energy and so an overlap of this type will destabilise the bond and is therefore called an *anti-bonding molecular orbital.*

We can therefore produce molecular orbital diagrams for some small diatomic molecules using an approach called the Linear Combination of Atomic Orbitals (LCAO). The following assumptions are necessary:
- Molecular orbitals are formed from the overlap of atomic orbitals.
- Only atomic orbitals of the same energy interact to a significant degree.
- When two atomic orbitals overlap, they interact in two extreme ways to form two molecular orbitals; a bonding molecular orbital (due to in-phase interaction) and an anti-bonding molecular orbital (due to out-of-phase interaction).

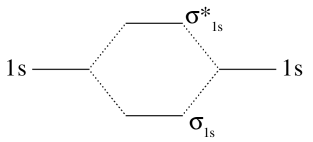
The simplest possible overlap results from the interaction of two 1s atomic orbitals.



σ^*_{1s} The sigma, σ, symbol indicates that the molecular orbital is symmetrical around the bond, while the asterisk indicates that this is an anti-bonding molecular orbital

σ_{1s} The sigma, σ, symbol indicates that the molecular orbital is symmetrical around the bond, while the lack of an asterisk indicates that it is a bonding molecular orbital

This diagram can be abbreviated to:

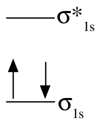


In order to complete the molecular orbital diagram a set procedure is followed:
- Count up the total number of electrons in the molecule, using the atomic numbers
- Assign the electrons to the orbitals from bottom (lowest energy) to top (highest energy) until all the electrons have been added.
- As in the familiar 'electron-in-boxes' notation used for atoms, the electrons are shown as arrows, with the first arrow in each orbital pointing up and the second pointing down (to indicate opposite spins).
- Orbitals of equal energy are half-filled before any pairing.

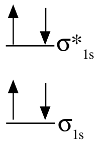
The stability of the bond is then described in terms of the bond order, where:
Bond Order = ½ (number of electrons in bonding MOs – number of electrons in anti-bonding MOs)

- If Bond Order = zero then the bond / molecule is unstable
- If Bond Order > zero then this suggests a stable molecule
- The higher the Bond Order the more stable the bond

The complete diagram for a hydrogen molecule, H_2, is therefore:



Therefore Bond Order = ½ (2 – 0) = 1 suggesting that H_2 is stable. Whereas, for the hypothetical diatomic helium molecule, He_2, we get:



Therefore Bond Order = ½ (2 – 2) = 0 suggesting that He_2 is unstable. Hence, as you know, it does do exist – a molecule of helium is just a single atom!

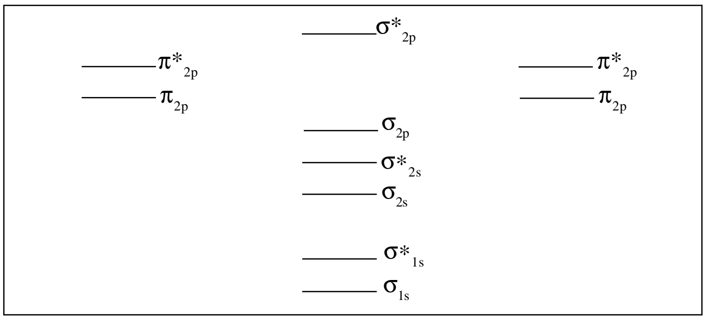
For the combination of larger atoms to form diatomic molecules, more atomic orbitals will interact. As above the 1s atomic orbital from each bonded atom will overlap to form a σ_{1s} bonding molecular orbital and a σ^*_{1s} anti-bonding molecular orbital.

Similarly the 2s atomic orbitals overlap to form a σ_{2s} bonding molecular orbital and a σ^*_{2s} anti-bonding molecular orbital. These are similar in shape to the ó$_{1s}$ bonding molecular orbital and σ^*_{1s} anti-bonding molecular orbital; but larger and of higher potential energy.

The p atomic orbitals can overlap in two different ways; parallel or end-on. The end-on overlap of the $2p_x$ atomic orbitals gives rise to sigma, σ, molecular orbitals; symmetrical about the axis of the bond. Parallel overlap of the $2p_y$ or $2p_z$ atomic orbitals, on the other hand, produces pi (π) molecular orbitals that are asymmetrical about the axis of the bond. These ideas should remind you of the bonding in molecules such as ethene and benzene.

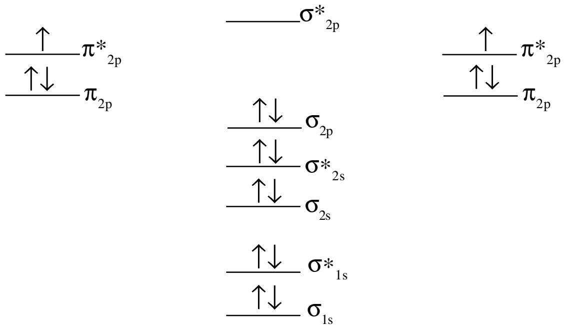
The parallel atomic orbitals overlap to a lesser extent than the end-on orbitals. The end result of this is that the in-phase interaction results in a higher potential energy for the pi bonding molecular orbital than for the sigma bonding molecular orbital. However, when the interaction is out-of-phase the pi anti-bonding molecular orbital will have a lower potential energy than the sigma anti-bonding molecular orbital.

The overall molecular orbital diagram for the overlap of 1s, 2s and 2p atomic orbitals is therefore:



So, for the oxygen molecule, O_2, with 16 electrons in total, the complete diagram is:

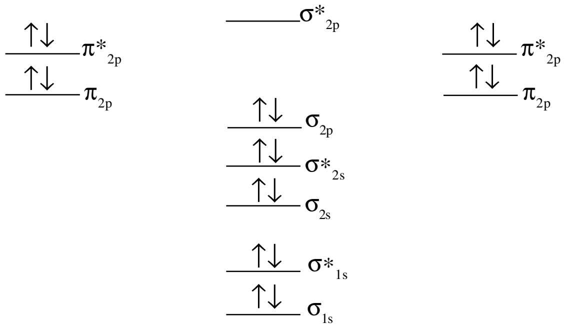
Molecular orbital diagram for an oxygen molecule, O_2.



This gives a Bond Order of ½ (10 – 6) = 2, suggesting that the oxygen molecule is stable.

For fluorine, F_2, with 18 electrons this becomes:

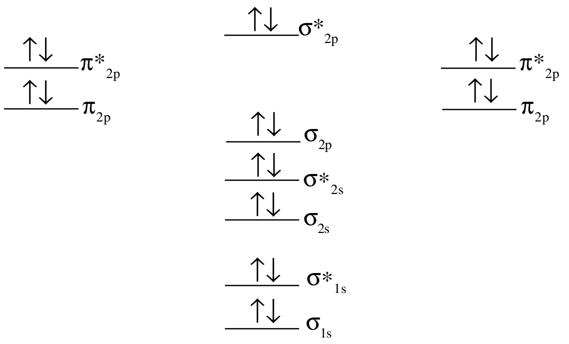
Molecular orbital diagram for an fluorine molecule, F_2.



Giving Bond Order = ½ (10 – 8) = 1 suggesting that the fluorine molecule is stable.

Finally, a diatomic neon molecule, Ne_2, with 20 electrons would give the following diagram:

Molecular orbital diagram for an neon molecule, Ne_2.



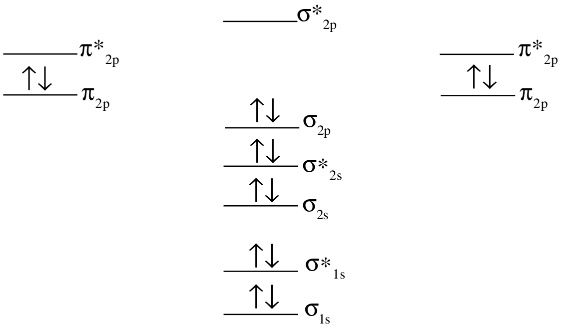
Hence Bond Order for Ne_2 = ½ (10-10) = 0; this confirms the instability of this molecule – as you should know, the neon molecule is just a single atom.

Practice Questions

1. Complete a molecular orbital diagram and calculate the bond order for a molecule of carbon monoxide, CO.
2. Complete a molecular orbital diagram and calculate the bond order for a molecule of nitrogen monoxide, NO.

Answers

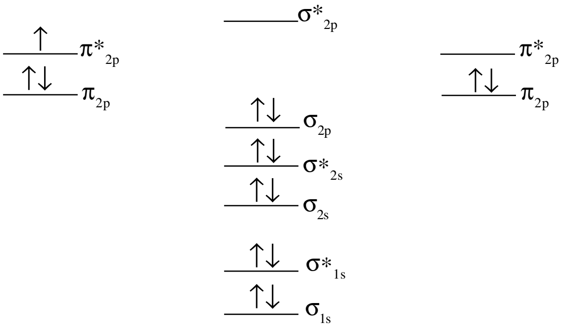
1. CO (6 + 8 electrons)



Bond Order CO = ½ (10 – 4) = 3

So CO is stable – note that CO's electron configuration is the same as N_2.

2. NO (7 + 8 electrons)



Bond order NO = ½ (10 - 5) = 2.5

So NO is stable.

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