### Bond Order

Simple models of bonding include the concepts of **single**, **double** and **triple bonds**. Molecular orbital theory provides us with a natural and general definition of bond order that includes all of these and also intermediate bonds as follows:

\[
\text{Bond Order} = \frac{1}{2} (\text{No. of bonding electrons} - \text{No. of anti-bonding electrons})
\]

**E.g.**
- \( \text{H}_2 \) bond order = 1 (2 electrons in a \( s \) orbital)
- \( \text{HF} \) bond order = 1 (2 electrons in a \( s \) orbital; 6 in non-bonding)
- \( \text{H}_2^+ \) bond order = 0.5 (1 electron in a \( s \) orbital)
- \( \text{H}_2^- \) bond order = 0.5 = \( \frac{1}{2} (2 - 1) \) (2 electrons in a bonding orbital, 1 antibonding)

**E.g.:**
- \( R = \bar{R} \) (H)
- \( R = \bar{R} \) (H)
- \( 2a \) (H)
- \( 1s \) (H)
- \( 0.735 \) Å (H)

**E.g.:**
- \( \text{H}_2^+ \) bond order = 0.5 (1 electron in a \( s \) orbital)
- \( \text{H}_2 \) bond order = 1 (2 electrons in a \( s \) orbital)
- \( \text{H}_2^- \) bond order = 0.5 = \( \frac{1}{2} (2 - 1) \) (2 electrons in a bonding orbital, 1 antibonding)
- \( \text{He}_2 \) is not bound
Molecular Orbitals in $F_2$: Where were we?

The lowest two molecular orbitals are $s$ and $s^*$. The other five filled orbitals have the same characteristics. Bonding orbitals have electrons delocalised between two nuclei, but in multiple lobes.

The next lowest energy orbitals are $p$ bonding - delocalised between the nuclei with nodes along the internuclear axis. This orbital is a $s$ bonding orbital. No node between the nuclei, and symmetric about the internuclear axis.

The highest energy occupied orbitals are $p^*$ antibonding (nodes between the nuclei). There are also nodes along the internuclear axis.

Molecular Orbitals in $F_2$: Where were we?

The bond order in $F_2$ is obtained by counting electrons in the various kinds of orbitals thus

\[
\frac{1}{2} (4 + 4 - 2) = 1, \text{ the same as } H_2. 
\]

The $p$ bonding orbitals and $p^*$ antibonding orbitals contribute nothing overall to the bond - that is, to the delocalisation of electrons between the nuclei.

The lower $s$ bonding and $s^*$ antibonding orbitals likewise contribute nothing overall to the bond.

The bond forms because the overall energy of $F_2$ is lower than $2F$.

The bond order of 1 arises from the filled (higher) $s$ bonding orbital.

Diatomic molecules with fewer electrons (in antibonding orbitals) will have a higher bond order.
Electron Densities in \( \text{H}_2, \text{F}_2 \), and \( \text{HF} \)

The square of a wavefunction tells us the charge density distribution in an orbital. If we add up the charge densities from all the molecular orbitals, then we get the overall charge density distribution in the molecule.

1. \( \text{H}_2 \)

This shows the surface within which the probability of finding an electron is 95%. It is simply the square of the \( \phi_{\text{HOMO}} \).

2. \( \text{F}_2 \)

In \( \text{F}_2 \) the 95% surface includes all the occupied MO’s. The general effect is seen by adding them together.

3. \( \text{HF} \)

In \( \text{HF} \) the 95% surface looks like a simple sigma bond, but the electrons accumulate more around the \( \text{F} \) atom (compare \( \text{H}_2 \)).

Bonding in \( \text{O}_2 \)

As two \( \text{O} \) atoms approach one another, some of the electrons become delocalised and the allowed energy levels change, lowering the total energy of the system.

Energy levels in \( \text{O}_2 \)

As the two nuclei approach each other, the energies of the valence electrons change, forming bonding and anti-bonding orbitals. The energy is a minimum at the equilibrium bond length (1.24 Å).

Note that 2p and 2s electrons are non-degenerate. Hund’s rule tells us to maximise the number of electrons with unpaired spins.

The energy of the core electrons does not change as the two nuclei approach and form a bond.
The O₂ ground electronic state has 12 (=16 total - 4 core) valence electrons and a bond order of 1.24 Å (O₂)

$$\text{O}_2 \text{ has two unpaired electrons in its p}^* \text{ orbitals, so it will be paramagnetic.}$$

$$\frac{1}{2} (4 \text{ s electrons} - 2 \text{ s}^* \text{ electrons} + 4 \text{ p electrons} - 2 \text{ p}^* \text{ electrons}) = 2$$

**Bonding in N₂**

N₂ has 14 valence electrons. The allowed energies and ground electron configuration of N₂ is shown below. Note that the orbitals are virtually identical in shape to O₂ and F₂. In N₂ the p* orbitals are empty

Bond order = ½ (8 - 3) = 2

**Worked Example: The Ground State Electronic Configuration of NO and its ions**

What are the ground state electron configurations and bond order in NO, NO⁺ and NO⁻?

NO has 5 + 6 = 11 valence electrons. Filling from the lowest energy gives the configuration shown.

The bond order is ½ (8 - 3) = 2.5 NO is paramagnetic.

NO⁺ has 10 valence electrons, so there is no electron in the p* orbital.

Bond order = ½ (8 - 2) = 3

NO⁻ has 12 valence electrons, so there are two electrons in the p* orbital.

Bond order = ½ (8 - 4) = 2
Types of Orbitals and Bonds

We now know of five kinds of molecular orbitals formed by valence electrons.

1. s (bonding) and s* (antibonding) orbitals
2. p (bonding) and p* (antibonding) orbitals
3. Non-bonding (nb) orbitals are localised on only one atom.

Bonding orbitals have electron density delocalised between two (or more) nuclei.

Antibonding orbitals have nodes between nuclei: electrons not as delocalised.

A filled bonding plus antibonding orbital has approximately the same effect on bond formation as two filled non-bonding orbitals, i.e. They contribute nothing to the bond order.

Orbitals in Heteronuclear Diatomics: NO

In homonuclear diatomics, all the bonding orbitals are symmetrical if reflected in the mid-plane of the internuclear axis.

We know that this is not true for HF, nor is it for other heteronuclear diatomics, including NO.

Charge Distribution in Heteronuclear Diatomics

The overall distribution of electron density in heteronuclear diatomic molecules is uneven due to the higher nuclear charge and electron configuration of the two different atoms.

In NO the distribution of charge slightly favours O.

Bonds between unlike atoms are said to be polar. Polar bonds can occur in diatomic or polyatomic molecules.

The bonding in HF is extremely polar: to the extent that the H atom is nearly bare!
Triatomic and Polyatomic Molecules

CO$_2$ is a simple triatomic molecule that can be represented O-C-O.

This representation says nothing about bond order or about molecular shape, only that in CO$_2$ both oxygen atoms are bonded to carbon.

Both C-O bonds in CO$_2$ are polar, as they are different atoms. Each polar bond can be characterised by a dipole, and described by a dipole moment. A dipole is represented by an arrow from the more positive to the more negative end of the molecule.

E.g. HF has a large dipole. (NO has a small one.)

The equilibrium structure of CO$_2$ is

Although each C-O bond is polar, the two bond dipoles are equal and opposite, so this linear triatomic molecule has no net dipole. The electron density distribution is symmetrical about the central C. (More examples later.)

Electronic Spectroscopy of Molecules

We have already noted that molecules absorb in broad bands rather than discrete lines, due to the existence of non-electronic quantum states (to be discussed later). However the electronic structure of molecules provides information about the transmission and colour associated with absorbance and emission due to transitions between electronic states.

As with atoms, absorbance occurs when an electron is promoted from an occupied molecular orbital into a vacancy in a higher molecular orbital by a photon of the correct wavelength.

The longest wavelength absorbance thus corresponds to the lowest energy transition

$$E = \frac{hc}{\lambda}$$

The lowest energy difference is a transition of an electron from the HOMO to the LUMO.

Electronic Spectroscopy of Molecules

Calculation of MO’s and their energies this give us direct predictions of absorbance energies (or wavelengths).

Conversely, measurements of absorbance spectra can yield experimental information about the electronic states of molecules (and test aspects of quantum theory and the accuracy of numerical calculations).

In the transitions shown in the schematic energy level diagram at right, DE is smallest for the HOMO $\rightarrow$ LUMO transition, higher for HOMO-1 $\rightarrow$ LUMO, and higher still for HOMO $\rightarrow$ LUMO+1, yielding increasingly shorter wavelengths.
Summary

You should now be able to

- Distinguish between various types of bonding, anti-bonding and non-bonding orbitals
- Distinguish between polar and apolar bonds in diatomic molecules and relate it to electron attraction of a nucleus.
- Draw out ground state electronic configurations for molecules and molecular ions given their allowed energy levels.
- Calculate bond order from molecular electronic configurations.
- Relate Electronic Absorbance Spectra to electronic structure.

Next Lecture

- Bonding in and properties of metals, semiconductors and insulators.