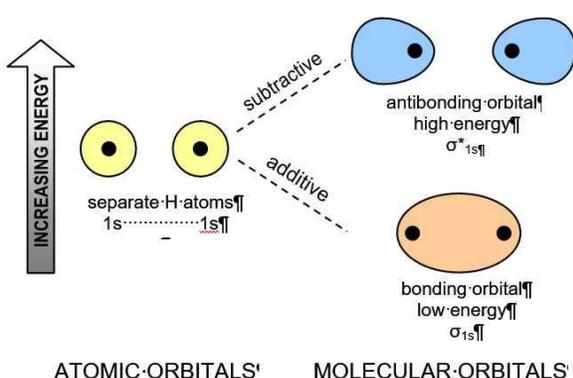


Molecular Orbitals

Molecular orbital theory describes molecules in a similar way to atoms, using orbitals, orbital diagrams and electron configurations. Molecular orbital theory provides an alternative model to valence bond theory that better describes the electron behaviour and physical/chemical properties of certain molecules. The key difference between the two models is that in valence bond theory, electrons are localized between two specific atoms in the molecule, whereas in molecular orbital theory, the electron pairs are distributed in sets of molecular orbitals which can extend over the entire molecule.

Atomic orbitals (AOs) are used to describe individual atoms or monatomic ions.

Molecular orbitals (MOs) are formed by overlapping atomic orbitals within a molecule. Only atomic orbitals of comparable energy levels can interact to any significant degree. MO theory predicts two ways for the individual atomic orbitals involved in molecular bonds to interact: an additive way (bonding) and a subtractive way (antibonding). The diagram below uses hydrogen atomic orbitals to show the two types of bonding.



When atomic orbitals overlap additively, the electrons spend the majority of their time in the space in between the two nuclei (indicated by the black dots in the diagram). Because the electrons are attracted to both nuclei, it's easier to maintain the electrons in this area, so it's a lower-energy position than the original atomic orbitals and it's more stable. (Remember: low energy = higher stability!) This type of overlap is called a **bonding**

orbital. For a single bond, or the primary bond in a multiple bond, it's called a σ (sigma) orbital. For a secondary bond within a multiple bond, it's called a π orbital. The subscript on the MO (1s, in this example) tells us which AO the electrons came from.

When atomic orbitals overlap in a subtractive way, the electrons spend the majority of their time in the space outside the two nuclei. There is now no negative force attracting the positive charge of the nuclei closer to the centre, so there is more repulsion between the nuclei themselves. Having electrons outside the space between the nuclei requires more energy than keeping those same electrons in their atomic orbitals. The bond is destabilized, so orbitals like this are called **antibonding orbitals**. Antibonding orbitals are marked with an asterisk, so there are σ^* (sigma-star) and π^* (pi-star) orbitals.

Just as in the hybridization model, the number of atomic orbitals you start with is the number of orbitals (MOs, in this case) you end up with. The same rules we applied for filling atomic orbitals also apply to molecular orbitals: (1) they are filled in a way that yields the lowest potential energy for the molecule, (2) the maximum number of electrons in each molecular orbital is two, and (3) orbitals of equal energy are filled



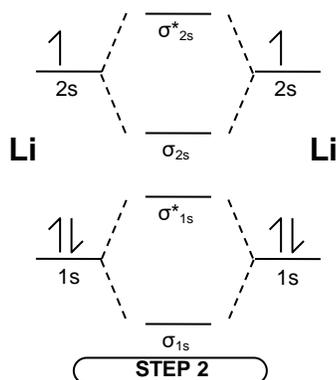
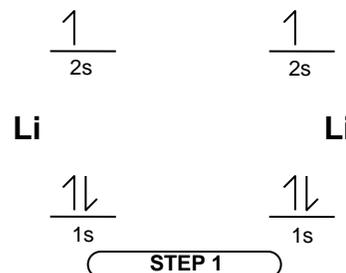
singly with parallel spin electrons before pairing up electrons.

THE MOLECULAR ORBITAL DIAGRAM

The molecular orbital diagram shows the creation and filling of MOs in a bond. Within the diagram, orbitals are represented by horizontal lines. The higher up an orbital is drawn, the higher an energy level it has. The lower down an orbital is drawn, the lower an energy level it has. When constructing the molecular orbital diagram, the atomic orbitals for each atom involved in the bond are drawn on the outside edges of the diagram; the MOs go between them.

Consider the MO diagram for Li_2 . This is a bond between two lithium atoms, which have an electron configuration of $1s^2 2s^1$. The 2s AO is at a higher energy level than the 1s AO, so it should be higher in the diagram.

The electrons are filled into their AOs. Now we combine the electrons into MOs to see what sort of bonding takes place.

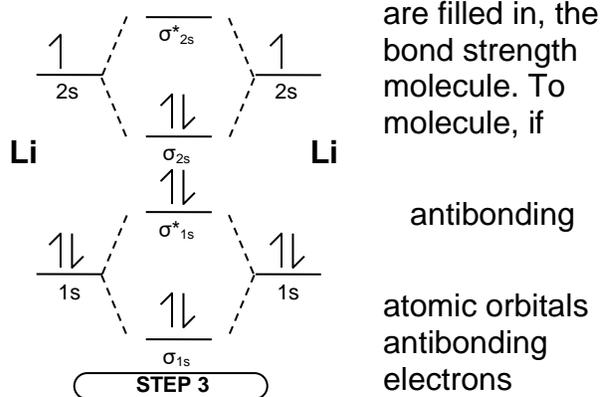


Draw dotted lines up and down from each set of atomic orbitals that have the same energy to the MOs that correspond to them. For s orbitals, σ and σ^* orbitals form in the bond, with the bonding orbitals at the lower energy position. The electrons from the atomic orbitals forming the molecular orbitals must be filled in according to the rules mentioned previously. One electron from each atom goes down to filling the bonding orbital first, and then extra electrons would fill the antibonding orbital. Remember that an electron from an atomic orbital can only follow a dotted line to get to an MO.

After the electrons diagram will tell you a few things like the and the magnetic properties of the find out what type of bonding exists in the any, we use the formula:

$$\text{bond order} = \frac{1}{2}(\# \text{ bonding electrons} - \# \text{ electrons})$$

You don't need to count electrons from where both the MO bonding and orbitals are filled since all non-valence cancel out to 0 using this calculation. This you know about valence electrons being the only ones involved in bonding.



are filled in, the bond strength molecule. To molecule, if antibonding atomic orbitals antibonding electrons confirms what

A **bond order** of 0 means that no bond forms and the molecule is unstable (will not exist). A bond order of more than 0 means bonding is stable; the molecule will exist, but it may be highly reactive. In our Li_2 diagram, there are 2 electrons in bonding orbital at level 2, and 0 electrons in the antibonding orbital at level 2. According to the formula above the bond order for this molecule would be $\frac{1}{2}(2 - 0) = 1$. A bond order of 1 means



there is a single bond. That means Li_2 could be stable, even though lithium is a metal and should therefore undergo metallic bonding instead of forming discrete molecules. In fact it is possible to create diatomic molecular lithium at extremely high temperatures. Molecular orbital theory can tell us about theoretical molecules and polyatomic ions, and whether they would be stable enough to exist.

A bond order of 2 represents a double bond, and 3 a triple bond. Molecular orbitals can also produce fractions for bond order, which can represent a delocalized bond (which is a more realistic way of describing what happens with resonance structures) or a stable bond within a highly reactive substance.

The magnetic properties of the molecule as shown by molecular orbital diagrams will be discussed in the next section after the formation of MO's from p level atomic orbitals.

MAGNETISM AND 2p ORBITALS

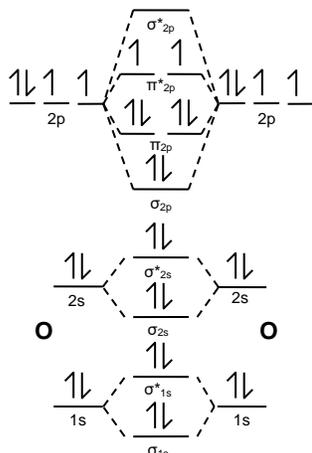
Molecular orbital structures involving p atomic orbitals are more complex. Overlapping p atomic orbitals form π and π^* MOs, along with the σ and σ^* MOs. Two atoms with six p AOs in total create six new MOs. Because MOs are drawn in energy order from highest to lowest, top to bottom, it is important to know which of these molecular orbitals have higher energy. It's fine to just memorize this information at this stage; you are *not* responsible for predicting the sequence for a particular atom.

You are only likely to be asked about the second-row elements: B, C, N, O, F, Ne. Among those elements there are some traits that are always true:

- The MOs that derive from 2p AOs have higher energy than those from 2s AOs.
- There is one σ_{2p} orbital, two π_{2p} orbitals, two π^*_{2p} orbitals and one σ^*_{2p} orbital.
- The π_{2p} orbitals have exactly the same energy (i.e., they are degenerate orbitals), and therefore are drawn next to each other in a molecular orbital diagram. The π^*_{2p} orbitals have equal energy as well, and are also drawn side by side.
- The σ^*_{2p} orbital has the highest energy, and is at the top of the diagram. The pair of π^*_{2p} orbitals have the next highest energy.

The only thing that changes is the energy level of the σ_{2p} orbital versus the π_{2p} orbitals.

In B_2 , C_2 and N_2 , σ_{2p} has a higher energy than π_{2p} and in O_2 and F_2 , π_{2p} has a higher energy than σ_{2p} .



Shown here is a complete molecular orbital diagram for O_2 . An oxygen atom by itself has the electron configuration $1s^2 2s^2 2p^4$. The configuration is shown in the AOs on the left and right sides of the diagram. The electrons in the 1s and 2s AOs completely fill the σ MOs that they create, so these electrons will not contribute to the bond order.

Each oxygen contributes 4 electrons from its 2p orbitals. The electrons completely fill the 3 bonding orbitals, with the remaining 2 electrons going into the π^*_{2p} antibonding orbitals. Hund's Rule still applies in MO's: each electron goes into a different orbital, rather than both electrons



going into the same one. Note that these 2 electrons have the same spin.

The fact that O_2 has two unpaired electrons explains a property of O_2 : when it is cooled to a liquid, it is attracted to the poles of a magnet. A molecular structure that results in unpaired electrons in degenerate MOs, like O_2 , is called **paramagnetic**. Li_2 has all of its electrons neatly paired up in the orbitals. Li_2 is **diamagnetic**.

EXERCISES

- Calculate the bond order of the O_2 molecule from the diagram on the previous page. What type of bond would you expect it to have?
- Construct a molecular orbital diagram for He_2 and calculate its bond order. What type of bond would you expect it to have?
- Construct a molecular orbital diagram for the “hydrogen molecule ion” H_2^+ by using an H atom on one side and an H^+ ion on the other side. Calculate the bond order for H_2^+ . What properties would you expect it to have?
- What is the main difference between the structures of the MO diagrams of N_2 and O_2 ?
- The acetylide ion has the structure C_2^{2-} . Construct its molecular orbital diagram by using C^- ions on both sides. Calculate acetylide’s bond order. Is it paramagnetic or diamagnetic?

SOLUTIONS

- $\frac{1}{2}(6 - 2) = 2$; double bond
- See orbital diagram #1. Bond order is $\frac{1}{2}(2 - 2) = 0$; no bond. He_2 would be unstable.
- See orbital diagram #2. Bond order is $\frac{1}{2}(1 - 0) = \frac{1}{2}$. It is paramagnetic, since it has an unpaired electron in the molecular orbitals, and it should be very reactive, since it has a low bond order.
- The order of the bonding orbitals derived from 2p atomic orbitals would be reversed: σ_{2p} would be above π_{2p} .
- See orbital diagram #3. $\frac{1}{2}(6 - 0) = 3$; triple bond. It is diamagnetic, since its electrons are balanced in terms of spin.

