Making Molecules

If we start off by thinking about making dihydrogen we know that, from much earlier in school, each hydrogen atom has one electron and each would like two, giving a full first shell. From our GCSE way of thinking of this we would draw a dot and cross diagram to show how this happens (see Figure 1).

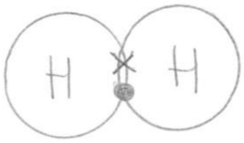

Figure 1. Dot and cross diagram of H_2.

Question: draw out dot and cross diagrams for N_2,CH_4, H_2O, CO_2 and CO

This dot and cross diagram shows that each hydrogen now has a full shell, but it doesn't explain how this lowers the energy of the electrons, making the molecule stable. To think about this we need to consider how the energy varies as we bring the two atoms together, this is shown in Figure 2. Here we can see that as we bring two atoms closer together we see a decrease in energy which is favourable until we reach a minimum which equates to the bond length (this is where the atoms are actually found). Past this point, moving the atoms closer together, leads to a massive increase in energy due to repulsion between the atoms.

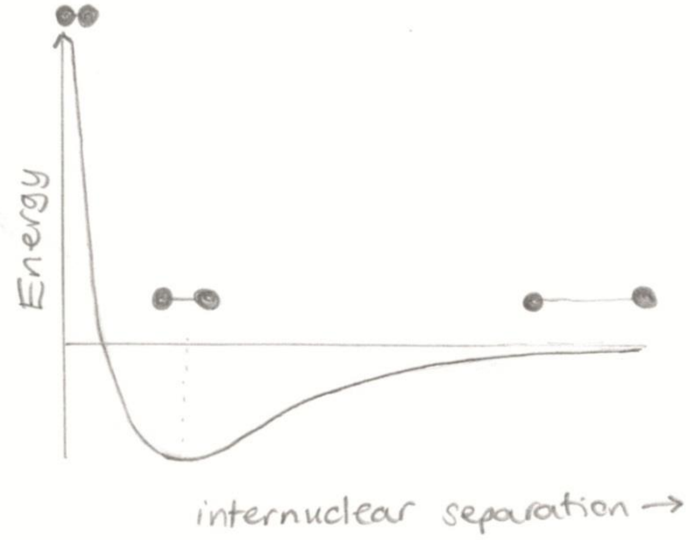

Figure 2. Showing how the energy varies as two atoms are brought closer and closer together. Here the lowest point on the graph is the most stable arrangement.

So what happens as we bring the atoms together; why do we see this decrease in energy? This is the point where we need to think about how the atomic orbitals, the orbitals on the individual atoms, combine together to form molecular orbitals. This happens through a process called the “linear combination of atomic orbitals”, i.e. simply adding them together. This is most easily shown pictorially, so see Figure 3.

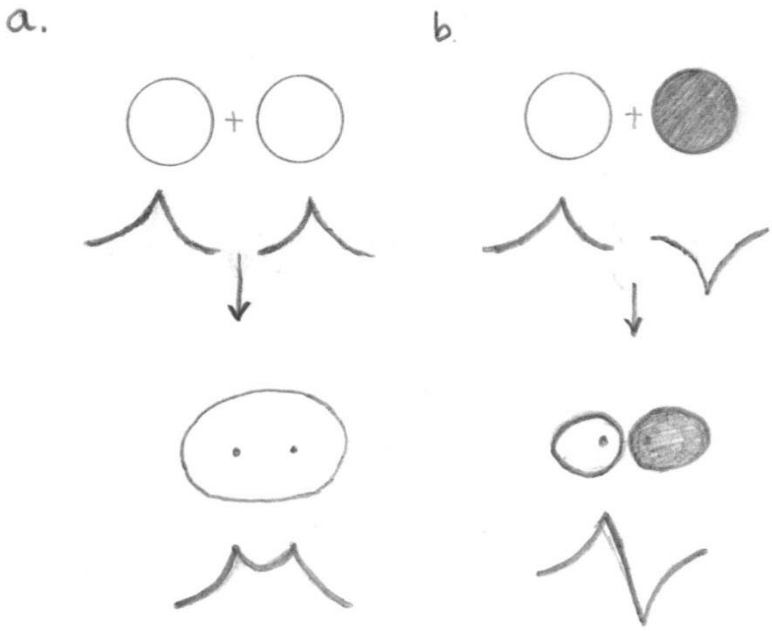

Figure 3. Showing the formation of the bonding and antibonding orbitals through the addition of a) in phase to give a bonding interaction and b) out of phase to give an antibonding interaction.

From Figure 3 we can see that if we start off with one electron in each of the hydrogen 1s-orbitals there are two ways these can combine; either in or out of phase. The in phase combination gives a favourable interaction which, due to the electrons now being attracted to both nuclei, is lower in energy, whilst the out of phase combination leads to a less favourable as the electron density is pushed away from the internuclear region, the most favourable place for the electrons to be as here they are attracted to both positive nuclei. As well as thinking about the existence of these molecular orbitals we have to be able to populate them with electrons. To do this we draw out an MO (molecular orbital) diagram showing the energies of the atomic orbitals and the molecular orbitals (see Figure 4). Each line in this MO diagram represents one orbital and we know that an orbital can hold two electrons so we put them in the lowest energy molecular orbital we can.

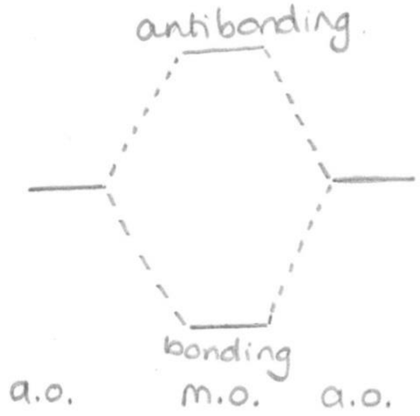

Figure 4. Showing how we represent the bonding and anti-bonding orbitals in a molecular orbital diagram (a.o. = atomic orbital, m.o. = molecular orbital)

Question: can you work out what the MO diagrams for H_2 and H_2^+ would look like with the electrons in. From the diagrams can you tell which will have the stronger bond?

(Answer 1 on the page below.)

Once we are happy with dihydrogen we can use the same analysis on helium. The orbital interactions are the same with two 1s-orbitals being available to overlap.

Question: Draw out the MO diagram for He_2 and put the electrons into the appropriate molecular orbitals. Using your diagram, do you think that He_2 exists? What about He_2^+? Explain your answers.

(Answer 2 on the page below)

From these examples we can see that electrons in the lower orbital contribute to bonding whilst those in the upper orbital take away from the bonding character. Therefore we call the favourable, lower orbital the “bonding” orbital and the unfavourable one the “antibonding” orbital. The bond order for a molecule is then given by:

$$\text{Bond order} = \frac{\text{no. of } e^- \text{ in bonding orbitals} - \text{no. of } e^- \text{ in antibonding orbitals}}{2}$$

This equation is useful to us as it can allow us to work out whether we have a single, double or triple bond, something in between, or indeed no bond at all.

For H_2 we would have bond order = (2 – 0)/2 = 1, i.e. a single bond.

For He_2 we would have bond order = (2 – 2)/2 = 0, i.e. no bond.

Question: What would the bond orders be for He_2^+ and H_2^+?

Answer 1: The MO diagrams will be as shown in Figure 1 in Activity 2, H_2 will have the stronger bond as it has two electrons in the favourable low energy orbital whilst H_2^+ has only one.

Answer 2: As He_2 would have two electrons in the bottom, favourable orbital and two in the top, unfavourable, orbital the effects cancel out and hence we would not expect He_2 to exist. The molecules would rather be separate. By removing and electron and forming He_2^+ we find that there are now more electrons in the favourable orbital than the unfavourable on and hence existing as a dimer is now favourable.