One More Problem…

Although this MO diagram is correct for O_2 and F_2, we find that for the earlier diatomics in the second row there is a problem which comes about from the fact that earlier on in the period the 2s and 2p-orbitals are closer together in energy. The elements from lithium to nitrogen where the atoms are close enough that the sigma anti-bonding orbital formed from the s-orbitals interacts with the sigma bonding orbital formed from the p-orbitals. This changes the order of the orbitals, raising the $2\sigma_g$ (see the labels in Figure 2) above the pi MOs, the outcome of this is shown in Figure 1.

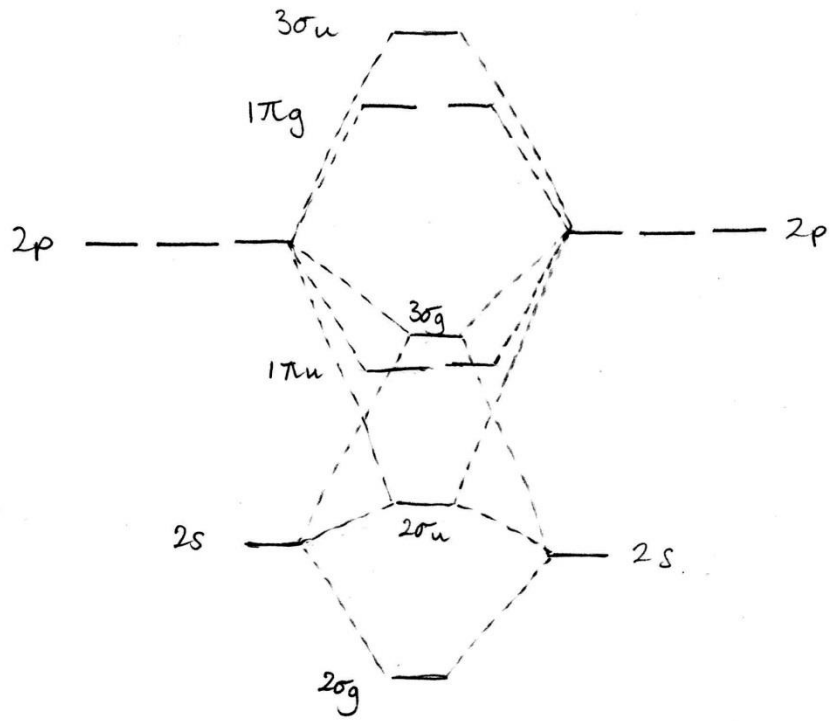

Figure 1. Showing the extra interaction which can occur between the sigma orbitals, lowering the energy of the $2\sigma_u$ whilst raising the $3\sigma_g$.

Bearing this change in mind, we now have MO diagrams which could be used for any of the 2nd row homonuclear (two of the same atom) diatomics. The final point we need to think about when putting the electrons into these orbitals is that we now have some degenerate (same energy) orbitals and so we have to consider how we fill these. As they are the same energy the most favourable arrangement of the electrons is to put one in each of the degenerate orbitals first and then they are paired up before moving onto the next energy level up.

Question: Using this information draw the MO diagram for all of the rest of the 2nd row homonuclear diatomics and work out their bond orders.

What happens when two different atoms join together?

When different atoms join together the energies of the atomic orbitals we are starting with are different from each other with the more electronegative atom being lower in energy. When we then make molecular orbitals from these atomic orbitals we find that the degree of stabilisation for the bonding orbital (how far down in energy it moves) and destabilisation (how far up in energy it moves) for the anti-bonding orbital is lessened, and the more different in energy our atomic orbitals are the smaller the change we see. This is shown in Figure 2.

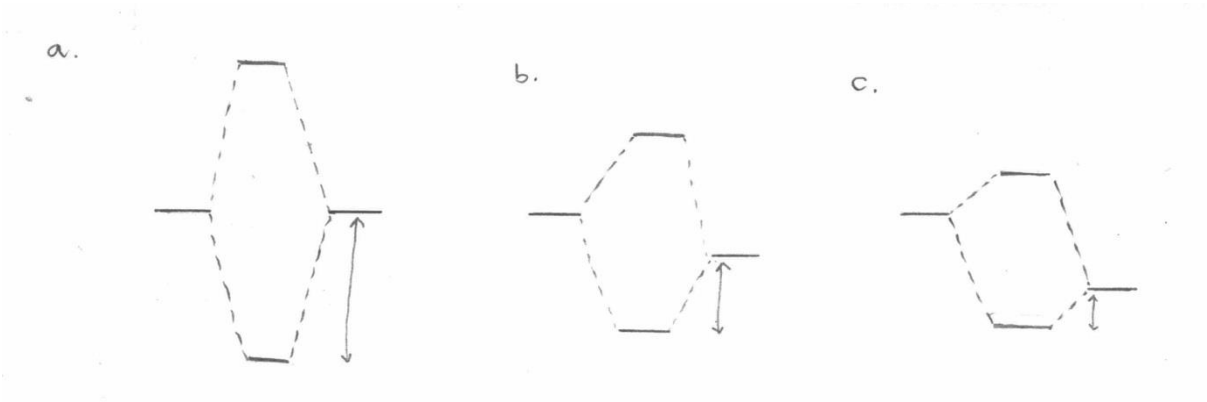

Figure 2. Showing how the stabilisation energy (shown by the arrow in each case) decreases as the energy difference between the two atomic orbitals increases.

Question: Could you use all of this information to draw out the MO diagrams for CO and LiH?