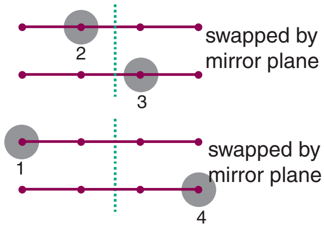
5 Electrons in molecules: polyatomics

5.1 Consider a hypothetical molecule in which four hydrogen atoms lie in a row. Like H_3^+, this molecule has a mirror plane down the middle. As shown opposite, atoms 2 and 3, and atoms 1 and 4 are swapped by the mirror plane. We therefore need to consider the AOs on atoms 2 and 3 together, and the AOs on atoms 1 and 4 together.



Draw sketches of the symmetric and antisymmetric combinations of AOs on atoms 2 and 3 (i.e. the symmetry orbitals), and then do the same for the AOs on atoms 1 and 4. Using the rule that only AOs of the same symmetry overlap, sketch the form of the four MOs, two symmetric and two antisymmetric, which are formed from the overlap of the SOs.

Arrange these MOs in order of increasing energy by looking at the number of nodes in the MOs. What does your MO diagram predict about the hypothetical molecule H_4?

5.2 Construct an MO diagram for a hypothetical linear water molecule, H–O–H, using a similar approach to that used for FHF^-; take the z-axis to be along the axis of the molecule. Sketch the form of the MOs, and indicate which will be occupied.

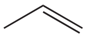
[Hints: The orbitals can be classified according to a mirror plane, as we did in FHF^-. The two hydrogen $1s$ form a symmetric and an antisymmetric SO, and the oxygen $2s$ and $2p_z$ can be classified individually. The oxygen $2p_x$ and $2p_y$ have the wrong symmetry to overlap with the hydrogen $1s$ (why?), and so remain nonbonding.]

Compare your MO diagram with that for 'bent' water. Using these two diagrams, rationalize why it is that water adopts a bent, rather than a linear, geometry.

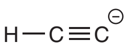
5.3 Using appropriate HAOs, described the bonding in each of the following molecules, being sure to specify the form of each occupied MO, and also making sure that you have accounted for all the electrons. Identify the HOMO and the LUMO for the first three molecules.

(a) $H_3C—CH_3$

(b)

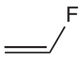


(c)

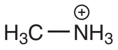


$H—C\equiv C^{\ominus}$

(d)

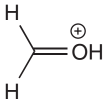


(e)



$H_3C—\overset{\oplus}{N}H_3$

(f)



5.4 Using a similar approach to that used in section 5.5 on page 159, construct an MO diagram for F_2 assuming that (i) the two fluorine atoms are sp hybridized and (ii) the two fluorine atoms are sp^3 hybridized. State which orbitals are occupied and compare the resulting descriptions of the bonding with that from the full MO picture (Fig. 4.27 on page 122).

Use a similar approach to construct an MO diagram for CO using sp hybrids on both atoms; remember to place the oxygen AOs and HAOs somewhat lower in energy than the corresponding orbitals on carbon. What does your diagram predict about the form of the HOMO and the LUMO? Compare your predictions about the MOs with the computed orbitals shown in Fig. 4.41 on page 137.

5.5 The MO diagram for the linear form of H_3^+ can be constructed by realizing that it is just three 1*s* orbitals in a row. The resulting MOs have the same form as the π MOs in the allyl cation, except that they are composed of 1*s* AOs. Compare the MOs deduced using this approach to those found in section 5.1.1 on page 143 using symmetry arguments.

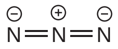
5.6 Using the graphical method described in section 5.8.1 on page 168, deduce the form of the π MOs of hexatriene (CH_2=CH–CH=CH–CH=CH_2). Which MOs are occupied?

Identify the contribution (in terms of bonding or antibonding) that each occupied MO makes to the π bonding between the end two carbons (numbered 1 and 2). Do the same for the bonding between carbons 2 and 3, and between 3 and 4. Based on your results, which of these bonds has the greatest net bonding interaction, and which has the least?

5.7 Using the graphical method described in section 5.8.1 on page 168, deduce the form of the π MOs of the cation (CH_2=CH–CH=CH–CH_2^+). Which MOs are occupied?

Adding one electron to this species gives a radical, and adding a further electron gives an anion. Explain what effect you would expect adding one or two extra electrons to have on the strength of the π bonding.

5.8 The azide ion, N_3^-, has a symmetrical linear structure. Describe the bonding in this ion by using *sp* hybrids on each atom, and by forming delocalized π MOs from the 2*p* orbitals which point perpendicular to the long axis (the *z*-axis) of the molecule. Note that there will be two separate π systems: one formed form the $2p_x$, and one from the $2p_y$ AOs. Identify the HOMO and the LUMO.



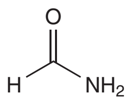
$\overset{\ominus}{N}{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}$

Compare your MO picture with the bonding shown in the localized structure of azide, shown opposite.

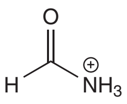
The molecules CO_2 and NO_2^+ are both symmetrical and linear, and can be described as being *isoelectronic* with N_3^-. What do you understand by this term? How does your MO description of the bonding in the azide ion need to be modified to describe CO_2 and NO_2^+?

5.9 Using appropriate HAOs, describe and compare the bonding in the following three molecules.

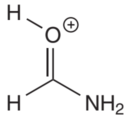
(a)



(b)



(c)



5.10 In the cyclopropenyl cation (shown below) a π system is formed from the overlap of an out-of-plane $2p_z$ AO from each carbon. The MOs formed from these AOs have exactly the same form as the MOs for triangular H_3^+ found in section 5.1.2 on page 144, except that they are formed from $2p_z$ AOs, rather than 1*s* AOs.

Carefully count up how many electrons there are in this molecule, and hence determine which of the π MOs are occupied. Compare the form of the occupied π MOs with those for the allyl cation, commenting on any relevant points of difference.