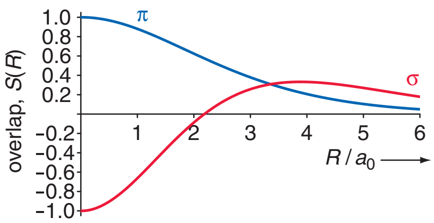
4 Electrons in molecules: diatomics

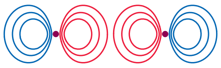
4.1 Explain how the bonding and antibonding MOs are formed in H_2^+, and rationalize why it is that the energy of the bonding MO shows a minimum when plotted as a function of the internuclear separation R, whereas the energy of the antibonding MO simply increases as R decreases.

Construct a MO diagram for H_2^+, and make rough sketches of the form of the MOs. Explain how symmetry labels are assigned to the two MOs.

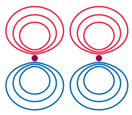
4.2 Explain what is meant by the overlap integral between two AOs, and also explain why this quantity goes to zero for large distances between the two AOs. How would you expect the plot of $S(R)$ to compare between two $1s$ AOs and two $2s$ AOs?

Shown below is a plot of the overlap integral between two $2p$ orbitals. The blue line is for the sideways-on overlap to give π MOs, whereas the red line is for the head-on overlap to give σ MOs. Explain the form of these two curves.





σ-type overlap



π-type overlap

4.3 Use MO diagrams to rationalize why He_2 is an unknown species, but the ion He_2^+ has been observed. Make what predictions you can about the stability of the molecules He_2^{2+} and H_2^{2-} with respect to dissociation.

4.4 Suppose that there is overlap between the $2p_z$ AOs from two atoms A and B, where z is the internuclear axis. Sketch the form of the MO diagram, and the form of the bonding and antibonding MOs, for the following cases: (a) A and B of very similar electronegativity; (b) A somewhat more electronegative than B; (c) A much more electronegative than B.

If the resulting bonding MO is occupied by a pair of electrons, what consequences would this have for the polarity of the A–B bond in these three cases?

4.5 Consider the overlap between a $3d_{xy}$ AO on one atom and a $2p$ AO on a second atom as these two approach one another along the x-axis. Explain, using sketches, whether or not there is overlap between the $3d_{xy}$ and each of the three $2p$ orbitals in turn. If there is overlap, classify the resulting MO as having σ or π symmetry.

Do the same for a $3d_{x^2-y^2}$ AO interacting with each of the $2p$ AOs.

4.6 Explain why the *overall* sign of the MO wavefunction is not important, whereas the relative signs of two AOs which are forming an MO is of significance.

4.7 In O_2 the lowest energy MO is given the label $1\sigma_g$ and the next lowest is $1\sigma_u$. Explain how these MOs are formed (i.e. from which AOs); sketch the form of the MOs.

Explain why it is that although both of these MOs are occupied, they make little contribution to the bonding in O_2.

4.8 The dissociation energy of N_2 is 942 kJ mol^{-1}, whereas that for N_2^+ is 842 kJ mol^{-1}; the dissociation energy of O_2 is 494 kJ mol^{-1}, whereas that for O_2^+ is 642 kJ mol^{-1}. rationalize these data.

4.9 Sketch an MO diagram for BeH. On the basis of your diagram, would you expect this molecule to be stable with respect to dissociation into atoms? Use your MO diagram to predict any other properties you can.

4.10 Construct an MO diagram for the diatomic molecule CH, label the MOs, indicate which orbitals are occupied, and sketch the form of the occupied orbitals. The relevant orbital energies are: H 1*s* −14 eV; C 2*s* −19 eV; C 2*p* −12 eV. To a first approximation, you can ignore the interaction between the H 1*s* and the C 2*s* (why?).

What does your MO diagram predict about CH and its ion CH^+?

4.11 Explain what you understand by the statement that CN^- is *isoelectronic* with CO.

Construct an approximate MO diagram for CN^-, indicate which MOs are occupied and explain what the diagram predicts about this molecule.

4.12 We argued that in H_2 the atoms are held together as a result of the build-up of electron density along the internuclear axis. However, in LiF there is practically no such build up. What, then, holds the atoms in LiF together, and in what way is this different to H_2?