6 Bonding in solids

6.1 In Fig. 6.1 on page 183 are shown the MOs (or COs) formed from a chain of *s* orbitals. We can just as well form such COs from chains of $2p$ AOs. Assuming that the chain is aligned along the z-axis, sketch the form of the *lowest* and *highest* energy COs for a chain composed of: (a) $2p_x$ AOs, and (b) $2p_z$ AOs. Comment on any differences between the COs you have drawn.

6.2 Use the idea of overlapping bands to rationalize why both lithium and beryllium are metallic conductors, and why the enthalpy of vaporization of beryllium (found to be 324 kJ mol^{-1}) is significantly greater than that of lithium (found to be 159 kJ mol^{-1}).

6.3 The bond length on the discrete (gaseous) Li_2 molecule is 267 pm, and the bond dissociation energy is 105 kJ mol^{-1} (i.e. 52.5 kJ is required to create one mole of Li atoms). For metallic lithium, the Li–Li spacing is 304 pm, and the enthalpy of vaporization is 159 kJ mol^{-1}(i.e. 159 kJ is required to create one mole of Li atoms). Discuss these data in the light of the different type of bonding in Li_2(g) and Li(m).

6.4 What is the difference between a metallic conductor and a semiconductor, and how can this difference be explained using band theory? Explain why diamond is an insulator, whereas silicon is a semiconductor.

If a small fraction of the Si atoms in solid silicon are replaced by phosphorus atoms, it is observed that the conductivity of the material increases significantly. Rationalize this observation (hint: how many electrons does a P atom have compared to a Si atom?).

6.5 What do you understand by the statement 'BN is isoelectronic with C_2'?

Solid boron nitride (BN) can exist in two forms. The α-form consists of hexagonal layers, is a soft material, and is an electrical insulator with a band gap of around 5.2 eV. The β-form is a very hard, abrasive material, which is also an insulator. By comparison with the allotropes of carbon, propose a structure for the β-form of BN, and explain why the α-form is an insulator.

6.6 Graphite can be 'doped' by exposing the material to potassium vapour. In the resulting materials the potassium atoms are found to fit *between* the layers of carbon atoms in the original structure, and it is also found that doping increases the electrical conductivity greatly. Use band theory to explain why doping with potassium increases the conductivity (hint: the outer electron from a K atom is easily removed: where might it be transferred to?).

Similarly, doping with bromine vapour leads to the incorporation of Br atoms between the layers, again accompanied by an increase in the conductivity. Explain why this is so.

6.7 Use the standard enthalpy changes given for the following processes to compute the lattice enthalpy of $MgBr_2(s)$:

$$\begin{array}{rcll}
\mathrm{Mg(s)} & \longrightarrow & \mathrm{Mg(g)} & 147\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Br_2(l)} & \longrightarrow & \mathrm{2\,Br(g)} & 224\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Mg(g)} & \longrightarrow & \mathrm{Mg^{+}(g)} & 738\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Mg^{+}(g)} & \longrightarrow & \mathrm{Mg^{2+}(g)} & 1451\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Br(g)} & \longrightarrow & \mathrm{Br^{-}(g)} & -325\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Mg(s) + Br_2(l)} & \longrightarrow & \mathrm{MgBr_2(s)} & -524\ \mathrm{kJ\ mol^{-1}}
\end{array}$$

6.8 (Requires a knowledge of elementary calculus) In section 6.2.1 on page 191 it was shown that the energy of a chain of ions with alternating charges is given by

$$E = -N_{\mathrm{A}}\mathcal{A}\frac{z^2e^2}{4\pi\varepsilon_0 r} + \frac{N_{\mathrm{A}}C}{r^n}.$$

The value of r at which this energy is a minimum, the equilibrium separation r_{e}, is found by computing the derivative with respect to r, and then setting this derivative equal to zero:

$$\frac{\mathrm{d}E}{\mathrm{d}r} = 0$$

Assuming that all of the other parameters do not depend on r (i.e. are constants), find the derivative and, by setting it equal to zero, show that the constant C is given by:

$$C = \frac{\mathcal{A}z^2e^2r^{n-1}}{4\pi\varepsilon_0 n}.$$

Substitute this expression for C into the original expression for the energy E and hence, after some tidying up, obtain Eq. 6.2 on page 193.

6.9 Use the Kapustinskii equation, Eq. 6.5 on page 197, along with the radii listed in Table 6.3 on page 196 to estimate the lattice enthalpy of $MgBr_2$. Compare your answer to the value obtained in question 6.7.

Calculate the lattice enthalpy using the full expression given in Eq. 6.4 on page 195 using the following values for the parameters: $r_{\mathrm{e}} = 270.7$ pm, $\mathcal{A} = 2.355$ and $n = 9$ (recall that $e = 1.602 \times 10^{-19}$ C and $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}). You need to be careful with units: r_{e} must be in m, and the energy will come out in J mol^{-1}.

6.10 (a) The discrete diatomic molecule MgO is known in the gas phase and has a bond length of 175 pm. If we *assume* that the this molecule consists of Mg^{2+} and O^{2-} ions held together by an electrostatic interaction then we can work out the energy change for

$$\mathrm{Mg^{2+}(g) + O^{2-}(g) \longrightarrow Mg^{2+}O^{2-}(g)}$$

by using Eq. 6.2 on page 193 with $\mathcal{A} = 1$:

$$E_{\mathrm{dimer}} = -N_{\mathrm{A}}\frac{z^2e^2}{4\pi\varepsilon_0 r_{\mathrm{e}}}\left(1 - \frac{1}{n}\right).$$

Taking $n = 7$ and $z = 2$, and being careful with the units, compute E_{dimer} in kJ mol^{-1}. Hence, given the following standard enthalpy changes

$$\begin{array}{rcll}
\mathrm{Mg(g)} & \longrightarrow & \mathrm{Mg^{2+}(g)} & 2188\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{O(g)} & \longrightarrow & \mathrm{O^{2-}(g)} & 703\ \mathrm{kJ\ mol^{-1}},
\end{array}$$

determine the enthalpy change for

$$\mathrm{Mg(g) + O(g) \longrightarrow Mg^{2+}O^{2-}(g)}.$$

(b) Solid MgO is a crystalline solid with an Mg–O spacing of 210.2 pm. Compute its lattice enthalpy using Eq. 6.4 on page 195 taking $\mathcal{A} = 1.7476$ and $n = 7$. Hence determine the enthalpy change for

$$\text{Mg(g)} + \text{O(g)} \longrightarrow \text{MgO(s)}.$$

(c) Compare and comment on your answers to (a) and (b).