1. (a) The electron configuration is shown on the diagram, including the parallel spins of the electrons in $1\pi^*$:

$$(1\sigma)^2 (1\sigma^*)^2 (1\pi)^4 (2\sigma)^2 $$(1\pi^*)^2$$

(b) bond order bond length / \AA

<table>
<thead>
<tr>
<th>species</th>
<th>electronic configuration</th>
<th>bond order</th>
<th>bond length / \AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>$\frac{1}{2} (8 - 4) = 2$</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>$\frac{1}{2} (8 - 3) = 5/2$</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>$\frac{1}{2} (8 - 5) = 3/2$</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>O$_2^{2-}$</td>
<td>$\frac{1}{2} (8 - 6) = 1$</td>
<td>1.49</td>
<td></td>
</tr>
</tbody>
</table>

The bond order is clearly related to the bond length – the larger the bond order, the shorter the bond. The bond order reflects the relative number of bonding and antibonding electrons.

Bonding electrons act to bind the atoms more strongly and reduce the bond length. Antibonding electrons act to weaken and hence lengthen the bond.

2.

<table>
<thead>
<tr>
<th>species</th>
<th>electronic configuration</th>
<th>bond order</th>
<th>change in bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$</td>
<td>$(1\sigma)^2$</td>
<td>$\frac{1}{2} (2 - 0) = 1$</td>
<td>(no bond)</td>
</tr>
<tr>
<td>Li$_2^+$</td>
<td>$(1\sigma)^1$</td>
<td>$\frac{1}{2} (1 - 0) = \frac{1}{2}$</td>
<td>increase</td>
</tr>
<tr>
<td>Li$_2^-$</td>
<td>$(1\sigma)^2(1\sigma^*)^1$</td>
<td>$\frac{1}{2} (2 - 1) = \frac{1}{2}$</td>
<td>increase (longer than Li$_2^+$)</td>
</tr>
<tr>
<td>Be$_2$</td>
<td>$(1\sigma)^2(1\sigma^*)^2$</td>
<td>$\frac{1}{2} (2 - 2) = 0$</td>
<td>(no bond)</td>
</tr>
<tr>
<td>Be$_2^+$</td>
<td>$(1\sigma)^2(1\sigma^*)^1$</td>
<td>$\frac{1}{2} (2 - 1) = \frac{1}{2}$</td>
<td>decrease</td>
</tr>
<tr>
<td>Be$_2^-$</td>
<td>$(1\sigma)^2(1\sigma^*)^2(2\pi)^1$</td>
<td>$\frac{1}{2} (3 - 2) = \frac{1}{2}$</td>
<td>decrease (longer than Be$_2^+$)</td>
</tr>
<tr>
<td>B$_2$</td>
<td>$(1\sigma)^2(1\sigma^*)^2(2\pi)^2$</td>
<td>$\frac{1}{2} (4 - 2) = 1$</td>
<td></td>
</tr>
<tr>
<td>B$_2^+$</td>
<td>$(1\sigma)^2(1\sigma^*)^1(2\pi)^1$</td>
<td>$\frac{1}{2} (3 - 2) = \frac{1}{2}$</td>
<td>increase</td>
</tr>
<tr>
<td>Molecular symbol</td>
<td>Electron Configuration</td>
<td>Bond Order</td>
<td>Type</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------------</td>
<td>------------</td>
<td>------</td>
</tr>
<tr>
<td>B$_2^-$</td>
<td>(1σ)$^3$(1σ*)$^2$</td>
<td>½ (4 – 2) = 3/2</td>
<td>decrease</td>
</tr>
<tr>
<td>C$_2$</td>
<td>(1σ)$^2$(1σ*)$^2$</td>
<td>½ (6 – 2) = 2</td>
<td></td>
</tr>
<tr>
<td>C$_2^+$</td>
<td>(1σ)$^2$(1σ*)$^1$</td>
<td>½ (5 – 2) = 3/2</td>
<td>increase</td>
</tr>
<tr>
<td>C$_2^-$</td>
<td>(1σ)$^2$(1σ*)$^1$</td>
<td>½ (7 – 2) = 5/2</td>
<td>decrease</td>
</tr>
<tr>
<td>N$_2$</td>
<td>(1σ)$^2$(1σ*)$^2$</td>
<td>½ (8 – 2) = 3</td>
<td></td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>(1σ)$^2$(1σ*)$^1$</td>
<td>½ (7 – 2) = 5/2</td>
<td>increase</td>
</tr>
<tr>
<td>N$_2^-$</td>
<td>(1σ)$^2$(1σ*)$^1$</td>
<td>½ (7 – 2) = 5/2</td>
<td>increase (longer than N$_2^+$)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^2$</td>
<td>½ (8 – 4) = 2</td>
<td></td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>(1σ)$^2$(1σ*)$^2$</td>
<td>½ (8 – 3) = 5/2</td>
<td>decrease</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>(1σ)$^2$(1σ*)$^1$(2π)$^3$</td>
<td>½ (8 – 5) = 1.5</td>
<td>increase</td>
</tr>
<tr>
<td>F$_2$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^2$</td>
<td>½ (8 – 6) = 1</td>
<td></td>
</tr>
<tr>
<td>F$_2^+$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^3$</td>
<td>½ (8 – 5) = 3/2</td>
<td>decrease</td>
</tr>
<tr>
<td>F$_2^-$</td>
<td>(1σ)$^2$(1σ*)$^2$</td>
<td>½ (8 – 7) = ½</td>
<td>increase</td>
</tr>
<tr>
<td>Ne$_2$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^4$</td>
<td>½ (8 – 8) = 1</td>
<td>(no bond)</td>
</tr>
<tr>
<td>Ne$_2^+$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^4$</td>
<td>½ (8 – 7) = ½</td>
<td>decrease</td>
</tr>
<tr>
<td>Ne$_2^-$</td>
<td>(1σ)$^2$(1σ*)$^2$(2π)$^4$(2σ)$^2$</td>
<td>½ (9 – 8) = ½</td>
<td>decrease but unlikely to exist (longer than Ne$_2^+$)</td>
</tr>
</tbody>
</table>

The bond order is a fairly good indication of the bond length. Due to the increasing nuclear charge, there is a trend towards shorter bonds as the period is crossed.

Ne$_2^-$ has an electron in the σ bonding orbital formed from overlap of the 3s orbitals. These are large and diffuse and it is unlikely that the ½ bond that results would be enough to hold the molecule together.

3. The ionic radii are: Na$^+$ (0.102 nm), Br$^-$ (0.196 nm), Cl$^-$ (0.181 nm). The radius ratio for NaBr, $r_+/r_-$ = 0.520, is smaller than for NaCl (0.563), suggesting that Na$^+$ can more easily fit into the octahedral interstices of the NaCl structure. There is insufficient space to fit 8 bromide ions around sodium so the CsCl structure is not formed.
4. The unit cell of a face-centred cubic or fcc lattice has an atom on each corner and an atom in centre of each face. There is no atom in the centre of the cube.

Although this might sound like it leaves a large hole in the centre, the structure is close packed. The diagram shows the close packed layers in different colours. The packing in these layers repeats every 4th layer.

An interactive version of the structure can be viewed at:
http://firstyear.chem.usyd.edu.au/calculators/solidstate

5. Using Planck’s relationship:

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{470 \times 10^{-9}} = 4.23 \times 10^{-19} \text{ J}$$

(As 1 eV = 1.602 × 10^{-19} J, $\Delta E = \frac{4.23 \times 10^{-19}}{1.602 \times 10^{-19}} = 2.60 \text{ eV}$)

A wavelength of 470 nm corresponds to blue light. This is the light that is absorbed by CdS. The colour observed is the complementary colour – white light with the absorbed colour removed as shown on the colour wheel opposite. The complementary colour of blue is orange and hence CdS is expected to be orange / yellow - a sample is shown on the right.

6. The NaCl unit is cubic with Cl⁻ ions on the corners and the centres of each face (i.e. a fcc lattice) and Na⁺ ions on the middle of each edge and in the centre of the cube (i.e. in the octahedral holes in the fcc lattice). The cations and anions ‘touch’ in the ionic model so the length of the cube side, a, is:

$$a = r_{\text{Cl}^-} + 2r_{\text{Na}^+} + r_{\text{Cl}^-} = (1.81 + 2 \times 1.02 + 1.81) \text{ Å} = 5.66 \text{ Å}$$

The cell is cubic so the volume, V, is:

$$V = a^3 = (5.66 \times 10^{-10})^3 \text{ m}^3 = 1.81 \times 10^{-28} \text{ m}^3$$
When working out the mass of the cube, it is important to only count the mass that is enclosed in this unit cell and is not in the neighbouring cells. Thus:

- the Cl\textsuperscript{−} ions on the corners of the cube are *shared* by 8 cells \( \rightarrow 8 \) corners
- the Cl\textsuperscript{−} ions on the faces of the cube are *shared* by 2 cells \( \rightarrow 6 \) faces

The total number of Cl\textsuperscript{−} ions is then:

\[
8 \times \frac{1}{8} (\text{corners}) + 6 \times \frac{1}{2} (\text{faces}) = 4
\]

Similarly, for Na\textsuperscript{+}:

- the Na\textsuperscript{+} ions on the edges of the cube are *shared* by *four* cells – there are 12 faces
- the Na\textsuperscript{+} ions in the centre of the cell is only in this cell. – there is 1 centre

The total number of Na\textsuperscript{+} ions is then:

\[
12 \times \frac{1}{4} (\text{edges}) + 1 \times 1 (\text{centre}) = 4
\]

The number of Na\textsuperscript{+} ions has to equal the number of Cl\textsuperscript{−} ions as the stoichiometry of NaCl is 1:1.

The atomic mass gives the mass of a mole of atoms. The mass of a Cl\textsuperscript{−} and a Na\textsuperscript{+} ion can therefore be worked out from the atomic mass and Avogadro’s number. The total mass of 4 Cl\textsuperscript{−} and 4 Na\textsuperscript{+} ions is therefore:

\[
\text{mass of cube} = 4 \times \frac{35.45 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \text{ (Cl)} + 4 \times \frac{22.99 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \text{ (Na)}
\]

\[
= 3.88 \times 10^{-22} \text{ g}
\]

Using the mass and the volume, the density can be calculated:

\[
\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{3.88 \times 10^{-22} \text{ g}}{1.81 \times 10^{-28} \text{ m}^3}
\]

\[
= 2.14 \times 10^6 \text{ g m}^{-3} = 2.14 \text{ g cm}^{-3} \text{ (as } 1 \text{ m}^3 = 10^6 \text{ cm}^3\text{)}
\]

If the number of cubes is doubled, the mass and the volume both double and the density is unaffected. Similarly, taking 10, 1000 or \(6.022 \times 10^{23}\) cubes will increase the mass and the volume by the same amount so the density is the same. The experimental density of a grain of salt is 2.14 g cm\textsuperscript{−3}. From microscopic information (atomic parameters (radii and masses) and a knowledge of the atomic positions), a macroscopic property has been determined!

This technique is used to check crystal structures determined from X-ray diffraction. Any difference in the density determined from the unit cell and that measured experimentally is likely to be due to atoms having been missed in the X-ray experiment or errors in the identification of the atoms present.