1 The iron atoms in haemoglobin are in the oxidation state +2 and are in an octahedral environment. Each iron atom is surrounded by five nitrogen-containing ligands, and one oxygen-containing ligand, which is H₂O in deoxyhaemoglobin and O₂ in oxyhaemoglobin.

In an octahedral environment, the \(d_{x^2-r^2}\) and \(d_{z^2}\) orbitals are at a higher energy than the \(d_{xy}\), \(d_{xz}\) and \(d_{yz}\) orbitals. The difference in energy between the two sets of d orbitals is known as the energy gap, \(\Delta E\).

(a) Draw a fully labeled diagram to show how the d-orbitals of Fe²⁺ are split in an octahedral environment such as haemoglobin, and use your diagram to outline the origin of the red colour of haemoglobin.

In the presence of ligands, the partially filled 3d orbitals of Fe²⁺ split into two different energy levels. The difference in the two energy levels, \(\Delta E\), is small, and falls within the visible region of the electromagnetic spectrum. An electron in a lower d orbital energy level can absorb radiation in the visible spectrum and be promoted to the higher d orbital energy level, where there are vacancies. This d→d electron transition gives rise to the red colour. The red colour seen is the complement of the absorbed green colour.

When the H₂O ligand in haemoglobin is changed to an O₂ ligand, the Fe²⁺ ion changes its electronic configuration from a ‘high spin’ state to a ‘low spin’ state.

In a ‘high spin’ state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a ‘low spin’ state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.
(b) Use diagrams like the one drawn in (a) to show the electronic distribution of a Fe\textsuperscript{2+} ion in a high spin state, and in a low spin state.

(c) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.  
Interelectronic repulsion would be present between electrons occupying the same orbital.

(d) Using this explanation, together with the information given above concerning the spins states of deoxyhaemoglobin and oxyhaemoglobin, state and explain which of the two haemoglobins will contain the larger energy gap, $\Delta E$, between its d-orbitals.

Oxyhaemoglobin would have the larger energy gap.

The electrons would pair up in the lower energy d-orbitals (low spin) if the energy gap, $\Delta E$, is greater than the repulsion energy between electrons occupying the same orbital.

For deoxyhaemoglobin, the energy gap is small enough such that it is energetically more favourable to occupy all the d-orbitals singly before pairing up (high spin).

(e) Would you expect a Cu\textsuperscript{2+} ion in an octahedral environment to be able to display both ‘high spin” and ‘low spin’ states? Explain your answer.

No. Cu\textsuperscript{2+} has 9 3d electrons. There is only one way to fill the two levels of d orbitals and hence high spin / low spin states are not possible.

Adapted from N2011 P3 Q4