- Determine the value of n that corresponds to the lowest excited state of He^+ from which radiation with a wavelength of 600 nm is able to ionise the electron (*i.e.* excite it to a state of $n = \infty$). Show all working. **2**

For a 1-electron atom or ion, the energy levels are given exactly by the equation,

$$E = -Z^2E_R\left(\frac{1}{n^2}\right)$$

Ionization corresponds to excitation from level n_1 to level $n_2 = \infty$:

$$\Delta E = -Z^2E_R\left(\frac{1}{\infty^2} - \frac{1}{n_1{}^2}\right) = Z^2E_R\left(\frac{1}{n_1{}^2}\right)$$

Radiation with wavelength 600 nm has energy:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s})(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{600 \times 10^{-9}\ \mathrm{m}} = 3.31 \times 10^{-19}\ \mathrm{J}$$

If this is able to provide the energy required to ionize He^+ ($Z = 2$) from level n_1:

$$Z^2E_R\left(\frac{1}{n_1{}^2}\right) = 2^2 \times (2.18 \times 10^{-18}\ \mathrm{J}) \times \left(\frac{1}{n_1{}^2}\right) = 3.31 \times 10^{-19}\ \mathrm{J}$$

This gives $n_1 = 5.13$. As n must be an integer, the radiation can ionize from $n = 6$ or above.

Answer: $\boldsymbol{n = 6}$

Marks 4

- Moseley discovered experimentally in 1913 that the atomic number, Z, of an element is inversely proportional to the square root of the wavelength, λ, of fluorescent X-rays emitted when an electron drops from the n = 2 to the n = 1 shell.

$$i.e. \quad \frac{1}{\sqrt{\lambda}} = kZ$$

Derive an expression for the constant of proportionality, k, for a hydrogen-like atom which would allow the value of k to be theoretically calculated.

Squaring Moseley's relationship gives $\frac{1}{\lambda} = (kZ)^2$ (1)

The energy of an X-ray with wavelength λ is given by $E = \frac{hc}{\lambda}$. Substituting in Moseley's value for $\frac{1}{\lambda}$ from (1) gives:

$$E = hc(kZ)^2 \quad (2)$$

For a hydrogen like atom, an electron in an orbital with quantum number n has energy $E = -Z^2E_R\left(\frac{1}{n^2}\right)$ where E_R is the Rydberg constant.

The energy *emitted* when an electron moves from an orbital with quantum number n = 2 to an orbital with quantum number n = 1 is:

$$E = [-Z^2E_R\left(\frac{1}{2^2}\right)] - [-Z^2E_R\left(\frac{1}{1^2}\right)] = Z^2E_R\left(\frac{3}{4}\right) \quad (3)$$

Equating equations (2) and (3) gives:

$$hc(kZ)^2 = Z^2E_R\left(\frac{3}{4}\right)$$

Rearranging for k gives:

$$k = \sqrt{\frac{3E_R}{4hc}}$$

- One problem with the Rutherford model of the atom was that there was nothing to stop the electrons from spiralling into the nucleus. Briefly explain how the quantum theory of the electrons resolved this problem. **2**

Classical theory held that a negatively charged particle orbiting a positive one would lose energy continuously.

In quantum theory, the energy of the electrons is quantised and only certain values are allowed. The lowest allowed energy level has *n* = 1. The most probable distance of finding an electron in this level is not at the nucleus.

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation emitted when the electron in Li^{2+} drops from an n = 4 state to an n = 2 state. **2**

As Li^{2+} has 1 electron, its energy levels are described by the equation $E_n = \frac{-E_R Z^2}{n^2}$ where $E_R = 2.18 \times 10^{-18}$ J and Z = 3.

The energies of the n = 4 and n =2 levels are:

$$E_4 = \frac{-E_R(3)^2}{(4)^2} = -\frac{9}{16}E_R \text{ and } E_2 = \frac{-E_R(3)^2}{(2)^2} = -\frac{9}{4}E_R = -\frac{36}{16}E_R$$

The energy separation is:

$$\Delta E = E_4 - E_2 = \left[-\frac{9}{16}E_R\right] - \left[-\frac{36}{16}E_R\right] = \frac{27}{16}E_R$$

$$= \frac{27}{16} \times (2.18 \times 10^{-18}) = 3.68 \times 10^{-18} \text{ J}$$

Using $E = \frac{hc}{\lambda}$, $\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^{8})}{(3.68 \times 10^{-18})} = 5.40 \times 10^{-8} \text{ m} = 54.0 \text{ nm}$

Energy = **3.68 × 10^{-18} J**	Wavelength = **54.0 nm**

- Identify two specific features of atomic structure that can only be explained by reference to the wave-like nature of electrons. Give reasons. **2**

Electrons occupy certain stable "orbits" that correspond to the standing waves obtained by solving the Schrödinger Equation. Each solution (orbital) corresponds to a different allowed energy level. As a consequence of this;

- **electrons do not spiral in towards the nucleus despite the electrostatic attraction between them**
- **the light emitted by excited atoms is a series of discrete spectral lines corresponding to the energy differences between the allowed energy states.**

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation emitted when the electron in Be^{3+} drops from an n = 3 state to an n = 2 state. **3**

Be^{3+} has only 1 e^- so the equation $E_n = \dfrac{-E_R Z^2}{n^2}$ where $E_R = 2.18 \times 10^{-18}$ J can be used. Be has Z = 4.

The energy of the n = 3 and n =2 levels are:

$$E_3 = \frac{-E_R (4)^2}{(3)^2} = -\frac{16}{9} E_R \text{ and } E_2 = \frac{-E_R (4)^2}{(2)^2} = -\frac{16}{4} E_R = -4E_R$$

The energy separation is $\dfrac{20}{9} E_R = \dfrac{20}{9} \times (2.18 \times 10^{-18}) = 4.84 \times 10^{-18}$ **J**

As $E = \dfrac{hc}{\lambda}$,

$$\lambda = \frac{hc}{E} = \frac{(6.634\times10^{-34})\times(2.998\times10^{8})}{(4.84\times10^{-18})} = 4.11\times10^{-8} \text{ m} = 41.1 \text{nm}$$

Energy = **4.84 × 10^{-18} J**	Wavelength = **41.1 nm**

- Identify one property used by Mendeleev to organise elements in his periodic table. 2

One from: atomic volume, stoichiometry of oxides, hydroxides, chloride and other compounds, melting points of elements and compounds, chemical reactivity and atomic mass

Provide a brief explanation of the origin of the periodicity of this property in terms of the quantum theory of atomic structure.

For atomic volume: atomic volume increases going down the groups of the table as new valence shells are filled.

For stoichiometry of compounds: compounds of elements in the same group show the same stoichiometry because they have the same configuration of valence electrons and therefore combine with the same number of atoms of another element to form a stable electronic configuration. Moving across a period, the stoichiometry changes as the number of valence electrons changes.

For melting points of elements and compounds: the type of bonding found in an element (metallic, covalent, dispersion) and in compounds (ionic, covalent, intermolecular) depends on the number of electrons in the outer shell. Elements on the left hand side of the periodic table have few valence electrons and relatively low nuclear charges favouring formation of metallic bonds in the element and ionic bonds in compounds. Elements on the right hand side have configurations just short of stable ones and tend to form covalent bonds with each other and ionic bonds with the metals.

2

- The lowest four energy levels of the He^+ ion are given.

Principal quantum number (n)	Energy (J)
1	-8.720×10^{-18}
2	-2.180×10^{-18}
3	-0.969×10^{-18}
4	-0.545×10^{-18}

An electronic transition is identified by specifying the value of n of the initial state and the value of n of the final state. Identify the electronic transition responsible for the emission of radiation from He^+ with a wavelength of 30.4 nm?

The wavelength of light is related to its energy through Planck's equation:

$$E = \frac{hc}{\lambda}$$

Substituting the values for Planck's constant (h), the speed of light (c) and the wavelength gives:

$$E = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})(2.998\times10^{8}\ \mathrm{m\ s^{-1}})}{(30.4\times10^{-19}\ \mathrm{m})} = 6.534 \times 10^{-18}\ \mathrm{J}$$

This corresponds to the energy difference between the n = 2 and n = 1 levels:

$$\Delta E = E_{n=2} - E_{n\text{-}1} = (-2.180\times10^{-18}\ \mathrm{J}) - (-8.720\times10^{-18}\ \mathrm{J}) = 6.534\times10^{-18}\ \mathrm{J}.$$

For the *emission* of light, the transition is from n = 2 to n = 1.

- The lowest four energy levels of the He^{+} ion are given. **3**

Principal quantum number (n)	Energy (J)
1	-8.720×10^{-18}
2	-2.180×10^{-18}
3	-0.969×10^{-18}
4	-0.545×10^{-18}

An electronic transition is identified by specifying the value of n of the initial state and the value of n of the final state. Identify the electronic transition responsible for the emission of radiation from He^{+} with a wavelength of 121.5 nm?

The wavelength of light is related to its energy through Planck's equation:

$$E = \frac{hc}{\lambda}$$

Substituting the values for Planck's constant (*h*), the speed of light (*c*) and the wavelength gives:

$$E = \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s})(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{(121.5 \times 10^{-9}\ \mathrm{m})} = 1.635 \times 10^{-18}\ \mathrm{J}$$

This corresponds to the energy difference between the *n* = 4 and *n* = 2 levels:

$$\Delta E = E_{n=4} - E_{n=2} = (-0.545 \times 10^{18}\ \mathrm{J}) - (-2.180 \times 10^{-18}\ \mathrm{J}) = 1.640 \times 10^{-18}\ \mathrm{J}$$

For the emission of light, the transition is from *n* = 4 to *n* = 2.

- Explain, in terms of the quantum theory of electrons, why the electronic energy is decreased by the delocalisation of the valence electrons in the metallic bond. 2

Electrons in atoms have wavelengths of similar length to the size of the atoms they are confined in. Delocalization of the electrons increases their wavelength. de Broglie's equation,

$$\mathbf{p = \frac{h}{\lambda}}$$

where h is Planck's constant, suggests that longer wavelengths are associated with lower momentum and hence *lower* kinetic energy (T) since this is related to the momentum and the electron mass, m_e:

$$T = \frac{p^2}{2m_e} = \frac{h^2}{2m_e\lambda^2}$$

Marks

- Explain why electrons in atoms occupy discrete energy levels rather than being able to possess any possible energy below that required for ionisation. **2**

Electrons, with insufficient energy to escape, are confined in atoms by the electrostatic attraction of the nucleus and have wave-like properties. The electron wave must fit into this confined space but this is only possible with certain wavelengths. As the wavelength is related to the momentum and hence the kinetic energy, through the de Broglie relationship, this means that only certain discrete energies are possible.

- A certain pigment is found to have an electronic excitation energy of 4.97×10^{-19} J. What is the wavelength at which this molecule will absorb radiation? **3**

The wavelength of light is related to its energy through Planck's equation:

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

Substituting the values for Planck's constant (h), the speed of light (c) and the value of excitation energy gives:

$$\lambda = \frac{(6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m s}^{-1})}{(4.97\times10^{-18}\text{ J})} = 4.00 \times 10^{-7}\text{ m} = 400.\text{ nm}$$

ANSWER: **4.00×10^{-7} m or 400. nm**

What colour do you expect this pigment to be? Explain your answer.

Absorption at 400. nm corresponds to blue light. The colour of the pigment will be white light with the blue removed – the complementary colour.

From Newton's wheel, the complementary colour of blue is orange.