Marks

- Explain why the electron on an H atom does not crash into the nucleus. 3

The negatively charged electron is attracted to the positively charged nucleus. The electron behaves like a standing wave (a matter wave) and as it approaches the nucleus it becomes more confined (or localised) and its wavelength decreases. As shown by the de Broglie equation ($\lambda = h/m\upsilon$), as the wavelength of a matter wave decreases, its momentum (and hence kinetic energy) increases. If it were at nucleus, its wavelength would become zero and its position would be known exactly. To do this, it would need to have infinite kinetic energy.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Explain the physical significance of the square of the wavefunction, ψ^2.

Marks
2

The square of the wavefunction provides a measure of electron density (*i.e.* the probability of finding an electron) at a given point around the nucleus of an atom.

d) When NO_2 absorbs UVA light in the atmosphere, at wavelengths shorter than 400 nm, it dissociates into NO + O: **2**

$$NO_2 + h\nu \rightarrow NO + O$$

What is the bond dissociation energy (in kJ mol^{-1}) of the N–O bond in NO_2?

The energy per molecule required to break the bond is given by Planck's relationship:

$$\boldsymbol{E = hc / \lambda}$$
$$\mathbf{= (6.626 \times 10^{-34}\ J\ s) \times (2.998 \times 10^{8}\ m\ s^{-1}) / (400 \times 10^{-9}\ m) = 5.0 \times 10^{-19}\ J}$$

The energy required per mole is therefore:

$$\boldsymbol{E} \mathbf{= 5.0 \times 10^{-19}\ J) \times (6.022 \times 10^{23}\ mol^{-1}) = 300\ kJ\ mol^{-1}}$$

Answer: **300 kJ mol^{-1}**

Marks 2

- In an electron microscope, to what minimum velocity must the electrons in the beam be accelerated in order to achieve a better spatial resolution (*i.e.*, have a shorter wavelength) than a visible light microscope? Assume an average wavelength of visible light of 500 nm.

The wavelength of the electrons must be shorter than 500 nm.

The de Broglie wavelength λ associated with a particle of mass *m* travelling with a velocity *v* is given by:

$$\lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}$$

Hence, the velocity required for a wavelength of 500 nm = 500 × 10^{-9} m is:

$$v = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.1094 \times 10^{-31} \text{ kg})(500 \times 10^{-9} \text{ m})} = 1 \times 10^{3} \text{ m s}^{-1}$$

Better resolution requires a shorter wavelength and so the velocity must be higher than this value.

Answer: **1 × 10^{3} m s^{-1}**

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.

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

If iron emits X-rays of 1.937 Å when a 2*s* electron drops back to the 1*s* shell, determine the identity of the elements contained in an alloy found to emit the same type of X-rays at 1.435 Å and 1.541 Å?

For iron, Z = 26. With λ = 1.937 Å = 1.937 × 10^{-10} m:

$$\frac{1}{\sqrt{1.937 \times 10^{-10}\ \text{m})}} = k \times (26) \quad \text{so } k = 2764\ \text{m}^{-1/2}$$

For λ = 1.435 Å = 1.435 × 10^{-10} m:

$$\frac{1}{\sqrt{1.435 \times 10^{-10}\ \text{m})}} = (2764\ \text{m}^{-1/2}) \times Z \quad \text{so } Z = 30 \text{ corresponding to Zn}$$

For λ = 1.541 Å = 1.541 × 10^{-10} m:

$$\frac{1}{\sqrt{1.541 \times 10^{-10}\ \text{m})}} = (2764\ \text{m}^{-1/2}) \times Z \quad \text{so } Z = 29 \text{ corresponding to Cu}$$

Answer: **Zn and Cu**

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.

The energy of an X-ray with wavelength λ is given by $E = \frac{hc}{\lambda}$ where h is Planck's constant and c is the speed of light. Using this and as $\frac{1}{\sqrt{\lambda}} = kZ$

$$\frac{1}{\lambda} = (kZ)^2$$

$$E = hc(kZ)^2 \quad (1)$$

For a hydrogen like atom, an electron in an orbital with quantum number n has energy $E = -Z^2E_R(\frac{1}{n^2})$ where E_R is the Rydberg constant. The energy *emitted* when an electron moves from an orbital with quantum number n_i to an orbital with quantum number n_f is:

$$E = E_{n_i} - E_{n_f} = [-Z^2E_R(\frac{1}{n_i^2})] - [-Z^2E_R(\frac{1}{n_f^2})] = Z^2E_R(\frac{1}{n_f^2} - \frac{1}{n_i^2}) \quad (2)$$

Equating (1) and (2) gives:

$$hc(kZ)^2 = Z^2E_R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

Rearranging for k gives:

$$k^2 = \frac{Z^2E_R}{hcZ^2}(\frac{1}{n_f^2} - \frac{1}{n_i^2}) = \frac{E_R}{hc}(\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

$$k = \sqrt{\frac{E_R}{hc}(\frac{1}{n_f^2} - \frac{1}{n_i^2})}$$

For the case where $n_i = 2$ and $n_f = 1$, this becomes

$$k = \sqrt{\frac{E_R}{hc}(\frac{1}{1^2} - \frac{1}{2^2})} = \sqrt{\frac{3E_R}{4hc}}$$

Marks 6

- Ozone in the upper atmosphere absorbs light with wavelengths of 220 to 290 nm. What are the frequency (in Hz) and energy (in J) of the most energetic of these photons?

The energy, E, and frequency, ν, are related to the wavelength, λ, of light by

$E = \frac{hc}{\lambda}$ and $\nu = \frac{c}{\lambda}$ respectively.

As energy is inversely proportional to wavelength, the most energetic of these photons has the shortest wavelength, λ = 220 nm = 220 × 10^{-9} m. Hence,

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{(220 \times 10^{-9}\ \text{m})} = 9.0 \times 10^{-19}\ \text{J}$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m s}^{-1}}{220 \times 10^{-9}\ \text{m}} = 1.4 \times 10^{15}\ \text{Hz}$$

Frequency: **1.4×10^{15} Hz**	Energy: **9.0×10^{-19} J**

Carbon-carbon bonds form the backbone of nearly every organic and biological molecule. The average bond energy of the C–C bond is 347 kJ mol^{-1}. Calculate the wavelength (in nm) of the least energetic photon that can break this bond.

A bond energy of 347 kJ mol^{-1} corresponds to a bond energy per molecule of

$$E = \frac{347 \times 10^{3}}{6.022 \times 10^{23}} \frac{\text{J mol}^{-1}}{\text{molecules mol}^{-1}} = 5.76 \times 10^{-19}\ \text{J molecule}^{-1}$$

As $E = \frac{hc}{\lambda}$, the corresponding wavelength is:

$$\lambda = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{(5.76 \times 10^{-19})} = 3.45 \times 10^{-7}\ \text{m} = 345\ \text{nm}$$

Wavelength: **3.45×10^{-7} m or 345 nm**

Compare this value to that absorbed by ozone and comment on the ability of the ozone layer to prevent C–C bond disruption.

345 nm is not blocked by ozone, so C–C bond disruption is still possible even with the presence of the ozone layer. Hence one still needs to wear sunblock creams.

	Marks
• Calculate the energy (in J) and wavelength (in nm) expected for an emission associated with an electronic transition from n = 4 to 3 in the B^{4+} ion.	3

For the one electron ion, B^{4+}, the energy levels are given by

$$E_n = \frac{-E_R Z^2}{n^2} \quad \text{where } E_R = 2.18\times10^{-18} \text{ J}$$

with atomic number Z = 5. The energies of the n = 3 and 4 levels are then:

$$E_3 = \frac{-E_R(5)^2}{(3)^2} = -\frac{25}{9}E_R \quad \text{and} \quad E_4 = \frac{-E_R(5)^2}{(4)^2} = -\frac{25}{16}E_R$$

The energy separation is 1.215E_R = 1.215 × (2.18 × 10^{-18} J) = 2.65 × 10^{-18} J

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 E from above gives:

$$\lambda = \frac{(6.626\times10^{-34}\text{ J s})(2.998\times10^{8}\text{ m s}^{-1})}{(2.65\times10^{-18}\text{ J})} = 7.50\times10^{-8}\text{ m} = 75.0\text{ nm}$$

Energy = **2.65 × 10^{-18} J**	Wavelength = **7.50 × 10^{-8} m or 75.0 nm**

	Marks
• Describe how EITHER the *photoelectric effect* OR the *visible spectrum of hydrogen* contributed to the development of quantum mechanics.	2

Photoelectric effect:
Certain aspects of the photoelectric effect could only be explained by considering light as particulate - a steam of photons. The energy of the photons was proportional to the frequency (not intensity) of the light. This explained the facts that there was a minimum threshold energy and that there was no time lag.

***Visible spectrum of hydrogen*:**
The visible spectrum of hydrogen showed distinct bands at certain wavelengths only. This showed that energy was quantised (ie not continuous) and that only certain energy levels were allowed.

Marks

- Describe how one of the following pieces of experimental evidence contributed to the development of quantum mechanics. 3

photoelectric effect OR *visible spectrum of hydrogen*

Photoelectric effect:
Certain aspects of the photoelectric effect could only be explained by considering light as particulate - a steam of photons. The energy of the photons was proportional to the frequency (not intensity) of the light. This explained the facts that there was a minimum threshold energy and that there was no time lag.

***Visible spectrum of hydrogen*:**
The visible spectrum of hydrogen showed distinct bands at certain wavelengths only. This showed that energy was quantised (ie not continuous) and that only certain energy levels were allowed.

- K-shell x-ray emission ($2p \rightarrow 1s$) from an unknown element is of the same wavelength as the shortest x-rays observed as *Bremsstrahlung* when electrons are accelerated by 52.9 keV into a copper target. What is the name of the unknown element? 4

As the emission is to the 1s core level, it can be treated with the hydrogen-like orbital energy equation

$$E_n = \frac{-E_R Z^2}{n^2} \quad \text{where } E_R = 2.18 \times 10^{-18} \text{ J}$$

For n = 1 (1s) and n = 2 (2p), the energies are:

$$E_1 = \frac{-E_R Z^2}{(1)^2} = -Z^2 E_R \quad \text{and} \quad E_2 = \frac{-E_R Z^2}{(2)^2} = -\frac{Z^2}{4} E_R$$

respectively. The separation, $E_1 - E_2$ is

separation = $\frac{3}{4} E_R Z^2 = \frac{3}{4} \times (2.18 \times 10^{-18}\text{ J})\, Z^2 = 1.64 \times 10^{-18} Z^2$ J.

The energy 52.9 keV corresponds to $(52.9 \times 10^3) \times (1.602 \times 10^{-19})$ J = 8.47×10^{-15} J.

If $1.64 \times 10^{-18} Z^2$ J = 8.47×10^{-15} J then Z^2 = 5183 so Z = 72. This is the atomic number of hafnium.

ANSWER: **Hafnium**