
Atomic structure and properties

Answers to worked examples

WE 3.1 Interconverting wavelength and frequency (on p. 118 in *Chemistry*³)

Radio *5 live* in the UK broadcasts at 909 **kHz**. What wavelength does this correspond to?

Strategy

Use Equation 3.1, $c = \lambda\nu$, and rearrange to find the wavelength, λ .

Remember that 1 **kHz** is equal to 1000 **Hz** (1000 s^{-1})

Solution

Rearranging Equation 3.1 by dividing both sides by ν gives

$$\lambda = \frac{c}{\nu}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\nu = 909 \text{ kHz} = 909 \times 10^3 \text{ Hz} = 909 \times 10^3 \text{ s}^{-1}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{909 \times 10^3 \text{ s}^{-1}}$$

$$\lambda = 330 \text{ m}$$

WE 3.2 Converting frequency to energy (on p. 121 in *Chemistry*³)

What is the energy of a mole of radio wave photons with a frequency of 909 **kHz**?

Strategy

The frequency can be converted to energy for a single photon using Equation 3.2, $E = h\nu$, and then multiplied by the Avogadro constant to find the energy of a mole of photons. (Where the Avogadro constant, N_A , is the number of entities in a mole, see Section 1.3, p.12).

Solution

Using Equation 3.2, $E = h\nu$, to calculate the energy of one photon where $h =$ Planck's constant $= 6.626 \times 10^{-34} \text{ J s}$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (909 \times 10^3 \text{ s}^{-1})$$

$$E = 6.023 \times 10^{-28} \text{ J}$$

The value for a single photon can then be converted into the energy for one mole of photons by multiplying by the Avogadro constant, $6.022 \times 10^{23} \text{ mol}^{-1}$

$$E = 6.023 \times 10^{-28} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E = 3.63 \times 10^{-4} \text{ J mol}^{-1}$$

WE 3.3 The photoelectric effect (on p. 122 in *Chemistry*³)

Calculate the kinetic energy of the ejected electrons (in kJ mol^{-1}) if ultraviolet radiation of wavelength 450 nm is used in this experiment.

Strategy

By rearranging Equation 3.1, $c = \lambda\nu$, the frequency, ν , can be calculated.

This value of ν , can then be combined with Equation 3.2, $E = h\nu$, to calculate the energy (in J) of a single photon.

The value of the work function, Φ , for sodium has already been calculated in Worked example 3.3 as $3.68 \times 10^{-19} \text{ J}$.

Using Equation 3.3, where $h\nu = \Phi + E_{\text{KE}}$, allows E_{KE} for a single electron to be calculated.

Finally, the value for a mole of electrons can be calculated by multiplying E_{KE} by the Avogadro constant.

Solution

Rearranging Equation 3.1 by dividing both sides by λ gives

$$\nu = \frac{c}{\lambda}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\lambda = 450 \text{ nm} = 450 \times 10^{-9} \text{ m}$$

$$\nu = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{450 \times 10^{-9} \text{ m}}$$

$$\nu = 6.66 \times 10^{14} \text{ s}^{-1}$$

Using Equation 3.2, $E = h\nu$, calculate the energy of one photon where $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J s}$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (6.66 \times 10^{14} \text{ s}^{-1})$$

$$E = 4.41 \times 10^{-19} \text{ J}$$

Since from Equation 3.3, $h\nu = \Phi + E_{\text{KE}}$, and the value of Φ , for sodium has already been calculated in the worked example (p.122) as $3.68 \times 10^{-19} \text{ J}$, rearranging for E_{KE} gives

$$E_{\text{KE}} = h\nu - \Phi$$

$$E = (4.41 \times 10^{-19} \text{ J}) - (3.68 \times 10^{-19} \text{ J})$$

$$E = 7.3 \times 10^{-20} \text{ J}$$

To convert this value for a single photon to a mole of electrons, requires multiplication by the Avogadro constant, N_{A} .

$$E_{\text{KE}} = (7.3 \times 10^{-20} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_{\text{KE}} = 4.4 \times 10^4 \text{ J mol}^{-1} \text{ or } 44 \text{ kJ mol}^{-1}$$

WE 3.4 The atomic spectrum of hydrogen (on p. 127 in *Chemistry*³)

What are the frequencies for the first three lines of the Brackett series, for which $n_1 = 4$?

Strategy

Use the Rydberg equation, Equation 3.6

$$\nu = R_{\text{H}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ and } R_{\text{H}} = 3.29 \times 10^{15} \text{ Hz}$$

In the Brackett series, $n_1 = 4$, and since n_2 must be greater than n_1 , the first three lines must be when $n_2 = 5, 6$ and 7 .

Solution

For the first line, $\nu = R_{\text{H}} \left[\frac{1}{4^2} - \frac{1}{5^2} \right] = R_{\text{H}} \left[\frac{1}{16} - \frac{1}{25} \right] = 7.40 \times 10^{13} \text{ Hz}$

For the second line, $\nu = R_{\text{H}} \left[\frac{1}{4^2} - \frac{1}{6^2} \right] = R_{\text{H}} \left[\frac{1}{16} - \frac{1}{36} \right] = 1.14 \times 10^{14} \text{ Hz}$

For the third line, $\nu = R_{\text{H}} \left[\frac{1}{4^2} - \frac{1}{7^2} \right] = R_{\text{H}} \left[\frac{1}{16} - \frac{1}{49} \right] = 1.38 \times 10^{14} \text{ Hz}$

WE 3.5 The ionization energy of hydrogen (on p. 127 in *Chemistry*³)

What is the ionization energy for an excited state of hydrogen in which the electron has already been promoted to the $n = 2$ level?

Strategy

Use the Rydberg equation, Equation 3.6, to work out the frequency of the line corresponding to the transition $n_1 = 2$ to $n_2 = \infty$ (infinity). Then use Equation 3.2, $E = h\nu$, to convert the frequency to the energy of the transition. Finally, this energy for a

single atom needs to be converted to a molar quantity by multiplying by the Avogadro constant.

Solution

Using Equation 3.6,

$$\nu = R_{\text{H}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ and } R_{\text{H}} = 3.29 \times 10^{15} \text{ Hz}$$

$n_1 = 2$ to $n_2 = \infty$ (infinity)

$$\nu = R_{\text{H}} \left[\frac{1}{2^2} - \frac{1}{\infty^2} \right] = \left[\frac{1}{4} - 0 \right] = 8.23 \times 10^{14} \text{ Hz (s}^{-1}\text{)}$$

Using Equation 3.2, $E = h\nu$, to find the energy of the transition.

$$E = (8.23 \times 10^{14} \text{ s}^{-1}) \times (6.626 \times 10^{-34} \text{ J s})$$

$$E = 5.45 \times 10^{-19} \text{ J or } 5.45 \times 10^{-22} \text{ kJ}$$

Finally multiply by the Avogadro constant to determine the value for a mole in kJ mol^{-1} .

$$E = (5.45 \times 10^{-22} \text{ kJ}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E = 328 \text{ kJ mol}^{-1}$$

WE 3.6 Using the de Broglie equation (on p. 132 in *Chemistry*³)

What is the wavelength of a neutron travelling at one tenth of the speed of light? (The mass of a neutron is given in Table 3.1, p.116.)

Strategy

Using Equation 3.9,

$$\lambda = \frac{h}{mv} \quad (\text{where } h = 6.626 \times 10^{-34} \text{ J s})$$

Remember $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$

When using SI units, masses are measured in **kg** (Section 1.2, p.7).

Solution

For a neutron, $m = 1.6749 \times 10^{-27} \text{ kg}$.

$v =$ one tenth the speed of light, that is $0.1 \times 2.998 \times 10^8 \text{ m s}^{-1} = 2.998 \times 10^7 \text{ m s}^{-1}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2} \text{ s}}{(1.6749 \times 10^{-27} \text{ kg}) \times (2.998 \times 10^7 \text{ m s}^{-1})}$$

$$\lambda = 1.320 \times 10^{-14} \text{ m}$$

WE 3.7 The Heisenberg uncertainty principle (on p. 133 in *Chemistry*³)

Calculate the uncertainty in the position of an electron whose velocity is known to within $1 \times 10^{-6} \text{ m s}^{-1}$.

Strategy

Since the momentum (p) = mass \times velocity, the uncertainty in the momentum is calculated using $\Delta p = m\Delta v$.

Rearrange Equation 3.10 and use it to calculate the uncertainty Δq , in the position of the electron.

Solution

The uncertainty in the momentum $\Delta p = m\Delta v$, where the mass of an electron = $9.1094 \times 10^{-31} \text{ kg}$ (Table 3.1, p.116)

$$\Delta p = (9.1094 \times 10^{-31} \text{ kg}) \times (1 \times 10^{-6} \text{ m s}^{-1})$$

$$\Delta p = 9.1094 \times 10^{-37} \text{ kg m s}^{-1}$$

Using Equation 3.10

$$\frac{h}{4\pi} \leq \Delta p \Delta q$$

Rearrange by dividing both sides by Δp to give:

$$\Delta q \geq \frac{h}{4\pi\Delta p}$$

$$\Delta q \geq \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.1416 \times 9.1094 \times 10^{-37} \text{ kg m s}^{-1}}$$

$$\Delta q \geq 57.9 \text{ m}$$

WE 3.8 Atomic orbitals (on p. 136 in *Chemistry*³)

What atomic orbital has the quantum numbers $n = 6$, $l = 2$?

Strategy

Use the definitions given in Section 3.5 (p.134) to identify the orbital.

Solution

n is the principal quantum number referring to the size of the orbital, therefore this means it is an orbital from the 6 orbital set. The secondary quantum number takes values from 0 (for an s orbital) upwards in integral increments. This means $l = 2$ corresponds to a d orbital. This orbital is therefore a $6d$ orbital.

WE 3.9 Radial wavefunctions (on p. 138 in *Chemistry*³)

How many radial nodes does a $7s$ orbital have?

Strategy

The number of radial nodes is directly related to the type of orbital. For an s orbital, there are $(n - 1)$ nodes where n is the principal quantum number.

Solution

As $n = 7$, the number of nodes for this s orbital is simply $(n - 1)$, therefore the $7s$ orbital has 6 nodes.

WE 3.10 Electronic configurations (on p. 148 in *Chemistry*³)

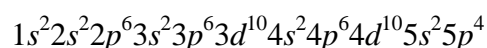
What is the electronic configuration of tellurium ($Z = 52$)?. Give both the full electronic configuration and the version using Group 18 element shorthand.

Strategy

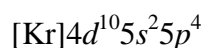
Use Figure 3.27 (p.144) to determine the order in which the orbitals are filled. Then use the Aufbau principle to put the electrons in the orbitals, starting from the lowest in energy. Use the Periodic Table (on the inside front cover) to find out the last full shell in the period before tellurium to produce the Group 18 shorthand.

Solution

Using the Aufbau principle and Figure 3.27, tellurium has the electronic configuration



The last group element before tellurium is krypton, therefore the shorthand becomes

**WE 3.11 Effective nuclear charge (on p. 152 in *Chemistry*³)**

What is the effective nuclear charges for (a) chlorine ($Z = 17$) and (b) bromine ($Z = 35$)?

Strategy

First establish the electronic configuration of the elements using the Aufbau principle and Figure 3.27. Consider one electron in the outer set of orbitals and the effect the other electrons has on it and apply Slater's rules to calculate the shielding constant, S . The other electrons in the same set of orbitals shield at 0.35, in the $(n - 1)$ set of orbitals shield at 0.85 and the $(n - 2)$ set of orbitals (or below) shield at 1.0. Finally, use Equation 3.19 to calculate Z_{eff} .

Solution

(a) The electronic configuration of chlorine ($Z = 17$) is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Considering one of the electrons in the $3p$ orbitals and the effect the other electrons have on it gives the following.

There are four other electrons in the $3p$ orbitals and two electrons in the $3s$ orbital. As these electrons are in orbitals of the same principal quantum number they shield at 0.35. i.e. 6×0.35 .

Each of the eight electrons in the $2s$ and $2p$ orbitals contribute 0.85 to the shielding as they are in the $(n - 1)$ set of orbitals. This gives 8×0.85 for this shielding contribution.

Finally the two $1s$ electrons are in the $(n - 2)$ set of orbitals and hence each contribute 1.0 to the shielding. This gives 2×1.0 .

Overall the shielding is therefore $(6 \times 0.35) + (8 \times 0.85) + (2 \times 1.0) = 10.9$.

Using Equation 3.19, where $Z_{\text{eff}} = Z - S$ gives $17 - 10.9 = 6.1$.

(b) The electronic configuration of bromine ($Z = 35$) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$.

Considering one of the electrons in the $4p$ orbitals and the effect the other electrons have on it gives the following.

There are four other electrons in the $4p$ orbitals and two electrons in the $4s$ orbital. As these electrons are in orbitals of the same principal quantum number they shield at 0.35. i.e. 6×0.35 .

Each of the eighteen electrons in the $3s$, $3p$ and $3d$ orbitals contribute 0.85 to the shielding as they are in the $(n - 1)$ set of orbitals. This gives 18×0.85 for this shielding contribution.

Finally there are ten electrons in a combination of the $1s$, $2s$ and $2p$ orbitals which are in the $(n - 2)$ (or below) set of orbitals and hence each contribute 1.0 to the shielding. This gives 10×1.0 .

Overall the shielding is therefore $(6 \times 0.35) + (18 \times 0.85) + (10 \times 1.0) = 27.4$.

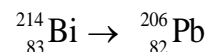
Using Equation 3.19, where $Z_{\text{eff}} = Z - S$ gives $35 - 27.4 = 7.6$.

WE 3.12 Nuclear decay (on p. 160 in *Chemistry*³)

$^{226}_{88}\text{Ra}$ is also unstable, and following a series of nine more radioactive intermediates it is eventually converted into the stable $^{206}_{82}\text{Pb}$ isotope. What combination of emissions occur in the latter part of this process to convert $^{214}_{83}\text{Bi}$ into $^{206}_{82}\text{Pb}$?

Strategy

Determine the product of each of the successive reactions, being mindful of the change in atomic number and mass numbers caused by α and β emission.



Solution

The difference in mass is eight atomic mass units, which must be due to two α emissions. However, the atomic number would be expected to have fallen by four and not one if this was the only process happening. Therefore the difference in atomic number must be due to three β emissions increasing the atomic number by one after each emission. Hence two α -emissions and three β -emissions convert $^{214}_{83}\text{Bi}$ into $^{206}_{82}\text{Pb}$.

Answers to boxes

Box 3.1 Radiation from the Sun (on p. 120 in *Chemistry*³)

Why does the Sun appear yellow?

Strategy

Examine the solar spectrum and examine the maximum intensity in comparison to the visible region.

Solution

All colours are present in sunlight, but the maximum intensity of the solar spectrum occurs at around 500 nm which is in the yellow region of the visible region.

Box 3.2 Lighting up the sky (on p. 128 in *Chemistry*³)

Why do excited atoms only emit radiation of certain frequencies?

Strategy

Consider how the observed transitions are being generated and refer to Section 3.3 (p.124).

Solution

As the electronic energies of atoms are quantised, they can only have fixed values (i.e. a bit like being on a ladder where you can only stand on the rungs and not between the rungs). The frequencies of the radiation emitted by electronically excited atoms are determined by the difference in energy between the excited electronic level and the lower electronic levels (refer to Equation 3.4).

Box 3.3 The composition of stars (on p. 131 in *Chemistry*³)

How would Slipher's observations have changed if the Universe was contracting?

Strategy

Read the details of the Doppler effect given in Box 3.3 (p.131). If the Universe was contracting, the objects emitting light would be moving towards the observer.

Solution

When an object emitting light is moving towards the observer the wavelength appears to decrease. This is known as a blue shift, and all of the lines would be at a shorter wavelength than expected.

Box 3.7 Exchange energy (on p. 147 in *Chemistry*³)

Given that the exchange energy for a pair of parallel electrons is K , calculate the exchange energy for the electronic configuration $3d^4$.

Strategy

For a $3d^4$ configuration there are four parallel electrons (Hund's rule). Determine how many pairs of parallel electrons there are.

Solution

Denoting the parallel electrons from 1 to 4, the pairs of electrons are as follows:

Electron 1 and electron 2

Electron 1 and electron 3

Electron 1 and electron 4

Electron 2 and electron 3

Electron 2 and electron 4

Electron 3 and electron 4

There are therefore six pairs of parallel electrons, and the exchange energy is $6K$.

Box 3.8 Atomic numbers and the Periodic Table (on p. 149 in *Chemistry*³)

Moseley showed that copper emits X-rays with $\lambda = 1.549 \times 10^{-10}$ m. Calculate the energy of a photon with this wavelength.

Strategy

Use Equation 3.1, $c = \lambda\nu$, to calculate the frequency of this X-ray and then Equation 3.2, $E = h\nu$, to calculate the energy of the photon.

Solution

Rearranging Equation 3.1 by dividing each side by λ gives and inputting the wavelength ($c = 2.998 \times 10^8 \text{ m s}^{-1}$)

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ ms}^{-1}}{1.549 \times 10^{-10} \text{ m}} = 1.935 \times 10^{18} \text{ s}^{-1} \text{ (Hz)}$$

Using Equation 3.2 to determine the energy of the photon where $E = h\nu$ and $h = 6.626 \times 10^{-34} \text{ J s}$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (1.935 \times 10^{18} \text{ s}^{-1})$$

$$E = 1.282 \times 10^{-15} \text{ J}$$

Box 3.9 Dating the Amesbury Archer (on p. 161 in *Chemistry*³)

In what year will the amount of ^{14}C be half its value when the Amesbury Archer was alive? Assume he died in 2300 BC.

Strategy

Calculate the radioactivity based on the half life of carbon-14 and the date of the Amesbury Archer's death taking into account that year zero of the calendar is 0 BC.

Solution

The half life of ^{14}C is 5730 years. This means that the radioactivity will be half its original value after one half life, i.e. 5730 years from the date of the archer's death. Since the archer passed away in 2300 BC, the radioactivity will have reached half its original level by $-2300 + 5730 \text{ years} = 3430$.

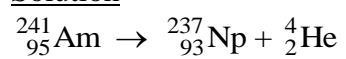
Box 3.10 Smoke detectors (on p. 163 in *Chemistry*³)

Write the nuclear equation for the α -decay of an atom of ^{241}Am ?

Strategy

An alpha decay (see Table 3.7, p.160) is associated with a change of 4 in the atomic number and 2 in the atomic mass (i.e. the same as a He atom). Therefore the product must reflect these changes.

Solution



Answers to end of chapter questions

1. What is the energy (in kJ mol^{-1}) of X-ray photons with a wavelength of 100 pm?

Strategy

Use Equation 3.1, $c = \lambda\nu$, and rearrange to find the frequency, ν . The wavelength, λ , must be in metres. The frequency can then be converted to energy for a single photon using Equation 3.2, $E = h\nu$ and then multiplied by the Avogadro constant to find the energy of a mole of photons. (Where the Avogadro constant, N_A , is the number of entities in a mole, see Section 1.3, p.12.)

Solution

Rearranging Equation 3.1 by dividing both sides by λ gives

$$\nu = \frac{c}{\lambda}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\lambda = 100 \text{ pm} = 100 \times 10^{-12} \text{ m}$$

$$\nu = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{100 \times 10^{-12} \text{ m}}$$

$$\nu = 2.998 \times 10^{18} \text{ s}^{-1} = 2.998 \times 10^{18} \text{ Hz}$$

Using Equation 3.2, $E = h\nu$ to then calculate the energy of one photon where

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J s}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{18} \text{ s}^{-1})$$

$$E = 1.986 \times 10^{-15} \text{ J}$$

The value for a single photon can then be converted into the energy for one mole of photons by multiplying by the Avogadro constant, $6.022 \times 10^{23} \text{ mol}^{-1}$.

$$E = 1.986 \times 10^{-15} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E = 1.20 \times 10^9 \text{ J mol}^{-1} \text{ or } 1.20 \times 10^6 \text{ kJ mol}^{-1}$$

2. The Cl–Cl bond in Cl₂ has a bond energy of 242 kJ mol⁻¹. Assuming that absorption of photons of this energy will break the bond, what is the minimum frequency of electromagnetic radiation that is required? What part of the electromagnetic spectrum does this correspond to?

Strategy

Firstly assume that the electromagnetic radiation must have the same energy to break this bond. The bond energy given is for one mole of chlorine atoms, therefore to work out the energy of a single bond, this value must be divided by the Avogadro constant. This energy for a single bond can then be converted into a frequency by using Equation 3.2, $E = h\nu$. The final numerical value can then be compared to the spectrum given in Figure 3.5 (p.119) to see what part of the spectrum this line lies in.

Solution

Dividing the bond energy of 242 kJ mol⁻¹ by Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$) gives the energy of a single Cl–Cl bond. Note that the bond energy must be converted to Joules to be used in the $E = h\nu$ equation.

$$E (\text{single bond}) = \frac{242000 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 4.02 \times 10^{-19} \text{ J}$$

Rearranging $E = h\nu$ by dividing both sides by h and substituting for E and h ($6.626 \times 10^{-34} \text{ J s}$)

$$\nu = \frac{E}{h} = \frac{4.02 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 6.07 \times 10^{14} \text{ s}^{-1}$$

Comparing this value with the spectrum given in Figure 3.5, shows that this frequency corresponds to the violet end of the visible spectrum.

3. What is the wavelength of light for a line in the atomic spectrum of hydrogen for which $n_1 = 2$ and $n_2 = 4$? What part of the electromagnetic spectrum does this correspond to?

Strategy

Comparing these data to Table 3.4 (p.126) shows that this line is from the Balmer series of the atomic spectrum of hydrogen. The wavelength can be calculated using Equation 3.6 to obtain the frequency of the line and then using Equation 3.1, $c = \lambda\nu$, to convert the frequency to wavelength.

Solution

Using Equation 3.6,

$$\nu = R_{\text{H}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ and } R_{\text{H}} = 3.29 \times 10^{15} \text{ Hz}$$

$$\nu = R_{\text{H}} \left[\frac{1}{2^2} - \frac{1}{4^2} \right] = R_{\text{H}} \left[\frac{1}{4} - \frac{1}{16} \right] = 6.169 \times 10^{14} \text{ Hz (s}^{-1}\text{)}$$

From Equation 3.1 dividing each side by ν gives

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ ms}^{-1}}{6.169 \times 10^{14} \text{ s}^{-1}} = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$$

This is at the violet end of the visible region.

4. Calculate the wavelengths for the first three lines in the Lyman series.

Strategy

Identify the value of n_1 for the Lyman series, then work out the values of n_2 for the first three lines. Use Equation 3.6 to calculate the frequencies of the lines, then use Equation 3.1 to convert these into wavelengths.

Solution

For the Lyman series, $n_1 = 1$, and for the first three lines $n_2 = 2, 3, 4$. Using Equation 3.6:

$$\nu = R_{\text{H}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ with } R_{\text{H}} = 3.29 \times 10^{15} \text{ Hz.}$$

For the first line,

$$\begin{aligned} \nu &= R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4} R_{\text{H}} \\ &= 2.47 \times 10^{15} \text{ Hz} \end{aligned}$$

Using Equation 3.1,

$$\begin{aligned} \lambda &= \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{2.47 \times 10^{15} \text{ s}^{-1}} \\ &= 1.21 \times 10^{-7} \text{ m} = 121 \text{ nm.} \end{aligned}$$

For the second line,

$$\begin{aligned} \nu &= R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{3^2} \right] = \frac{8}{9} R_{\text{H}} \\ &= 2.92 \times 10^{15} \text{ Hz} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{2.92 \times 10^{15} \text{ s}^{-1}} \\ &= 1.03 \times 10^{-7} \text{ m} = 103 \text{ nm.} \end{aligned}$$

For the third line,

$$\begin{aligned} \nu &= R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{4^2} \right] = \frac{15}{16} R_{\text{H}} \\ &= 3.08 \times 10^{15} \text{ Hz} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{3.08 \times 10^{15} \text{ s}^{-1}} \\ &= 9.73 \times 10^{-8} \text{ m} = 97 \text{ nm.} \end{aligned}$$

5. What is the wavelength of a helium atom with a velocity of $1.00 \times 10^3 \text{ m s}^{-1}$?

Strategy

The wavelength of a particle is related to its mass through the de Broglie equation, Equation 3.9, $E = \frac{h}{mv}$. A helium atom consists of two electrons, two protons and two neutrons, therefore the mass can be calculated using the data given in Table 3.1 (p.116).

Solution

Mass of the helium atom

$$= [2 \times (9.1094 \times 10^{-31})] + [2 \times (1.6726 \times 10^{-27})] + [2 \times (1.6749 \times 10^{-27})] \text{ kg}$$

$$= 6.697 \times 10^{-27} \text{ kg}$$

$$h = 6.626 \times 10^{-34} \text{ Js (kg m}^2 \text{ s}^{-1}\text{)}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(6.697 \times 10^{-27} \text{ kg}) \times (1.00 \times 10^3 \text{ m s}^{-1})}$$

$$= 9.89 \times 10^{-11} \text{ m} = 98.9 \text{ pm.}$$

6. Which of the following sets of quantum numbers are allowed? What atomic orbitals do the allowed combinations correspond to?
- $n = 2, l = 2, m_l = 2$
 - $n = 5, l = 3, m_l = -2$
 - $n = 3, l = -1, m_l = 1$
 - $n = 2, l = 1, m_l = 1$
 - $n = 4, l = 0, m_l = 1$

Strategy

Use the definitions given for n , l and m_l on page 135 to identify permitted values: n takes integral values starting from 1 upwards and l can then take value from 0 up to $(n - 1)$. m_l can take integral values between $+l$ and $-l$.

Solution

- These values are not allowed, the maximum value of l is $(n - 1)$.
- These values are allowed and with $n = 5$ and $l = 3$, combine to give a $5f$ orbital.

- (c) These values are not allowed as l cannot be negative.
- (d) These values are allowed and with $n = 2$ and $l = 1$, combine to give a $2p$ orbital.
- (e) The values are not allowed as m_l can only take values from $+l$ to $-l$. In this case as l is zero, $m_l = 1$ is not allowed.

7. How many orbitals are possible for $n = 5$? Identify the orbital types giving the numbers of each?

Strategy

Use the definitions given for n , l and m_l on page 135 to identify permitted values: n takes integral values starting from 1 upwards and l can then take value from 0 up to $(n - 1)$. m_l can take integral values between $+l$ and $-l$.

Solution

When $n = 5$, l can take integral values 0 to $(n - 1)$. This means 0, 1, 2, 3 and 4.

For each value of l , m_l can take integral values between $+l$ and $-l$.

When $l = 0$, $m_l = 0$ (an s orbital)

When $l = 1$, $m_l = 1, 0, -1$ (three p orbitals)

When $l = 2$, $m_l = 2, 1, 0, -1, -2$ (five d orbitals)

When $l = 3$, $m_l = 3, 2, 1, 0, -1, -2, -3$ (seven f orbitals)

When $l = 4$, $m_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$ (nine g orbitals)

Therefore in total there are $1 + 3 + 5 + 7 + 9 = 25$ orbitals.

8. The value of m_l for a particular orbital is -2 . What are the smallest possible values for n and l ?

Strategy

Use the definitions given for n , l and m_l on page 135 to identify permitted values: n takes integral values starting from 1 upwards and l can then take value from 0 up to $(n - 1)$. m_l can take integral values between $+l$ and $-l$.

Solution

For m_l to have a value of -2 , where m_l takes values from $+l$ to $-l$, the smallest l can be is 2. As l takes values up to $(n - 1)$, the smallest value of n where $l = 2$, must be $l + 1 = 3$.

9. For the following atomic orbitals, give the values of the quantum numbers n and l . In each case indicate what values for m_l are allowed.

- a) $2s$
- b) $5f$
- c) $6p$

Strategy

Use the definitions given for n , l and m_l on page 135 to identify permitted values: n takes integral values starting from 1 upwards and l can then take value from 0 up to $(n - 1)$. m_l can take integral values between $+l$ and $-l$.

Solution

a) For the $2s$ orbital, $n = 2$ and $l = 0$. Since m_l takes values from $+l$ to $-l$, the only value possible if $l = 0$ is $m_l = 0$.

b) For the $5f$ orbital, $n = 5$ and $l = 3$. Since m_l takes values from $+l$ to $-l$, the possible values for m_l are $+3, +2, +1, 0, -1, -2$ and -3 .

c) For the $6p$ orbital, $n = 6$ and $l = 1$. Since m_l takes values from $+l$ to $-l$, the possible values for m_l are $+1, 0$ and -1 .

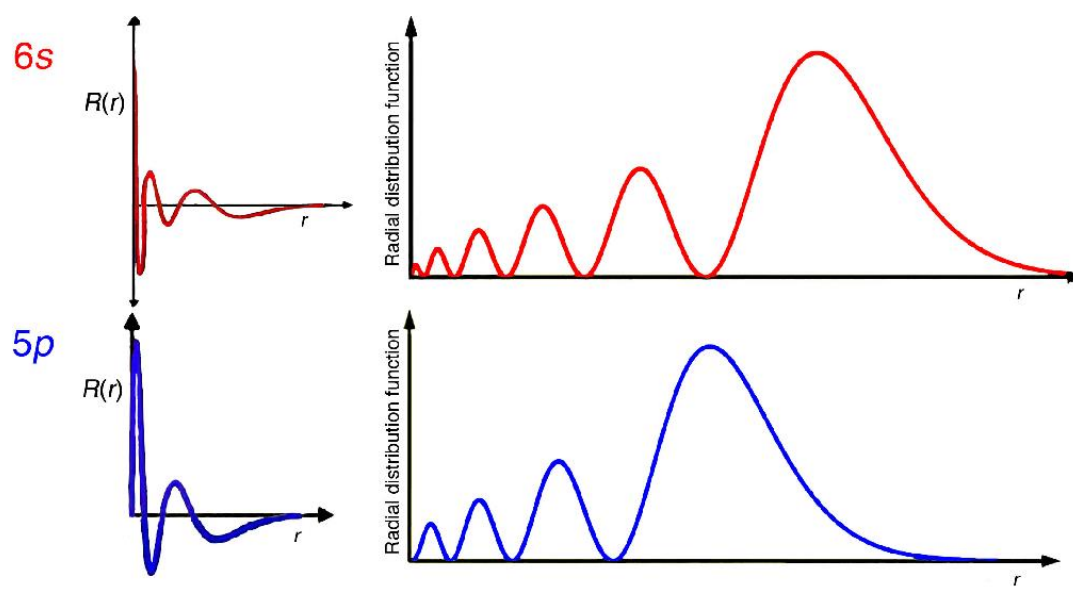
10. Sketch radial wavefunctions, radial distribution functions and boundary diagrams for $6s$ and $5p$ electrons.

Strategy

Apply Equation 3.15 (p.137) and use the plots given in Figure 3.16 (p.138).

Solution

An s orbital has $(n - 1)$ radial nodes, therefore for the $6s$ orbital there will be five radial nodes. In contrast, a p orbital has $(n - 2)$ radial nodes for $r > 0$ and as $n = 5$, this means the p orbital will have three radial nodes. As $R(r)$ is non zero at $r = 0$, the s orbital is spherical whereas for the p orbital $R(r)$ is zero at $r = 0$ and has one angular nodal plane.



Boundary diagrams for the s and p orbitals are shown on pages 140 and 141.

11. Explain why the $2s$ orbital is at a lower energy than the $2p$ orbital for lithium, whereas the $2s$ and $2p$ orbitals have the same energy for Li^{2+} .

Strategy

A lithium atom has three electrons, whereas a Li^{2+} ion has only one electron. Consider the effect of the additional electrons in the Li atom.

Solution

For lithium, the $1s$ orbital is occupied. This orbital shields the $2s$ and $2p$ orbitals from the nuclear charge. Because of the radial node, the $2s$ orbital is able to penetrate the $1s$ electron density, so experiences a greater effective nuclear charge than the $2p$

orbital, hence the lower energy. The Li^{2+} ion contains only a single electron, so there is no shielding. This ion has hydrogen-like orbitals.

- 12.** Of the following arrangement of p electrons, which represents the ground state, which are excited states and which are impossible?

Strategy

Apply the Pauli exclusion principle (no two electrons may have the same four quantum numbers) and Hund's Rule (the lowest energy configuration is the one with maximum number of parallel electrons) to the different configurations to determine which are allowed. Note in the answers that the difference between an allowed excited state (in violation of Hund's Rule) as opposed to a disallowed state (in violation of the Pauli exclusion principle).

Solution

- (a) As one of the electrons could be placed in another orbital in a spin parallel configuration (according to Hund's rule) this is not the lowest energy configuration. This is therefore an excited state.
- (b) This is the ground state configuration with a maximum number of parallel electrons in agreement with Hund's rule.
- (c) Although electrons are in separate orbitals, the spins are not parallel and hence this configuration does not obey Hund's rule. It is therefore an excited state.
- (d) This configuration has two electrons with the same four quantum numbers and disobeys the Pauli exclusion principle. This configuration is disallowed.
- 13.** Using the Group 18 element shorthand, give the electronic configurations for the following elements or ions: (a) arsenic, (b) cobalt, (c) holmium and (d) bromide ion. How many unpaired electrons are there in each case?

Strategy

Use Figures 3.26 and 3.27 (p.144) to determine the order in which the orbitals are filled. Then use the Aufbau principle to put the electrons in the orbitals, starting from the lowest in energy. Use the Periodic Table (on the inside front cover) to find out the last full shell in the period before the element/ion in question to produce the Group 18 shorthand. Be careful to add/remove electrons before noting the Group 18 configuration for ions.

Solution

- (a) [Ar] $4s^2 3d^{10} 4p^3$ (3 unpaired electrons)
- (b) [Ar] $4s^2 3d^7$ (2 unpaired electrons)
- (c) [Xe] $6s^2 4f^{11}$ (3 unpaired electrons)
- (d) [Kr] (0 unpaired electrons)

14. Which elements would you expect to have the following electronic configurations: (a) [Ar] $4s^2$, (b) [Ne] $3s^2 3p^5$, (c) [Kr] $4d^7 5s^2$.

The actual configuration for the element in (c) is [Kr] $4d^8 5s^1$. Suggest a reason for this.

Strategy

Use Figures 3.26 and 3.27 (p.144) to determine the order in which the orbitals are filled. Use the Periodic Table (on the inside front cover) to pinpoint the period of the element in question. *i.e.* from the noble gas configuration shorthand the element must be in the period after the last full noble gas configuration.

Solution

- (a) This element has two more electrons than argon, it is therefore calcium.
- (b) This element has seven more electrons than neon, it is therefore chlorine.
- (c) This element has nine more electrons than krypton, it is therefore rhodium.

The unexpected configuration for rhodium is due to Hund's rule. This configuration has a greater number of parallel electrons.

15. Considering the number of parallel electron pairs, calculate the exchange energy for the d^5 and f^7 configurations. Assume that the exchange energy for a pair of parallel electrons is K .

Strategy

Use Hund's rule to work out how many parallel electrons there are in these configurations, and then for each case determine how many pairs of parallel electrons there are.

Solution

(i) d^5

In this case there are five parallel electrons. Denoting the parallel electrons from 1 to 5, the pairs of electrons are as follows:

Electron 1 and electron 2

Electron 1 and electron 3

Electron 1 and electron 4

Electron 1 and electron 5

Electron 2 and electron 3

Electron 2 and electron 4

Electron 2 and electron 5

Electron 3 and electron 4

Electron 3 and electron 5

Electron 4 and electron 5

There are therefore ten pairs of parallel electrons, and the exchange energy is $10K$.

(ii) f^7

In this case there are seven parallel electrons. Denoting the parallel electrons from 1 to 7, the pairs of electrons are as follows:

Electron 1 and electron 2

Electron 1 and electron 3

Electron 1 and electron 4

Electron 1 and electron 5

Electron 1 and electron 6

Electron 1 and electron 7

Electron 2 and electron 3

Electron 2 and electron 4

Electron 2 and electron 5

Electron 2 and electron 6

Electron 2 and electron 7

Electron 3 and electron 4

Electron 3 and electron 5

Electron 3 and electron 6

Electron 3 and electron 7

Electron 4 and electron 5

Electron 4 and electron 6

Electron 4 and electron 7

Electron 5 and electron 6

Electron 5 and electron 7

Electron 6 and electron 7

There are therefore 21 pairs of parallel electrons, and the exchange energy is $21K$.

- 16.** Use Slater's rules to calculate the effective nuclear charge for phosphorus and for arsenic. Do the values account for the difference in atomic radius for these elements (Figure 3.34, p.154).

Strategy

Use Figure 3.26 and 3.27 (p.144) and the Periodic Table (on the inside front cover) to work out electronic configurations for phosphorus and arsenic. Then use Slater's rules (p.151) to calculate Z_{eff} for these elements.

Solution

For phosphorus, the electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$.

The four electrons (the outermost electron cannot shield itself) in the $3s$ and $3p$ orbitals contribute 0.35 each to S . The eight electrons in the $2s$ and $2p$ orbitals contribute 0.85 each to S . The two $1s$ electrons contribute 1 each to S .

$$S = (4 \times 0.35) + (8 \times 0.85) + (2 \times 1) = 10.2.$$

$$Z_{\text{eff}} = Z - S = 15 - 10.2 = 4.8.$$

For arsenic, the electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^3$.

The four electrons (the outermost electron cannot shield itself) in the $4s$ and $4p$ orbitals contribute 0.35 each to S . The eighteen electrons in the $3s$, $3p$ and $3d$ orbitals

contribute 0.85 each to S . The ten electrons in the $1s$, $2s$ and $2p$ orbitals contribute 1 each to S .

$$S = (4 \times 0.35) + (18 \times 0.85) + (10 \times 1) = 26.7.$$

$$Z_{\text{eff}} = Z - S = 33 - 26.7 = 6.3.$$

The atomic radius for arsenic is greater than that for phosphorus. This is not really related to Slater's rules. The most important factor is the occupation of atomic orbitals with higher values of n , that are further away from the nucleus.

17. For each of the following pairs of elements, which has the larger first ionization energy: (a) sodium and magnesium, (b) magnesium and aluminium (c) magnesium and calcium?

Strategy

The ease of ionization for elements depends on both their electronic configuration and the amount of shielding. Elements with more shielding will be more easily ionised as their valence electrons are more shielded from the nuclear charge of the nucleus.

Solution

- (a) As the period is crossed from left to right, the effective nuclear charge increases and electrons become generally more difficult to remove. This means magnesium will have a higher ionization energy than sodium.
- (b) The configurations of magnesium and aluminium are $[\text{Ne}]3s^2$ and $[\text{Ne}]3s^22p^1$ respectively. For aluminium, the p orbital is less well shielded than the s orbital and hence will be easier to remove. This means magnesium will have the higher ionization energy.
- (c) The ionization energy falls as a group is descended as there are more electrons to shield the valence electrons from the nuclear charge. As calcium is below magnesium in the same group, magnesium will have the higher ionization energy.

- 18.** Account for the following trends in ionization energy.
- (a) the increase from oxygen to fluorine
 - (b) the decrease from nitrogen to phosphorus
 - (c) the decrease from phosphorus to sulfur

Strategy

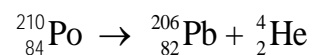
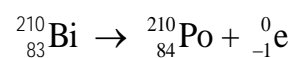
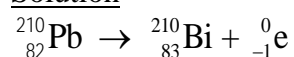
Review the factors leading to trends in ionization energy (Section 3.7, p.154).

Solution

- (a) The increase in ionization energy from oxygen to fluorine is expected from the general trend of increasing ionization energies across each period. This is due to the greater value for Z_{eff} for fluorine, itself a consequence of poor shielding of the nuclear charge by the $2p$ electrons.
 - (b) The decrease in ionization energy from nitrogen to phosphorus is expected from the general trend of decreasing ionization energies down each group. This is due to the larger more diffuse orbitals for phosphorus, which are further from the nuclear charge.
 - (c) The decrease in ionization energy from phosphorus to sulfur is counter to the general trend of increasing ionization energies across each period. Removal of a paired electron for sulfur (p^4) compared to an unpaired electron for phosphorus (p^3) leads to a greater reduction in electron-electron repulsion.
- 19.** ^{210}Pb decays into ^{206}Pb in a pathway involving two β emissions followed by an α emission. What are the two intermediate isotopes?

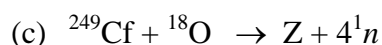
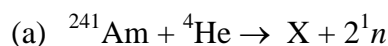
Strategy

A β emission causes a rise by 1 unit in the atomic number and no change in the atomic mass. An α emission causes a decrease of 2 in the atomic number and 4 in the atomic mass. Use the Periodic Table (on the inside front cover) to determine which two elements are created after each emission.

Solution

The two intermediate isotopes are bismuth-210 and polonium-210.

20. Identify the transuranic element isotopes X, Y and Z that were prepared by the following nuclear reactions.

Strategy

Use the Periodic Table (inside front cover) to identify the atomic number for the elements in the nuclear reactions. Work out the atomic number and the atomic mass for X, Y and Z by balancing the equations so that the total number of protons and neutrons is the same on the left and right sides. Finally, use the Periodic Table to identify the elements from their atomic numbers.

Solution

(a) The atomic numbers for Am and He are 95 and 2 respectively. This means X has atomic number 97 (Bk). There are 245 protons and neutrons on the left hand side of the equation, so the atomic mass of Bk is $245 - 2 = 243$. X is ${}^{243}\text{Bk}$.

(b) The atomic numbers for Pb and Ni are 82 and 28 respectively. This means Y has atomic number 110 (Ds). There are $208 + 64 = 272$ protons and neutrons on the left hand side of the equation, so the atomic mass of Bk is $272 - 1 = 271$. Y is ${}^{271}\text{Ds}$.

- (c) The atomic numbers for Cf and O are 98 and 8 respectively. This means Z has atomic number 106 (Sg). There are $249 + 18 = 267$ protons and neutrons on the left hand side of the equation, so the atomic mass of Bk is $267 - 4 = 263$. Z is ^{263}Sg .