02 Atomic structure

Essential ideas

2.1 The mass of an atom is concentrated in its minute, positively charged nucleus.

2.2 The electron configuration of an atom can be deduced from its atomic number.

12.1 The quantized nature of energy transitions is related to the energy states of electrons in atoms and molecules.

Picture of individual atoms. This is a scanning tunnelling micrograph of gold atoms on a graphite surface. The gold atoms are shown in yellow, red, and brown and the graphite (carbon) atoms are shown in green.

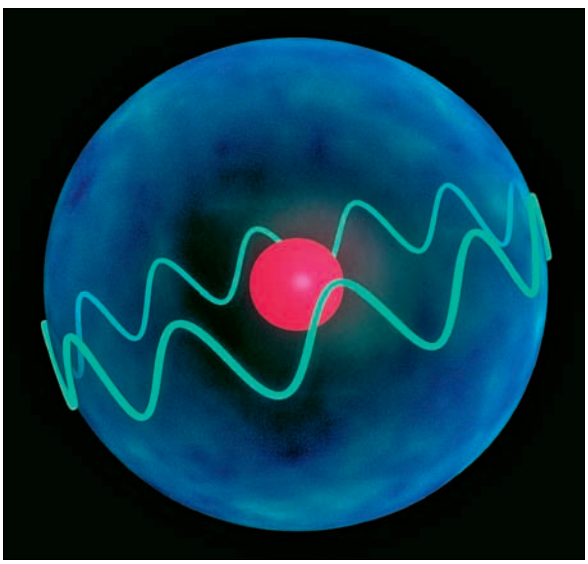
'All things are made from atoms.' This is one of the most important ideas that the human race has learned about the universe. Atoms are everywhere and they make up everything. You are surrounded by atoms – they make up the foods you eat, the liquids you drink, and the fragrances you smell. Atoms make up you! To understand the world and how it changes you need to understand atoms.

The idea of atoms has its origins in Greek and Indian philosophy nearly 2500 years ago, but it was not until the 19th century that there was experimental evidence to support their existence. Although atoms are too small ever to be seen directly by a human eye, they are fundamental to chemistry. All the atoms in a piece of gold foil, for example, have the same chemical properties. The atoms of gold, however, have different properties from the atoms of aluminium. This chapter will explain how they differ. We will explore their structure and discover that different atoms are made from different combinations of the same sub-atomic particles.

This exploration will take us into some difficult areas because our everyday notion of particles following fixed trajectories does not apply to the microscopic world of the atom. To understand the block structure of the Periodic Table we need to use **quantum theory** and adopt a wave description of matter. These ideas are revolutionary. As Niels Bohr, one of the principal scientists involved in the development of quantum theory said, 'Anyone who is not shocked by quantum theory has not understood it.'

TOK

Richard Feynman: "… if all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis … that *all things are made of atoms.*" Are the models and theories which scientists create accurate descriptions of the natural world, or are they primarily useful interpretations for prediction, explanation, and control of the natural world?



The hydrogen atom shown as a nucleus (a proton, pink), and an electron orbiting in a wavy path (light blue). It is necessary to consider the wave properties of the electron to understand atomic structure in detail.

A billion of your atoms once made up Shakespeare, another billion made up Beethoven, another billion St. Peter and another billion the Buddha. Atoms can rearrange in chemical reactions but they cannot be destroyed.

2.1 The nuclear atom

Understandings:

- Atoms contain a positively charged dense nucleus composed of protons and neutrons (nucleons).

Guidance
Relative masses and charges of the sub-atomic particles should be known, actual values are given in section 4 of the IB data booklet. The mass of the electron can be considered negligible.

- Negatively charged electrons occupy the space outside the nucleus.
- The mass spectrometer is used to determine the relative atomic mass of an element from its isotopic composition.

Guidance
The operation of the mass spectrometer is not required.

Applications and skills:

- Use of the nuclear symbol notation $^{A}_{Z}X$ to deduce the number of protons, neutrons, and electrons in atoms and ions.
- Calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.

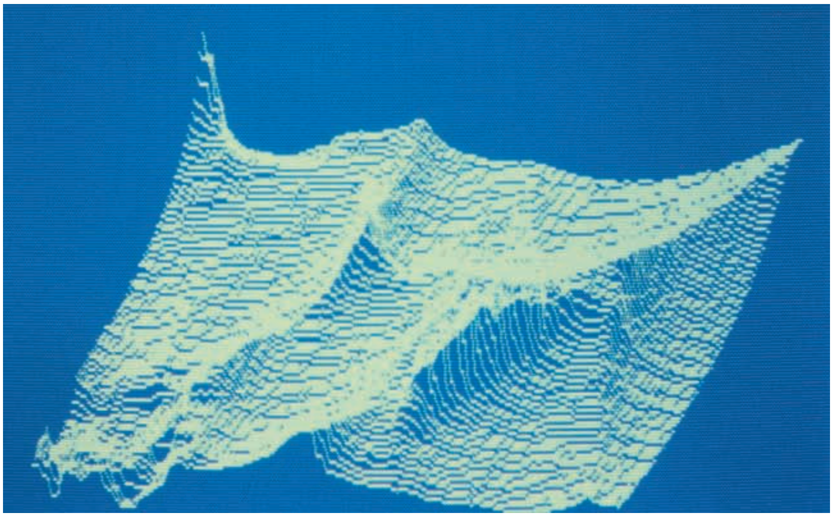
Guidance
Specific examples of isotopes need not be learned.

Dalton's model of the atom

An element is a substance that cannot be broken down into simpler substances by a chemical reaction.

The word 'atom' comes from the Greek words for 'not able to be cut'.

One of the first great achievements of chemistry was to show that all matter is built from about 100 **elements**. As mentioned in Chapter 1, the elements are substances which cannot be broken down into simpler components by chemical reactions. They are the simplest substances and their names are listed in your IB data booklet (section 5). Different elements have different chemical properties but gold foil, for example, reacts in essentially the same way as a single piece of gold dust. Indeed if the gold dust is cut into smaller and smaller pieces, the chemical properties would remain essentially the same until we reached an **atom**. This is the smallest unit of an element. There are only 92 elements which occur naturally on earth and they are made up from only 92 different types of atom. (This statement will be qualified when isotopes are discussed later in the chapter.)



Scanning tunnelling microscope (STM) image of the surface of pure gold. STM provides a magnification of 250 000 times, which records the surface structure at the level of the individual atoms. Gold exists in many forms – gold foil, nuggets, blocks, etc., which all contain the same type of atoms. The 'rolling hills' structure seen here is the result of changes in the surface energy as the gold cooled from its molten state. STM is based on quantum mechanical effects, and is described on page 92.

NATURE OF SCIENCE

The idea that matter is made up from elements and atoms dates back to the Indian philosophy of the sixth century BCE and the Greek philosophy of Democritus (460 BCE to 370 BCE). These ideas were speculative as there was little evidence to support them. A significant development for chemistry came with the publication of Robert Boyle's *Skeptical Chemist* of 1661 which emphasized the need for scientific knowledge to be justified by evidence from practical investigations. Boyle was the first to propose the modern concept of an element as a substance which cannot be changed into anything simpler.

The modern idea of the atom dates from the beginning of the 19th century. John Dalton noticed that the elements hydrogen and oxygen always combined together in fixed proportions. To explain this observation he proposed that:

- all matter is composed of tiny indivisible particles called atoms;
- atoms cannot be created or destroyed;
- atoms of the same element are alike in every way;
- atoms of different elements are different;
- atoms can combine together in small numbers to form **molecules**.

Using this model we can understand how elements react together to make new substances called **compounds**. The compound water, for example, is formed when two hydrogen atoms combine with one oxygen atom to produce one water molecule. If we repeat the reaction on a larger scale with $2 \times 6.02 \times 10^{23}$ atoms of hydrogen and 6.02×10^{23} atoms of oxygen, 6.02×10^{23} molecules of water will be formed. This leads to the conclusion (see Chapter 1) that 2.02 g of hydrogen will react with 16.00 g of oxygen to form 18.02 g of water. This is one of the observations Dalton was trying to explain.

NATURE OF SCIENCE

Dalton was a man of regular habits. 'For fifty-seven years... he measured the rainfall, the temperature... Of all that mass of data, nothing whatever came. But of the one searching, almost childlike question about the weights that enter the construction of simple molecules – out of that came modern atomic theory. That is the essence of science: ask an impertinent question: and you are on the way to the pertinent answer.' (J. Bronowski)

Dalton was the first person to assign chemical symbols to the different elements.

CHALLENGE YOURSELF

2 It is now known that some of these substances are not elements but compounds. Lime, for example, is a compound of calcium and oxygen. Can you find any other examples in this list and explain why the elements had not been extracted at this time?

John Dalton's symbols for the elements.

CHALLENGE YOURSELF

1 Can you think of any evidence based on simple observations that supports the idea that water is made up from discrete particles?

Although John Dalton (1766–1844) was a school teacher from Manchester in England, his name has passed into other languages. The internationally recognized term for colour-blindness, *Daltonisme* in French, for example, derives from the fact the he suffered from the condition.

TOK

'What we observe is not nature itself but nature exposed to our mode of questioning.' (Werner Heisenberg). How does the knowledge we gain about the natural world depend on the questions we ask and the experiments we perform?

A compound is a substance made by chemically combining two or more elements. It has different properties from its constituent elements.

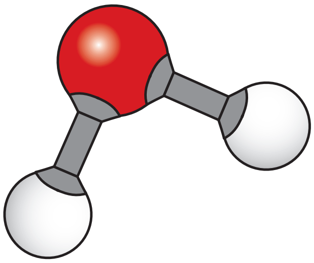


Figure 2.1 A model of a water molecule made from two hydrogen atoms and one oxygen atom. Dalton's picture of the atom as a hard ball is the basis behind the molecular models we use today.

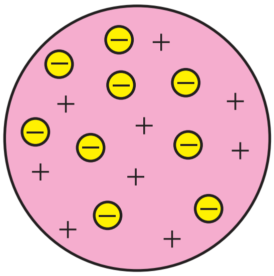


Figure 2.2 Thomson's 'plum pudding' model of the atom. The electrons (yellow) are scattered in a positively charged sponge-like substance (pink).

TOK

When Geiger and Marsden reported to Rutherford that they had seen nothing unusual with most of the alpha particles passing straight through the gold and a small number being deflected by small angles, he asked them to look and see if any of the alpha particles had bounced back. This was a very unusual suggestion to make at the time, with little logical justification. What is the role of intuition in the pursuit of scientific knowledge?

Following his example, the formation of water (described above) can be written using modern notation:

$$2H + O \rightarrow H_2O$$

But what are atoms really like? It can be useful to think of them as hard spheres (Figure 2.1), but this tells us little about how the atoms of different elements differ. To understand this, it is necessary to probe deeper.

NATURE OF SCIENCE

Dalton's atomic theory was not accepted when it was first proposed. Many scientists, such as Kelvin for example, considered it as nothing more than a useful fiction which should not be taken too seriously. Over time, as the supporting evidence grew, there was a general shift in thinking which led to its widespread acceptance. These revolutions in understanding or '**paradigm shifts**' are characteristic of the evolutions of scientific thinking.

Atoms contain electrons

The first indication that atoms were destructible came at the end of the 19th century when the British scientist J. J. Thomson discovered that different metals produce a stream of negatively charged particles when a high voltage is applied across two electrodes. As these particles, which we now know as **electrons**, were the same regardless of the metal, he suggested that they are part of the make-up of all atoms.

NATURE OF SCIENCE

The properties of electrons, or cathode rays as they were first called, could only be investigated once powerful vacuum pumps had been invented – and once advances had been made in the use and understanding of electricity and magnetism. Improved instrumentation and new technology have often been the drivers for new discoveries.

As it was known that the atom had no net charge, Thomson pictured the atom as a 'plum pudding', with the negatively charged electrons scattered in a positively charged sponge-like substance (Figure 2.2).

Rutherford's model of the atom

Ernest Rutherford (1871–1937) and his research team working at Manchester University in England, tested Thomson's model by firing alpha particles at a piece of gold foil. We now know that alpha particles are helium nuclei, composed of two protons and two neutrons, with a positive charge. They are emitted by nuclei with too many protons to be stable. If Thomson's model was correct, the alpha particles should either pass straight through or get stuck in the positive 'sponge'. Most of the alpha particles did indeed pass straight through, but a very small number were repelled and bounced back. Ernest Rutherford recalled that 'It was quite the most incredible thing that has happened to me. It was as if you had fired a (artillery) shell at a piece of tissue paper and it came back and hit you.'

The large number of undeflected particles led to the conclusion that the atom is mainly empty space. Large deflections occur when the positively charged alpha particles collide with and are repelled by a dense, positively charged centre called the **nucleus** (Figure 2.3). The fact that only a small number of alpha particles bounce back suggests that the nucleus is very small.

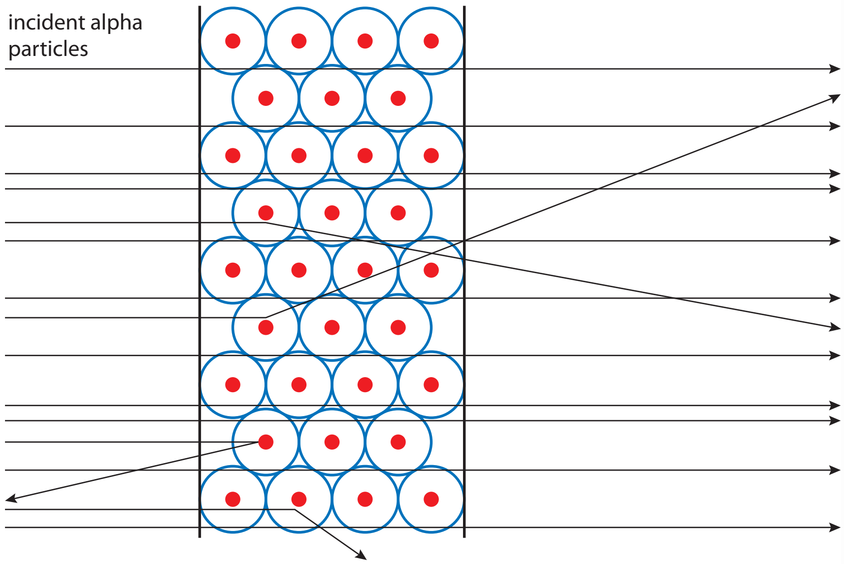


Figure 2.3 Rutherford's model of the atom accounts for the experimental observations. Most of the alpha particles pass straight through but a small number collide with and are repelled by a positively charged nucleus.

NATURE OF SCIENCE

Our knowledge of the nuclear atom came from Rutherford's experiments with the relatively newly discovered alpha particles. Scientific knowledge grows as new evidence is gathered as a result of new technologies and instrumentation.

The European Organization for Nuclear Research (CERN) is run by twenty European Member States, with involvements from scientists from many other countries. It operates the world's largest particle physics research centre, including particle accelerators and detectors used to study the fundamental constituents of matter.

PET (positron-emission tomography) scanners give three-dimensional images of tracer concentration in the body, and can be used to detect cancers. The patient is injected with a tracer compound labelled with a positron-emitting isotope. The positrons collide with electrons after travelling a short distance (≈1 mm) within the body. Both particles are destroyed with the production of two photons, which can be collected by the detectors surrounding the patient, and used to generate an image.

Sub-atomic particles

A hundred or so years after Dalton first proposed his model, these experiments and many others showed that atoms are themselves made up from smaller or **sub-atomic** particles. The nucleus of an atom is made up of **protons** and **neutrons**, collectively called **nucleons**. Both the protons and neutrons have almost the same mass as a hydrogen nucleus and account for the most of the mass of the atom. **Electrons**, which have a charge equal and opposite to that of the proton, occupy the space in the atom outside of the nucleus.

These particles are described by their *relative* masses and charges which have no units. The absolute masses and charges of these fundamental particles are given in section 4 of the IB data booklet.

Particle	Relative mass	Relative charge
proton	1	+1
electron	0.0005	−1
neutron	1	0

NATURE OF SCIENCE

The description of sub-atomic particles offered here is sufficient to understand chemistry but incomplete. Although the electron is indeed a fundamental particle, we now know that the protons and neutrons are both themselves made up from more fundamental particles called quarks. We also know that all particles have anti-particles. The positron is the anti-particle of an electron; it has the same mass but has an equal and opposite positive charge. When particles and anti-particles collide they destroy each other and release energy in the form of high-energy photons called gamma rays. Our treatment of sub-atomic particles is in line with the principle of Occam's razor, which states that theories should be as simple as possible while maximizing explanatory power.

View of a patient undergoing a positron-emission tomography (PET) brain scan. A radioactive tracer is injected into the patient's bloodstream, which is then absorbed by active tissues of the brain. The PET scanner detects photons emitted by the tracer and produces 'slice' images.

As you are made from atoms, you are also mainly empty space. The particles which make up your mass would occupy the same volume as a flea if they were all squashed together, but a flea with your mass. This gives you an idea of the density of the nucleus.

TOK

None of these sub-atomic particles can be (or ever will be) directly observed. Which ways of knowing do we use to interpret indirect evidence gained through the use of technology.

Bohr model of the hydrogen atom

The Danish physicist Niels Bohr pictured the hydrogen atom as a small 'solar system', with an electron moving in an orbit or energy level around the positively charged nucleus of one proton (Figure 2.4). The electrostatic force of attraction between the oppositely charged sub-atomic particles prevents the electron from leaving the atom. The nuclear radius is 10^{-15} m and the atomic radius 10^{-10} m, so most of the volume of the atom is empty space.

The existence of neutrally charged neutrons is crucial for the stability of nuclei of later elements, which have more than one proton. Without the neutrons, the positively charged protons would mutually repel each other and the nucleus would fall apart.

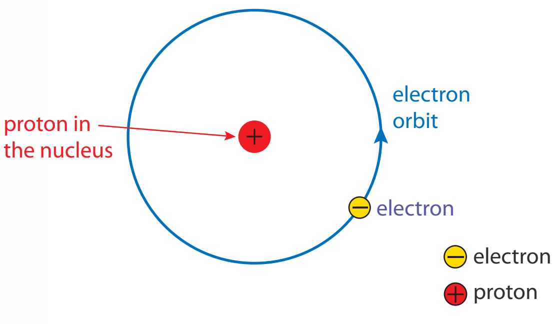


Figure 2.4 The simplest atom. Only one proton and one electron make up the hydrogen atom. The nuclear radius is 10^{-15} m and the atomic radius 10^{-10} m. Most of the volume of the atom is empty – the only occupant is the negatively charged electron. It is useful to think of the electron orbiting the nucleus in a similar way to the planets orbiting the sun. The absence of a neutron is significant – it would be essentially redundant as there is only one proton.

Atomic number and mass number

We are now in a position to understand how the atoms of different elements differ. They are all made from the same basic ingredients, the sub-atomic particles. The only difference is the recipe – how many of each of these sub-atomic particles are present in the atoms of different elements. If you look at the Periodic Table, you will see that the elements are each given a number which describes their relative position in the table. This is their **atomic number**. We now know that the atomic number, represented by **Z**, is the defining property of an element as it tells us something about the structure of the atoms of the element. The atomic number is defined as the number of protons in the atom.

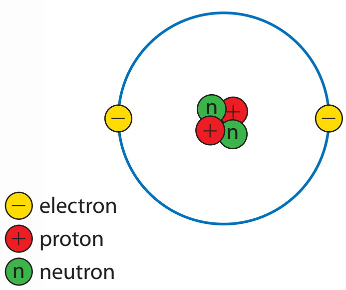


Figure 2.5 A helium atom. The two neutrons allow the two protons, which repel each other, to stay in the nucleus.

The atomic number (Z) is defined as the number of protons in the nucleus.

As an atom has no overall charge, the positive charge of the protons must be balanced by the negative charge of the electrons. The atomic number is also equal to the number of electrons.

The electron has such a very small mass that it is essentially ignored in mass calculations. The mass of an atom depends on the number of protons and neutrons only. The **mass number**, given the symbol **A**, is defined as the number of protons plus the number of neutrons in an atom. An atom is identified in the following way:

$${}^{A}_{Z}X$$

$A \rightarrow$ mass number

$X \rightarrow$ symbol of element

$Z \rightarrow$ atomic number

We can use these numbers to find the composition of any atom.

$$\text{number of protons (p)} = \text{number of electrons} = Z$$
$$\text{number of neutrons (n)} = A - \text{number of protons} = A - Z$$

Consider an atom of aluminium:

$${}^{27}_{13}Al$$

$n = 27 - 13 = 14$

$p = 13$
$e = 13$

An aluminium atom is made from 13 protons and 13 electrons. An atom of gold on the other hand has 79 protons and 79 electrons. Can you find gold in the Periodic Table?

Isotopes

Find chlorine in the Periodic Table. There are two numbers associated with the element, as shown below.

8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 24.16
16 **S** Sulfur 32.06	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
34 **Se** Selenium 78.95	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80

Atomic number = 17

Relative atomic mass = 35.45

How can an element have a fractional relative atomic mass if both the proton and neutron have a relative mass of 1? One reason is that atoms of the same element with different mass numbers exist, so it is necessary to work within an average value – as discussed in Chapter 1.

To have different mass numbers, the atoms must have different numbers of neutrons – all the atoms have the same number of protons as they are all chlorine atoms. Atoms of the same element with different numbers of neutrons are called **isotopes**.

The isotopes show the same chemical properties, as a difference in the number of neutrons makes no difference to how they react and so they occupy the same place in the Periodic Table.

Make sure you have a precise understanding of the terms identified in the subject guide. The atomic number, for example, is defined in terms of the number of protons, not electrons.

The mass number (A) is the number of protons plus the number of neutrons in an atom. As it gives the total number of nucleons in the nucleus, it is sometimes called the nucleon number.

Isotopes are atoms of the same element with different mass numbers.

The word 'isotope' derives from the Greek for 'same place'. As isotopes are atoms of the same element, they occupy the same place in the Periodic Table.

A common error is to misunderstand the meaning of 'physical property'. A difference in the number of neutrons is not a different physical property. A physical property of a substance can be measured without changing the chemical composition of the substance, e.g. melting point, density.

Chlorine exists as two isotopes, ^{35}Cl and ^{37}Cl. The average relative mass of the isotopes is, however, not 36, but 35.45. This value is closer to 35 as there are more ^{35}Cl atoms in nature – it is the more abundant isotope. In a sample of 100 chlorine atoms, there are 77.5 atoms of ^{35}Cl and 22.5 atoms of the heavier isotope, ^{37}Cl.

To work out the average mass of one atom we first have to calculate the total mass of the hundred atoms:

$$\text{total mass} = (77.5 \times 35) + (22.5 \times 37) = 3545$$

$$\text{relative average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{3545}{100} = 35.45$$

The two isotopes are both atoms of chlorine with 17 protons and 17 electrons.

- ^{35}Cl; number of neutrons = 35 – 17 = 18
- ^{37}Cl; number of neutrons = 37 – 17 = 20

Although both isotopes essentially have the same chemical properties, the difference in mass does lead to different physical properties such as boiling and melting points. Heavier isotopes move more slowly at a given temperature and these differences can be used to separate isotopes.

Exercises

1 State two physical properties other than boiling and melting point that would differ for the two isotopes of chlorine.

2 Explain why the relative atomic mass of tellurium is greater than the relative atomic mass of iodine, even though iodine has a greater atomic number.

Radioisotopes are used in nuclear medicine for diagnostics, treatment, and research, as tracers in biochemical and pharmaceutical research, and as 'chemical clocks' in geological and archaeological dating.

Uranium exists in nature as two isotopes, uranium-235 and uranium-238. One key stage in the Manhattan Project (the development of the atomic bomb during World War II) was the enrichment of uranium with the lighter and less abundant isotope, as this is the atom which splits more easily. It is only 0.711% abundant in nature. First the uranium was converted to a gaseous compound (the hexafluoride UF_6). Gaseous molecules with the lighter uranium isotope move faster than those containing the heavier isotope at the same temperature and so the isotopes could be separated. Isotope enrichment is employed in many countries as part of nuclear energy and weaponry programmes. This is discussed in more detail in Chapter 14.

Radioactive isotopes are extremely hazardous and their use is of international concern. The International Atomic Energy Agency (IAEA) promotes the peaceful use of nuclear energy. The organization was awarded the Nobel Peace Prize in 2005.

NATURE OF SCIENCE

Science is a collaborative endeavour and it is common for scientists to work in teams between disciplines, laboratories, organizations, and countries. The Manhattan Project, which produced the first nuclear bomb, employed more than 130 000 people working in secret at different production and research sites. Today such collaboration is facilitated by virtual communication which allows scientists around the globe to work together.

Ions

The atomic number is defined in terms of number of protons because it is a fixed characteristic of the element. The number of protons identifies the element in the same way your fingerprints identify you. The number of protons and neutrons never changes during a chemical reaction. It is the electrons which are responsible for chemical change. Chapter 4 will examine how atoms can lose or gain electrons to form **ions**. When the number of protons in a particle is no longer balanced by the number of electrons, the particles has a non-zero charge. When an atom loses electrons it forms a positive ion or **cation**, as the number of protons is now greater than the number of electrons. Negative ions or **anions** are formed when atoms gain electrons. The magnitude of the charge depends on the number of electrons lost or gained. The

When an atom loses electrons, a positive ion is formed and when it gains electrons, a negative ion is formed. Positive ions are called cations and negative ions are called anions.

loss or gain of electrons makes a very big difference to the chemical properties. You swallow sodium ions, Na^+, every time you eat table salt, whereas (as you will discover in Chapter 3) sodium atoms, Na, are dangerously reactive.

An aluminium ion is formed when the atom loses three electrons. There is no change in the atomic or mass numbers of an ion because the number of protons and neutrons remains the same.

$${}^{27}_{13}Al^{3+}$$

The atom has lost 3 electrons.
$e = 13 - 3 = 10$

$p = 13$
$n = 27 - 13 = 14$

Oxygen forms the oxide ion when the atom gains two electrons.

$${}^{16}_{8}O^{2-}$$

The atom has gained 2 electrons.
$e = 8 + 2 = 10$

$p = 8$
$n = 16 - 8 = 8$

The element radium was first discovered by the Polish–French scientist Marie Curie. She is the only person to win Nobel Prizes in both Physics and Chemistry. The Curies were a remarkable family for scientific honours – Marie shared her first prize with husband Pierre, and her daughter Irène shared hers with her husband Frédéric. All the Curies' prizes were for work on radioactivity.

Worked example

Identify the sub-atomic particles present in an atom of ${}^{226}Ra$.

Solution

The number identifying the atom is the atomic number. We can find the atomic number from the IB data booklet (section 5).

We have $Z = 88$ and $A = 226$

In other words:

- number of protons (p) = 88
- number of electrons (e) = 88
- number of neutrons (n) = 226 – 88 = 138

Worked example

Most nutrient elements in food are present in the form of ions. The calcium ion ${}^{40}Ca^{2+}$, for example, is essential for healthy teeth and bones. Identify the sub-atomic particles present in the ion.

Solution

We can find the atomic number from the IB data booklet (section 5). We have $Z = 20$ and $A = 40$:

- number of protons (p) = 20
- number of neutrons (n) = 40 – 20 = 20

As the ion has a positive charge of 2+ there are two more protons than electrons:

- number of electrons = 20 – 2 = 18

Worked example

Identify the species with 19 protons, 20 neutrons and 18 electrons.

Solution

- the number of protons tells us the atomic number; $Z = 19$ and so the element is potassium: K
- the mass number $= p + n = 19 + 20 = 39$: $^{39}_{19}K$
- the charge will be $= p - e = 19 - 18 = +1$ as there is one extra proton: $^{39}_{19}K^{+}$

Exercises

3 Use the Periodic Table to identify the sub-atomic particles present in the following species.

	Species	No. of protons	No. of neutrons	No. of electrons
(a)	^{7}Li			
(b)	^{1}H			
(c)	^{14}C			
(d)	$^{19}F^{-}$			
(e)	$^{56}Fe^{3+}$			

4 Isoelectronic species have the same number of electrons. Identify the following isoelectronic species by giving the correct symbol and charge. You will need a Periodic Table.

The first one has been done as an example.

	Species	No. of protons	No. of neutrons	No. of electrons
	$^{40}Ca^{2+}$	20	20	18
(a)		18	22	18
(b)		19	20	18
(c)		17	18	18

5 Which of the following species contain more electrons than neutrons?

A $^{2}_{1}H$ **B** $^{11}_{5}B$ **C** $^{16}_{8}O^{2-}$ **D** $^{19}_{9}F^{-}$

6 Which of the following gives the correct composition of the $^{71}Ga^{+}$ ion present in the mass spectrometer when gallium is analysed.

	Protons	Neutrons	Electrons
A	31	71	30
B	31	40	30
C	31	40	32
D	32	40	31

Relative atomic masses of some elements

An instrument known as a **mass spectrometer** can be used to measure the mass of individual atoms. The mass of a hydrogen atom is 1.67×10^{-24} g and that of a carbon atom is 1.99×10^{-23} g. As the masses of all elements are in the range 10^{-24} to 10^{-22} g and these numbers are beyond our direct experience, it makes more sense to use relative values. The mass needs to be recorded relative to some agreed standard. As carbon is a very common element which is easy to transport and store because it is a solid, its isotope, ^{12}C, was chosen as the standard in 1961. As discussed in Chapter 1 this is given a relative mass of exactly 12, as shown below.

Element	Symbol	Relative atomic mass
carbon	C	12.011
chlorine	Cl	35.453
hydrogen	H	1.008
iron	Fe	55.845
Standard isotope	**Symbol**	**Relative atomic mass**
carbon-12	^{12}C	12.000

Carbon-12 is the most abundant isotope of carbon but carbon-13 and carbon-14 also exist. This explains why the average value for the element is greater than 12.

The relative atomic mass of an element (A_r) is the average mass of an atom of the element, taking into account all its isotopes and their relative abundance, compared to one atom of carbon-12.

Mass spectra

The results of the analysis by the mass spectrometer are presented in the form of a **mass spectrum**. The horizontal axis shows the mass/charge ratio of the different ions on the carbon-12 scale, which in most cases can be considered equivalent to their mass. The percentage abundance of the ions is shown on the vertical scale.

The mass spectrum of gallium in Figure 2.6 shows that in a sample of 100 atoms, 60 have a mass of 69 and 40 have a mass of 71.We can use this information to calculate the relative atomic mass of the element.

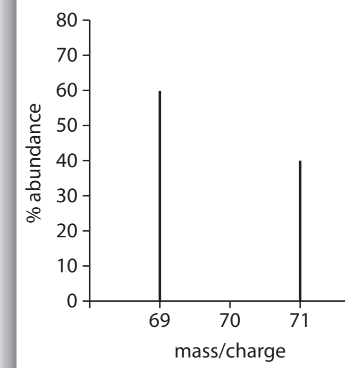


Figure 2.6 Mass spectrum for gallium. The number of lines indicates the number of isotopes (two in this case), the value on the *x*-axis indicates their mass number (69 and 71) and the *y*-axis shows the percentage abundance.

total mass of 100 atoms = (60 × 69) + (40 × 71) = 6980

$$\text{relative average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{6980}{100} = 69.80$$

Worked example

Deduce the relative atomic mass of the element rubidium from the data given in Figure 2.7.

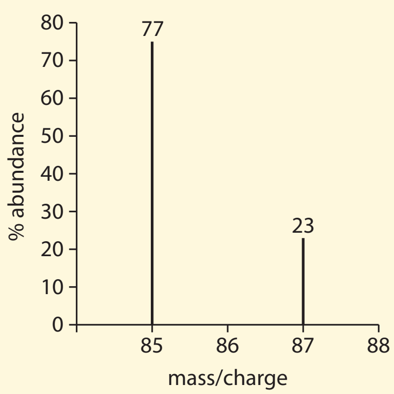


Figure 2.7 Mass spectrum for rubidium.

Solution

Consider a sample of 100 atoms.

total mass of 100 atoms = (85 × 77) + (87 × 23) = 8546

$$\text{relative atomic mass} = \text{average mass of atom} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{8546}{100} = 85.46$$

Worked example

Boron exists in two isotopic forms, ^{10}B and ^{11}B. ^{10}B is used as a control for nuclear reactors. Use your Periodic Table to find the abundances of the two isotopes.

Solution

Consider a sample of 100 atoms.

Let x atoms be ^{10}B atoms. The remaining atoms are ^{11}B.

number of ^{11}B atoms $= 100 - x$

total mass of 100 atoms $= x \times 10 + (100 - x) \times 11 = 10x + 1100 - 11x = 1100 - x$

$$\text{average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{1100 - x}{100}$$

From the Periodic Table, the relative atomic mass of boron = 10.81.

$$10.81 = \frac{1100 - x}{100}$$

$1081 = 1100 - x$

$x = 1100 - 1081 = 19$

The abundances are ^{10}B = 19% and ^{11}B = 81%

Exercises

7 What is the same for an atom of phosphorus-26 and an atom of phosphorus-27?

A atomic number and mass number
B number of protons and electrons
C number of neutrons and electrons
D number of protons and neutrons

8 Use the Periodic Table to find the percentage abundance of neon-20, assuming that neon has only one other isotope, neon-22.

9 The relative abundances of the two isotopes of chlorine are shown in this table:

Isotope	Relative abundance
^{35}Cl	75%
^{37}Cl	25%

Use this information to deduce the mass spectrum of chlorine gas, Cl_2.

10 Magnesium has three stable isotopes – ^{24}Mg, ^{25}Mg, and ^{26}Mg. The lightest isotope has an abundance of 78.90%. Calculate the percentage abundance of the other isotopes.

11 The Geiger–Marsden experiment, supervised by Ernest Rutherford, gave important evidence for the structure of the atom. Positively charged alpha particles were fired at a piece of gold foil. Most of the particles passed through with only minor deflections but a small number rebounded from the foil.

How did this experiment change our knowledge of the atom?

A It provided evidence for the existence of discrete atomic energy levels.
B It provided evidence for a positively charged dense nucleus.
C It provided evidence that electrons move in unpredictable paths around the nucleus.
D It provided evidence for the existence of an uncharged particle in the nucleus.

In 1911, a 40 kg meteorite fell in Egypt. Isotopic and chemical analysis of oxygen extracted from this meteorite show a different relative atomic mass to that of oxygen normally found on Earth. This value matched measurements made of the Martian atmosphere by the Viking landing in 1976, showing that the meteorite had originated from Mars.

2.2 Electron configuration

Understandings:

- Emission spectra are produced when photons are emitted from atoms as excited electrons return to a lower energy level.
- The line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher energies.

Guidance
The names of the different series in the hydrogen line spectrum are not required.

- The main energy level or shell is given an integer number, n, and can hold a maximum number of electrons, $2n^2$.
- A more detailed model of the atom describes the division of the main energy level into s, p, d, and f sub-levels of successively higher energies.
- Sub-levels contain a fixed number of orbitals, regions of space where there is a high probability of finding an electron.
- Each orbital has a defined energy state for a given electronic configuration and chemical environment and can hold two electrons of opposite spin.

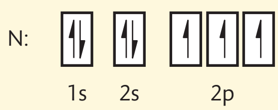
Applications and skills:

- Description of the relationship between colour, wavelength, frequency, and energy across the electromagnetic spectrum.

Guidance
Details of the electromagnetic spectrum are given in the IB data booklet in section 3.

- Distinction between a continuous spectrum and a line spectrum.
- Description of the emission spectrum of the hydrogen atom, including the relationships between the lines and energy transitions to the first, second, and third energy levels.
- Recognition of the shape of an s orbital and the p_x, p_y, and p_z atomic orbitals.
- Application of the Aufbau principle, Hund's rule, and the Pauli exclusion principle to write electron configurations for atoms and ions up to $Z = 36$.

Guidance
- *Full electron configurations (e.g. $1s^22s^22p^63s^23p^4$) and condensed electron configurations (e.g. [Ne] $3s^23p^4$) should be covered.*
- *Orbital diagrams should be used to represent the character and relative energy of orbitals. Orbital diagrams refer to arrow-in-box diagrams, such as the one given below.*



The electron configurations of Cr and Cu as exceptions should be covered.

Atoms of different elements give out light of a distinctive colour when an electric discharge is passed through a vapour of the element. Similarly, metals can be identified by the colour of the flame produced when their compounds are heated in a Bunsen burner. Analysis of the light emitted by different atoms has given us insights into the electron configurations within the atom.

To interpret these results we must consider the nature of electromagnetic radiation.


(a)


(b)


(c)

Flame tests on the compounds of (a) sodium, (b) potassium, and (c) copper.

Flame colours can be used to identify unknown compounds.

The electromagnetic spectrum

Electromagnetic radiation comes in different forms of differing energy. The visible light we need to see the world is only a small part of the full spectrum, which ranges from low-energy radio waves to high-energy gamma rays. All electromagnetic waves

All electromagnetic waves travel at the same speed, $c = 3.00 \times 10^8$ m s^{-1}. This is the cosmic speed limit as, according to Einstein's Theory of Relativity, nothing in the universe can travel faster than this.

travel at the same **speed** (c) but can be distinguished by their different **wavelengths** (λ) (Figure 2.8). Different colours of visible light have different wavelengths; red light, for example, has a longer wavelength than blue light. The full electromagnetic spectrum is given in section 3 of the IB data booklet.

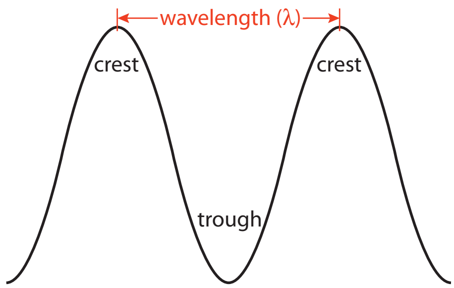


Figure 2.8 Snapshot of a wave at a given instant. The distance between successive crests or peaks is called the wavelength (λ).

The number of waves which pass a particular point in 1 s is called the **frequency** (ν); the shorter the wavelength, the higher the frequency. Blue light has a higher frequency than red light.

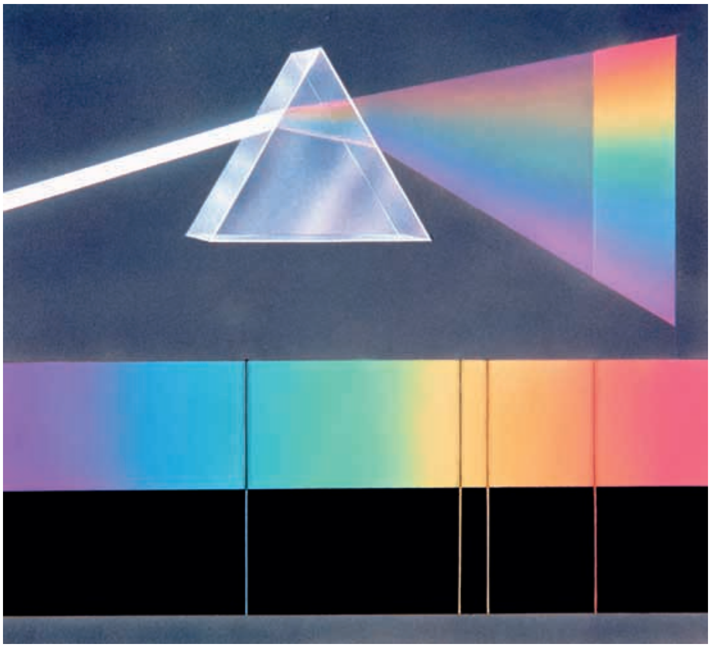
The distance between two successive crests (or troughs) is called the wavelength (λ). The frequency (ν) of the wave is the number of waves which pass a point in one second. The wavelength and frequency are related by the equation $c = \nu\lambda$ where c is the speed of light.

The wavelength and frequency are related by the equation:

$$c = \nu \lambda$$

where c is the speed of light.

White light is a mixture of light waves of differing wavelengths or colours. We see this when sunlight passes through a prism to produce a **continuous spectrum** or as a rainbow when light is scattered through water droplets in the air.



A continuous spectrum is produced when white light is passed through a prism. The different colours merge smoothly into one another. The two spectra below the illustration of the prism show, (top) a continuous spectrum with a series of discrete absorption lines and (bottom) a line emission spectrum.

As well as visible light, atoms emit infrared radiation, which has a longer wavelength than red light, and ultraviolet radiation, with a shorter wavelength than violet light. The complete electromagnetic spectrum is shown in Figure 2.9.

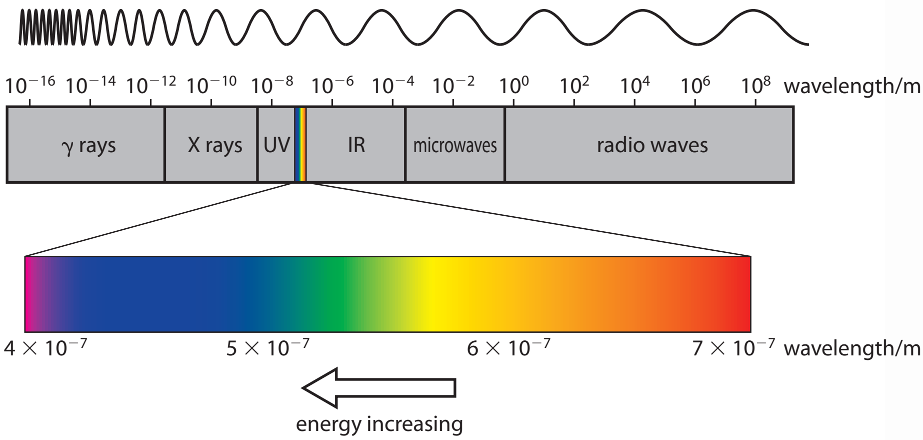


Figure 2.9 The changing wavelength (in m) of electromagnetic radiation through the spectrum is shown by the trace across the top. At the short wavelength end (on the left) of the spectrum are γ rays, X rays, and ultraviolet light. In the centre of the spectrum are wavelengths that the human eye can see, known as visible light. Visible light comprises light of different wavelengths, energies, and colours. At the longer wavelength end of the spectrum (on the right) are infrared radiation, microwaves, and radio waves. The visible spectrum gives us only a small window to see the world.

Atomic absorption and emission line spectra

When electromagnetic radiation is passed through a collection of atoms some of the radiation is absorbed and used to excite the atoms from a lower energy level to a higher energy level. The spectrometer analyses the transmitted radiation relative to the incident radiation and an **absorption spectrum** is produced.

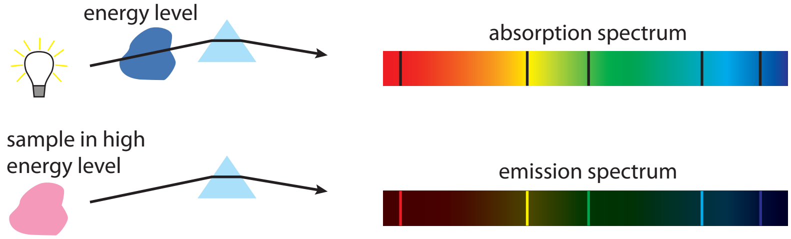


Figure 2.10 The origin of absorption and emission spectra. An absorption spectrum shows the radiation absorbed as atoms move from a lower to a higher energy level. An emission spectrum is produced when an atom moves from a higher to a lower level.

When white light is passed through hydrogen gas, an absorption **line spectrum** is produced with some colours of the continuous spectrum missing. If a high voltage is applied to the gas, a corresponding **emission** line spectrum is produced.

Visible emission spectrum of hydrogen. These lines form the Balmer series and you should note that they converge at higher energies. Similar series are found in the ultraviolet region – the Lyman Series – and in the infrared region – the Paschen series.

The colours present in the emission spectrum are the same as those that are missing from the absorption spectra. As different elements have different line spectra they can be used like barcodes to identify unknown elements. They give us valuable information about the electron configurations of different atoms.

Investigating flame tests

Full details of how to carry out this experiment with a worksheet are available online.

Emission spectra could be observed using discharge tubes of different gases and a spectroscope.

Electromagnetic waves allow energy to be transferred across the universe. They also carry information. Low-energy radio waves are used in radar and television, for example, and the higher energy gamma rays are used as medical tracers. The precision with which we view the world is limited by the wave lengths of the colours we can see. This is why we will never be able to see an atom directly; it is too small to interact with the relatively long waves of visible light. What are the implications of this for human knowledge?

The elemental composition of stars can be determined by analysing their absorption spectra. This is discussed in more detail in Chapter 14.

The element helium was discovered in the Sun before it was found on Earth. Some unexpected spectral lines were observed when the absorption spectra of sunlight was analysed. These lines did not correspond to any known element. The new element was named after the Greek word *helios*, which means 'Sun'. Emission and absorption spectra can be used like barcodes to identify the different elements.

Evidence for the Bohr model

How can a hydrogen atom absorb and emit energy? A simple picture of the atom was considered earlier with the electron orbiting the nucleus in a circular energy level. Niels Bohr proposed that an electron moves into an orbit or higher energy level further from the nucleus when an atom absorbs energy. The **excited state** produced is, however, unstable and the electron soon falls back to the lowest level or **ground state**. The energy the electron gives out when it falls into lower levels is in the form of electromagnetic radiation. One packet of energy (quantum) or **photon** is released for each electron transition (Figure 2.11). Photons of ultraviolet light have more energy than photons of infrared light. The energy of the photon is proportional to the frequency of the radiation.

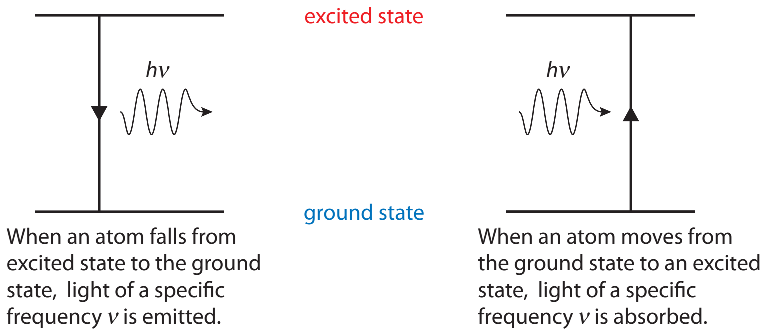


Figure 2.11 Emission and absorption spectra are the result of an energy transition between the ground and excited states.

The energy of the photon of light emitted is equal to the energy change in the atom:

$$\Delta E_{\text{electron}} = E_{\text{photon}}$$

It is also related to the frequency of the radiation by the Planck equation:

$$E_{\text{photon}} = h\,\nu$$

This equation and the value of h (the Planck constant) are given in sections 1 and 2 of the IB data booklet.

This leads to:

$$\Delta E_{\text{electron}} = h\,\nu$$

This is a very significant equation as it shows that line spectra allow us to glimpse the inside of the atom. The atoms emit photons of certain energies which give lines of certain frequencies, because the electron can only occupy certain orbits. The energy levels can be thought of as a staircase. The electron cannot change its energy in a continuous way, in the same way that you cannot stand between steps; it can only change its energy by discrete amounts. This energy of the atom is **quantized**. The line spectrum is crucial evidence for quantization: if the energy were not quantized, the emission spectrum would be continuous.

- **A continuous spectrum shows an unbroken sequence of frequencies, such as the spectrum of visible light.**
- **A line emission spectrum has only certain frequencies of light as it is produced by excited atoms and ions as they fall back to a lower energy level.**
- **A line absorption spectrum is a continuous spectrum except for certain colours which are absorbed as the atoms are excited to higher energy levels.**

NATURE OF SCIENCE

The idea that electromagnetic waves can be thought of as a stream of photons or quanta is one aspect of quantum theory. The theory has implications for human knowledge and technology. The key idea is that energy can only be transferred in discrete amounts or quanta. Quantum theory shows us that our everyday experience cannot be transferred to the microscopic world of the atom and has led to great technological breakthroughs such as the modern computer. It has been estimated that 30% of the gross national product of the USA depends on the application of quantum theory. In the modern world our scientific understanding has led to many technological developments. These new technologies in their turn drive developments in science. The implications of the quantum theory for the electron are discussed in more detail later (page 74). Note that 'discrete' has a different meaning to 'discreet'.

When asked to distinguish between a line spectrum and a continuous spectrum, references should be made to discrete or continuous energy levels and all or specific colours, wavelengths, or frequencies.

The amount of light absorbed at particular frequency depends on the identity and concentration of atoms present. Atomic absorption spectroscopy is used to measure the concentration of metallic elements.

The hydrogen spectrum

The hydrogen atom gives out energy when an electron falls from a higher to a lower energy level. Hydrogen produces visible light when the electron falls to the second energy level (n = 2). The transitions to the first energy level (n = 1) correspond to a higher energy change and are in the ultraviolet region of the spectrum. Infrared radiation is produced when an electron falls to the third or higher energy levels (Figure 2.12).

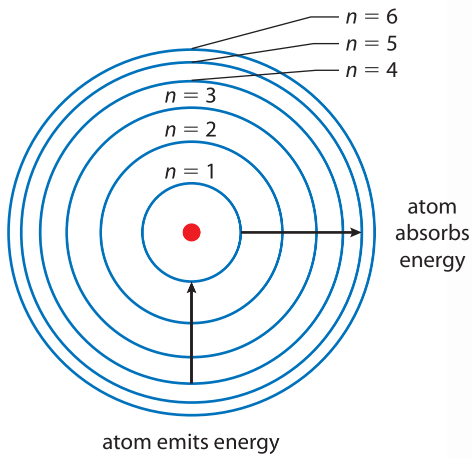


Figure 2.12 When an electron is excited from a lower to a higher energy level, energy is absorbed and a line in an absorption spectrum is produced. When an electron falls from a higher to a lower energy level, radiation is given out by the atom and a line in an emission spectrum is produced.

The pattern of the lines in Figure 2.12 gives us a picture of the energy levels in the atom. The lines **converge** at higher energies because the energy levels inside the atoms are closer together at higher energy. When an electron is at the highest energy $n = \infty$, it is no longer in the atom and the atom has been ionized. The energy needed to remove an electron from the ground state of an atom in a mole of gaseous atoms, ions, or molecules is called the **ionization energy**. Ionization energies can also be used to support this model of the atom (see page 85).

The energy of a photon of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength. It can be calculated from the Planck equation ($E = h\nu$), which is given in section 1 of the IB data booklet.

The first ionization energy of an element is the minimum energy needed to remove one mole of electrons from one mole of gaseous atoms in their ground state.

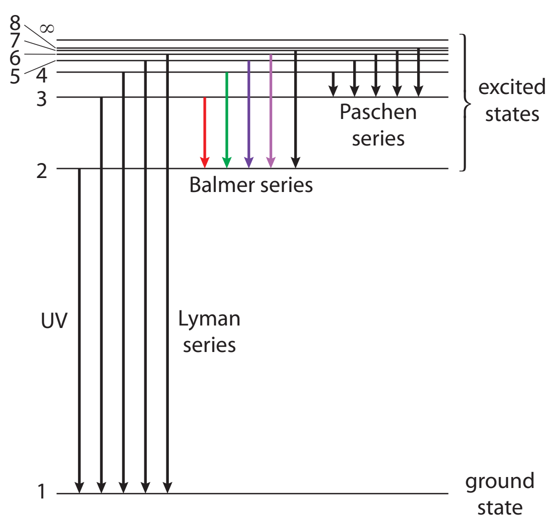
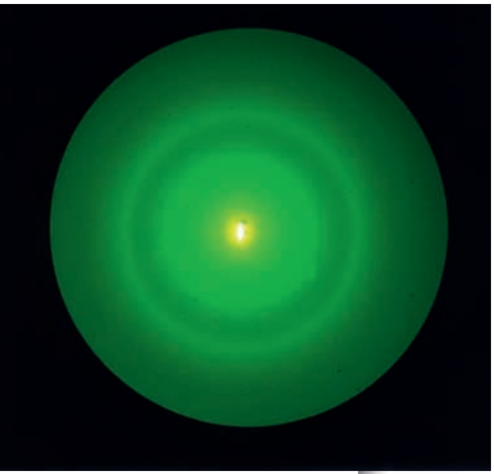


Figure 2.13 Energy levels of the hydrogen atom showing the transitions which produce the Lyman, Balmer, and Paschen series. The transition 1 → ∞ corresponds to ionization:

$$H(g) \rightarrow H^+(g) + e^-$$

This is discussed in more detail later.



Demonstration of wave–particle duality. An electron gun has been fired at a thin sheet of graphite. The electrons passed through the graphite and hit a luminescent screen, producing the pattern of rings associated with diffraction. Diffraction occurs when a wave passes through an aperture similar in size to its wavelength. Quantum theory shows that electrons have wavelengths inversely proportional to their momentum (momentum is the product of their mass and velocity).

Wave and particle models

Although the Bohr model of the atom was able to explain the emission spectrum of hydrogen with great success, it failed to predict the spectral lines of atoms with more than one electron. The model is a simplification. To develop the model of the atom further, we need to reconsider the nature of light and matter.

We saw earlier that light could either be described by its frequency, ν, which is a wave property, or by the energy of individual particles, E (called photons or quanta of light), which make up a beam of light. The two properties are related by the Planck equation $E = h\,\nu$. Both wave and particle models have traditionally been used to explain scientific phenomena and you may be tempted to ask which model gives the 'true' description of light. We now realize that neither model gives a complete explanation of light's properties – both models are needed.

- The diffraction, or spreading out, of light that occurs when light passes through a small slit can only be explained by a wave model.
- The scattering of electrons that occurs when light is incident on a metal surface is best explained using a particle model of light.

In a similar way, quantum theory suggests that it is sometimes preferable to think of an electron (or indeed any particle) as having wave properties. The diffraction pattern produced when a beam of electrons is passed through a thin sheet of graphite demonstrates the wave properties of electrons. To understand the electron configurations of atoms it is useful to consider a wave description of the electron.

NATURE OF SCIENCE

Models are used in science to explain processes that may not be observable. The models can be simple or complex in nature but must match the experimental evidence if they are to be accepted. The power of the wave and particle models is that they are based on our everyday experience, but this is also their limitation. We should not be too surprised if this way of looking at the world breaks down when applied to the atomic scale, as this is beyond our experience. The model we use depends on the phenomena we are trying to explain.

When differences occur between the theoretical predictions and experimental data, the models must be modified or replaced by new models. Bohr's model of the hydrogen atom was very successful in explaining the line spectra of the hydrogen atom but had some difficulties. It could not explain the spectra of more complex atoms, or the relative intensities of the lines in the hydrogen spectra. It also suffered from a fundamental weakness in that it was based on postulates which combined ideas from classical and quantum physics in an ad hoc manner, with little experimental justification: ideally models should be consistent with the assumptions and premises of other theories. A modification of Bohr's model could only be achieved at the expense of changing our model of the electron as a particle. Dalton's atomic model and quantum theory are both examples of such radical changes of understanding, often called **paradigm shifts**.

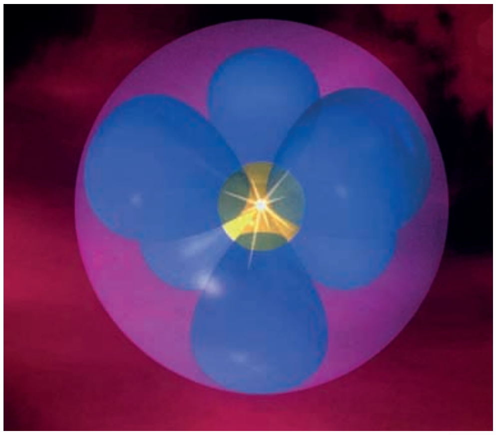
TOK

The Uncertainty Principle can be thought of as an extreme example of the observer effect discussed on page 958. The significance of the Uncertainty Principle is that it shows the effect cannot be decreased indefinitely by improving the apparatus. There is an inherent uncertainty in our measurements. What are the implications of this for the limits of human knowledge?

The Uncertainty Principle

Another fundamental problem with the Bohr model is that it assumes the electron's trajectory can be precisely described. This is now known to be impossible, as any attempt to measure an electron's position will disturb its motion. The act of focusing radiation to locate the electron gives the electron a random 'kick' which sends it hurtling off in a random direction.

According to Heisenberg's **Uncertainty Principle** we cannot know where an electron is at any given moment in time – the best we can hope for is a probability picture of where the electron is *likely* to be. The possible positions of an electron are spread out in space in the same way as a wave is spread across a water surface.



Representation of atomic orbitals in an atom of neon, Ne. The nucleus is shown by a flash of light and the 1s orbital as a yellow sphere. The 2s orbital is shown as a pink sphere, and the 2p orbitals as blue lobes. According to Heisenberg's Principle, the exact position of an electron cannot be defined; atomic orbitals represent regions where there is a high probability of finding an electron.

Schrödinger model of the hydrogen atom

We have seen that the electron can be considered to have wave properties and that only a probability description of its location is possible at a given time. Both of these ideas are encapsulated in the Schrödinger model of the hydrogen atom. Erwin Schrödinger (1887–1961) proposed that a wave equation could be used to describe the behaviour of an electron in the same way that a wave equation could be used to described the behaviour of light. The equation can be applied to multi-electron systems and its solutions are known as **atomic orbitals**. An atomic orbital is a region around an atomic nucleus in which there is a 90% probability of finding the electron. The shape of the orbitals will depend on the energy of the electron. When an electron is in an orbital of higher energy it will have a higher probability of being found further from the nucleus.

TOK

In our efforts to learn as much as possible about the atom, we have found that certain things can never be known with certainty. Much of our knowledge must always remain uncertain. Some suggest that Heisenberg's Uncertainty Principle has major implications for *all* areas of knowledge. Does science have the power to inform thinking in other areas of knowledge such as philosophy and religion? To what extent should philosophy and religion take careful note of scientific developments?

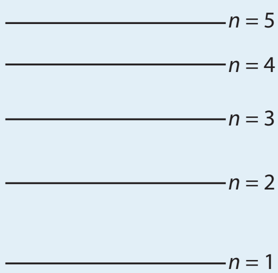
The progressive nature of scientific knowledge is illustrated by the Nobel Prizes awarded between 1922 and 1933. The Physics prize was awarded to Bohr in 1922, Heisenberg in 1932, and Schrödinger in 1933.

Exercises

12 Emission and absorption spectra both provide evidence for:

A the existence of neutrons
B the existence of isotopes
C the existence of atomic energy levels
D the nuclear model of the atom

13 The diagram shows the lowest five electron energy levels in the hydrogen atom.



Deduce how many different frequencies in the visible emission spectrum of atomic hydrogen would arise as a result of electron transitions between these levels.

A 3 **B** 4 **C** 6 **D** 10

14 Identify which of the following provide evidence to support the Bohr model of the hydrogen atom?

I The energy of the lines in the emission spectra of atomic hydrogen.
II The energy of the missing lines in the absorption spectra of helium as seen from the sun.
III The relative intensity of the different spectral lines in the emission spectrum of atomic hydrogen.

A I only **B** II only **C** I and II **D** I and III

Our model of the atom owes a great deal to the work of Niels Bohr and Werner Heisenberg, who worked together in the early years of quantum theory before World War II. But they found themselves on different sides when war broke out. The award-winning play and film *Copenhagen* is based on their meeting in the eponymous city in 1941 and explores their relationship, the uncertainty of the past, and the moral responsibilities of the scientist.

CHALLENGE YOURSELF

3 State **two** ways in which the Schrödinger model of the hydrogen atom differs from that of the Bohr model.

Atomic orbitals

The first energy level has one 1s orbital

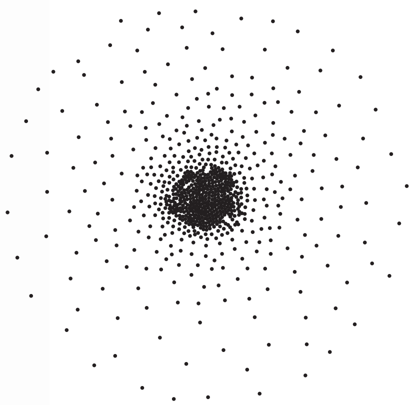
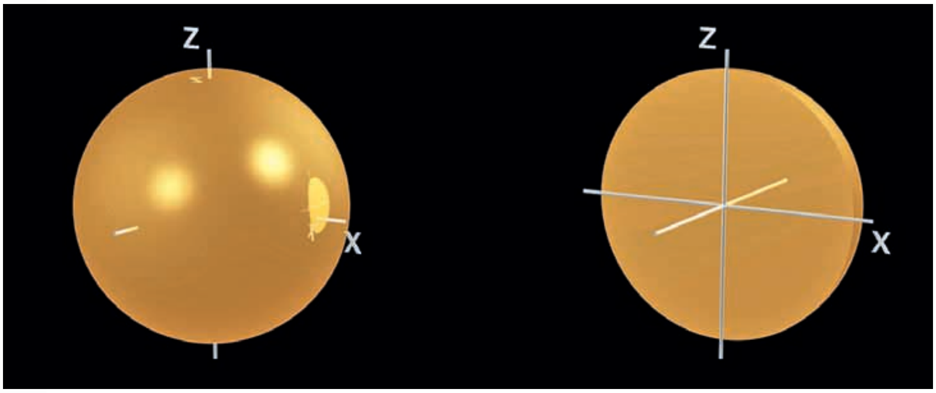


Figure 2.14 An electron in a 1s atomic orbital. The density of the dots gives a measure of the probability of finding the electron in this region.

We saw that the electron in hydrogen occupies the first energy level in the ground state, which can hold a maximum of two electrons. To highlight the distinction between this wave description of the electron provided by the Schrödinger model and the circular orbits of the Bohr atom, we say the electron occupies a 1s orbital.

The dots in Figure 2.14 represent locations where the electron is most likely to be found. The denser the arrangement of dots, the higher the probability that the electron occupies this region of space. The electron can be found anywhere within a spherical space surrounding the nucleus.

The first energy level consists of a 1s atomic orbital which is spherical in shape.

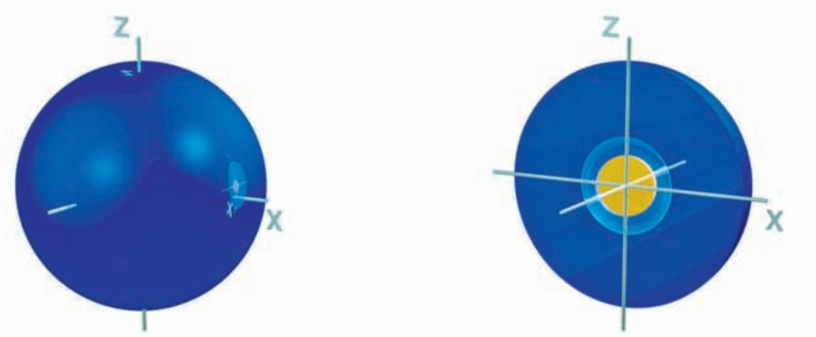


The electrons in the Bohr model occupy orbits, which are circular paths. An orbital, which is a wave description of the electron, shows the volume of space in which the electron is likely to be found.

The second energy level has a 2s and 2p level

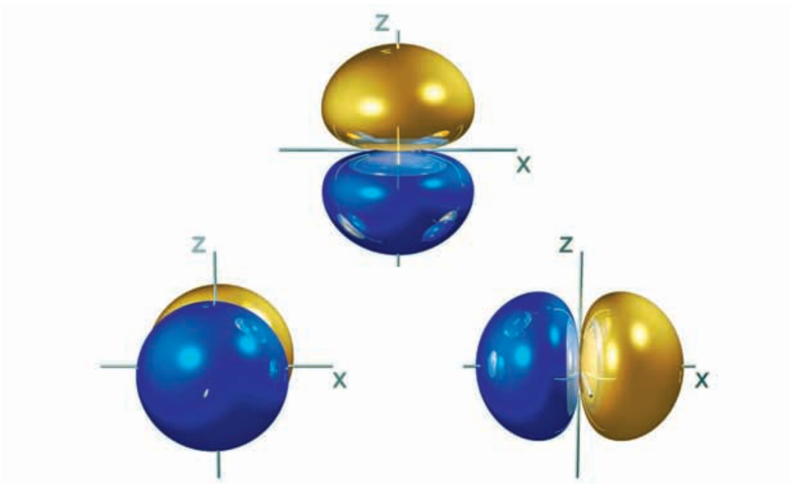
The second energy level of the Bohr model is split into two **sub-levels** in the Schrödinger model. Further evidence of sub-shells comes from a consideration of patterns in first ionization energies, which will be discussed on page 90. The 2s sub-level is made up from one 2s orbital and can hold a maximum of two electrons, and the 2p sub-level is made up from three 2p orbitals and can hold six electrons.

The 2s orbital has the same symmetry as a 1s orbital but extends over a larger volume. So electrons in a 2s orbital are, on average, further from the nucleus than electrons in 1s orbitals and are at higher energy.



The 2s electron orbital. Just as a water wave can have crests and troughs, an orbital can have positive and negative areas. The blue area shows positive values, and the gold area negative. As it is the magnitude of the wave, not the sign, which determines the probability of finding an electron at particular positions, the sign is often not shown.

The 2p sub-level contains three 2p atomic orbitals of equal energy which are said to be **degenerate**. They all have the same dumbbell shape; the only difference is their orientation in space. They are arranged at right angles to each other with the nucleus at the centre.

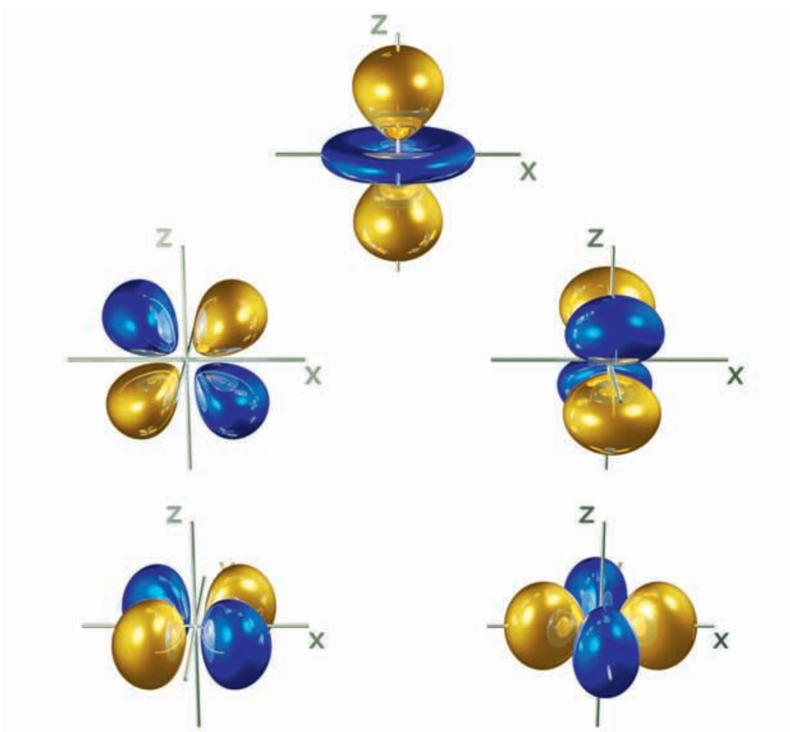


From left to right, the p_y, p_z, and p_x atomic orbitals, localized along the *y*, *z*, and *x*-axes respectively (the *y*-axis comes out of the page). As they have the same energy, they are said to be degenerate. They form the 2p sub-level.

If you wanted to be absolutely 100% sure of where the electron is you would have to draw an orbital the size of the universe.

d and f orbitals

We have seen that the first energy level is made up from one sub-level and the second energy level is made up from two sub-levels. This pattern can be generalized; the *n*th energy level of the Bohr atom is divided into *n* sub-levels. The third energy level is made up from three sub-levels: the 3s, 3p, and 3d. The d sub-level is made up from five d atomic orbitals.



The five electron orbitals found in the 3d sub-level. Four of the orbitals are made up of four lobes, centred on the nucleus.

You are expected to know the shapes and names of the s and p atomic orbitals, but not of the d atomic orbitals.

The labels s, p, d, and f relate to the nature of the spectral lines the model was attempting to explain. The corresponding spectroscopic terms are *sharp*, *principal*, *diffuse*, and *fine*.

The letters **s**, **p**, **d**, and **f** are used to identify different sub-levels and the atomic orbitals which comprise them. The fourth level ($n = 4$) is similarly made up from four sub-levels. The 4f sub-levels are made up from seven f atomic orbitals, but you are not required to know the shapes of these orbitals.

Worked example

Draw the shapes of a 1s orbital and a $2p_x$ orbital.

Solution

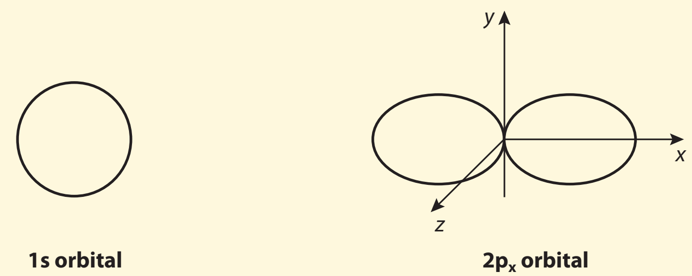


Figure 2.15 A simple two-dimensional drawing is sufficient.

Electron spin and the Pauli Exclusion Principle

The atomic orbitals associated with the different energy levels are shown in Figure 2.16. This diagram is a simplification, as the relative energy of the orbitals depends on the atomic number. This is discussed in more detail later. The relative energies of the 4s and 3d atomic orbitals is chemically significant.

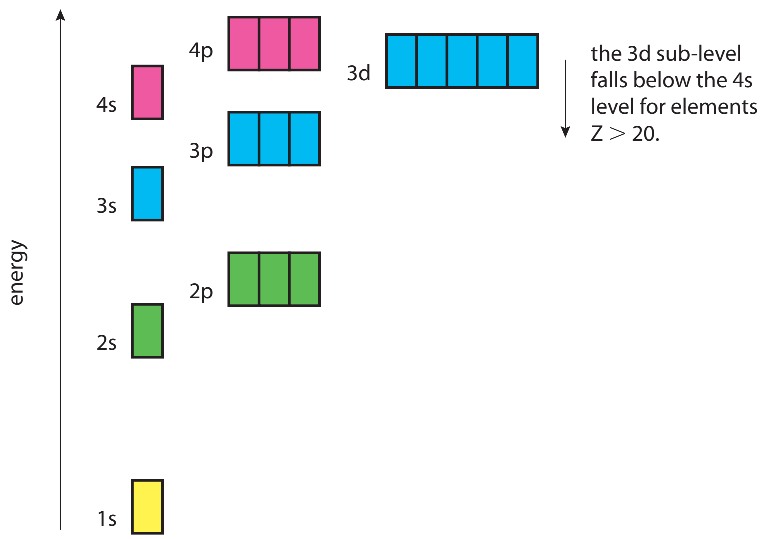


Figure 2.16 The relative energies of the atomic orbitals up to the 4p sub-level. The 3d sub-level falls below the 4s level for elements $Z > 20$.

The Pauli Exclusion Principle states that no more than two electrons can occupy any one orbital, and if two electrons are in the same orbital they must spin in opposite directions.

An electron is uniquely characterized by its atomic orbital and spin. If two electrons occupied the same orbital spinning in the same direction, they would be the same electron.

Each atomic orbital can hold a maximum of two electrons. These electrons can occupy the same region of space despite their mutual repulsion as they spin in opposite directions.

Exercises

15 List the 4d, 4f, 4p, and 4s atomic orbitals in order of increasing energy.

16 State the number of 4d, 4f, 4p, and 4s atomic orbitals.

Sub-levels of electrons

The number of electrons in the sub-levels of the first four energy levels are shown in the table below.

Level	Sub-level	Maximum number of electrons in sub-level	Maximum number of electrons in level
$n = 1$	1s	2	2
$n = 2$	2s	2	8
	2p	6	
$n = 3$	3s	2	18
	3p	6	
	3d	10	
$n = 4$	4s	2	32
	4p	6	
	4d	10	
	4f	14	

We can see the following from the table.

- The nth energy level of the Bohr atom is divided into n sub-levels. For example, the fourth level ($n = 4$) is made up from four sub-levels. The letters s, p, d, and f are used to identify different sub-levels.
- Each main level can hold a maximum of $2n^2$ electrons. The 3rd energy level, for example, can hold a maximum of 18 electrons ($2 \times 3^2 = 18$).
- s sub-levels can hold a maximum of 2 electrons.
- p sub-levels can hold a maximum of 6 electrons.
- d sub-levels can hold a maximum of 10 electrons.
- f sub-levels can hold a maximum of 14 electrons.

Aufbau Principle: orbital diagrams

The electron configuration of the ground state of an atom of an element can be determined using the **Aufbau Principle**, which states that electrons are placed into orbitals of lowest energy first. Boxes can be used to represent the atomic orbitals, with single-headed arrows to represent the spinning electrons. The **electron configurations** of the first five elements are shown in Figure 2.17. The number of electrons in each sub-level is given as a superscript.

Aufbau means 'building up' in German.

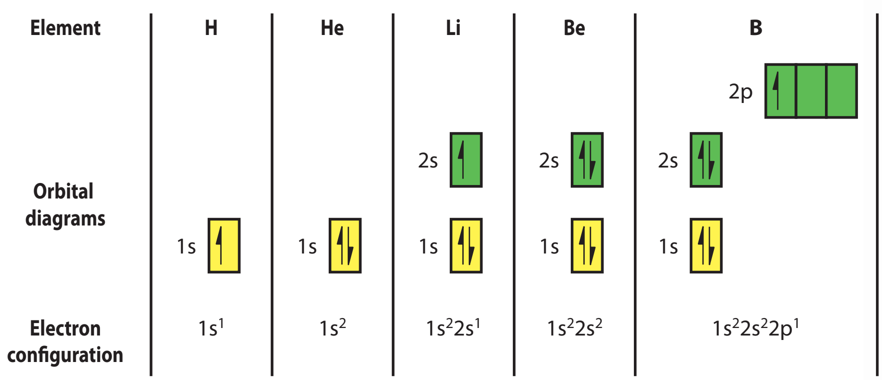
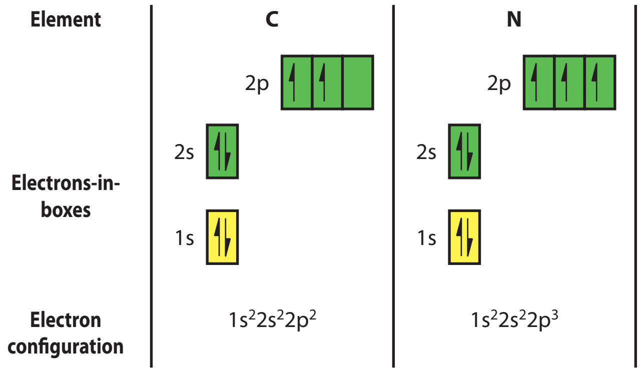


Figure 2.17 The electron configuration of the first five elements.

The next element in the Periodic Table is carbon. It has two electrons in the 2p sub-level. These could either pair up, and occupy the same p orbital, or occupy separate p orbitals. Following **Hund's third rule**, we can place the two electrons in separate orbitals because this configuration minimizes the mutual repulsion between them. As the 2p orbitals are perpendicular to each other and do not overlap, the two 2p electrons are unlikely to approach each other too closely. The electrons in the different 2p orbitals have parallel spins, as this leads to lower energy. The electron configurations of carbon and nitrogen are shown in Figure 2.18.

Figure 2.18 Electron configurations of carbon and nitrogen.



Hund's rule: If more than one orbital in a sub-level is available, electrons occupy different orbitals with parallel spins.

Do you need a useful mnemonic to the order of filling orbitals? Figure 2.19 shows orbitals filled to sub-level 7s. Follow the arrows to see the order in which the sub-levels are filled.

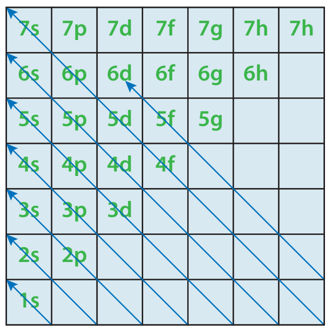
The 2p electrons begin to pair up for oxygen ($1s^22s^22p_x^{\,2}2p_y^{\,1}2p_z^{\,1}$) and fluorine ($1s^22s^22p_x^{\,2}2p_y^{\,2}2p_z^{\,1}$). The 2p sub-shell is completed for neon ($1s^22s^22p_x^{\,2}2p_y^{\,2}2p_z^{\,2}$).

Exercises

17 Apply the *orbital diagram* method to determine the electron configuration of calcium.

18 Deduce the number of unpaired electrons present in a phosphorus atom.

Figure 2.19 Order of filling sub-levels: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7s.



The mathematical nature of the orbital description is illustrated by some simple relationships:

- **number of sub-levels at *n*th main energy level = *n***
- **number of orbitals at *n*th energy level = n^2**
- **number of electrons at *n*th energy level = $2n^2$**
- **number of orbitals at *l*th sub-level = $(2l + 1)$ where *n* and *l* are sometimes known as quantum numbers.**

Sub-level	s	p	d	f
l	0	1	2	3

The relative energy of the orbitals depends on the atomic number

The energy of an orbital depends on the attractions between the electrons and the nucleus and inter-electron repulsions. As these interactions change with the nuclear charge and the number of the electrons, that is the atomic number, so does the relative energy of the orbitals. All the sub-levels in the third energy level (3s, 3p, and 3d), for example, have the same energy for the hydrogen atom and only become separated as extra protons and electrons are added. The situation is particularly complicated when we reach the d block elements. The 3d and 4s levels are very close in energy and their relative separation is very sensitive to inter-electron repulsion. For the elements potassium and calcium, the 4s orbitals are filled before the 3d sub-level. Electrons are, however, first lost from the 4s sub-level when transitional metals form their ions, as once the 3d sub-level is occupied the 3d electrons push the 4s electrons to higher energy.

When the transition metal atoms form ions they lose electrons from the 4s sub-level before the 3d sub-level.

Worked example

State the full electron configuration of vanadium and deduce the number of unpaired electrons.

Solution

The atomic number of vanadium gives the number of electrons: Z = 23.

So the electronic configuration is: $1s^22s^22p^63s^23p^64s^23d^3$. Note: the 3d sub-level is filled after the 4s sub-level.

It is useful, however, to write the electronic configuration with the 3d sub-shell before the 4s: $1s^22s^22p^63s^23p^63d^34s^2$ as the 3d sub-level falls below the 4s orbital once the 4s orbital is occupied (i.e. for elements after Ca).

Three 3d orbitals each have an unpaired electron. Number of unpaired electrons = 3.

TOK

The abstract language of mathematics provides a powerful tool for describing the behaviour of electrons in the atom. The shapes and equations it generates have elegance and symmetry. What do such results tell us about the relationship between the natural sciences, mathematics, and the natural world?

The worked example asked for the full electron configuration. Sometimes it is convenient to use an abbreviated form, where only the outer electrons are explicitly shown. The inner electrons are represented as a noble gas core. Using this notation, the electron configuration of vanadium is written [Ar] $3d^34s^2$, where [Ar] represents the electron configuration of Ar, which is $1s^22s^22p^63s^23p^6$.

The electron configurations of the first 30 elements are tabulated below.

Element	Electron configuration	Element	Electron configuration	Element	Electron configuration
$_1H$	$1s^1$	$_{11}Na$	$1s^22s^22p^63s^1$	$_{21}Sc$	[Ar] $3d^14s^2$
$_2He$	$1s^2$	$_{12}Mg$	$1s^22s^22p^63s^2$	$_{22}Ti$	[Ar] $3d^24s^2$
$_3Li$	$1s^22s^1$	$_{13}Al$	$1s^22s^22p^63s^23p^1$	$_{23}V$	[Ar] $3d^34s^2$
$_4Be$	$1s^22s^2$	$_{14}Si$	$1s^22s^22p^63s^23p^2$	$_{24}Cr$	[Ar] $3d^54s^1$
$_5B$	$1s^22s^22p^1$	$_{15}P$	$1s^22s^22p^63s^23p^3$	$_{25}Mn$	[Ar] $3d^54s^2$
$_6C$	$1s^22s^22p^2$	$_{16}S$	$1s^22s^22p^63s^23p^4$	$_{26}Fe$	[Ar] $3d^64s^2$
$_7N$	$1s^22s^22p^3$	$_{17}Cl$	$1s^22s^22p^63s^23p^5$	$_{27}Co$	[Ar] $3d^74s^2$
$_8O$	$1s^22s^22p^4$	$_{18}Ar$	$1s^22s^22p^63s^23p^6$	$_{28}Ni$	[Ar] $3d^84s^2$
$_9F$	$1s^22s^22p^5$	$_{19}K$	$1s^22s^22p^63s^23p^64s^1$	$_{29}Cu$	[Ar] $3d^{10}4s^1$
$_{10}Ne$	$1s^22s^22p^6$	$_{20}Ca$	$1s^22s^22p^63s^23p^64s^2$	$_{30}Zn$	[Ar] $3d^{10}4s^2$

The term 'valence' is derived from the Latin word for 'strength'.

The electrons in the outer energy level are mainly responsible for compound formation and are called **valence electrons**. Lithium has one valence electron in the outer second energy level ($2s^1$), beryllium has two ($2s^2$), boron has three ($2s^2p^1$), etc. The number of valence electrons follows a periodic pattern, which is discussed fully in Chapter 3. Atoms can have many other electron arrangements when in an excited state. Unless otherwise instructed, assume that you are being asked about ground-state arrangements.

For the d block elements three points should be noted:

- the 3d sub-level is written with the other $n = 3$ sub-levels as it falls below the 4s orbital once the 4s orbital is occupied (i.e. for elements after Ca), as discussed earlier;
- chromium has the electron configuration [Ar] $3d^5 4s^1$;
- copper has the electron configuration [Ar] $3d^{10} 4s^1$.

To understand the electron configurations of copper and chromium it is helpful to consider the orbital diagram arrangements in Figure 2.20. As the 4s and 3d orbitals are close in energy, the electron configuration for chromium with a half-full d sub-level is relatively stable as it minimizes electrostatic repulsion, with six singly occupied atomic orbitals. This would be the expected configuration using Hund's rule if the 4s and 3d orbitals had exactly the same energy. Half-filled and filled sub-levels seem to be particularly stable: the configuration for copper is similarly due to the stability of the full d sub-level.

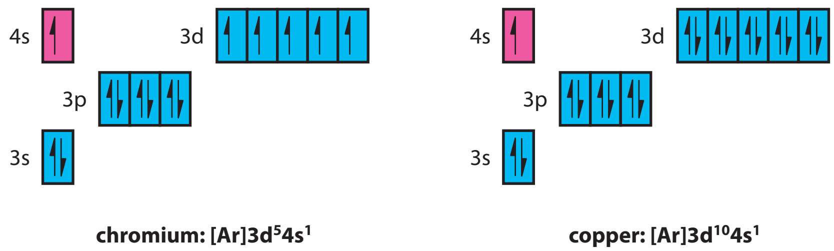


Figure 2.20 The electron configuration of the 3rd and 4th energy levels for chromium and copper.

Exercises

19 Identify the sub-level which does not exist.

A 5d **B** 4d **C** 3f **D** 2p

20 Which is the correct order of orbital filling according to the Aufbau Principle?

A 4s 4p 4d 4f **B** 4p 4d 5s 4f **C** 4s 3d 4p 5s **D** 4d 4f 5s 5p

21 State the full ground-state electron configuration of the following elements.

(a) V **(b)** K **(c)** Se **(d)** Sr

22 Determine the total number of electrons in d orbitals in a single iodine atom.

A 5 **B** 10 **C** 15 **D** 20

23 Identify the excited state (i.e. not a ground state) in the following electron configurations.

A [Ne] $3s^2 3p^3$ **B** [Ne] $3s^2 3p^3 4s^1$ **C** [Ne] $3s^2 3p^6 4s^1$ **D** [Ne] $3s^2 3p^6 3d^1 4s^2$

24 Deduce the number of unpaired electrons present in the ground state of a titanium atom.

A 1 **B** 2 **C** 3 **D** 4

Electron configuration of ions

As discussed earlier, positive ions are formed by the loss of electrons. These electrons are lost from the outer sub-levels. The electron configurations of the different aluminium ions formed when electrons are successively removed are for example:

- Al^{+} is $1s^2 2s^2 2p^6 3s^2$
- Al^{2+} is $1s^2 2s^2 2p^6 3s^1$
- Al^{3+} is $1s^2 2s^2 2p^6$, etc.

When positive ions are formed for transition metals, the outer 4s electrons are removed before the 3d electrons, as discussed earlier.

For example, Cr is [Ar] $3d^5 4s^1$ and Cr^{3+} is [Ar] $3d^3$

The electron configuration of negative ions is determined by adding the electrons into the next available electron orbital:

S is $1s^2 2s^2 2p^6 3s^2 3p^4$ and S^{2-} is $1s^2 2s^2 2p^6 3s^2 3p^6$

Worked example

State the ground-state electron configuration of the Fe^{3+} ion.

Solution

First find the electron configuration of the atom. Fe has 26 electrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

As the 3d sub-level is below the 4s level for elements after calcium we write this as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Now remove the two electrons from the 4s sub-level and one electron from the 3d sub-level.

Electron configuration of Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Note the abbreviated electron configuration using the noble gas core is not acceptable when asked for the *full* electron configuration.

Exercises

25 State the full ground-state electron configuration of the following ions.

(a) O^{2-} **(b)** Cl^{-} **(c)** Ti^{3+} **(d)** Cu^{2+}

26 State the electron configuration of the following transition metal ions by filling in the boxes below. Use arrows to represent the electron spin.

	Ion	3d					4s
(a)	Ti^{2+}						
(b)	Fe^{2+}						
(c)	Ni^{2+}						
(d)	Zn^{2+}						

27 **(a)** State the full electron configuration for neon.

(b) State the formulas of two oppositely charged ions which have the same electron configuration as neon.

Electronic configuration and the Periodic Table

We are now in a position to understand the structure of the Periodic Table (Figure 2.21):

- elements whose valence electrons occupy an s sub-level make up the **s block**;
- elements with valence electrons in p orbitals make up the **p block**;
- the **d block** and the **f block** are similarly made up of elements with outer electrons in d and f orbitals.

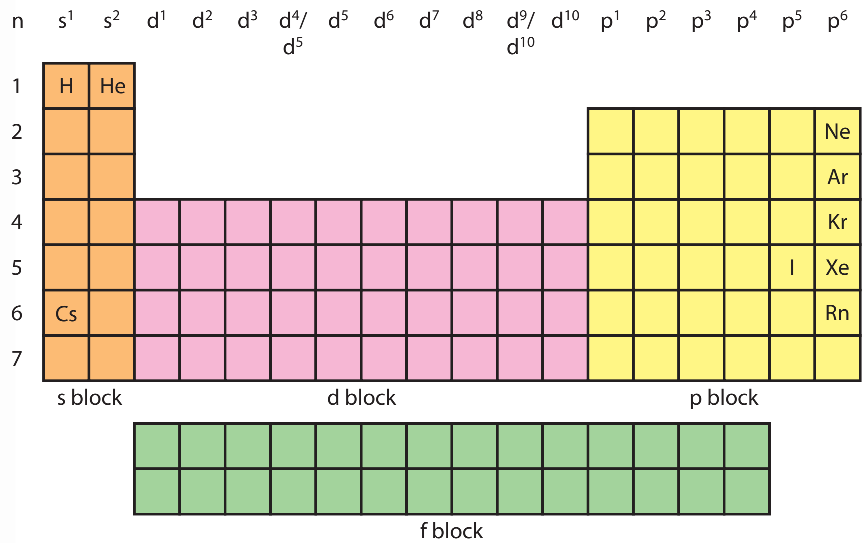


Figure 2.21 The block structure of the Periodic Table is based on the sub-levels of the atom. H and He are difficult elements to classify. Although they have electron configurations that place them in the s block, their chemistry is not typical of Group 1 or Group 2 elements.

The *ns* and *np* sub-levels are filled for elements in Period *n*. However the (*n* – 1)d sub-level is filled for elements in Period *n*.

The position of an element in the Periodic Table is based on the occupied sub-level of highest energy in the ground-state atom. Conversely, the electron configuration of an element can be deduced directly from its position in the Periodic Table.

Here are some examples.

- Caesium is in Group 1 and Period 6 and has the electronic configuration: [Xe] $6s^1$.
- Iodine is in Group 17 and in Period 5 and has the configuration: [Kr] $5s^2 4d^{10} 5p^5$. Placing the 4d sub-level before the 5s gives [Kr] $4d^{10} 5s^2 5p^5$. Iodine has 7 valence electrons in agreement with the pattern discussed on page 82.

Some versions of the Periodic Table use the numbering 3–7 for Groups 13–17. In this version Group 3 elements have 3 valence electrons and Group 7 elements have 7 valence electrons. Although this is simpler in some respects it can lead to problems. How do you refer to the d-block elements? After extensive discussions, the IUPAC concluded that the 1 to 18 numbering provides the most clear and unambiguous labelling system. The Periodic Table has to meet the needs of young students and Nobel Prize winners alike.

Exercises

28 Use the Periodic Table to find the full ground-state electron configuration of the following elements.

(a) Cl **(b)** Nb **(c)** Ge **(d)** Sb

29 Identify the elements which have the following ground-state electron configurations.

(a) [Ne] $3s^2 3p^2$ **(b)** [Ar] $3d^5 4s^2$ **(c)** [Kr] $5s^2$
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

30 State the total number of p orbitals containing one or more electrons in tin.

31 How many electrons are there in all the d orbitals in an atom of barium?

32 State the electron configuration of the ion Cd^{2+}.

TOK

Do atomic orbitals exist or are they primarily useful inventions to aid our understanding? What consequences might questions about the reality of scientific entities have for the public perception and understanding of the subject? If they are only fictions, how is it that they can yield such accurate predictions?

CHALLENGE YOURSELF

4 Only a few atoms of element 109, meitnerium, have ever been made. Isolation of an observable quantity of the element has never been achieved, and may well never be. This is because meitnerium decays very rapidly.

(a) Suggest the electron configuration of the ground-state atom of the element.

(b) There is no g block in the Periodic Table as no elements with outer electrons in g orbitals exist in nature or have been made artificially. Suggest a minimum atomic number for such an element.

5 State the full electron configuration of U^{2+}.

6 Consider how the shape of the Periodic Table is related to the three-dimensional world we live in.

(a) How many 3p and 3d orbitals would there be if there were only the *x* and *y* dimensions?

(b) How many groups in the p and d block would there be in such a two-dimensional world?

NATURE OF SCIENCE

We have seen how the model of the atom has changed over time. All these theories are still used today. Dalton's model adequately explains many properties of the states of matter, the Bohr model is used to explain chemical bonding, and the structure of the Periodic Table is explained by the wave description of the electron. In science we often follow Occam's razor and use the simplest explanation which can account for the phenomena. As Einstein said 'Explanations should be made as simple as possible, but not simpler.'

12.1 Electrons in atoms

Understandings:

- In an emission spectrum, the limit of convergence at higher frequency corresponds to the first ionization energy.
- Trends in first ionization energy across periods account for the existence of main energy levels and sub-levels in atoms.
- Successive ionization energy data for an element give information that shows relations to electron configurations.

Applications and skills:

- Solving problems using $E = h\nu$.

  Guidance

  The value of Planck's constant and $E = h\nu$ *are given in the IB data booklet in sections 1 and 2.*
- Calculation of the value of the first ionization energy from spectral data which gives the wavelength or frequency of the convergence limit.

  Guidance

  Use of the Rydberg formula is not expected in calculations of ionization energy.
- Deduction of the group of an element from its successive ionization energy data.
- Explanation of the trends and discontinuities in data on first ionization energy across a period.

Ionization energy

The first ionization energy is the energy needed to remove one mole of electrons from the ground state of one mole of the gaseous atom. For hydrogen it corresponds to the following change with the electron being removed from the 1s orbital:

$$H(g) \rightarrow H^+(g) + e^-$$

Once removed from the atom, the electron is an infinite distance away from the nucleus and can considered to be in the $n = \infty$ energy level.

We saw earlier that the energy levels in the hydrogen converge at higher energy. This allows us to calculate the ionization energy from the convergence limit at higher frequency.

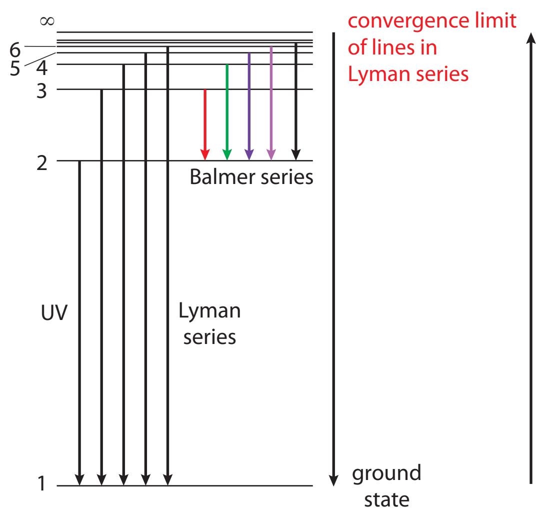


Figure 2.22 The transition from $n = 1$ to $n = \infty$ corresponds to ionization.

NATURE OF SCIENCE

The best data for making accurate and precise descriptions is often quantitative as it is then amenable to mathematical analysis. The data can often be presented in a variety of formats that can be analysed. Scientists look for patterns in an attempt to discover relationships. The frequencies of the lines in the Lyman series, for example, can be analysed in different ways.

Method 1

The frequencies of the lines in the Lyman series are shown below. All the transitions involve the electron falling from the excited levels with $n \geq 1$ to the $n = 1$ energy level. The difference between the frequencies in successive lines is given in the third column.

Excited energy level	Frequency, ν / × 10^{14} s^{-1}	$\Delta\nu$ / × 10^{14} s^{-1}
2	24.66	4.57
3	29.23	1.60
4	30.83	0.74
5	31.57	0.40
6	31.97	0.24
7	32.21	0.16
8	32.37	

As we are interested in the frequency of the line at which convergence occurs ($\Delta\nu = 0$), we have plotted a graph of ν against $\Delta\nu$ (Figure 2.23).

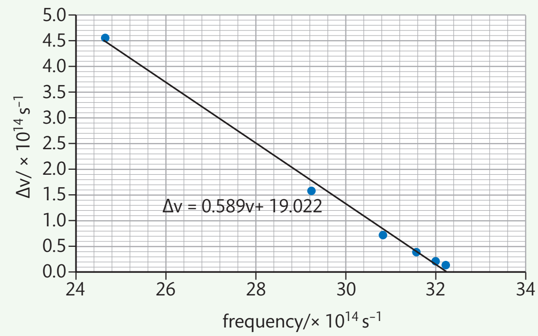


Figure 2.23 A graph showing the frequency of the line emitted against the difference in frequency between successive lines in the Lyman series of the hydrogen atom.

As we can see, the points fit an approximate straight line with the equation:

$$\Delta\nu = -0.5897\nu + 19.022$$

This allows us to find the frequency at which convergence occurs ($\Delta\nu = 0$):

$$-0.5897\nu + 19.022 = 0$$

$$\nu = \frac{19.022}{0.5897} \times 10^{14}\ s^{-1} = 32.26 \times 10^{14}\ s^{-1}$$

Method 2

Alternatively, a graph of the frequencies of the lines plotted against $1/n^2$ produces a straight line (Figure 2.24).

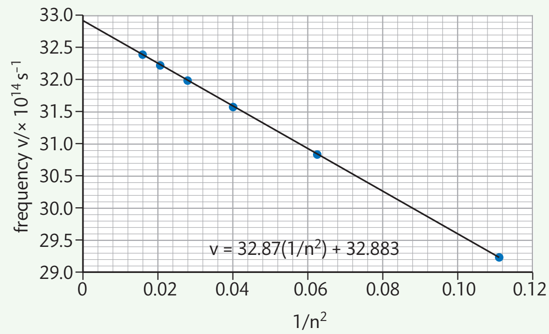


Figure 2.24

continued

NATURE OF SCIENCE

continued ....

The frequency corresponding to $n = \infty$ can be read as the intercept on the y-axis and equals $32.883 \times 10^{14}\ s^{-1}$.

The second method produced the best-fit straight line. We can use the frequency obtained to calculate the ionization energy.

Using the equation $E = h\nu$ we have the ionization energy for one atom:

$$E = 32.883 \times 10^{14}\ s^{-1} \times 6.63 \times 10^{-34}\ J\ s$$

So for one mole the ionization energy is given by:

$$I.E. = 32.883 \times 10^{14}\ s^{-1} \times 6.63 \times 10^{-34}\ J\ s \times 6.02 \times 10^{23}\ mol^{-1}$$
$$= 1312\ kJ\ mol^{-1}$$

This agrees with the value given in section 8 of the IB data booklet.

CHALLENGE YOURSELF

7 Use the graph produced by method 1 to calculate the ionization energy of hydrogen.

8 The convergence limit in the Balmer series corresponds to a frequency of $8.223 \times 10^{14}\ s^{-1}$. Use this value along with other data given above to calculate the ionization energy.

NATURE OF SCIENCE

The Bohr model of the atom (1913) was able to explain the relationship between the frequency of the lines and the n values for the energy levels, but Bohr was unable to provide experimental evidence to support his postulates. They were inconsistent as they came from an unjustified mixture of classical and quantum physics. In general scientists strive to develop hypotheses and theories that are compatible with accepted principles and that simplify and unify existing ideas. A deeper understanding needed the wave description of the electron suggested by de Broglie (1926).

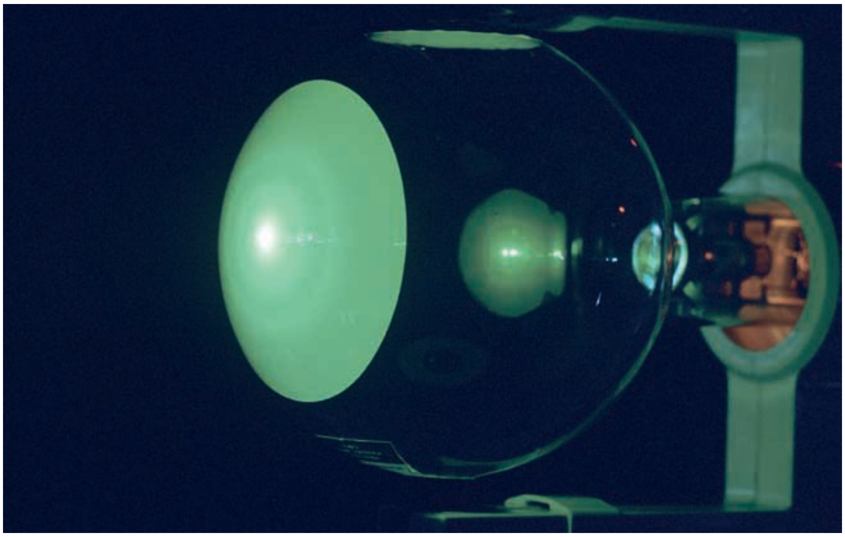
Many scientific discoveries have involved flashes of intuition and many have come from speculation or simple curiosity about particular phenomena. Broglie speculated on the wave properties of particles by combining results from Einstein's theory of relativity with Planck's quantum theory.

Given that $E = h\nu$ from the Planck equation and $E = mc^2$ from Einstein's theory of special relativity, we have: $h\nu = mc^2$

This can be simplified to $h\nu/c = mc$ (for a photon mc is the momentum p) to give

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

de Broglie suggested this result could be generalized for all particles; particles with greater momentum will have an associated shorter wavelength. Using this idea the energy levels of the hydrogen atom can be associated with standing waves of specific wavelength. The circumference of the orbit of the $n = 1$ energy level, for example, is equal to the wavelength of the de Broglie wave. The wave properties of the electrons, first suggested by de Broglie, were confirmed later by the **Davisson–Germer experiment** in which electrons were diffracted. To be scientific, an idea (e.g. a theory or hypothesis) must be testable.



An electron diffraction tube. The electrons fired at a thin sheet of graphite produce the patterns of rings associated with diffraction. de Broglie (1892–1987) correctly deduced that the electrons would have wavelengths inversely proportional to their momentum.

TOK

The de Broglie equation shows that macroscopic particles have too short a wavelength for their wave properties to be observed. Is it meaningful to talk of properties which can never be observed from sense perception?

Ionization energies can also be used to support this model of the atom.

Patterns in successive ionization energies give evidence for the energy levels in the atom

Additional evidence for electron configuration in atoms comes from looking at patterns of successive ionization energies. For aluminium, the first ionization energy corresponds to the following process:

$$Al(g) \rightarrow Al^{+}(g) + e^{-}$$

The second ionization energy corresponds to the change:

$$Al^{+}(g) \rightarrow Al^{2+}(g) + e^{-}$$

and so on …

The ionization energies for aluminium are shown in Figure 2.25 and follow a similar pattern to the electron configuration.

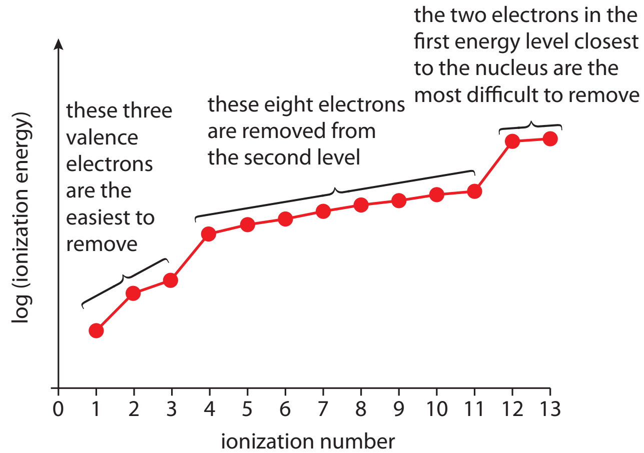


Figure 2.25 Successive ionization energies for aluminium. Note the jumps between the 3rd and 4th and between the 11th and 12th ionization energies as electrons are removed from lower energy levels. The wide range in values is best presented on a log scale.

TOK

How does the method of data presentation influence how the data are interpreted? The use of scale can clarify important relationships but can also be used to manipulate data. How can you as a knower distinguish between the use and abuse of data presentation?

The electron configurations of aluminium ions as electrons are successively removed are shown in the table below.

Ion	Electron configuration	Ion	Electron configuration
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	Al^{6+}	$1s^2 2s^2 2p^3$
Al^{+}	$1s^2 2s^2 2p^6 3s^2$	Al^{7+}	$1s^2 2s^2 2p^2$
Al^{2+}	$1s^2 2s^2 2p^6 3s^1$	Al^{8+}	$1s^2 2s^2 2p^1$
Al^{3+}	$1s^2 2s^2 2p^6$	Al^{9+}	$1s^2 2s^2$
Al^{4+}	$1s^2 2s^2 2p^5$	Al^{10+}	$1s^2 2s^1$
Al^{5+}	$1s^2 2s^2 2p^4$	Al^{11+}	$1s^2$

The graph in Figure 2.25 shows two key points.

1 There is an increase in successive ionization energies. The first ionization energy involves the separation of an electron from a singly charged ion and the second the separation of an electron from a doubly charged ion. The process becomes more difficult as there is increasing attraction between the higher charged positive ions and the oppositely charged electron.

2 There are jumps when electrons are removed from levels closer to the nucleus. The first three ionization energies involve the removal of electrons from the third level.

The 3p electron is removed first, followed by the electrons from the 3s orbital. An electron is removed from the second level for the fourth ionization energy. This electron is closer to the nucleus and is more exposed to the positive charge of the nucleus and so needs significantly more energy to be removed. There is similarly a large jump for the 12th ionization energy as it corresponds to an electron being removed from the 1s orbital.

TOK

Which of Dalton's five proposals (page 59) do we now hold to be 'true'? How does scientific knowledge change with time? Are the models and theories of science accurate descriptions of the natural world, or just useful interpretations to help predict and explain the natural world?

A closer look at successive ionization energies gives evidence for the sub-levels

A closer look at the successive ionization energies shows evidence of the sub-levels present with each level. The log graph of all 13 ionization energies showed a 2, 8, 3 pattern in successive ionization energies, which reflects the electron arrangement of the atom, with two electrons in the first level, eight electrons at the second energy level, and three valence electrons in the outer shell. Now we will consider the fourth to eleventh ionization energies in more detail. These correspond to the removal of the eight electrons in the second energy level (Figure 2.26).

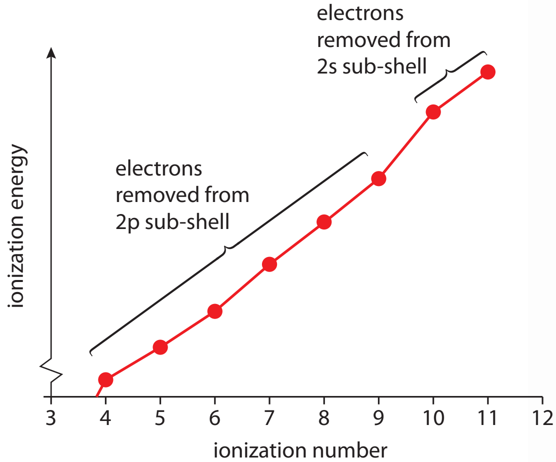


Figure 2.26 Successive ionization energies for aluminium. The jump between the ninth and tenth ionization energies indicates that the second energy level is divided into sub-levels. The smaller jump between the sixth and seventh ionization energies should also be noted and is discussed more fully in the text.

The jump between the ninth and tenth ionization energies shows that the eleventh electron is more difficult to remove than we would expect from the pattern of the six previous electrons. This suggests that the second energy level is divided into two **sub-levels**.

This evidence confirms that the **2s sub-level** can hold a maximum of two electrons, and the **2p sub-level** can hold six electrons.

Worked example

A graph of some successive ionization energies of aluminium is shown in Figure 2.26.

(a) Explain why there is a large increase between the ninth and tenth ionization energies.

(b) Explain why the increase between the sixth and seventh values is greater than the increase between the fifth and sixth values.

Solution

(a) The ninth ionization energy corresponds to the change:

$$Al^{8+}(g) \rightarrow Al^{9+}(g) + e^-$$

Al^{8+} has the configuration $1s^2 2s^2 2p^1$. The electron is removed from a 2p orbital.

The tenth ionization energy corresponds to the change:

$$Al^{9+}(g) \rightarrow Al^{10+}(g) + e^-$$

Al^{9+} has the configuration $1s^22s^2$. The electron is removed from a 2s orbital.

Electrons in a 2s orbital are of lower energy. They are closer to the nucleus and experience a stronger force of electrostatic attraction and so are more difficult to remove.

(b) The sixth ionization energy corresponds to the change:

$$Al^{5+}(g) \rightarrow Al^{6+}(g) + e^-$$

Al^{5+} has the configuration $1s^22s^22p^4$ ($1s^22s^22p_x^{\,2}2p_y^{\,1}2p_z^{\,1}$). The electron is removed from a doubly occupied 2p orbital.

The seventh ionization energy corresponds to the change:

$$Al^{6+}(g) \rightarrow Al^{7+}(g) + e^-$$

The electron is removed from singly occupied 2p orbital.

An electron in a doubly occupied orbital is repelled by its partner, as it has the same negative charge, and so is easier to remove than electrons in half-filled orbitals, which do not experience this force of repulsion (Figure 2.27).

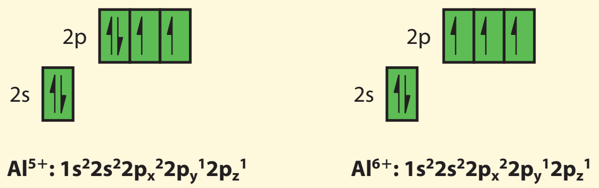
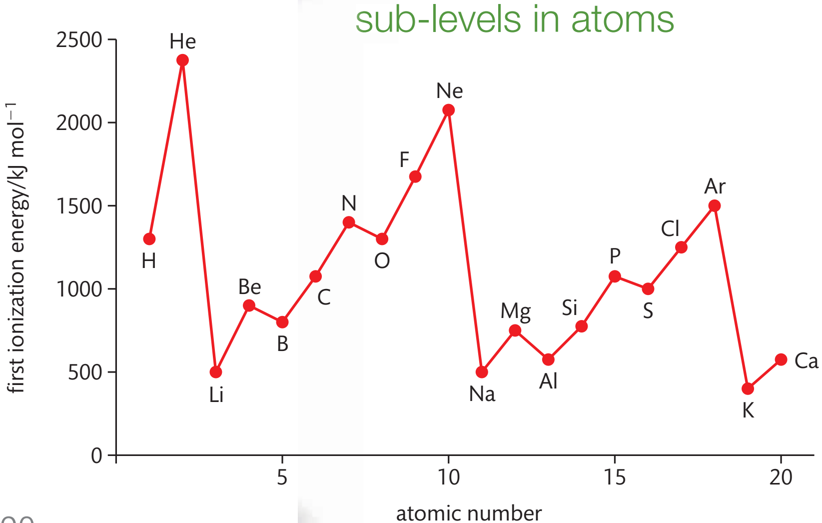


Figure 2.27 The electron removed from the Al^{5+} ion is removed from a doubly occupied 2p orbital. This is easier to remove as it is repelled by its partner.

Further evidence of sub-shells comes from a consideration of patterns in first ionization energies.

Figure 2.28 The first ionization energies of the first 20 elements.



Trends in first ionization energy across periods accounts or the existence of main energy levels and sub-levels in atoms

The periodic arrangement of the elements in the Periodic Table is also reflected by patterns in first ionization energies.

1 Ionization energy generally increases from left to right across a period, as the nuclear charge increases. As the electrons are removed from the same main energy level, there is an increase in the force of electrostatic attraction between the nucleus and outer electrons.

2 Ionization energy decreases down a group as a new energy level, which is further from the nucleus, is occupied. Less energy is required to remove outer electrons that are further from the attractive pull of the nucleus.

3 There are regular discontinuities in the trend across a period, which are explored below. These provide further evidence for the existence of sub-shells.

Worked example

Further evidence for the existence of sub-shells comes from a study of first ionization energies.

(a) In Period 2 there is a decrease in first ionization energies between Be and B, and in Period 3 there is a decrease between Mg and Al. Explain this decrease in ionization energies between Group 2 and Group 13 elements.

(b) In Period 2 there is a decrease in first ionization energies between N and O, and in Period 3 a decrease between P and S. Explain the decrease in ionization energies between Group 15 and Group 16 elements.

Solution

(a) The Group 2 elements have the electron configuration ns^2. The Group 13 elements have the electron configuration ns^2np^1.

The electron removed when the Group 13 elements are ionized is a p electron. The electron removed when the Group 2 elements are ionized is an s electron. Electrons in p orbitals are of higher energy and further away from the nucleus than s electrons and so are easier to remove than electrons in an s orbital.

(b) Group 15 elements have the configuration $ns^2np_x^1np_y^1np_z^1$. Group 16 elements have the configuration $ns^2np_x^2np_y^1np_z^1$. For Group 16 elements, the electron is removed from a doubly occupied 2p orbital. An electron in a doubly occupied orbital is repelled by its partner and so is easier to remove than an electron in a half-filled orbital.

TOK

Patterns in successive ionization energies of a given element and in first ionization energies of different elements both provide evidence to support the orbital model of electron configuration. Which source do you find most compelling? What constitutes good evidence within the natural sciences?

Databases could be used for compiling graphs of trends in ionization energies.

Exercises

33 The first four ionization energies for a particular element are 738, 1450, 7730, and 10 550 kJ mol^{-1} respectively. Deduce the group number of the element.

A 1 **B** 2 **C** 3 **D** 4

34 Successive ionization energies for an unknown element are given in the table below.

First ionization energy / kJ mol^{-1}	Second ionization energy / kJ mol^{-1}	Third ionization energy / kJ mol^{-1}	Fourth ionization energy / kJ mol^{-1}
590	1145	4912	6491

Identify the element.

A K **B** Ca **C** S **D** Cl

35 The successive ionization energies (in kJ mol^{-1}) for carbon are tabulated below.

1st	2nd	3rd	4th	5th	6th
1086	2352	4619	6220	37820	47280

(a) Explain why there is a large increase between the fourth and fifth values.
(b) Explain why there is an increase between the second and third values.

36 Sketch a graph to show the expected pattern for the first seven ionization energies of fluorine.

Exercises

37 The first ionization energies of the Period 3 elements Na to Ar are given in Section 8 of the IB data booklet.

(a) Explain the general increase in ionization energy across the period.
(b) Explain why the first ionization energy of magnesium is greater than that of aluminium.
(c) Explain why the first ionization energy of sulfur is less than that of phosphorus.

One of the first advances in nanotechnology was the invention of the **scanning tunnelling microscope** (STM). The STM does not 'see' atoms, but 'feels' them. An ultra-fine tip scans a surface and records a signal as the tip moves up and down depending on the atoms present. The STM also provides a physical technique for manipulating individual atoms. They can be positioned accurately in just the same way as using a pair of tweezers.

The head of a variable temperature scanning tunnelling microscope.

TOK

The use of the scanning tunnelling microscope has allowed us to 'see' individual atoms. Does technology blur the distinction between simulation and reality?

Waves can be thought of as a carrier of information. The precision of the information they provide is based on their wavelength or the momentum of the associated particles. Electrons can be accelerated to high momenta which allows electron microscopy to be used to show more precise detail than that provided by light microscopy. This has led to many advances in biology, such as the ultrastructure of cells and viruses. The scanning tunnelling microscope (STM) uses a stylus of a single atom to scan a surface and provide a three-dimensional image at the atomic level.

CERN, the European Organization for Nuclear Research, an international organization set up in 1954, is the world's largest particle physics laboratory. The laboratory, situated near Geneva, shares data with scientists of over 100 nationalities from 600 or more universities and research facilities.

NATURE OF SCIENCE

This chapter has highlighted the need for experimental evidence to support our scientific theories:

- the hydrogen emission spectra provides evidence for the existence of energy levels;
- patterns in ionization energies provided evidence for the sub-levels in other elements;
- the Davisson–Germer experiment supports de Broglie's hypothesis.

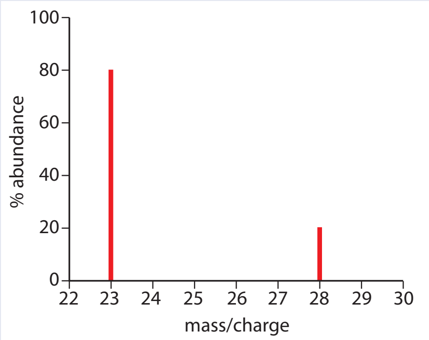
Scientific ideas often start as speculations which are only later confirmed experimentally. The existence of the Higgs' boson was, for example, first suggested by the physicist Peter Higgs after he had spent a weekend walking in the Scottish mountains in 1964 thinking about the missing pieces in the jig-saw of the standard model of particle physics and why the fundamental particles have mass. It was, however, only detected in 2012 when two separate international teams working at the Large Hadron Collider at CERN independently announced that they had collected evidence to support the existence of the Higgs' boson. This discovery was greatly facilitated by the growth in computing power and sensor technology. Experiments in CERN's Large Hadron Collider regularly produce 23 petabytes of data per second, which is equivalent to 13.3 years of high definition TV content per second.

Practice questions

1 What is the electron configuration of the Cr^{2+} ion?

A [Ar] $3d^5 4s^1$ **B** [Ar] $3d^3 4s^1$ **C** [Ar] $3d^6 4s^1$ **D** [Ar] $3d^4 4s^0$

2 What is the relative atomic mass of an element with the following mass spectrum?



A 24 **B** 25 **C** 26 **D** 27

3 Which is correct for the following regions of the electromagnetic spectrum?

	Ultraviolet (UV)		Infrared (IR)	
A	high energy	short wavelength	low energy	low frequency
B	high energy	low frequency	low energy	long wavelength
C	high frequency	short wavelength	high energy	long wavelength
D	high frequency	long wavelength	low frequency	low energy

4 An ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$. Which ion could it be?

A Ni^{2+} **B** Cu^+ **C** Cu^{2+} **D** Co^{3+}

5 Which describes the visible emission spectrum of hydrogen?

A a series of lines converging at longer wavelength
B a series of regularly spaced lines
C a series of lines converging at lower energy
D a series of lines converging at higher frequency

6 Which statements about the isotopes of chlorine, $^{35}_{17}Cl$ and $^{37}_{17}Cl$, are correct?

I They have the same chemical properties.
II They have the same atomic number.
III They have the same physical properties.

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

7 Which statement about the numbers of protons, electrons, and neutrons in an atom is always correct?

A The number of neutrons minus the number of electrons is zero.
B The number of protons plus the number of neutrons equals the number of electrons.
C The number of protons equals the number of electrons.
D The number of neutrons equals the number of protons.

8 Which quantities are the same for all atoms of chlorine?

I number of protons
II number of neutrons
III number of electrons

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

9 In the emission spectrum of hydrogen, which electronic transition would produce a line in the visible region of the electromagnetic spectrum?

A $n = 2 \rightarrow n = 1$ **B** $n = 3 \rightarrow n = 2$ **C** $n = 2 \rightarrow n = 3$ **D** $n = \infty \rightarrow n = 1$

10 How many electrons does the ion ${}^{31}_{15}P^{3-}$ contain?

A 12 **B** 15 **C** 16 **D** 18

11 A sample of iron has the following isotopic composition by mass.

Isotope	^{54}Fe	^{56}Fe	^{57}Fe
Relative abundance / %	5.95	91.88	2.17

Calculate the relative atomic mass of iron based on this data, giving your answer to two decimal places. (2)

(*Total 2 marks*)

12 The electron configuration of chromium can be expressed as $[Ar]4s^x3d^y$.

(a) Explain what the square brackets around argon, [Ar], represent. (1)

(b) State the values of x and y. (1)

(c) Annotate the diagram below showing the 4s and 3d orbitals for a chromium atom using an arrow, $\upharpoonleft$ and $\downharpoonright$, to represent a spinning electron.

(1)

(*Total 3 marks*)

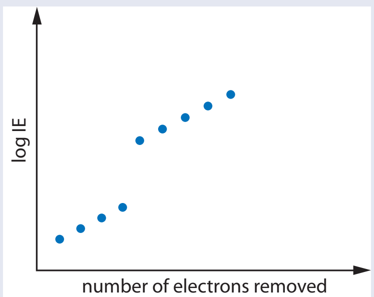
13 **(a)** Explain why the relative atomic mass of cobalt is greater than the relative atomic mass of nickel, even though the atomic number of nickel is greater than the atomic number of cobalt. (1)

(b) Deduce the numbers of protons and electrons in the ion Co^{2+}. (1)

(c) Deduce the electron configuration for the ion Co^{2+}. (1)

(*Total 3 marks*)

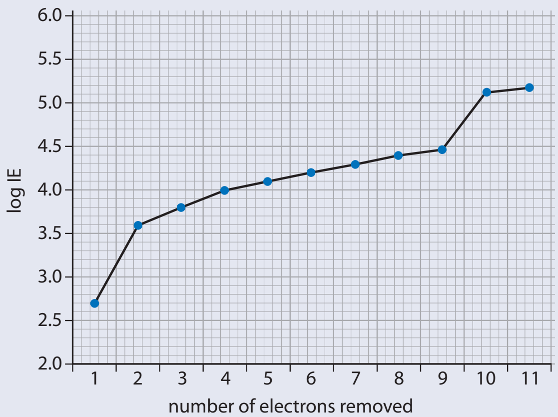
14 The graph represents the energy needed to remove nine electrons, one at a time, from an atom of an element. Not all of the electrons have been removed.



Which element could this be?

A C **B** Si **C** P **D** S

15 The graph below represents the successive ionization energies of sodium. The vertical axis plots log (ionization energy) instead of ionization energy to allow the data to be represented without using an unreasonably long vertical axis.



State the full electron configuration of sodium and explain how the successive ionization energy data for sodium are related to its electron configuration.

(*Total 4 marks*)

To access weblinks on the topics covered in this chapter, please go to www.pearsonhotlinks.com and enter the ISBN or title of this book.