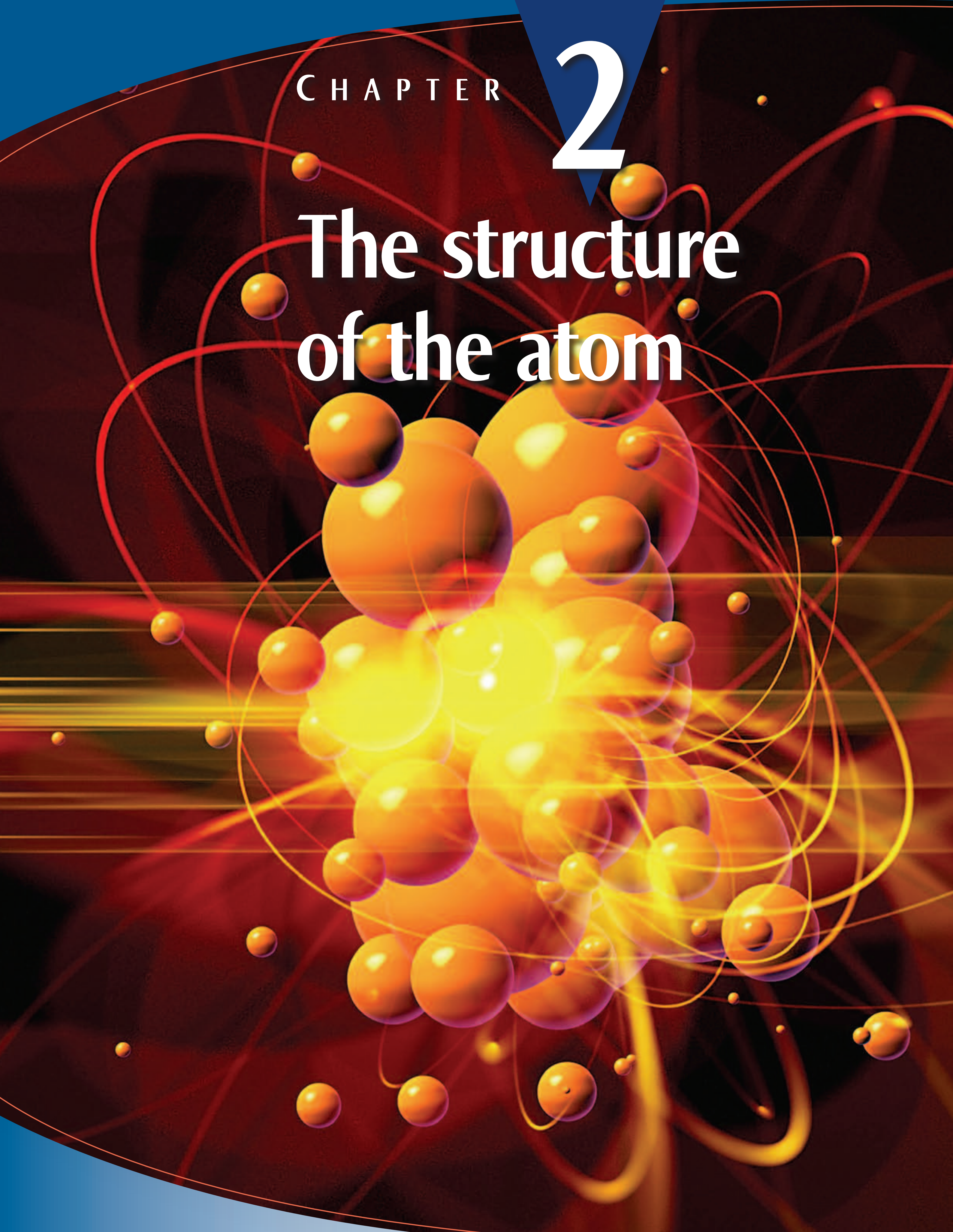
CHAPTER 2

The structure of the atom



Key Knowledge

Atomic theory

- historical development of the model of atomic theory with contributions from Dalton to Chadwick
- limitations of the model of atomic theory

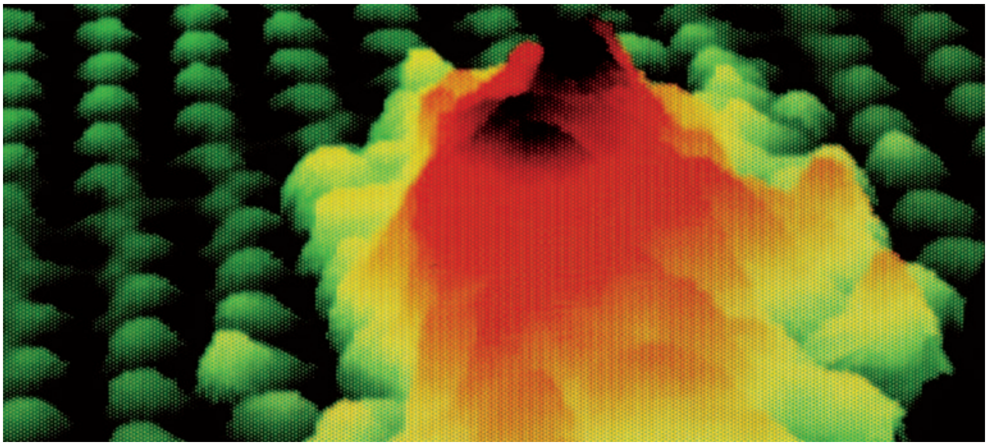


Figure 2.1 An image of gold atoms, taken with an electron tunnelling microscope

Dalton's theory that the atom is indivisible set a challenge for scientists of the day. Was he right, or could they find a way to split the atom or find evidence that it breaks up of its own accord? By the early 1900s, with the discovery of the electron, this challenge was met. But then, of course, the knowledge that the atom contains even smaller particles posed far more questions than it answered. What different kinds of particles are present in the atom, and how are they arranged?

Cathode rays

In 1838, the well-known British scientist Michael Faraday noticed that when he passed a large electric current through a glass tube that had had most of its air pumped out, a strange light was produced between the two electrodes. The region behind the negatively charged electrode, however, was dark. Physicists love solving intriguing puzzles, so you can imagine, the discovery of this light inspired much experimentation.

In 1855 the German scientist Heinrich Geissler invented a new kind of vacuum pump and developed a special glass tube in which the strange light could be investigated under much lower gas pressures. This piece of apparatus was known as a Geissler tube. Its design was later modified by the English physicist Sir William Crookes. His tube was, of course, called the Crookes tube.

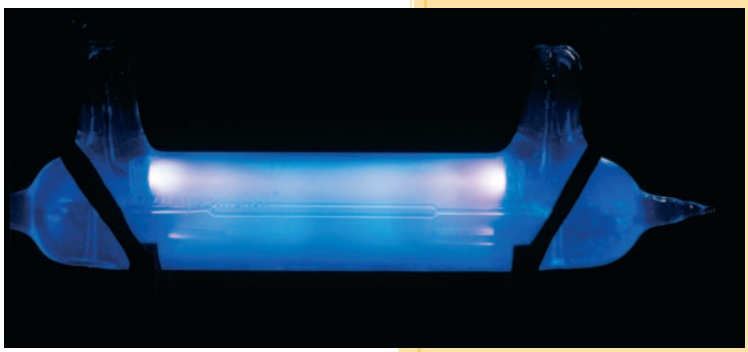


Figure 2.2 The strange light caused by passing an electric current through a gas at low pressure

Experiments soon showed that the mysterious glow first seen by Faraday was produced by rays that streamed from the **cathode** (the negatively charged electrode) towards the **anode** (the positively charged electrode). As a result they were called **cathode rays**.

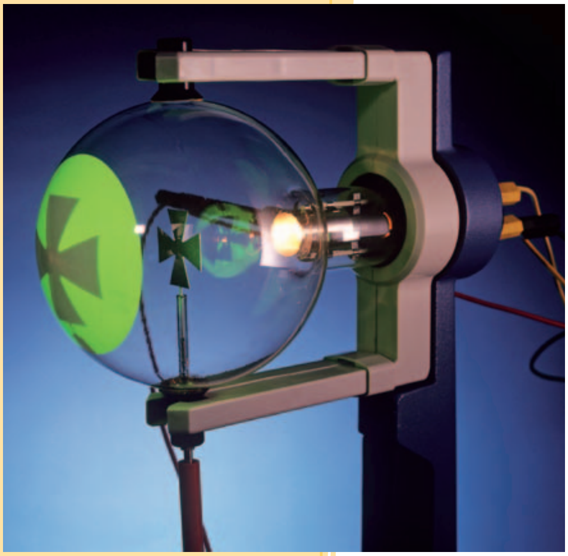


Figure 2.3 The Maltese cross experiment

Light—or particles?

The big question now was, what were cathode rays actually made of? Were light rays or particles streaming out of the cathode? It was known that oppositely charged objects attract one another. The direction of movement of the cathode rays towards the positively charged electrode suggested that if the rays consisted of particles, then they would be negatively charged.

One experiment that was conducted to determine the nature of the rays was to attach a Maltese cross made of metal to the anode. A sharp shadow of the cross formed at the end of the tube, showing that the rays must travel from the cathode in straight lines (Figure 2.3).

In other experiments, an opaque barrier with a slit in it was placed between the cathode and the anode. This meant that only a narrow beam of cathode rays could pass through. When electric plates were placed above and below the anode on the outside of the tube, the beam always bent towards the positively charged plate. Magnets also were able to bend the beam.

From these and many other experiments, physicists concluded that cathode rays consist of negatively charged particles that move in straight lines unless they are subjected to electrical or magnetic forces. The story behind working out the nature of these particles is told next. The tube came to be known as a **gas discharge tube** (or simply a **discharge tube**) or a **cathode ray tube**.

Cathode rays

Click on the link to **Cathode rays** and see the structure of a discharge tube. Pass the hand over each part and find out its function. Watch the short movie and observe what happens to the cathode rays when a magnet is passed over the outside of the tube.

The discovery of the electron

One physicist who investigated cathode rays was Joseph John Thomson. Thomson was Cavendish Professor of Experimental Physics at Cambridge University, England, from 1884 to 1919. In 1897, the same year that Braun invented the cathode ray oscilloscope (CRO), Thomson positioned electrodes and a magnet around a discharge tube to investigate the charge and mass of the particles that make up cathode rays (Figure 2.4).

By measuring how much the particles in the cathode rays were deflected (moved from their normal path) by different electrical and magnetic fields (Figure 2.5), Thomson was able to calculate the ratio of their mass to their charge. He then tested to see what would happen when the conditions were changed, and discovered that no matter what metal the electrodes were made of or what type of gas was in the tube, this mass to charge ratio was unchanged.

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What an invention!

It is hard to imagine that televisions, automated teller machines, computers, monitors, video game machines, video cameras and a number of other devices all owe their existence to the invention of the cathode ray tube! While experimenting on them, the German physicist Karl Braun invented the first cathode ray scanning device—the cathode ray oscilloscope. His discharge tube was the forerunner of television and radar tubes.

See page 44 in Chapter 3 for an explanation of the term 'mass' and how this is related to but different from weight.

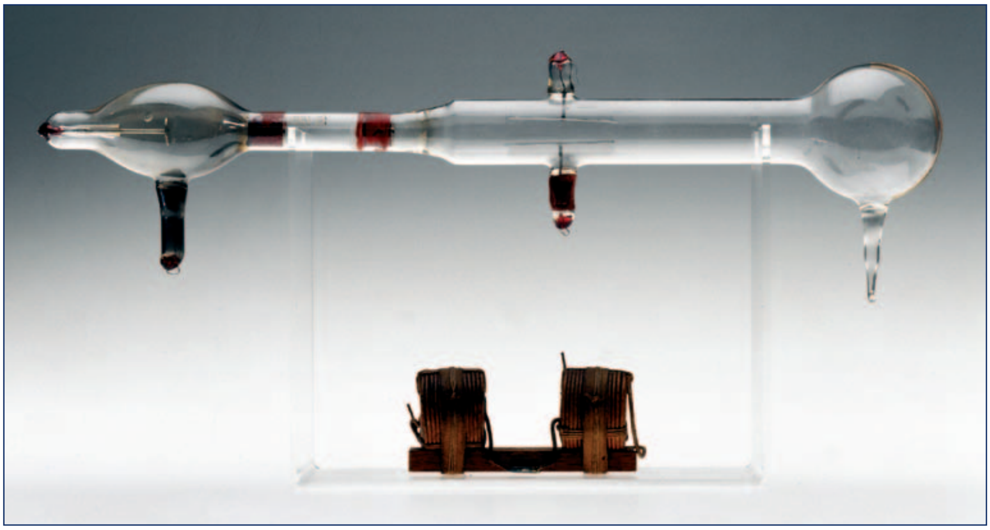

Figure 2.4 The gas discharge tube used by Thomson in his experiments. It was about 1 metre long and had been made entirely by hand for him by a very gifted glassblower. Note the long glass 'finger' through which almost all of the gas was pumped out of the tube before it was sealed.

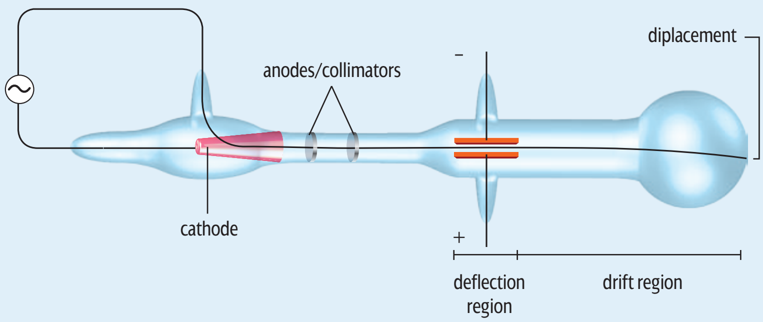

Figure 2.5 This diagram of Thomson's experiment appeared in an article he wrote about his discoveries in 1897.

Dalton was wrong!

From the direction in which the particle beam was deflected, Thomson deduced that the particles that made up cathode rays were negatively charged. When they streamed from the cathode, they hit the atoms of the gas present in the tube and knocked the same type of negatively charged particle out of these atoms.

From this and the fact that atoms have no net charge, Thomson concluded that atoms consist of two parts which are held together by electrostatic attraction:

1 A heavy part with a positive charge, which is almost entirely responsible for the mass of the atom. (At this stage the proton and neutron were still to be discovered.)
2 Negatively charged 'corpuscles', which are present in all atoms, but in different numbers. These corpuscles were later called **electrons**.

This of course meant that Dalton's model of the atom was incorrect, since the atom was *not* the smallest possible particle. Thomson was awarded the 1906 Nobel Prize in Physics for his work.

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A man of influence

During his time at Cambridge, Thomson is reputed to have trained some 72 professors of physics and chemistry, who went on to lead departments in universities around the world.

The Cavendish Laboratory he headed for so long is still a leading research centre and is a popular destination for those interested in the story behind the atom.

Discovering the electron

Click on the link to **Discovering the electron**. See cathode rays glowing. Click on the different options and find out how Faraday's discovery led to the invention of the forerunner of today's neon lights. Learn more about the discovery of the electron and hear Thomson himself talking about the electron.

The Thomson plum pudding model

The question that immediately arose from Thomson's work was, how are the parts of the atom arranged?

Thomson reasoned that the positively charged material in the atom and the negatively charged electrons would be so strongly attracted to one another that the electrons would be pulled into and embedded within the positive material. He therefore proposed that the atom was similar to a plum pudding, with negatively charged electrons scattered throughout the positively charged material like currants through a pudding.

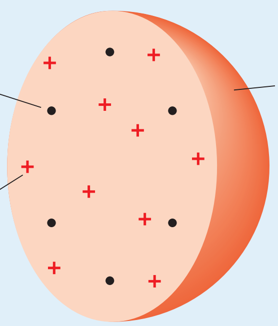

Figure 2.6 The Thomson 'plum pudding' model of the atom, proposed in 1906

He also proposed that repulsion between the electrons would impose some ordered structure on the 'pudding'. If there were only one electron, it would be in the centre, two electrons would be at opposite sides, and larger numbers would be located in rings (Figure 2.6). This model of the atom is known as the **Thomson plum pudding model**.

This was a reasonable theory in the light of the evidence available at that time. Physicists had observed that charged objects moved towards each other and that energy was required to keep them apart.

The alpha-particle scattering experiment

Ernest Rutherford, a New Zealander, had won a scholarship to study under Thomson, conducting important research on radioactive substances. He then worked in Canada before returning to England in 1907 to take up an appointment as Professor of Physics at the University of Manchester.

By this time Rutherford knew that many radioactive substances naturally emitted alpha radiation that could pass through very thin layers of materials but was stopped by thicker layers. This radiation consisted of **alpha-particles** (**α-particles**), atoms of helium that have lost their electrons and hence are positively charged.

We now know that α-particles are helium nuclei, and consist of two protons and two neutrons bound together by very powerful nuclear forces.

At Manchester, Rutherford worked in collaboration with a colleague in his department, the German physicist Hans Geiger. Together they devised a method for detecting a single α-particle and for counting the number of α-particles emitted by a radioactive source. They then set up an experiment that was to become one of the most famous experiments ever conducted.

The experiment

Rutherford and Geiger fired a narrow beam of high-speed α-particles into a fine tissue-like sheet of gold. The α-particles were detected on a moveable curved screen that was coated in zinc sulfide. This substance is fluorescent and gives a tiny flash of light (called a scintillation) when hit by an electron (Figure 2.8).

At first they placed the screen behind the gold foil. Rutherford reasoned that if the positively charged material in each gold atom is spread out over the entire volume of the atom, as Thomson had proposed, its electric field would not be intense enough to repel the tiny, very fast moving positively charged α-particles to any significant degree. Instead, they would virtually pass straight through the much larger gold atoms. That is, they would be only slightly **scattered** (moved off their path in a new direction).

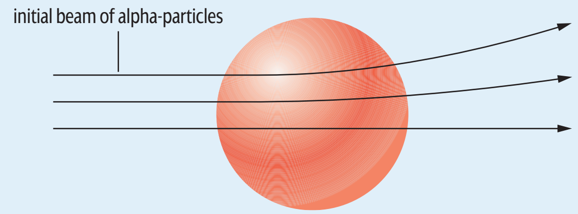

Figure 2.7 What the 'plum pudding atom' would do

The results

At first, it appeared that the prediction came true. Then, in 1909, a remarkable discovery was made. In a later speech, Rutherford told the story:

> *I had observed the scattering of alpha-particles, and Dr Geiger in my laboratory had examined it in detail. He found, in thin pieces of heavy metal, that the scattering was usually small, of the order of one degree.*
>
> *One day Geiger came to me and said, 'Don't you think that young Marsden, whom I am training in radioactive method, ought to begin a small research?' Now, I had thought that too, so I said, 'Why not let him see if any alpha-particles can be scattered through a large angle?'*
>
> *I may tell you in confidence that I did not believe that they would be, since we knew the alpha-particle was a very fast, massive particle with a great deal of energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings, the chance of an alpha-particle being scattered backwards was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying 'We have been able to get some of the alpha-particles coming backward.' It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.*

Explaining the results

It would have been tempting to dismiss this unexpected result as being due to experimental error, but it was reproducible and had no obvious cause. It was time to modify Thomson's model of the atom.

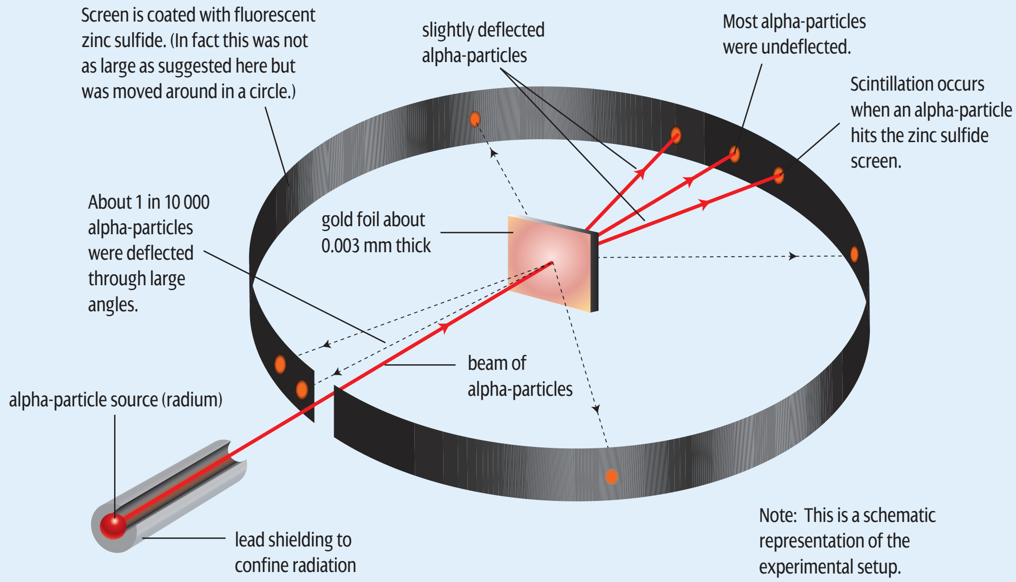

Figure 2.8 The now famous alpha-particle scattering experiment

The Rutherford nuclear model

Rutherford concluded that the results of the α-particle scattering experiment could be explained only if the positive charge of the atom was not spread over its whole volume but concentrated in a small volume at the centre. He called this concentrated region of positive charge the **nucleus**.

Rutherford proposed, therefore, that most of the atom is empty space and when an α-particle moves through this empty space the nucleus will have little effect on its movement. The α-particle will only deviate to a significant extent when it comes near a nucleus.

Rutherford

Click on the link to **Rutherford**. Hear Rutherford talking about breaking up the atom.

Scattering α-particles

Click on the link to **Scattering α-particles** and see the animation of how an α-particle is deviated when it comes near a nucleus.

Ironically, Ernest Marsden, the graduate student whose research project precipitated the discovery of the nucleus, emigrated from England to Rutherford's birthplace, New Zealand, where he became a Professor of Physics. He, too, was eventually knighted.

Hans Geiger returned to Germany and is best known for the invention that bears his name—the Geiger counter.

How big is the nucleus?

Rutherford then designed a series of experiments to determine the size of the nucleus compared with that of the atom. He measured the angles of scattering and their frequency by using slits of various widths and foils of different metal. He used mathematical modelling to deduce that the positive charge had to be concentrated in a sphere less than 10^{-14} m in diameter!

Rutherford's experiment

Click on the link to **Rutherford's experiment** and see the animation of some of Rutherford's experimentation. The animation shows the proposed nuclear model of the atoms of the foil. Move the bar to see the effect on the scattering of the α-particles when the slit is widened.

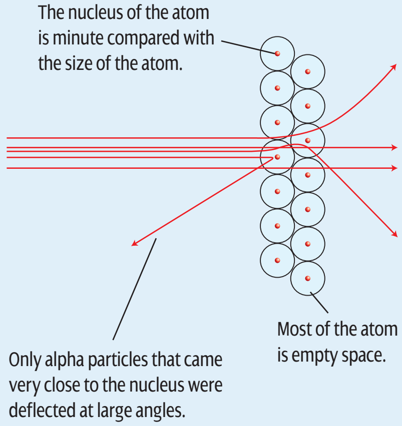

Figure 2.9 Explaining the results of the alpha-particle scattering experiment

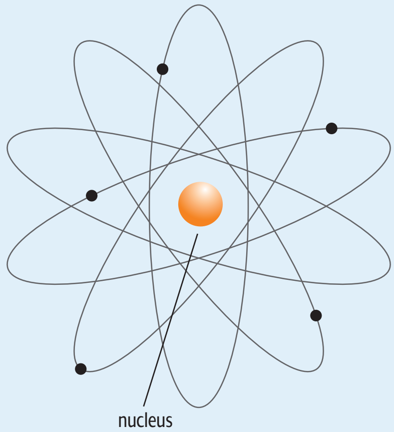

Figure 2.10 The Rutherford nuclear model of the atom

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Atomic Illusions

If the atom were the size of a large classroom, then the nucleus would be the size of a very small full stop.

Like a fan with rotating blades, atoms only appear the size they are because their electrons are moving so rapidly around their nucleus. This implies that all objects only give an illusion of size; like the atoms from which they are constructed, they are mostly empty space!

The electrons

Rutherford was fascinated by the nucleus and investigated it further. He concluded that the electrons travel around the nucleus in random orbits like the planets around the Sun, but he did not study them. This model of the atom is termed the **Rutherford nuclear model**, although it is sometimes called the **planetary model** of the atom.

Ernest Rutherford was awarded the 1908 Nobel Prize in Chemistry for his work. Like Thomson, he was later knighted and is now buried in Westminster Abbey.

QUESTIONS 2.1

1 Copy and complete Table 2.1.

Feature of the model	Thomson's 'plum pudding' model	Rutherford's nuclear model
What is present inside the atom?		
Where are these particles or this material located within the atom?		
What is responsible for most of the weight of the atom?		
What discovery led to the proposal of this model?		

Table 2.1 A comparison of the Thomson and Rutherford models of the atom

continues on next page

continued from previous page

2 a Draw a sketch of the two models of the atom featured in Table 2.1.
  b Although Thomson's model was later found to be incorrect, it was consistent with what was known about charged objects at that time. State the reasoning behind Thomson's model.
  c Were any features of the Dalton model of the atom (page 13) retained in these two models? Discuss.

3 a Draw a schematic diagram of the experimental setup for the α-particle scattering experiment.
  b State how α-particles were detected in this experiment.
  c Explain why Rutherford was astonished at the results of this experiment.
  d Draw a sketch to show how the Rutherford nuclear model was able to explain the occasional large angle at which α-particles were deflected.
  e Suggest what the term 'reproducible results' means and discuss why such results are considered to provide reliable experimental evidence.

4 Scientific discoveries usually result from scientists collaborating with one another and building on one another's experiments and hypotheses.
  a Identify two previous discoveries that made it possible for cathode rays to be seen for the first time.
  b Design a flow chart that shows the series of discoveries that led to the Rutherford nuclear model of the atom.

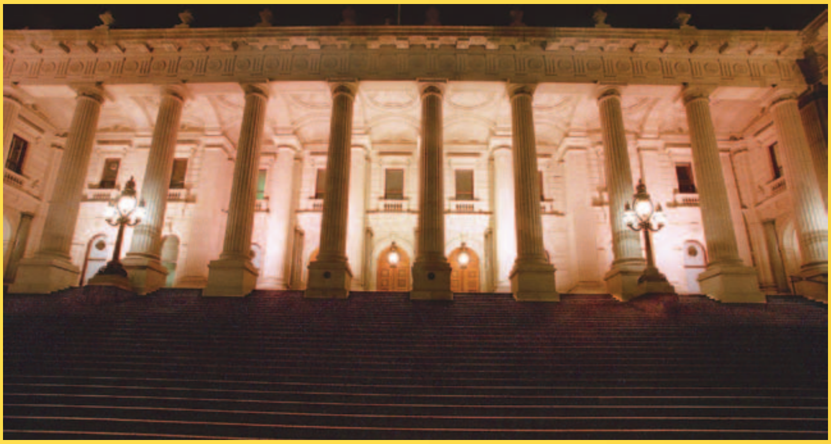


Figure 2.11 Victoria's Parliament House

5 According to Rutherford's nuclear model of the atom, if all the atoms that make up Victoria's Parliament House were compressed to the size of their nuclei alone, this Parliament House would occupy approximately the volume of a die.
  a Explain why such a large building would 'shrink' like this.
  b If the Rutherford nuclear model is correct, would you be able to pick up this die? Discuss.

6 No matter what model we build of something, it will not be able to completely and accurately represent the object we are modelling. We say the model has its limitations. What are three limitations to the illustrations of the Dalton, Thomson and Rutherford models of the atom drawn in this book?

Problems with the Rutherford nuclear model

Rutherford's model of the atom posed a problem that Thomson had already identified and tried to solve with his model. An object moving in a circle is continuously changing direction. From Sir Isaac Newton's time onwards, physicists had known that this means it is continuously accelerating. If the object is uncharged and its speed does not change, this acceleration causes no change in energy. However, from their experiments with electric currents, scientists had observed that if a charged particle accelerates, it radiates energy as radio waves.

An orbiting charged particle such as an electron should, therefore, continuously radiate energy. This would make it lose speed (because the energy would have to come from its motion) and so the electron would be drawn inwards by the forces of attraction from the nucleus. The electrons in Rutherford's model of the atom should therefore spiral into the nucleus after only about 1×10^{-9} (0.000 000 001) seconds! This would result in the collapse of all matter. Clearly, this has not happened. Why not?

Spectral evidence

It had been known for some time that when different elements are heated or subjected to a very high voltage in a gas discharge tube (page 17) they emit light. If this light is viewed with a **spectroscope**, a device that breaks up light into its different wavelengths, the image obtained is a set of coloured lines on a black background. This image is termed an **emission spectrum**. Each element produces a unique emission spectrum. An example is shown in Figure 2.12.

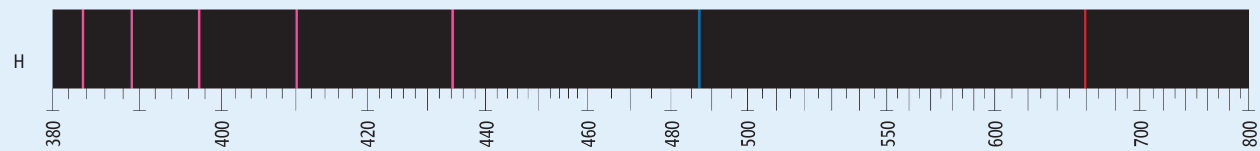


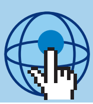
Figure 2.12 The emission spectrum of hydrogen. This image only shows the light in the visible region that is emitted by hydrogen atoms. Any ultraviolet and infrared light emitted by the hydrogen atom is not shown.

Bohr's proposals are often described in older chemistry books as his 'radical postulates'.

Each coloured line on an emission spectrum represents light of a particular wavelength. We therefore say that only **discrete** wavelengths of light are emitted; that is, only a certain set of particular wavelengths is present in the emitted light.

In 1913, while working in Rutherford's department in Manchester, Danish physicist Niels Bohr analysed the spectral lines of hydrogen (Figure 2.12). Since the spectrum was not continuous (like a rainbow), the electrons could not be giving off energy continuously. Bohr concluded that objects on the atomic scale do not behave like normal-sized objects, and so the laws of classical physics cannot possibly apply to particles found inside the atom. This was very radical thinking at the time. He proposed a new model to explain the emission spectrum of hydrogen.

Spectra



Click on the link to **Spectra**. View the emission spectra of the elements shown. By first clicking on one element and then clicking on the side bar, you can view even more spectra. (Absorption spectra will be studied in Unit 3.)

The Bohr model of the atom

Bohr agreed with Rutherford's proposals that in the atom the electrons revolve around a central positively charged nucleus that is responsible for most of the weight of the atom. But from his spectral evidence, he concluded that electrons are found at only certain distances from the nucleus and have particular values of energy. The further they are from the nucleus, the greater the amount of energy they possess. While in their orbit, electrons do not lose any energy.

Electron shells

Bohr called the collection of electron orbits at any given distance an **electron shell**.

From the nucleus outwards, these electron shells are called the K shell, L shell, M shell, N shell and so on. These shells and the electrons they contain obey certain conditions. These conditions are listed below and illustrated in Figure 2.13.

- The shells get closer and closer to one another, the further they are from the nucleus. Electrons always occupy the lowest energy shells first. Bohr called this the **ground state** of the atom.
- A maximum number of electrons can occupy any given shell. This number is related to the shell number (Table 2.2). However, the outermost occupied shell can only contain a maximum of 8 electrons.

Table 2.2 Maximum number of electrons in each electron shell

Shell number	1	2	3	4	n
Maximum number of electrons	2	8	18	32	$2n^2$

This model of the atom is known as the **Bohr model**. Bohr won the 1922 Nobel Prize for Physics for his work on the structure of the atom.

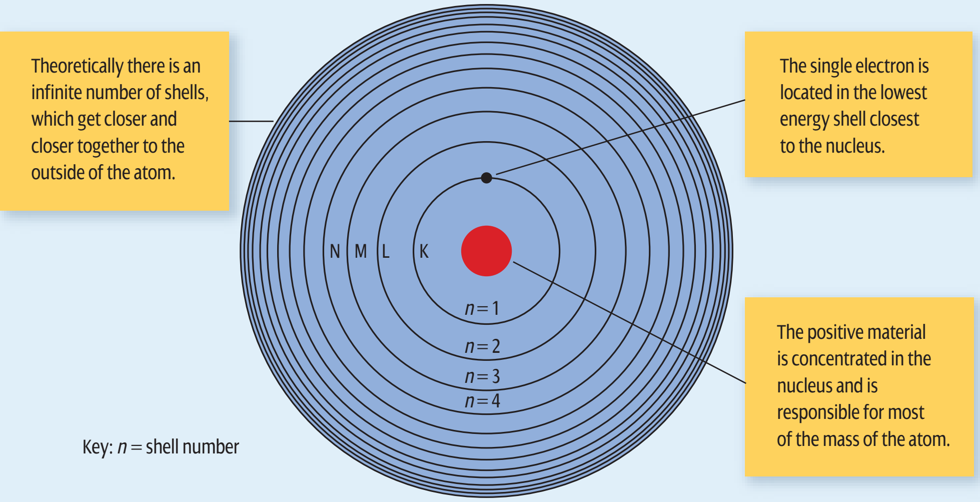


Figure 2.13 The Bohr model of the hydrogen atom

Explaining spectra using the Bohr model

Bohr explained the discrete lines on the hydrogen spectrum by proposing that if a hydrogen atom is given energy, by heating it for example, the electron can jump to a higher energy level further from the nucleus. When it does so, it absorbs an exact **quantum** (or 'packet') of energy that is equal to the difference in the energy of the two levels.

When any electron absorbs energy and jumps to a higher energy level, we say it has been **excited**. The atom is then described as being in an excited state. Figure 2.14 shows one possible jump the electron of a hydrogen atom may make when it is excited.

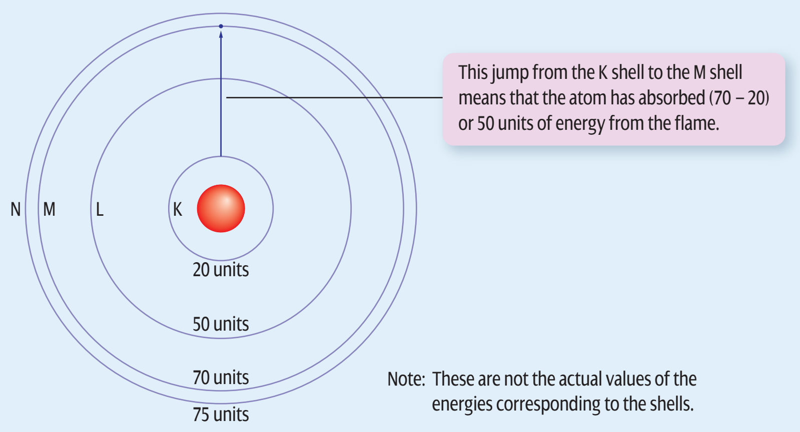


Figure 2.14 Exciting a hydrogen atom, using hypothetical energy values

Returning to the ground state

Excited atoms are unstable and in less than a millionth of a second they will give out the energy they have absorbed to return to the stable ground state. They emit this energy in the form little 'packets' of light energy known as **photons**. Each photon has a particular energy and hence a particular wavelength.

In each excited hydrogen atom, for example, the electron jumps back to the K shell either in a single leap or in stages. For each jump, a photon of light is emitted, with energy corresponding to the energy difference between the two levels. Figure 2.15 illustrates this using the hypothetical energy values shown in Figure 2.14.

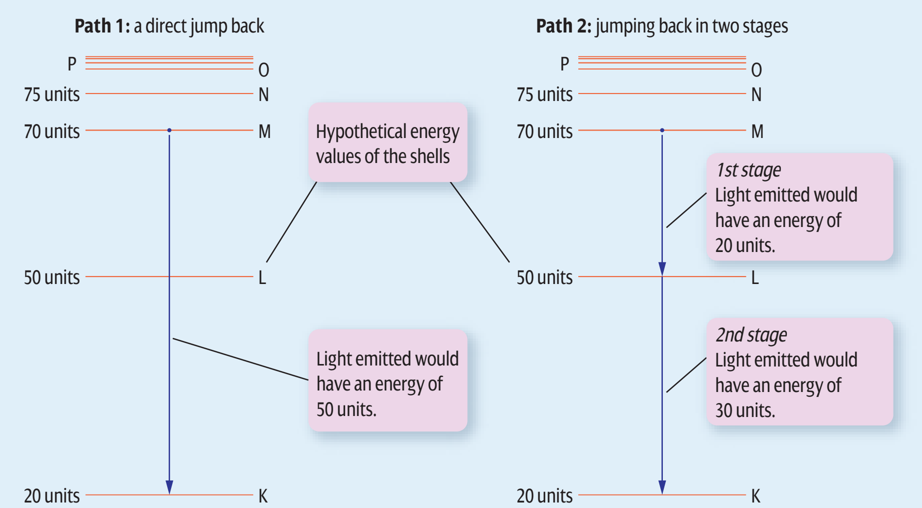


Figure 2.15 Returning to the ground state. Some atoms will follow Path 1, and others will follow Path 2. This will account for three of the spectral lines of hydrogen; that is, it accounts for three different wavelengths of light emitted by the excited atoms.

If you heat a sample of hydrogen, different atoms will absorb different amounts of energy. In this atom, the electron has been excited from the K shell to the M shell. In another atom it may have been excited to the L shell, which would have required 30 units of energy, and in another it has been excited to the N shell, which would require 55 units.

It is important to note, however, that the actual energy value of electrons in a given electron shell is mathematically related to the radius of the shell and depends on the element. That is, the electron in the K shell of a hydrogen atom has a different energy to an electron in the K shell of, say, a sodium atom.

In hydrogen, any jumps directly to the K shell release high-energy photons that have wavelengths in the ultraviolet band. These therefore are not seen in Figure 2.12.

Electron configurations

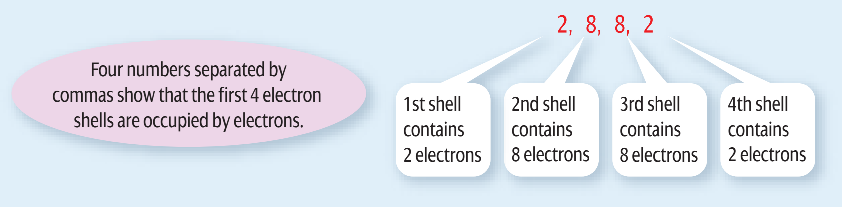


Figure 2.16 Interpreting an electron configuration

The arrangement of electrons in their shells is termed the **electron configuration** of the atom. Figure 2.16 shows a typical electron configuration based on the Bohr model, and explains how it is interpreted.

Applying the Bohr model

SKILLS

We now know how electrons are allocated to the electron shells in the Bohr model, therefore we can:

- determine the electron configuration of an atom, if we know how many electrons are present
- distinguish between an electron configuration that represents an atom in its ground state and one that represents an excited atom
- deduce how many different jumps are possible between two particular electron shells and hence predict the number of spectral lines that would arise from these jumps.

Examples of these different types of problems are shown next.

Example 1

The uncharged sodium atom contains 11 electrons. State its electron configuration according to the Bohr model.

Solution

We work through the shells, placing the maximum number of electrons in each of the lowest energy shells.

- The 1st shell can hold 2 electrons, so the first 2 electrons go here. This leaves 9 electrons to place.
- The 2nd shell can hold 8 electrons, so the next 8 electrons go here. This leaves 1 electron to place.
- The remaining electron must be placed in the 3rd shell.

Answer

The electron configuration of the uncharged sodium atom according to the Bohr model is 2, 8, 1.

Example 2

Which of the following electron configurations represent an atom in its excited state?

A 2, 8, 5
B 2, 4
C 2
D 2, 7, 2

Solution

If a configuration obeys Bohr's rules then we know it represents an atom in its ground state. If it does not obey the rules, it must represent an atom in its excited state.

- Configurations A, B and C all show electrons placed according to the rules (see Example 1).
- Configuration D shows a total of 11 electrons, but according to the rules this should have the configuration shown in Example 1.

Answer

D represents an atom in its excited state. A, B and C represent atoms in their ground state.

Example 3

What are the possible jumps back to the ground state for an electron excited from the 2nd electron shell to the 5th electron shell of an atom? Hence, how many possible spectral lines will be produced over the series of atoms as excited electrons jump back to the 2nd shell from the 5th shell?

Solution

In this type of question, drawing a schematic diagram will enable you to picture and hence identify the possible jumps. This is shown in Figure 2.17. Remember that each different jump will lead to the emission of a unique amount of energy and hence produce light of a unique wavelength.

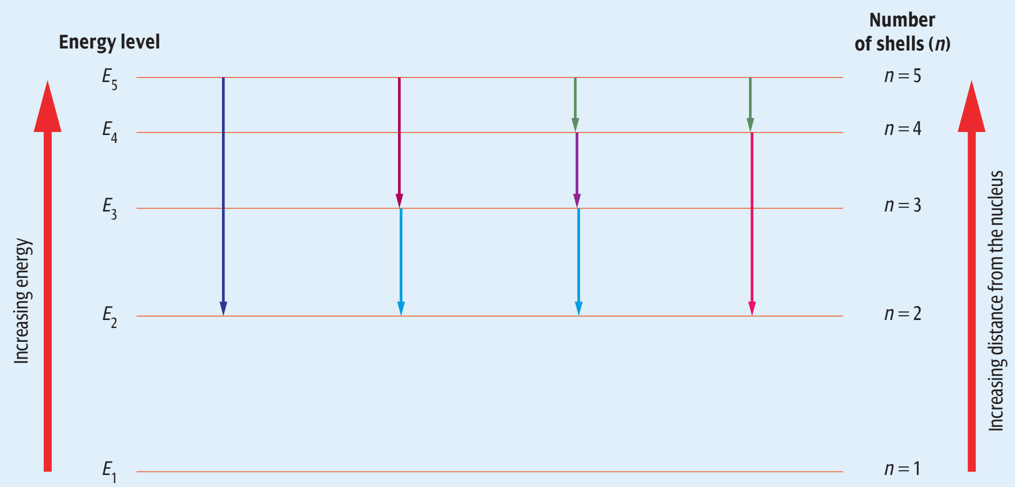
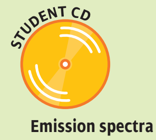


Figure 2.17 The possible pathways (or sequences of jumps) as electrons jump from the 5th electron shell back to the 2nd electron shell



From Figure 2.17 we can see that the following different jumps are possible: 5 ⟶ 2, 5 ⟶ 3, 3 ⟶ 2, 5 ⟶ 4, 4 ⟶ 3 and 4 ⟶ 2

Answer

There are 6 different possible jumps and hence 6 possible spectral lines that can arise when electrons jump back from the 5th shell to the 2nd shell over a sample of atoms.

QUESTIONS 2.2

1 Copy and complete the flow chart in Figure 2.18 by inserting the correct missing term. Choose from *light energy, heat energy, ground, excited, stable, unstable, photon.*

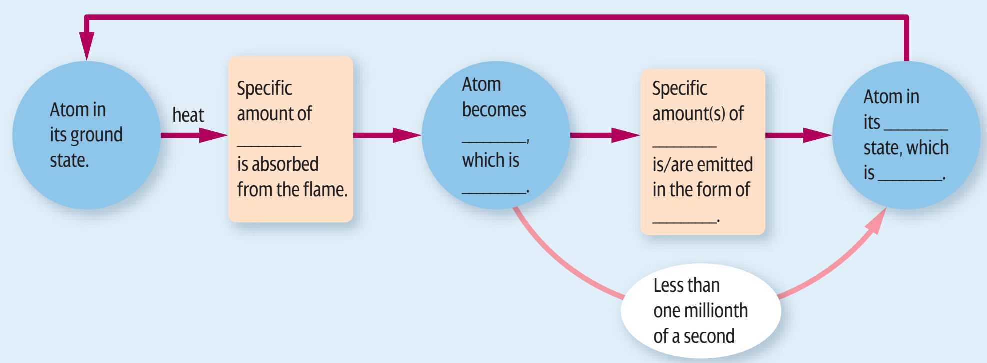


Figure 2.18 What happens when we heat a sample of atoms

continues on next page

continued from previous page

2 Niels Bohr retained much of the Rutherford nuclear model when he created his model of the atom.
   a Outline the problem posed by the Rutherford model that Thomson had tried to solve with his model.
   b What was Bohr's radical conclusion about the laws of classical physics known at that time?
   c What experimental evidence led Bohr to propose his model of the atom?
   d State the key similarity and the key difference between the Rutherford and Bohr models.
3 a State what is an electron shell.
   b Predict the maximum possible number of electrons that can occupy the 6th electron shell according to the Bohr model of the atom.
   c What is the 6th electron shell of an atom also called?
   d If the 6th electron shell was the outermost occupied shell of an atom in its ground state, what would be the maximum number of electrons it could contain?
4 Write the electron configurations of the uncharged atoms of the elements listed in Table 2.3, according to the Bohr model of the atom.

Table 2.3 The electrons present in the uncharged atoms of a number of elements

Name of element	Carbon	Fluorine	Aluminium	Phosphorus	Calcium
Total number of electrons in its uncharged atoms	6	9	13	15	20

5 a Create an annotated 2D or 3D model of the carbon atom based on your answer to Question 4.
   b Identify two limitations of the model you have created.
   c Explain the difference between the ground state and excited state of an atom.
   d Hence write one possible electron configuration for an excited atom of carbon.
6 Give explanations for the following:
   a When atoms of elements are heated they give off light, though sometimes this light is not visible.
   b When the light from heated atoms is passed through a spectroscope, the image it produces consists of a number of separate coloured lines on a black background.
   c The emission spectrum of an element can be used to identify it.
7 Predict the number of possible spectral lines that might arise from a jump between the following sets of shells. Show all reasoning.
   a 4th shell back to 2nd shell
   b 6th shell back to 2nd shell

CHEMBOX

The discovery of the proton

The **proton** is the positively charged particle found in the nucleus of all atoms. Like the electron, its discovery started with experiments with cathode ray tubes and ended in one very cleverly designed experiment from which brilliant deductions were made.

In 1886, the German physicist Eugen Goldstein was experimenting with gas discharge tubes. He had already discovered that cathode rays are affected by moving a magnet near them and, in fact, was the person who named them cathode rays.

In one experiment Goldstein placed holes in the cathode and observed glowing yellow streamers emanating from the holes in the opposite direction to the anode. He called these **canal rays** since they passed through 'channels' in the cathode. Since they move in the opposite direction to cathode rays, it was deduced that canal rays were positively charged (Figure 2.19).

CHEMBOX

After Thomson's experiments with cathode rays and the discovery of the electron, physicists started to perform similar experiments on canal rays.

They found that the rays consisted of positively charged particles with a mass to charge ratio that varied with the gas in the tube. The smallest ratio was obtained when hydrogen was in the tube. When the physicists assumed the particles of other gases would have the same charge as the hydrogen particles, they calculated that their mass was a multiple of that of the hydrogen particle.

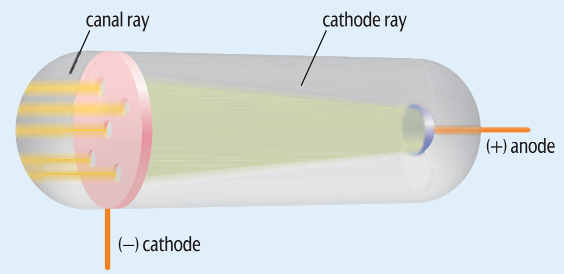


Figure 2.19 Goldstein's experiment—a schematic diagram

It was suggested that these positively charged particles were produced when atoms of the gas in the discharge tube lost an electron due to their interaction with the cathode rays. This electron was absorbed by the anode. The atoms that lost a negatively charged electron from within them were now positively charged.

The fact that the masses of the atoms appeared to be multiples of that of the hydrogen atom suggested that the nuclei of other elements contain multiple copies of a fundamental particle present in the hydrogen nucleus. But it took another famous experiment by Ernest Rutherford to show that this was the case.

In his experiment, Rutherford sealed a small glass tube into a brass box that had a zinc sulfide scintillation screen (page 22) at one end. The brass box was filled with nitrogen gas and then α-particles were passed through the glass tube into the box.

Rutherford was greatly excited to discover that the scintillations produced could not be distinguished from those produced by hydrogen. Yet no hydrogen was present. He concluded that bombardment by α-particles had caused nitrogen atoms to be split into hydrogen atoms.

Figure 2.20 Ernest Rutherford

Newspaper headlines of the time proclaimed 'Rutherford splits the atom!' Far more importantly, however, Rutherford realised the significance of his discovery. It meant that, like the electron, the hydrogen nucleus must be a fundamental particle from which other particles are made. Rutherford named it the proton, from the Greek *protos*, meaning 'first'. Rutherford published his conclusions in 1919.

Questions

1 What is the origin of the word 'proton'?
2 Why is the proton described as a fundamental (or elementary) particle?
3 Explain the difference between a cathode ray and a canal ray.
4 Describe the experiment that first showed that the atom contains positively charged material.
5 Outline how Rutherford showed that the proton existed and the reasoning he used.

Atomic number

We now know that the total number of protons in the nucleus of the atoms of an element is unique for that element. For example, all sodium atoms contain 11 protons. If an atom contains 11 protons in its nucleus, it must be an atom of sodium. Thus we identify elements by the number of protons they contain.

The number of protons in the nucleus of an atom is termed its **atomic number**, symbol **Z**. The atomic number of sodium therefore is 11. The atomic numbers of the elements are listed in the Periodic Table inside the front cover of this book.

Element number 111 (roentgenium, Rg) is named after Röntgen, to honour his work. This element was only officially accredited in December 2004.

The charge on the proton is equal to that on the electron, except that it is positive, not negative. Note that these charges are actually measured in coulombs, but for most purposes we only need to represent the charge on a proton as 1+ and the charge on an electron as 1–.

In an uncharged atom, the number of electrons in the atom must equal its number of protons. Thus all uncharged sodium atoms, for example, contain 11 electrons.

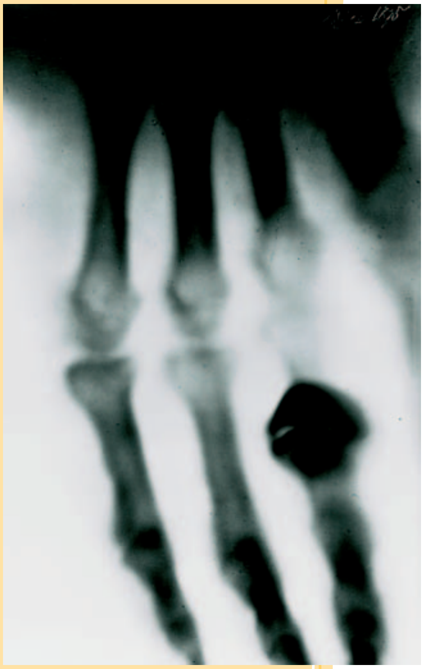


Figure 2.21 The first X-ray ever seen

Why *Z*?

From the many experiments on cathode ray tubes, it was found that, when the anode was made of certain metals, X-rays were produced when these metals were bombarded by cathode rays. X-rays were first discovered by Wilhelm Röntgen in 1895 and were so named because they were mysterious, unknown rays. Röntgen soon discovered that these mysterious rays could penetrate his wife's hand and produce an image of her bones and rings on a photographic plate (Figure 2.21). This was the first X-ray ever taken!

Before long, it was found that, like light, X-rays are a form of electromagnetic radiation and are composed of many different wavelengths which can be separated by prisms and viewed as a spectrum. When studying the spectra of the X-rays produced by different elements, Robert Moseley found that the frequencies of certain similar lines in their spectra were mathematically related to a number that depended on the weight of their atoms. He happened to use Z to represent this number in his formula for the frequencies of the lines:

$$\gamma = a(Z - b)^2$$

where γ = frequency and a and b are constants

Eventually Z was found to correspond to the charge of the nucleus of the atoms of an element, rather than their weight, and so it became known as the atomic number of the element. It was to play a key role in the growing understanding of the atom.

Problems with the Bohr model

Bohr's model of the atom is very helpful in explaining in simple terms many aspects of how atoms interact. However, as more accurate spectroscopes were developed, it was found that what had appeared to be one line on an emission spectrum was often a number of fine lines located close together.

Bohr's model could explain how the coloured lines on the emission spectrum of hydrogen arose, but it could not explain these additional lines or the different intensities of the lines present in the spectra of other elements. Moreover, it did not give any reasons for the electron's stable orbits, and there was no theoretical justification for his proposal that the **orbits** of the atoms (the paths they trace out as they move around the nucleus) should be circular.

So, like the models that came before it, it had to be modified. The model that replaced it is considered next, but first we will examine the limitations of any drawings representing the Bohr model.

Limitations to drawings of Bohr's model

Consider the representation of the Bohr model shown in Figure 2.13. Here are some of its limitations:

- Atoms are not coloured.
- Electron shells are invisible.
- The atom could not be drawn to scale. For the hydrogen atom to be sufficiently magnified so that its electron is visible in a drawing, the atom would need to be much bigger than your school!
- The nucleus is represented by a red circle to show it is positively charged, but in fact for all atoms other than this simple hydrogen atom the nucleus contains a number of protons and neutrons.
- The atom is spherical; we can only show a two-dimensional image.
- Electrons spin around the nucleus at almost the speed of light; we have to 'freeze' them in a particular position to make them visible.

The Schrödinger model

When the emission spectra of elements other than hydrogen were examined with high resolution spectroscopes, what had appeared to be single lines were found to be clusters of lines. These indicated that the electrons occupying a particular shell did not all have exactly the same amount of energy. In all but the first shell they could have different, though closely related, energies.

In this way, it was discovered that electron shells are divided into **subshells**—regions within a shell in which the electrons have the same energy.

The subshells

The number of subshells depends on the number of the shell in a simple way. Similarly, the maximum possible number of electrons in any given subshell follows a simple mathematical pattern. This is shown in Table 2.4.

Table 2.4 The subshells of an atom

Electron shell	Number of shell (n)	Total number of subshells present in the shell	Names of subshells	Maximum number of electrons in the subshell	Maximum number of electrons present in the shell
K	1	1	1*s*	2	2
L	2	2	2*s* 2*p*	2 6	8
M	3	3	3*s* 3*p* 3*d*	2 6 10	18
N	4	4	4*s* 4*p* 4*d* 4*f*	2 6 10 14	32

The letters used to label the subshells come from spectroscopy and the appearance of lines in spectra: *s* = sharp, *p* = principal, *d* = diffuse and *f* = fine.

It can be seen from Table 2.4 that:

- The number of the shell, *n*, equals the number of subshells present. Thus the 5th shell will contain 5 subshells, and so on.
- All *s* subshells can contain up to 2 electrons; all *p* subshells can contain up to 6 electrons, and so on. These numbers go up in steps of 4.
- The maximum total number of electrons in a shell is the same as that for the Bohr model (Table 2.2); that is, it is given by $2n^2$.

Atomic orbitals

The other new feature of this model of the atom is that electrons are no longer confined to circular orbits. Instead, they move in regions of space called **atomic orbitals**. Each atomic orbital cannot contain more than 2 electrons, a rule that is called the **Pauli Exclusion Principle**. If there are two electrons present, these electrons spin in opposite directions.

The names of the atomic orbitals and where they are located is shown in Table 2.5.

In this table you can see there is a simple pattern to the number of atomic orbitals present in any given type of subshell. (They form an arithmetic series.) This accounts for the pattern in the maximum number of electrons in a subshell.

Table 2.5 The atomic orbitals found in the atom

Type of subshell	Type of atomic orbital present	Number of atomic orbitals present in the subshell	Maximum number of electrons present in the subshell
s	*s* orbital	1	2
p	*p* orbital	3	6
d	*d* orbital	5	10
f	*f* orbital	7	14
g	*g* orbital	9	18

This produces a far more complex picture of the atom, because the atomic orbitals have a range of different shapes. For example, *s* orbitals are spherical and *p* orbitals are dumbbell shaped. The three *p* orbitals found within a given *p* subshell each have the same shape but are located at right angles to one another (Figure 2.22). The size and location of these orbitals, of course, depends on the subshell in which they are located and the actual element.

An occupied atomic orbital is also called a **charge cloud**.

In fact, the atom is even more complex than is suggested in Figure 2.22, since the boundaries of atomic orbitals are not as sharply defined as implied in the drawings. An electron in the 3*s* subshell, for example, might occasionally move in close to the nucleus, then way out to the outer boundaries of the atom. The drawings therefore represent the boundaries of the regions in which the electrons are found about 95 per cent of the time. Hence we define an atomic orbital as a region in the atom in which there is a high probability of finding an electron at any moment of time.

Figure 2.23 shows a two-dimensional representation of how successive *s* orbitals are arranged in a particular atom. The greater the density of the image, the higher is the probability of finding an electron at those distances from the nucleus.

This model of the atom is known as the **Schrödinger model** or the **quantum mechanical model**. It was built up from very sophisticated mathematical analysis of spectral lines. The German scientist Erwin Schrödinger discovered the fundamental

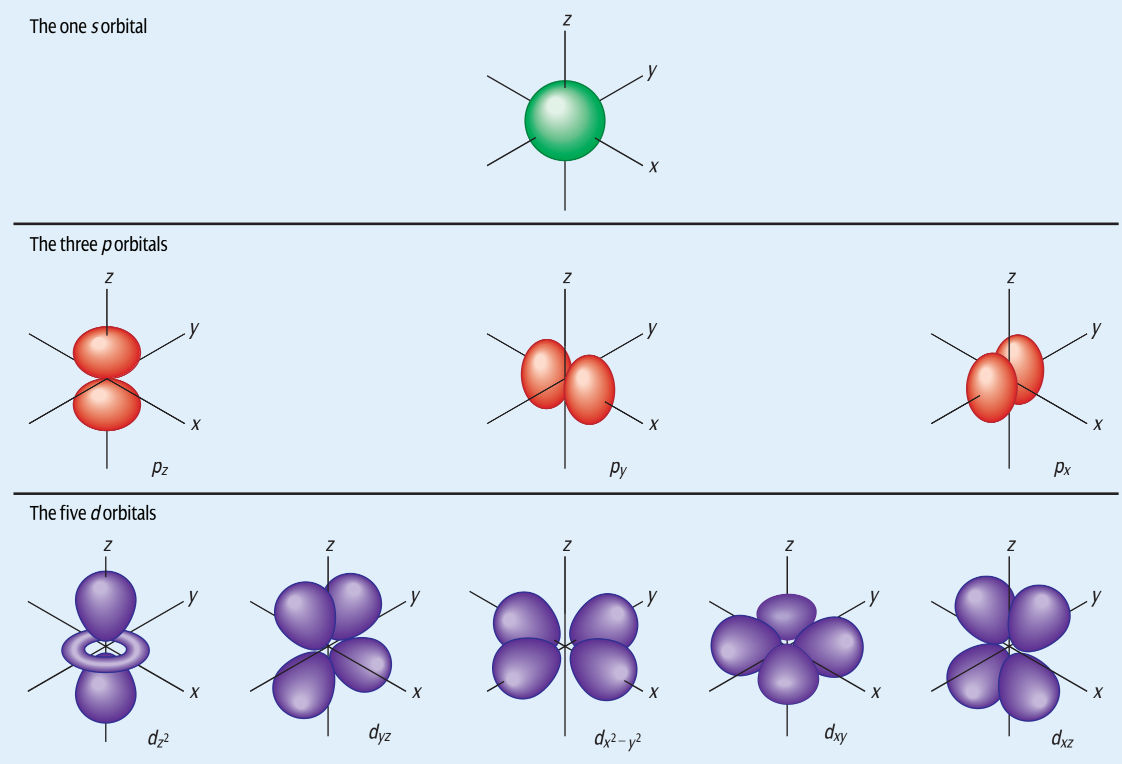


Figure 2.22 The shapes of *s*, *p* and *d* orbitals

equation for analysing these lines in 1926. This is all the more remarkable when you remember that he did not have computers to assist him. For this work he shared the 1933 Nobel Prize for Physics.

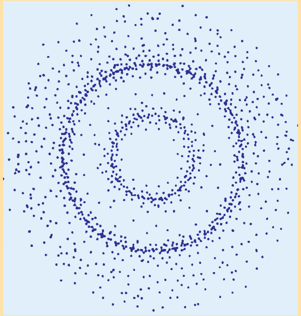


Figure 2.23 The first two *s* orbitals of an atom. The nucleus is located at the centre.

Quantum mechanics is the study of matter at the atomic level. It provides a theoretical framework for many fields of chemistry and physics.

Electron configurations using the Schrödinger model

When determining the location of electrons for an atom in its ground state, we use the same principle as for the Bohr model. The atom is most stable when all electrons are in the lowest possible energy levels. They are therefore placed in successive subshells in order of their increasing energy. This is termed the **Aufbau Principle**. (*Aufbau* means 'building up'.)

The energies of the subshells

For a given shell, the energies of electrons in the subshells increases from *s* to *p* to *d* to *f*. For example, in the 3rd shell, the order of increasing energy is $3s < 3p < 3d$.

However, there are 'crossovers' in the energies of the subshells. For example, electrons in the $3d$ subshell have higher energy than those in the $4s$ subshell.

One useful way of remembering the order of the energies of the subshells is to follow the diagram in Figure 2.24. Joining the arrows head to tail (beginning with arrow a, then arrow b, and so on) gives the order of energies and hence the order in which the subshells are filled. Another useful diagram that shows the order of energies of the subshells and the number of electrons they can contain is shown in Figure 2.25.

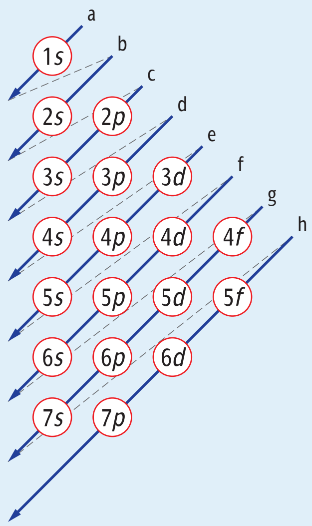


Figure 2.24 The order of increasing energy of the subshells—a schematic representation

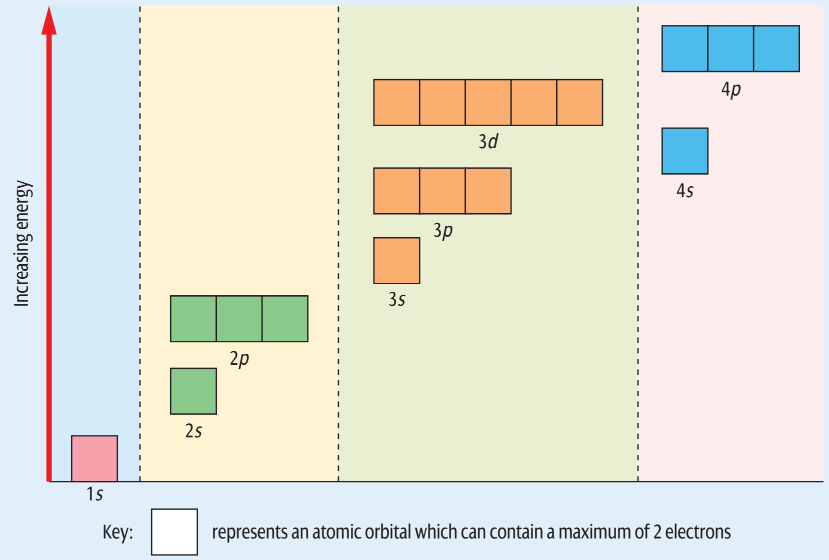


Figure 2.25 The subshells and atomic orbitals of atoms—a schematic representation

Filling convention

When filling a particular subshell, one electron is placed in each atomic orbital before the second electron is placed in any of them. In diagrams like Figure 2.25, a box represents an atomic orbital. An upward arrow in the box represents the first electron added to that atomic orbital. When the second electron is added, its arrow points the opposite way to show it is spinning in the opposite direction to the first electron. (This convention can be seen in the example shown in Figure 2.27, page 37.)

A sample electron configuration

Figure 2.26 shows an example of an electron configuration based on the Schrödinger model and explains how it can be interpreted. Notice that the number of electrons in each subshell is stated as a superscript and commas are not used.

This shows that 2 electrons are placed in the 1*s* subshell.

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^5$

This shows that in this atom there is a total of 7 electrons in the 3rd shell.

Figure 2.26 A typical electron configuration based on the Schrödinger model

Giving an electron its 'address'

Chemists actually use a set of four numbers to define the location of an electron in the atom. These are termed **quantum numbers**. They are based on:

1 its shell. (This is the **principal quantum number**, n, where $n = 1, 2, 3$ …)
2 its subshell
3 its atomic orbital
4 its direction of spin.

No two electrons in an atom can have the same set of quantum numbers, because even if they occupy the same atomic orbital they must spin in opposite directions.

WRITING ELECTRON CONFIGURATIONS

SKILLS

The following examples show two different approaches to determining an electron configuration. You should be able to use both methods, though you may find one easier than the other.

Example 1

Write the electron configuration of an uncharged sodium atom, which has 11 electrons.

Solution

In this example we will use Figure 2.24 to remind us of the order in which subshells are filled, and our knowledge of the limit to the number of electrons that can be placed in each subshell (Table 2.4, page 33).

- The first 2 electrons will fit in the lowest energy level, the 1*s* subshell. This leaves 9 more electrons to place.
- The next 2 electrons will fit in the second lowest energy level, the 2*s* subshell. This leaves 7 more electrons to place.
- The next 6 electrons will fit in the third lowest energy level, the 2*p* subshell. This leaves 1 more electron to place.
- The last electron will fit in the fourth lowest energy level, the 3*s* subshell.

Answer

The electron configuration of an uncharged atom of sodium is $1s^2\ 2s^2\ 2p^6\ 3s^1$.

Example 2

Write the electron configuration of an uncharged iron atom, which has an atomic number of 26.

Solution

In this example, we will use the chart in Figure 2.25 to assist us. The iron atom is uncharged, so it will contain 26 electrons. These are placed as shown in Figure 2.27. Notice that a total of 26 arrows have been drawn.

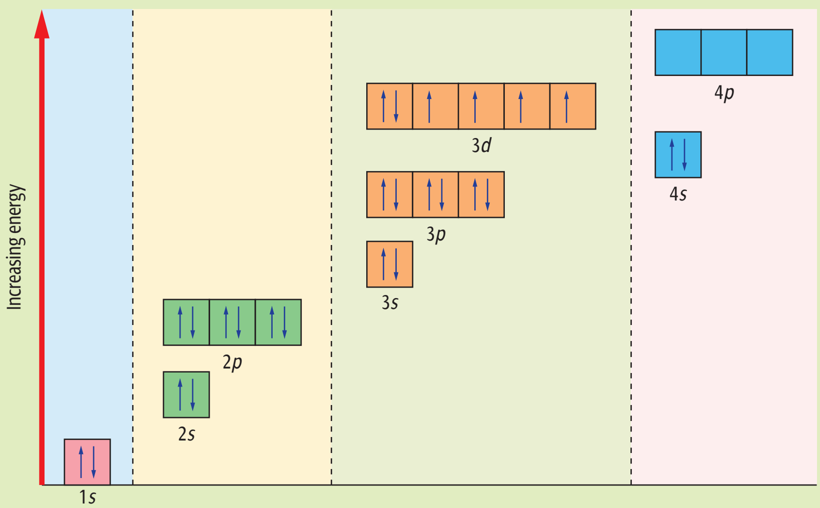


Figure 2.27 Placing the electrons of an uncharged atom of iron into their subshells

Answer

The electron configuration of an uncharged atom of iron is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$.

Note: Even though the 4*s* subshell was filled before the 3*d* subshell, the 3*d* subshell is listed first, because the convention is that the subshells are grouped into their shells in the electron configuration.

Modern atomic theory

Click on the link to **Modern atomic theory** to find the latest theories about the atom. Learn about the particles which theoretical physicists believe are even more fundamental particles of matter—that have the strange name of quarks.

Zooming in

Click on the link to **Zooming in**. See this fascinating movie that shows a view that starts from the Milky Way and zooms in by successive powers of 10 until you reach inside the nucleus of a carbon atom.

QUESTIONS 2.3

1 **a** Identify the two major new features of the quantum mechanical model of the atom that are not features of the Bohr model of the atom.

b What experimental evidence led to the modification of Bohr's model of the atom?

2 A certain element has an atomic number of 17.

a What can you deduce about the atoms of this element from this information?

b Explain why elements are identified by their atomic number.

3 Write the electron configuration of the uncharged atoms of the following elements according to the quantum mechanical model of the atom, given their atomic number.

a hydrogen ($Z = 1$)

b nitrogen ($Z = 7$)

c neon ($Z = 10$)

d chlorine ($Z = 17$)

e potassium ($Z = 19$)

f nickel ($Z = 28$)

g krypton ($Z = 36$)

4 The uncharged atoms of a certain element have the following electron configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

a Draw a representation like that shown in Figure 2.27 of the placement of electrons in this atom.

b Use the Periodic Table inside the front cover of this book to identify the element and show your reasoning.

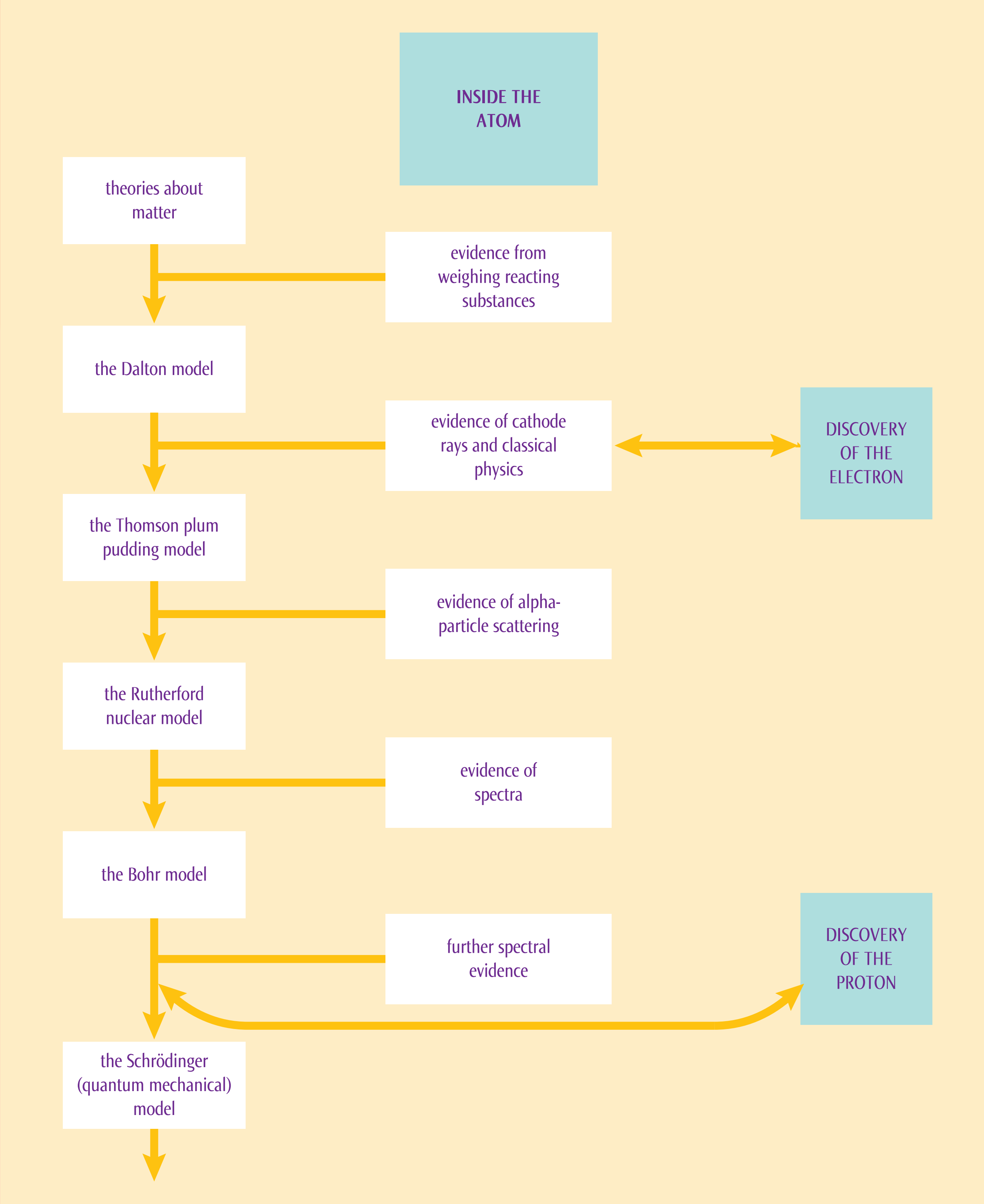
c Write one possible electron configuration of an excited atom of this element.

d Suggest why it is specified that the atoms of the element are uncharged.

5 Bohr could not explain why the outermost occupied shell of an atom could not hold more than 8 electrons (page 26). Use Figure 2.25 to suggest why this is the case.

6 Identify and describe some limitations of drawing or constructing a model of an atom based on the quantum mechanical model.

Visual summary



Key terms

alpha-particles (α-particles)	discrete	photons
anode	electron configuration	principal quantum number, n
atomic number, Z	electron shell	proton
atomic orbitals	electrons	quantum
Aufbau Principle	emission spectrum	quantum numbers
Bohr model	excited	Rutherford nuclear model (planetary model)
canal rays	gas discharge tube (discharge tube)	scattered
cathode	ground state	Schrödinger model (quantum mechanical model)
cathode ray tube	nucleus	spectroscope
cathode rays	orbits	subshells
charge cloud	Pauli Exclusion Principle	Thomson plum pudding model

Review questions

1 Copy and complete Table 2.6. You do not need to elaborate the experimental evidence; summarise it in one sentence only.

Table 2.6 Models of the atom

Feature of the model	Thomson plum pudding model	Rutherford nuclear model	Bohr model	Schrödinger model
When the model was proposed	1898	1911	1913	1926
Experimental evidence that led to this modification of the previous model of the atom				
Key features of the model in which it differed from the previous model				
Key features of the models that they held in common				

2 Copy and complete Table 2.7 by stating the electron configurations of uncharged atoms of the elements according to the Bohr and the Schrödinger models of the atom.

Table 2.7 Electron configurations of uncharged atoms

	Element	Atomic number	Electron configuration according to the Bohr model	Electron configuration according to the Schrödinger model
a	Helium	2		
b	Oxygen	8		
c	Magnesium	12		
d	Sulfur	16		
e	Calcium	20		
f	Zinc	30		
g	Bromine	35		

3 A study of the history of the development of models of the structure of the atom shows that scientific theories and models do not develop in a vacuum. Rather, they develop in a step-by-step approach through the sharing of discoveries and the exchange of ideas between scientists. For each of the following scientists, summarise in one sentence the contribution they made to our knowledge of the atom.

a Goldstein	**c** Faraday	**e** Thomson	**g** Bohr	**i** Geiger
b Dalton	**d** Rutherford	**f** Pauli	**h** Schrödinger	**j** Marsden

4 A number of famous experiments and the brilliant deductions that were made from them led to the discovery of the electron and the proton, and to the development of the successive models of the atom. Imagine that you have been asked to make a multimedia presentation on one of these experiments at a conference of modern chemists. Devise a presentation in which you give the background of the experiment (what led to it) and of the scientist(s) who performed the experiment, describe the results that were obtained and the conclusions that were drawn and then discuss why this experiment was important. Test your presentation by presenting it to your class.

5 **a** It has been claimed that were it not for the invention of air pumps and the discovery of how to harness and generate electrical currents, we would still accept the Dalton model of the atom as being correct. Would you agree with this statement? Discuss.

b Were any of Dalton's assertions retained in the later models of the atom? Discuss.

6 Were it not for the discovery of the nucleus, physicists would not have gone on to discover the incredible power of the atom. We therefore would not have nuclear power stations—or the threat posed by nuclear weapons. But of course Rutherford could not have predicted that this would happen. In your opinion, should scientists control the extent to which they seek new knowledge in case their discoveries are later used for destructive purposes?

Figure 2.28 The power of the atom