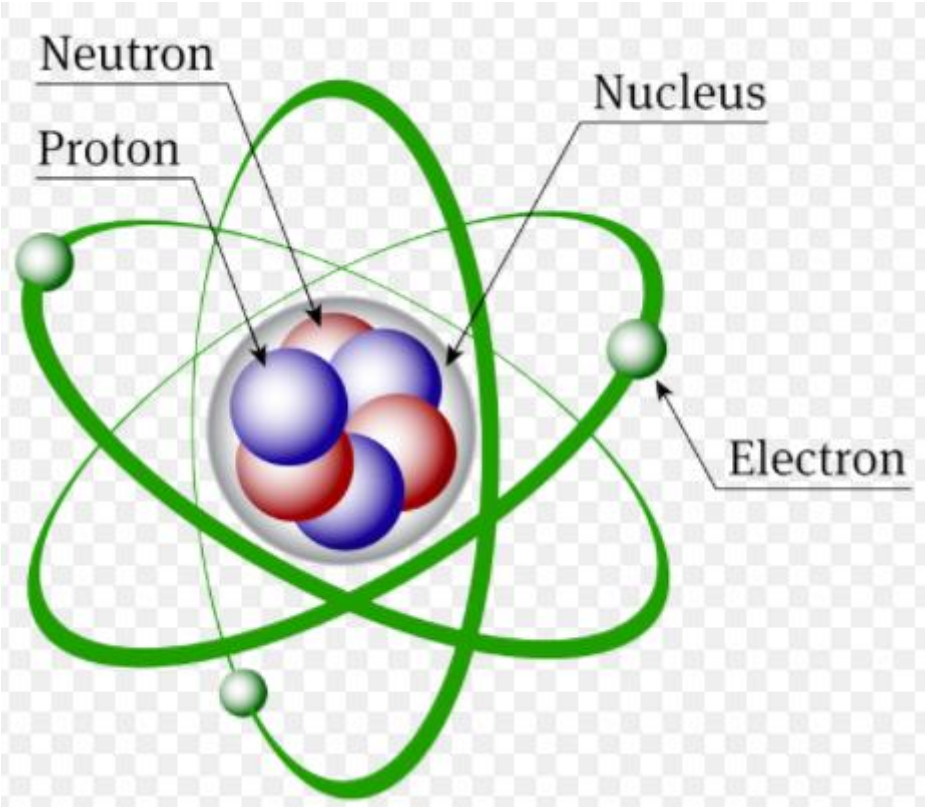
UNIT 1

ATOMIC STRUCTURE AND THE PERIODIC TABLE

PART 1 – INTRODUCTION TO ATOMIC STRUCTURE



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Key words: Dalton, Thomson, Rutherford, proton, neutron, electron, nucleon, isotopes, relative atomic mass, atom, ion, energy level, energy sub-level, orbital, shell, line spectrum, Pauli Exclusion Principle, Aufbau Principle, Hund's Rule of Maximum Multiplicity, electronic configuration

1) Early models of the atom

Since ancient times, scientists have been trying to explain what the universe is made of. Several theories have been developed as scientists try to explain observations that they make. If a theory is accepted, it becomes "science" until subsequent observations are made which disprove the theory, and a new theory, consistent with the new observations, is developed to replace it.

A typical cycle for the development of theories and models in science could be summarised as follows:

- make an observation which contradicts an existing theory/model
- develop a new theory/model which is consistent with all existing observations
- communicate the new theory or model and encourage others to test it
- the new theory/model will either be rejected or be accepted
- continue to make observations until the theory/model is disproved

The development of the model of the atom is a good example of how scientific understanding develops in this way:

When	Who	Why/How	Features of theory/model
5th century BC	Democritus and Leucippus	No evidence	The "atomos" is an indivisible building block of matter
1805	Dalton	Observed the Law of Multiple Proportions	**Dalton's atomic theory**: - atoms are indivisible (from Democritus and Leucippus) - all atoms of the same element are identical - atoms of different elements have different sizes and masses - atoms of different elements combine chemically in fixed proportions to form compounds
1897	Thomson	Discovered that metals, when heated in sealed tubes, emit negatively charged particles which are much smaller than the smallest atom	**Thomson's atomic model:** - atoms are divisible - atoms contain electrons distributed inside a uniform sea of positive charge (also known as the "plum pudding" model)
1909	Rutherford	Fired alpha particles at gold foil and discovered that most passed straight through but that a small number were hugely deflected	**Rutherford's atomic model:** - small positive nucleus concentrated at centre of atom - cloud of negatively electrons around nucleus

Dalton, Thomson and Rutherford all used observations from experiments to make major contributions towards our understanding of atomic structure. Later observations were made (most notably by Bohr and Schrodinger) and the accepted model of the atom was amended again as a result.

Research task: How did Niels Bohr and Edwin Schrodinger contribute to our understanding of atomic structure?

2) Nuclear Structure, Isotopes and Atomic Mass

a) Protons, neutrons and electrons

Atoms are made up of three fundamental particles: **protons**, **neutrons** and **electrons**.

Protons and neutrons are found in the nucleus and are collectively called **nucleons**. Electrons orbit the nucleus in a similar (but not identical) way to that in which planets orbit a sun. In between the electrons and nucleus there is nothing (empty space). The nucleus is very small; if an atom were the size of a football pitch, the nucleus would be the size of a drawing pin.

The basic properties of these three particles can be summarized in the following table:

Particle	Charge	Mass
Proton	+1 unit	Approx 1 unit
Neutron	No charge	Approx 1 unit
Electron	-1 unit	Approx 1/1840 units (very small)

1 unit of charge is 1.602×10^{-19} coulombs. A proton is given a charge of +1 and an electron a charge of -1. All charges are measured in these units.

1 unit of mass is 1.661×10^{-27} kg. This is also not a convenient number, so we use “atomic mass units”. Since the mass of protons and neutrons varies slightly depending on the nucleus, then in order to define an “atomic mass unit” we need to choose one nucleus as a standard. For this purpose $^{12}_{6}C$, or “carbon-12”, was chosen. **An atomic mass unit is thus defined as 1/12th of the mass of one atom of carbon-12**. All atomic masses are measured relative to this quantity.

b) Atomic numbers, mass numbers and isotopes

An atom is named after the number of protons in its nucleus. If the nucleus of an atom has 1 proton, it is hydrogen; if it has two protons, it is helium; if it has 3, it is lithium etc. The number of protons in the nucleus of an atom is called the atomic number. It has the symbol Z.

The **atomic number** is the number of protons in the nucleus of an atom

Not all atoms of the same element have equal numbers of neutrons. The sum of the number of protons and neutrons in the nucleus of an atom is called its **mass number**. It is represented by the symbol A.

The **mass number** is the sum of the number of protons and neutrons in the nucleus of an atom

The nucleus of an atom can thus be completely described by its mass number and its atomic number. It is generally represented as follows:

$$^{A}_{Z}E$$

Eg. $^{9}_{4}Be$, $^{12}_{6}C$, $^{24}_{12}Mg$

Atoms with the same atomic number but with different mass numbers (ie different numbers of neutrons) are called **isotopes**.

Isotopes are atoms with the same atomic number but with different mass numbers

Eg magnesium (atomic number 12) has 3 naturally occurring isotopes:
$^{24}_{12}Mg$: 12 protons, 12 neutrons
$^{25}_{12}Mg$: 12 protons, 13 neutrons
$^{26}_{12}Mg$: 12 protons, 14 neutrons

Test Your Progress: Topic 1 Part 1 Exercise 1

1. Deduce the number of protons, electrons and neutrons in the following atoms:
   (a) $^{1}_{1}H$ (b) $^{17}_{8}O$ (c) $^{132}_{54}Xe$ (d) $^{235}_{92}U$ (e) $^{14}_{6}C$

2. Deduce the symbol of the following atoms:
   (a) 19 protons, 20 neutrons
   (b) 8 protons, 8 neutrons
   (c) 1 proton, 2 neutrons, 1 electron
   (d) 82 protons, 126 neutrons
   (e) 53 protons, 74 neutrons, 54 electrons

c) Relative atomic mass

Atoms of the same element do not all have the same mass, as they can contain different numbers of neutrons (different isotopes).

The **atomic mass** of an atom is therefore an **average** value which depends on the mass numbers of the different isotopes and their relative abundances. It can be calculated by the formula:

$$\text{Atomic mass} = \Sigma \frac{\text{(perentage abundance of each isotope x mass of each isotope)}}{100}$$

eg neon is an element consisting of ^{20}Ne (90%) and ^{22}Ne (10%)

so the atomic mass of Ne = (90 x 20 + 10 x 22)/100 = 20.2

All atomic masses in the Periodic Table have been calculated in this way.

Atomic mass is measured in atomic mass units (amu) - one amu is 12th of the mass of one atom of carbon-12. It is referred to as **relative atomic mass**.

The **relative atomic mass** of an atom is the ratio of the average mass of one atom of that element to $1/12^{th}$ of the mass of one atom of carbon-12.

Test Your Progress: Topic 1 Part 1 Exercise 2

1. Deduce the relative atomic masses of the following elements.
   (a) Silicon (^{28}Si 92.21%, ^{29}Si 4.70%, ^{30}Si 3.09%)
   (b) Silver (^{107}Ag 51.88%, ^{109}Ag 48.12%)
   (c) Boron (^{10}B 19.7%, ^{11}B 80.7%)
   (d) Gallium (^{69}Ga 60.2%, ^{71}Ga 39.8%)
   (e) Chlorine (^{35}Cl 75.8%, ^{71}Ga 24.2%)

2. Bromine has two isotopes, with mass numbers 79 and 81. Its relative atomic mass is often given as 80. What does that tell you about the relative abundance of the two isotopes?

d) Atoms and ions

In a neutral atom, the number of protons and electrons are the same. However, many elements do not exist as neutral atoms, but exist as **ions**. Ions are species in which the proton and electron numbers are not the same, and hence have an overall positive or negative charge. The number of electrons in a species can be deduced from its charge:

Eg
$^{24}_{12}Mg^{2+}$: 12p, 12n, 10e
$^{24}_{12}Mg^{+}$: 12p, 12n, 11e
$^{24}_{12}Mg$ 12p, 12n, 12e
$^{24}_{12}Mg^{-}$: 12p, 12n, 13e

Ions with a positive charge are called CATIONS
Ions with a negative charge are called ANIONS.

Test Your Progress: Topic 1 Part 1 Exercise 3

1. Deduce the number of protons, neutrons and electrons in the following species:
   (a) $^{4}_{2}He^{2+}$ (b) $^{27}_{13}Al^{3+}$ (c) $^{1}_{1}H^{-}$

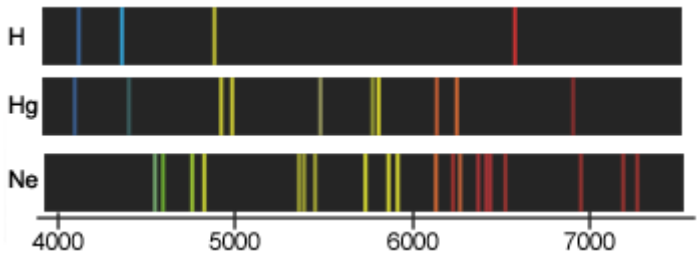
2. Deduce the symbols of the following ions:
   (a) 8 protons, 8 neutrons, 10 electrons
   (b) 82 protons, 126 neutrons, 80 electrons
   (c) 53 protons, 74 neutrons, 54 electrons

3) Energy levels, orbitals and electronic configuration

a) Energy Levels

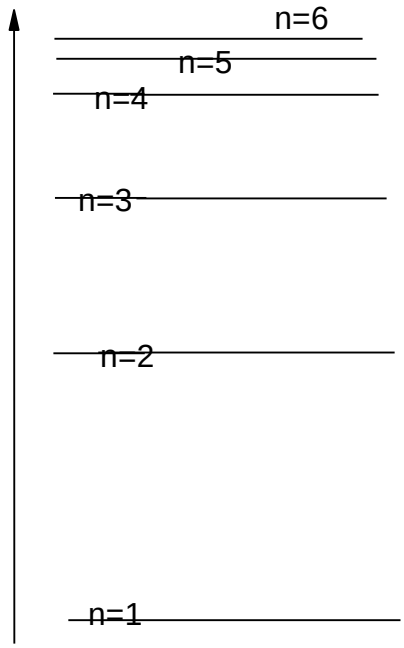
Electrons do not orbit the nucleus randomly; they occupy certain fixed energy levels. Each atom has its own unique set of energy levels, which are difficult to calculate but which depend on the number of protons and electrons in the atom.

There is clear experimental evidence for this in the form of **line spectra**. When atoms are heated or subjected to radiation, electrons are excited from lower energy levels into higher energy levels. When they return to the lower energy level, they emit radiation with energy equal to the energy difference between the two levels. Because specific lines are visible and not a continuous spectrum, it shows that only certain energy levels can exist in the atom. Each atom has a unique set of energy levels and so gives a distinct line spectrum, which can be used to identify the atom. The analysis of emission or absorption of radiation in order to identify substances is known as **spectroscopy**.



Line spectra of some different atoms

Energy levels in an atom can be numbered 1,2,3,…. To infinity. Level 1 (or the K level) is the lowest energy level (closest to the nucleus), followed by Level 2 (or the L level) and Level 3 (or the M level). Energy level infinity corresponds to the energy of an electron which is not attracted to the nucleus at all. The energy levels thus converge as they approach infinity:



b) Orbitals and sub-levels

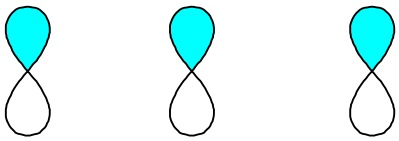
Electrons do not in fact orbit the nucleus in an orderly way. In fact they occupy areas of space known as **orbitals**. The exact position of an electron within an orbital is impossible to determine; an orbital is simply an area of space in which there is a high probability of finding an electron.

Orbitals can have a number of different shapes, the most common of which are as follows:

s-orbitals: these are spherical.

Every energy level contains one s-orbital.
An s-orbital in the first energy level is a 1s orbital.
An s-orbital in the second energy level is a 2s orbital, etc

p-orbitals: these are shaped like a 3D figure of eight. They exist in groups of three:



Every energy level except the first level contains three p-orbitals. Each p-orbital in the same energy level has the same energy but different orientations: x, y and z.
The p-orbitals in the second energy level are known as 2p orbitals ($2p_x$, $2p_y$, $2p_z$)
The p-orbitals in the third energy level are known as 3p orbitals ($3p_x$, $3p_y$, $3p_z$), etc

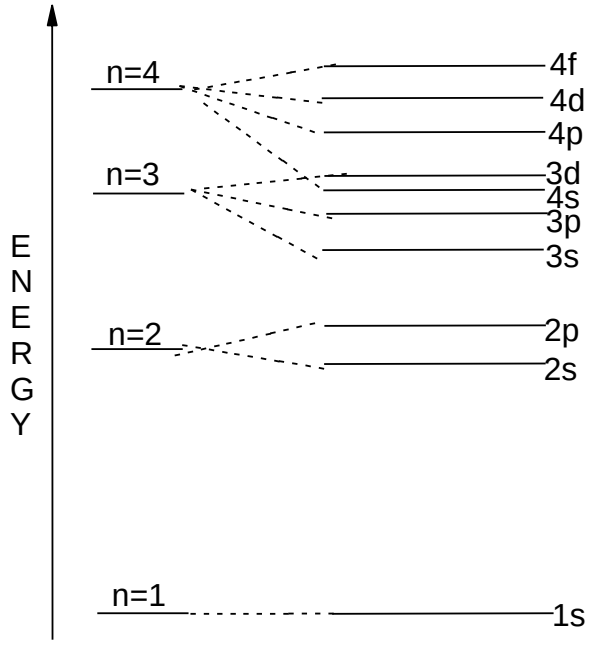
In addition, the third and subsequent energy levels each contain five d-orbitals, the fourth and subsequent energy levels contain seven f-orbitals and so on. Each type of orbital has its own characteristic shape.

S, p and d orbitals do not all have the same energy. In any given energy level, s-orbitals have the lowest energy and the energy of the other orbitals increases in the order p < d < f etc. Thus each energy level must be divided into a number of different sub-levels, each of which has a slightly different energy.

The number and type of orbitals in each energy level can thus be summarised as follows:

	Number and type of orbital		
Energy level	1st sub-level	2nd sub-level	3rd sub-level
1 (K)	1 x 1s		
2 (L)	1 x 2s	3 x 2p	
3 (M)	1 x 3s	3 x 3p	5 x 3d

Since the different sub-levels have different energies, and the energies of the different levels get closer together with increasing energy level number, the high energy sub-levels of some energy levels soon overlap with the low energy sub-levels of higher energy levels, resulting in a more complex energy level diagram:



Starting with the lowest energy, the orbitals can thus be arranged as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f

Many of these sub-levels have similar energy, and can be grouped together.
A collection of sub-levels of similar energy is called a **shell**.

1s | 2s 2p | 3s 3p | 4s 3d 4p | 5s 4d 5p | 6s 4f 5d 6p

The arrangement of shells and orbitals/sub-levels can be summarised as follows:

Shell number	Orbitals/sub-levels in shell
1	1 x1s
2	1 x 2s, 3 x 2p
3	1 x 3s, 3 x 3p
4	1 x 4s, 5 x 3d, 3 x 4p

c) Rules for electrons occupying orbitals, sub-levels and shells

There are three rules which determine how electrons occupy orbitals:

(i) Pauli Exclusion Principle

Electrons repel each other. In a small space such as an orbital, it is impossible to put more than two electrons.

Since electrons are charged particles, and moving charges create a magnetic field, it is possible to create a small magnetic attraction between two electrons if they are spinning in opposite directions in the same orbital. This is the reason two electrons, and not one, are permitted in the same orbital. They must be spinning in opposite directions.

The **Pauli Exclusion Principle** states that **a maximum of two electrons can occupy the same orbital, and they must do so with opposite spins**.

It is thus possible to calculate the maximum possible number of electrons in each sub-level, and thus in each energy level:

Shell	Number of electrons in each sub-level	Max. no of electrons
1	2 x 1s	2
2	2 x 2s, 6 x 2p	8
3	2 x 3s, 6 x 3p	8
4	2 x 4s, 10 x 3d, 6 x 4p	18
5	2 x 5s, 10 x 4d, 6 x 5p	18
6	2 x 6s, 14 x 4f, 10 x 5d, 6 x 6p	32

Note that although the third energy level (Level M – 3s, 3p and 3d) can accommodate 18 electrons, the 3d sub-level is actually in the fourth shell, so the third shell only contains 8 electrons.

(ii) Aufbau Principle

The **Aufbau principle** states that **electrons always fill the lowest energy orbitals first**. So 1s is filled first, followed by 2s, 2p, 3s, 3p, 4s, 3d and then 4p.

(iii) Hund's rule of Maximum Multiplicity

Hund's Rule of Maximum Multiplicity states that electrons never pair up in the same orbital until all orbitals of the same energy are singly occupied, and that all unpaired electrons must have parallel spin.

(d) Electronic Configuration

The arrangement of electrons in an atom is known as its **electronic configuration**. It can be represented in two ways:

The **arrow and box method** represents each orbital as a box and each electron as an arrow. The direction of spin is shown by the orientation of the arrow.

The electronic configuration of the first 18 elements using the arrow in box method is as follows:

	1s	2s	2p			3s	3p		
H	↑								
He	↑↓								
Li	↑↓	↑							
Be	↑↓	↑↓							
B	↑↓	↑↓	↑						
C	↑↓	↑↓	↑	↑					
N	↑↓	↑↓	↑	↑	↑				
O	↑↓	↑↓	↑↓	↑	↑				
F	↑↓	↑↓	↑↓	↑↓	↑				
Ne	↑↓	↑↓	↑↓	↑↓	↑↓				
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↑			
Mg	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			
Al	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		
Si	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	
P	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
S	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑
Cl	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

The **orbital method** indicates the number of electrons in each orbital with a superscript written immediately after the orbital.

The electronic configurations of the first eighteen elements can be shown with the orbital method as follows:

H:	$1s^1$
He:	$1s^2$
Li:	$1s^2 2s^1$
Be:	$1s^2 2s^2$
B:	$1s^2 2s^2 2p^1$
C:	$1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
N:	$1s^2 2s^2 2p^3$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
O:	$1s^2 2s^2 2p^4$ or $1s^2 2s^2 2p^6 3s^2 3p^2 3p_x^2 3p_y^1 3p_z^1$
F:	$1s^2 2s^2 2p^5$
Ne:	$1s^2 2s^2 2p^6$
Na:	$1s^2 2s^2 2p^6 3s^1$
Mg:	$1s^2 2s^2 2p^6 3s^2$
Al:	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si:	$1s^2 2s^2 2p^6 3s^2 3p^2$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
P:	$1s^2 2s^2 2p^6 3s^2 3p^3$ or $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
S:	$1s^2 2s^2 2p^6 3s^2 3p^4$ or $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Cl:	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar:	$1s^2 2s^2 2p^6 3s^2 3p^6$

A shorthand form is often used for both the above methods. Full shells are not written in full but represented by the symbol of the element to which they correspond, written in square brackets.

Eg. $1s^2 2s^2 2p^6$ is represented as [Ne] and $1s^2 2s^2 2p^6 3s^2 3p^6$ is represented as [Ar].

The shorthand electronic configuration of the elements with atomic numbers 18 to 36 can be written as follows:

		4s	3d					4p		
K	[Ar]	↑								
Ca	[Ar]	↑↓								
Sc	[Ar]	↑↓	↑							
Ti	[Ar]	↑↓	↑	↑						
V	[Ar]	↑↓	↑	↑	↑					
Cr	[Ar]	↑	↑	↑	↑	↑	↑			
Mn	[Ar]	↑↓	↑	↑	↑	↑	↑			
Fe	[Ar]	↑↓	↑↓	↑	↑	↑	↑			
Co	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑			
Ni	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	↑			
Cu	[Ar]	↑	↑↓	↑↓	↑↓	↑↓	↑↓			
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			
Ga	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		
Ge	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	
As	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
Se	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑
Br	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Kr	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Note the unusual structures of chromium and copper. This is because the difference in energy between the 3d and 4s electrons is very small.

In chromium the energy required to promote and electron from 4s to 3d is recovered in the reduced repulsion which results from the fact that they are no longer paired. Thus the $4s^1 3d^5$ structure in Cr is preferred.

In copper, the 3d orbitals are actually lower in energy than the 4s orbital, so the $4s^1 3d^{10}$ structure in Cu is preferred.

(e) Electronic Configuration of Ions

The electronic configuration of ions can be deduced by simply adding or removing the appropriate number of electrons. The order in which electrons are to be removed can be deduced from the following rules:

- remove outer shell electrons first
- remove p-electrons first, then s-electrons and then d-electrons
- remove paired electrons before unpaired electrons in the same sub-level

(f) Effect of electronic configuration on chemical properties

The chemical properties of an atom depend on the strength of the attraction between the outer electrons and the nucleus. These in turn depend on the number of protons and on the electronic configuration, and so it follows that these two factors are instrumental in determining the chemical properties of an atom.

This is in contrast with the neutron number however, which has no effect on the chemical properties of an atom. Neutrons have no charge and hence exert no attractive force on the nucleus.

Isotopes, therefore, tend to have very similar chemical properties since they have the same atomic number and the same electronic configuration. They differ only in number of neutrons, which do not directly influence the chemical properties of an element.

Test Your Progress: Topic 1 Part 1 Exercise 4

1. Explain how line spectra provide evidence for fixed energy levels in atoms.

2. Deduce the full electronic configurations of:
   (a) C (b) Cu (c) Mg^{+} (d) N^{3-} (e) Ar

3. Deduce the abbreviated electronic configurations of:
   (a) Sc^{3+} (b) Mn^{2+} (c) Fe (d) Cl^{-} (e) Br