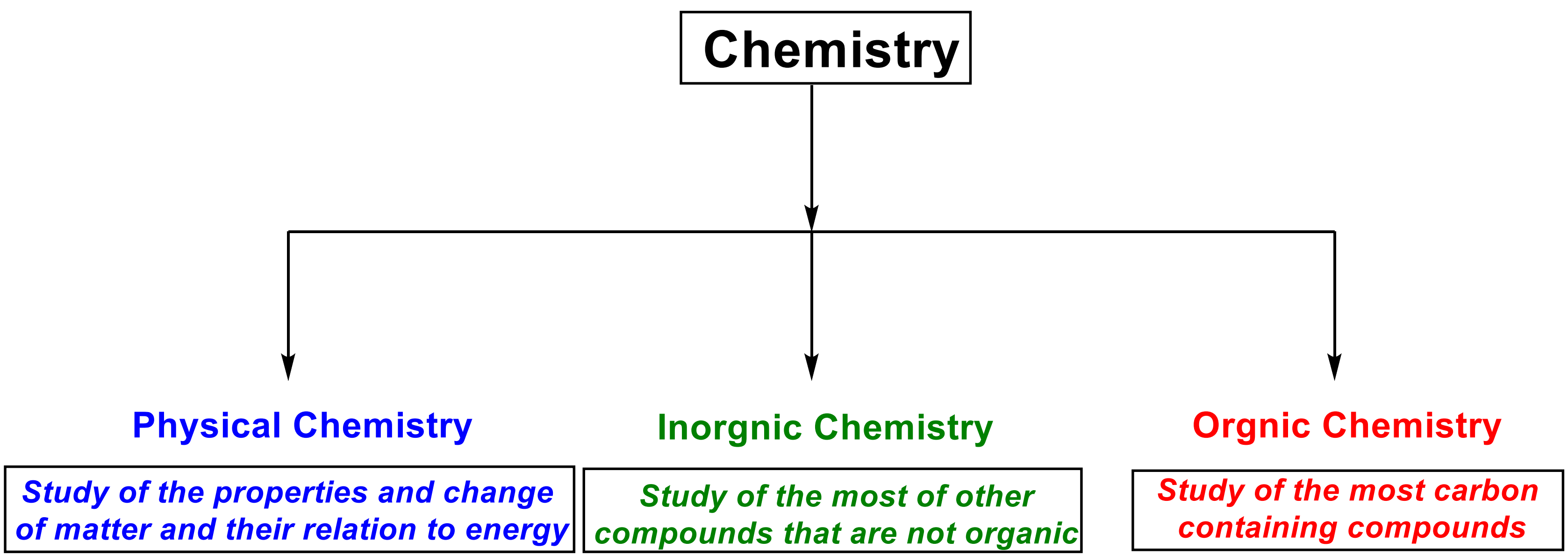
Introduction

■ What is Chemistry?

→ Chemistry is the study of ***matter and the changes it undergoes***.

Chemistry is often called the central science, because a basic knowledge of chemistry is essential for students of biology, physics, geology, ecology, and many other subjects.

■ Classification of chemistry



Introduction

■ **Impact on society and on you as an individual:**

→ **Health and Medicine:**

Chemists in the pharmaceutical industry are researching potent drugs with few or no side effects to treat cancer, AIDS, and many other diseases as well as drugs to increase the number of successful organ transplants.

→ **Energy and the Environment:**

Energy is a by-product of many chemical processes, and as the demand for energy continues to increase. Chemists are actively trying to find new energy sources.

Photovoltaic cells → Conversion of sunlight directly to electricity

Hydrogen from water → *Fuel cell* → Generate electricity

Nuclear fission → Potential source of energy

Introduction

→ **Materials and Technology:**

Chemical research and development in the twentieth century have provided us with new materials.

A few examples are polymers (including rubber and nylon), ceramics (such as cookware), liquid crystals (like those in electronic displays), adhesives (used in your Post-It notes), and coatings (for example, latex paint).

For the future, scientists have begun to explore the prospect of "***molecular computer***" replacing silicon with molecules.

→ **Food and Agriculture:**

Chemists can devise ways to increase the production of fertilizers that are less harmful to the environment and substances that would selectively kill weeds.

Atomic Structure

■ What is Atom?

→ John Dalton (1805) considered that all matter was composed of **small particles called atoms**.

→ A hard solid individual particle **incapable of subdivision**.

→ At the end of the nineteenth century, experimental evidence shows that the atom is made of still **smaller particles**.

→ These subatomic particles are called the **fundamental particles**.

→ For us, the three most important are the **proton**, **neutron** and **electron**.

Atomic Structure

■ **The main landmarks in the evolution of atomic structure are:**

→ **1896**; J.J. Thomson's discovery of the electron and the proton.

→ **1909** Rutherford's Nuclear Atom

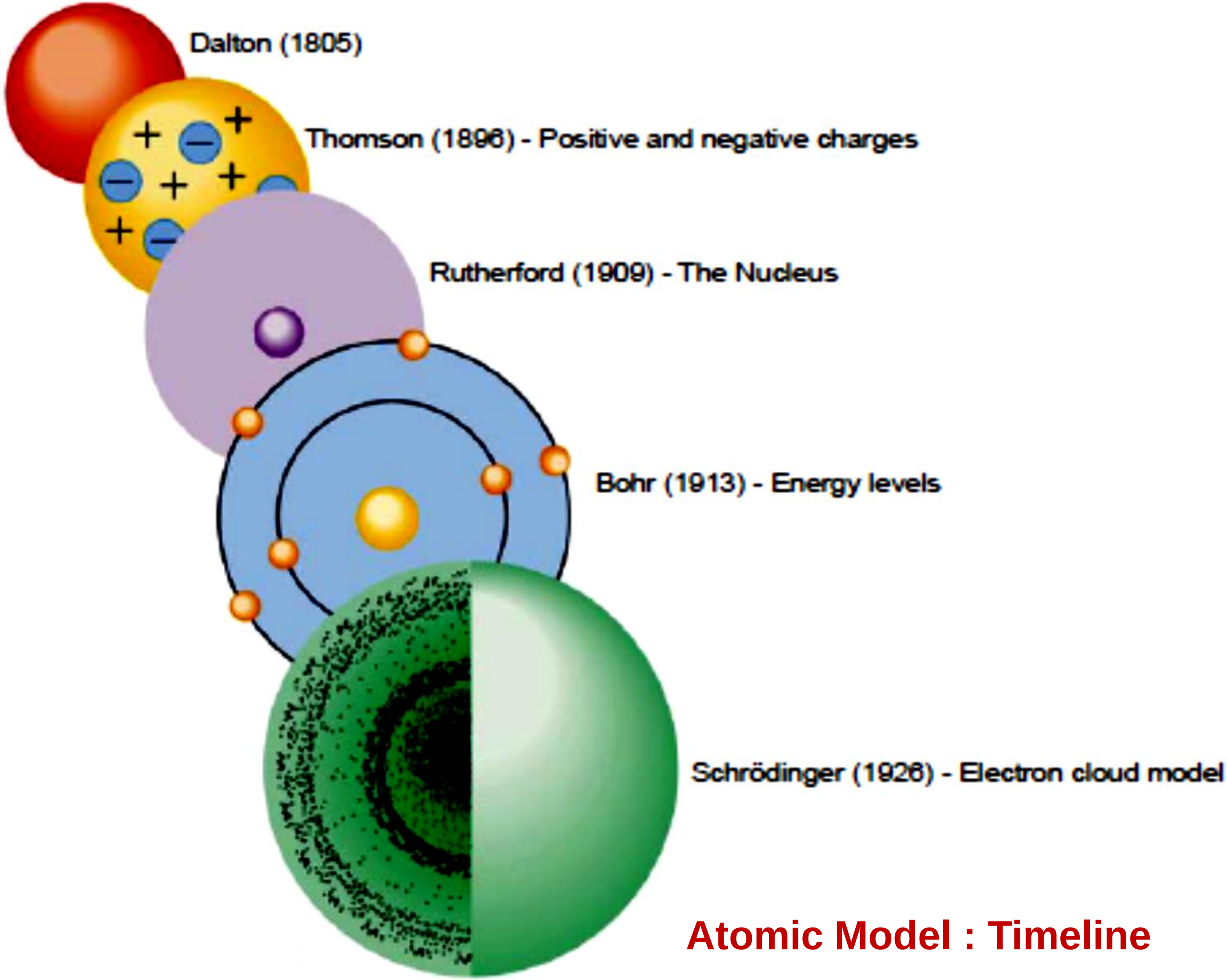
→ **1913** Mosley's determination of Atomic Number

→ **1913** Bohr Atom

→ **1921** Bohr-Bury Scheme of Electronic Arrangement

→ **1932** Chadwick's discovery of the neutron.

Atomic Structure



Atomic Model : Timeline

Atomic Structure

■ Postulates of Dalton's Atomic Theory:

→ **All matter** is composed of indivisible atoms. An atom is an extremely small particle of matter that retains its identity during chemical reactions.

→ **An element** is a type of matter composed of only one kind of atom, each atom of a given kind having the same properties. Mass is one such property. Thus, the atoms of a given element have a characteristic mass.

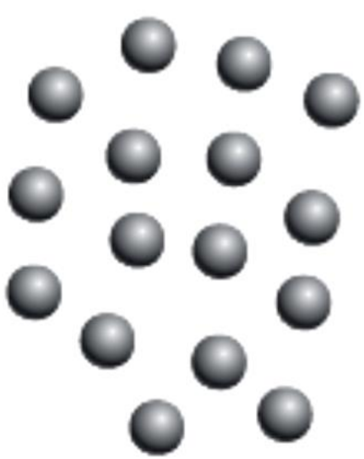
→ **A compound** is a type of matter composed of atoms of two or more elements chemically combined in fixed proportions. The relative numbers of any two kinds of atoms in a compound occur in simple ratios.

Atomic Structure

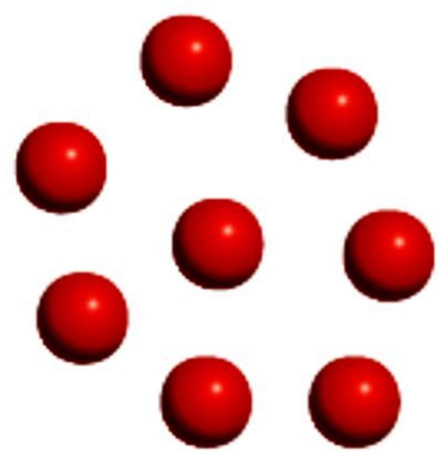
→ **A chemical reaction** consists of the rearrangement of the atoms present in the reacting substances to give new chemical combinations present in the substances formed by the reaction.

Atoms are not created, destroyed, or broken into smaller particles by any chemical reaction.

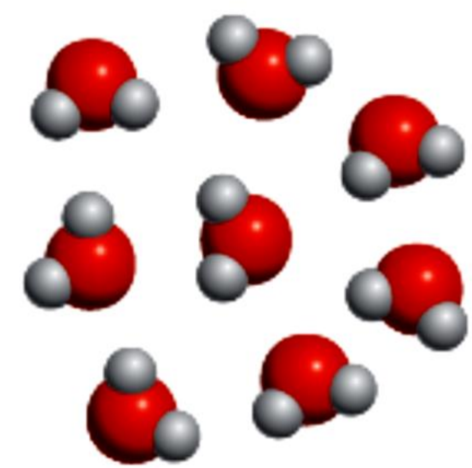
Today we know that atoms are not truly indivisible; they are themselves made up of particles.



Atoms of element X



Atoms of element Y



Compounds of elements X and Y

Atomic Structure

■ The Structure of the Atom:

→ Although Dalton had postulated that atoms were indivisible particles, experiments conducted around the beginning of the last century showed that atoms themselves consist of particles.

TABLE 1.1. CHARGE AND MASS OF ELECTRON, PROTON AND NEUTRON

Particle	Symbol	Mass		Charge	
		amu	grams	Units	Coloumbs
Electron	e^-	$\frac{1}{1835}$	9.1×10^{-28}	-1	-1.60×10^{-19}
Proton	p^+	1	1.672×10^{-24}	$+1$	$+1.60 \times 10^{-19}$
Neutron	n or n^0	1	1.674×10^{-24}	0	0

■ Other Subatomic Particles:

Besides fundamental particles, many other subatomic particles such as **mesons**, **positrons**, **neutrinos** and **antiprotons** have been discovered.

■ Alpha Particles:

→ Alpha particles are shot out from radioactive elements with very high speed. For example, they come from radium atoms at a speed of 1.5×10^7 m/sec.

Rutherford identified them to be di-positive helium ions, He^{2+} or ${}_{2}^{4}He$. Thus an alpha particle has 2+ charge and 4 amu mass.

$$He \longrightarrow He^{2+} + 2e^{-}$$

α-Particles are also formed in the discharge tube that contains helium.

α-particle is not a fundamental particle of the atom (or subatomic particle) but Rutherford thought of firing them like bullets at atoms and thus obtain information about the structure of the atom.

Atomic Structure

■ Rutherford's Atomic Model – The Nuclear Atom:

→ Having known that atom contains electrons and a positive ion, Rutherford proceeded to perform experiments to know as to how and where these were located in the atom.

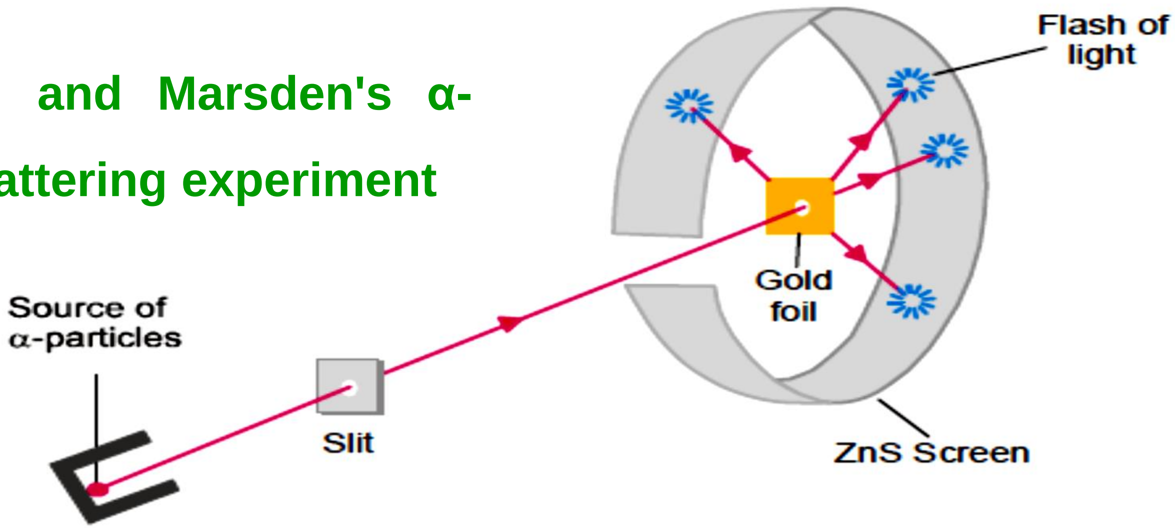
→ In 1909 Rutherford and Marsden performed their historic **Alpha Particle-Scattering Experiment**,

→ They directed a stream of very highly energetic α-particles from a radioactive source against a thin gold foil provided with a circular fluorescent zinc sulphide screen around it.

Whenever an α-particle struck the screen, a tiny flash of light was produced at that point.

Atomic Structure

Rutherford and Marsden's α-particle scattering experiment



→ Rutherford and Marsden noticed that most of the α-particles passed straight through the gold foil and thus produced a flash on the screen behind it. This indicated that gold atoms had a structure with plenty of empty space.

→ Tiny flashes were also seen on other portions of the screen, some time in front of the gold foil. This showed that gold atoms deflected or 'scattered' α-particles through large angles so much so that some of these bounced back to the source.

Atomic Structure

■ Rutherford's Atomic Model – The Nuclear Atom:

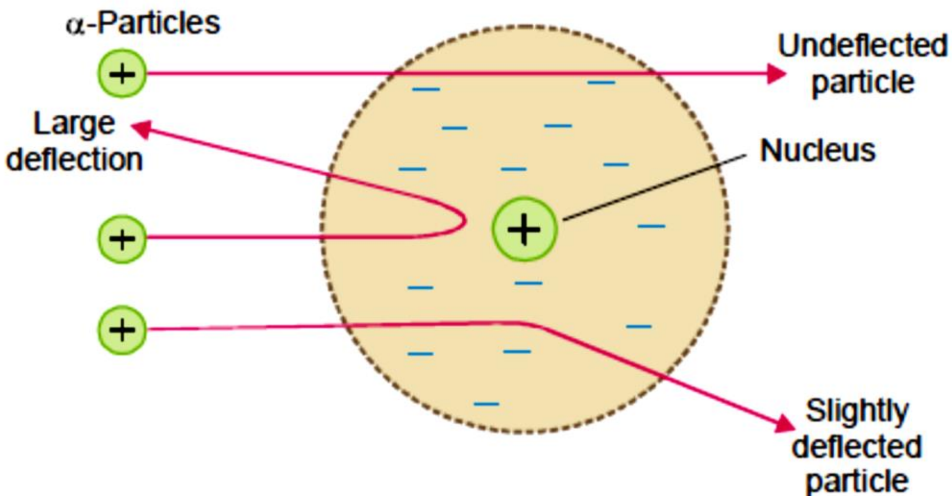
→ Based on these observations, Rutherford proposed a model of the atom which is named after him. This is also called the Nuclear Atom. According to it :

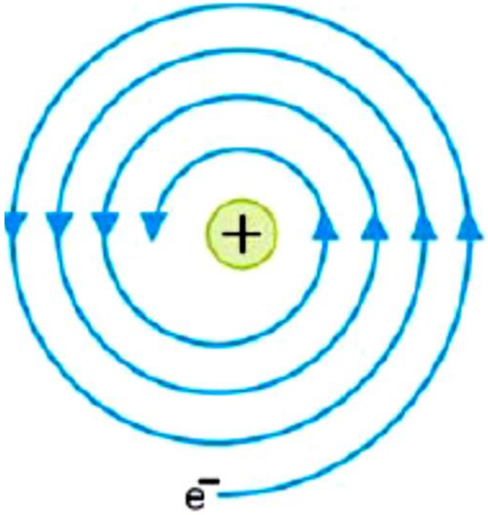
(1) **Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom, leaving the rest of the atom almost empty.**

(2) **The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around.**

(3) **The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.**

Atomic Structure





■ Weakness of Rutherford Atomic Model:

→ The assumption that electrons were orbiting around the nucleus was unfortunate. According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen actually as then the atom would be unstable which it is not.

Atomic Structure

■ The Bohr Theory of Atomic Structure:

→ In 1913, Niels Bohr combined Rutherford's ideas and suggested that the atomic nucleus was surrounded by electrons moving in orbits like planets round the sun . He was awarded the Nobel Prize for Physics in 1922 for his work on the structure of the atom. Several problems arise with this concept:

1. The electrons might be expected to slow down gradually.

2. Why should electrons move in an orbit round the nucleus?

3. Since the nucleus and electrons have opposite charges, they should attract each other. Thus one would expect the electrons to spiral inwards until eventually they collide with the nucleus.

Atomic Structure

■ The Bohr Theory of Atomic Structure:

→ To explain these problems Bohr postulated:

1. An electron did not radiate energy if it stayed in one orbit, and therefore did not slow down.

2. When an electron moved from one orbit to another it either radiated or absorbed energy. If it moved towards the nucleus energy was radiated and if it moved away from the nucleus energy was absorbed.

3. For an electron to remain in its orbit the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit .

■ The Bohr Theory of Atomic Structure:

→ For an electron of mass m, moving with a velocity v in an orbit of radius r,

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

If the charge on the electron is *e*. the number of charges on the nucleus *Z*. and the permittivity of a vacuum ε_o.

$$\text{Coulombic attractive force} = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

Now;

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_o mr}$$

Atomic Structure

■ The Bohr Theory of Atomic Structure:

(1) **Electrons travel around the nucleus in specific permitted circular orbits and in no others.**

→ Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus. The orbits are given the letter designation n and each is numbered 1, 2, 3, etc. (or K, L, M, etc.) as the distance from the nucleus increases.

(2) **While in these specific orbits, an electron does not radiate (or lose) energy.**

→ Therefore in each of these orbits the energy of an electron remains the same i.e. it neither loses nor gains energy. Hence the specific orbits available to the electron in an atom are referred to as stationary energy levels or simply energy levels.

■ The Bohr Theory of Atomic Structure:

(3) **An electron can move from one energy level to another by quantum or photon jumps only.**

→ When an electron resides in the orbit which is lowest in energy, the electron is said to be in the ground state. When an electron is supplied energy, it absorbs one quantum or photon of energy and jumps to a higher energy level. The electron then has potential energy and is said to be in an excited state.

The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom

$$\Delta E = E_{high} - E_{low} = h\text{v}$$

where h is Planck's constant and v the frequency of a photon emitted or absorbed energy.

Atomic Structure

■ The Bohr Theory of Atomic Structure:

(4) **The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π.**

→ Angular momentum = mvr = $n\dfrac{h}{2\pi}$

where m = mass of electron, v = velocity of the electron, r = radius of the orbit ; n = 1, 2, 3, etc., and h = Planck's constant.

By putting the values 1, 2, 3, etc., for n, we can have respectively the angular momentum,

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \text{ etc}$$

There can be no fractional value of h/2π. Thus the angular momentum is said to be quantized. The integer n corresponding energy level n is called the atom's **Principal quantum number**.

Quantum Number

■ Quantum Numbers:

→ Like the energy states of Bohr, designated by n = 1, 2, 3..., these states are also identified by numbers and specify the position and energy of the electron. Thus there are in all four such identification numbers called **quantum numbers** which fully describe an electron in an atom. Each one of these refers to a particular character.

(1) **Principal Quantum Number '*n*':**

→ This quantum number denotes the principal shell to which the electron belongs. This is also referred to as major energy level. The principal quantum number 'n' can have non-zero, positive, integral values n = 1, 2, 3... increasing by integral numbers to infinity. An electron with n = 1 has the lowest energy and is bound most firmly to the nucleus.

Quantum Number

The letters K, L, M, N, O, P and Q are also used to designate the energy levels or shells of electrons with a n value of 1, 2, 3, 4, 5, 6, 7 respectively. There is a limited number of electrons in an atom which can have the same principal quantum number and is given by $2n^2$, where n is the principal quantum number concerned. Thus,

Principal quantum number ($n =$)	1	2	3	4
Letter designation	K	L	M	N
Maximum number of electrons ($2n^2 =$)	2	8	18	32

(2) **Azimuthal Quantum Number ‘l ’**

→ This is also called secondary or subsidiary quantum number. the quantum number l defines the shape of the orbital occupied by the electron and the angular momentum of the electron. It is for this reason that ‘l’ is sometimes referred to as orbital or angular quantum number. For any given value of the principal quantum number n, the

Quantum Number

For any given value of the principal quantum number n, the azimuthal quantum number l may have all integral values from 0 to (n – 1), each of which refers to an energy sublevel or sub-shell. The total number of such possible sublevels in each principal level is numerically equal to the principal quantum number of the level under consideration. These sublevel are also symbolised by letters s, p, d, f etc. For example, for principal quantum number n = 1, the only possible value for l is 0 i.e., there is only one possible subshell i.e. s-subshell (n = 1, l = 0). For n = 2, there are two possible values of l, l = 0 and l = 2 – 1 = 1.

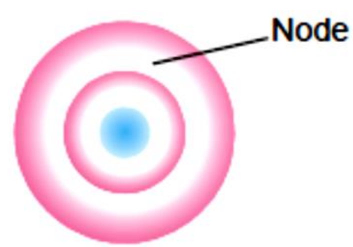
$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$l = 0\ (1s)$	$l = 0\ (2s)$	$l = 0\ (3s)$	$l = 0\ (4s)$	$l = 0\ (5s)$
	$l = 1\ (2p)$	$l = 1\ (3p)$	$l = 1\ (4p)$	$l = 1\ (5p)$
		$l = 1\ (3d)$	$l = 2\ (4d)$	$l = 2\ (5d)$
			$l = 3\ (4f)$	$l = 3\ (5f)$
				$l = 5\ (5g)$

(3) **Magnetic Quantum Number ‘*m*’:**

→ This is also called **Orientation Quantum Number** because it gives the orientation or distribution of the electron cloud. For each value of the azimuthal quantum number ‘l’, the magnetic quantum number m, may assume all the integral values between + l to – l through zero i.e., + l, (+ l – 1),... 0..., (– l + 1), – l. Therefore for each value of l there will be (2l + 1) values of m.

Thus when l = 0, m = 0 and no other value. This means that for each value of principal quantum number ‘n’, there is only one orientation for l = 0 (s orbital) or there is only one s orbital.

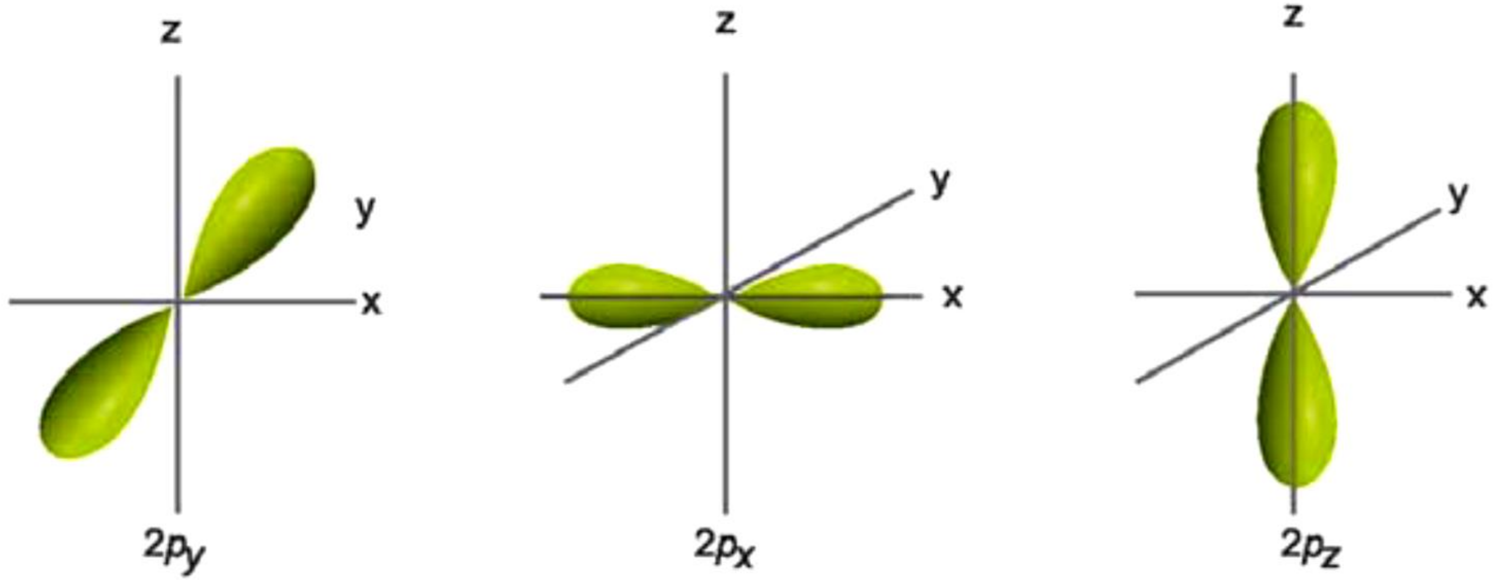
1s Orbital



2s Orbital

Quantum Number

For l = 1 (p orbital), the magnetic quantum number m will have three values : + 1, 0 and – 1; so there are three orientations for p orbitals. These three types of p orbitals differ only in the value of magnetic quantum number and are designated as p_x, p_y, p_z depending upon the axis of orientation.

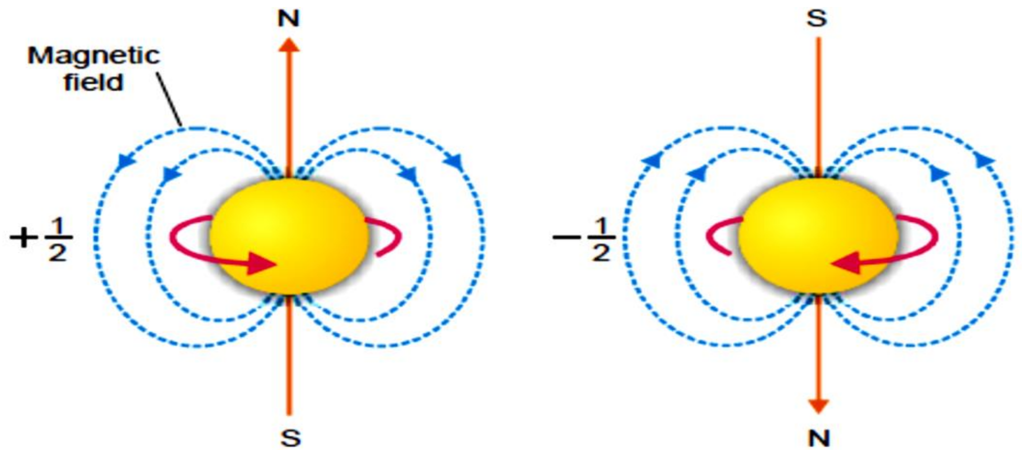


Quantum Number

(4) **Spin Quantum Number '*s*':**

→ This quantum number has been introduced to account for the spin of electrons about their own axis. Since an electron can spin clockwise or anticlockwise (in two opposite directions), there are two possible values of s that are equal and opposite.

As quantum numbers can differ only by unity from each other, there are two values given to s ; +1/2 + and -1/2 depending upon whether the electron spins in one direction or the other. These spins are also designated by arrows pointing upwards and downward as ↓↑.



Quantum Number

TABLE 2.1. QUANTUM NUMBERS AND ELECTRON ACCOMMODATION

Principal Q-number *n*		Azimuthal Q-number *l*		Magnetic Quantum Number *m*	Spin Quantum Number *s*	Number of Electrons accommodated	
1	K	0	*s*	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
2	L	0	*s*	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
		1	*p*	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	
3	M	0	*s*	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
		1	*p*	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	
		2	*d*	$+2, +1, 0, -1, -2,$	$+\frac{1}{2}, -\frac{1}{2}$	10	
4	N	0	*s*	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
		1	*p*	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	
		2	*d*	$+2, +1, 0, -1 \;\; -2$	$+\frac{1}{2}, -\frac{1}{2}$	10	
		3	*f*	$+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$	14	

Quantum Number

SOLVED PROBLEM. List all possible values of l and m for $n = 2$.

SOLUTION. Here, the principal quantum number $n = 2$. The azimuthal quantum number can have only two values. These are 0 and 1

When	$l = 0$	$m = 0$
and	$l = 1$	$m = +1, 0, -1$

SOLVED PROBLEM. Which of the following sets of quantum numbers are not allowable and why?

(*a*)	$n = 2$	$l = 2$	$m = 0$	$s = +\frac{1}{2}$
(*b*)	$n = 3$	$l = 1$	$m = 0$	$s = -\frac{1}{2}$
(*c*)	$n = 1$	$l = 1$	$m = +1$	$s = +\frac{1}{2}$
(*d*)	$n = 2$	$l = 0$	$m = -1$	$s = 0$
(*e*)	$n = 3$	$l = 2$	$m + 2$	$s = -\frac{1}{2}$

SOLUTION

(*a*) Not allowable as l cannot have value equal to 2 when $n = 2$.

(*b*) Allowable

(*c*) Not allowable as l cannot have value equal to 1 when $n = 1$

(*d*) Not allowable as s cannot have value equal to 0.

(*e*) Allowable

Ground-state Electron Configuration of Elements

Rule 1. Each electron shell can hold a maximum of $2n^2$ electrons where n is the shell number.

Rule 2. These electrons are accommodated in s, p, d and f orbitals, the maximum number of electrons in each type of orbitals being determined by its electron-holding capacity (for s = 2, p = 6, d = 10 and f = 14).

Rule 3. In the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first.

The increasing order of energy of various orbitals is as follows :

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s ......

Ground-state Electron Configuration of Elements

The energy of an orbital is determined by the sum of principal quantum number (n) and the azimuthal quantum number (l). This rule is called (n + l) rule. There are two parts of this rule:

(a) The orbitals with the lower value of (n + l) has lower energy than the orbitals of higher (n + l) value.

(b) When two orbitals have same (n + l) value, the orbital with lower value of n has lower energy.

For example, let us compare the (n + l) value for 3d and 4s orbitals.

For 3d orbital n = 3, l = 2 and n + l = 5 and for 4s orbital n = 4, l = 0 and n + l = 4.

Therefore, 4s orbital is filled before 3d orbital.

Ground-state Electron Configuration of Elements

Rule 4. Any orbital may have one or two electrons at the most. Two electrons can occupy the same orbital only if they have opposite spins **(Pauli's exclusion principle).**

Rule 5. When several orbitals of equal energy (degenerate orbitals) are available, electrons prefer to occupy separate orbitals rather than getting paired in the same orbital. Such electrons tend to have same spins **(Hund's rule).**

Heisenberg's Uncertainty Principle

■ According to the uncertainty principle, it is impossible to know simultaneously both the conjugate properties accurately.

For example, **both the position and the momentum** of the particle at any instant cannot be determined with absolute exactness or certainty. If the momentum (or velocity) be measured very accurately, a measurement of the position of the particle correspondingly becomes less precise.

On the other hand if position is determined with accuracy or precision, the momentum becomes less accurately known or uncertain.

Thus certainty of determination of one property introduces uncertainty of determination of the other.

Heisenberg's Uncertainty Principle

■ The uncertainty in measurement of position, Δx, and the uncertainty of determination of momentum, Δp (or Δmv), are related by Heisenberg's relationship as;

$$\Delta x \times \Delta p \geq \frac{h}{2\pi}$$

or, $$\Delta x \times m\,\Delta v \geq \frac{h}{2\pi}$$

Where, h is plank's constant.

The uncertainty product is negligible in case of large objects.

→ For a moving ball of iron weighing 500 g, the uncertainty expression assumes the form;

$$\Delta x \times m\,\Delta v \geq h/2\pi \quad \text{or} \quad \Delta x \times \Delta v \geq h/2\pi m$$

$$\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 500} = 5 \times 10^{-31} \text{ erg sec g}^{-1}$$

Heisenberg's Uncertainty Principle

→ But for an electron of mass m = 9.109 × 10^{-28} g, the product of the uncertainty of measurements is quite large as

$$\Delta x \times m\,\Delta v \geq h/2\pi \quad \text{or} \quad \Delta x \times \Delta v \geq h/2\pi m$$

$$\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.109 \times 10^{-28}} = 0.3 \text{ erg sec g}^{-1}$$

SOLVED PROBLEM. Calculate the uncertainty in position of an electron if the uncertainty in velocity is 5.7×10^5 m sec^{-1}.

SOLUTION. According to Heisenberg's uncertainty principle

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

or $$\Delta x \times m\,\Delta v = \frac{h}{4\pi}$$

or $$\Delta x = \frac{h}{4\pi m \times \Delta v}$$

Here $\Delta v = 5.7 \times 10^5$ m sec^{-1}

$h = 6.6 \times 10^{-34}$ kg m^2 sec^{-1}

$m = 9.1 \times 10^{-31}$ kg

On substitution we get

$$\Delta x = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg})(5.7 \times 10^5 \text{ m sec}^{-1})}$$

$$= \frac{6.6 \times 10^{-8}}{4 \times 3.14 \times 9.1 \times 5.7} m$$

$$= 1 \times 10^{-10} \text{ m}$$