Atomic Structure

Atom and Fundamental Particles

The smallest unit of an element which does not have its own existence in nature but takes part in chemical reactions is called an atom.

Fine particles that are present in every atom of the element are called the fundamental particles of an atom.

Types of fundamental particles: Fundamental particles are of three types

(1) **Stable particles:** These are the fundamental particles which are present in every atom of element. There are three particles which are: proton, neutron and electron.
(2) **Unstable particles:** these particles remain present in the atoms of some elements for a very short time. There are about a two hundred of these particles which are neutrino, anti-neutrino, positron, meson etc.
(3) **Composite particles:** Other than the stable and unstable fundamental particles there are other heavy particles known as composite particles. Examples of composite particles are deuteron and alpha particles.

Particle	Symbol	Mass (kg)	Relative Mass (pro-ton =1)	Relative Charge
Proton	p^+	1.673×10^{-27}	1	+1
Neutron	n^0	1.675×10^{-27}	1	0
Electron	e^-	9.109×10^{-31}	0.00055	-1

Atomic Symbol:

The atom of each element is made up of electrons, protons and neutrons. All atoms of the same neutral element have the same number of protons and electrons but the number of neutrons can differ. Atoms of the same element but different neutrons are called isotopes. Because of these isotopes it becomes necessary to develop a notation to distinguish one isotope from another - the atomic symbol. The atomic symbol has three parts to it:

$$ {}^{\mathbf{Z}}_{\mathbf{A}}\mathbf{X}^{\pm \mathbf{n}} $$

(1) The symbol **X**: the usual element symbol
(2) The atomic number **A**: equal to the number of protons (placed as a left subscript)
(3) The mass number **Z**: equal to the number of protons and neutrons in the isotope (placed as a left superscript)
(4) Charge number **±n:** equal to the number of electrons donated or accepted by the atom

Isotope, Isobar and Isotone:

Isotope: Atoms of the same element which have same atomic number but different mass number are called isotopes. Hydrogen is the common example which has three isotopes.

Hydrogen (H): Z=1, A=1 (one proton only)

Deuterium (D): Z=1, A=2 (one proton and one neutron)

Tritium (T): Z=1, A=3 (one proton and two neutron)

Isobar: Isobars are the atom of different elements having the same mass number but different atomic numbers. For example, tellurium and the iodine isotope, ^{127}Te and ^{127}I are isobars to each other.

Isotone: Isotones are the atoms of different elements that have the same neutron number but different proton numbers, hence different atomic masses. For example, ^{32}Si and ^{32}P have 16 neutrons in each of the atom, and so they are called isotones.

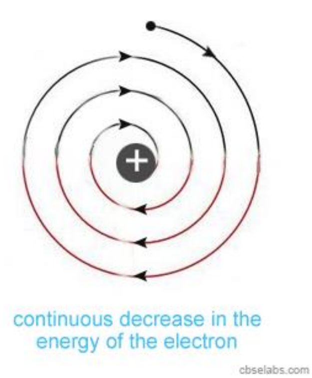
Rurherford Atom Model:

Postulates of Rutherford atomic model-

(1) An atom is composed of positively charged particles. Majority of the mass of an atom was concentrated in a very small region. This region of the atom was called as the nucleus of an atom. It was found out later that the very small and dense nucleus of an atom is composed of neutrons and protons.
(2) Atoms nucleus is surrounded by negatively charged particles called electrons. The electrons revolve around the nucleus in a fixed circular path at very high speed. These fixed circular paths were termed as "orbits."
(3) An atom has no net charge or they are electrically neutral because electrons are negatively charged and the densely concentrated nucleus is positively charged. A strong electrostatic force of attractions holds together the nucleus and electrons.
(4) The size of the nucleus of an atom is very small in comparison to the total size of an atom.

Limitations of Rutherford Atomic Model-

(1) Rutherford's model was unable to explain the stability of an atom. According to Rutherford's postulate, electrons revolve at a very high speed around a nucleus of an atom in a fixed orbit. However, Maxwell explained accelerated charged particles release electromagnetic radiations. Therefore, electrons revolving around the nucleus will release electromagnetic radiation.
(2) The electromagnetic radiation will have energy from the electronic motion as a result of which the orbits will gradually shrink. Finally, the orbits will shrink and collapse in the nucleus of an atom. According to the calculations, if Maxwell's explanation is followed Rutherford's model will collapse with 10-8 seconds. Therefore, Rutherford atomic model was not following Maxwell's theory and it was unable to explain an atom's stability.



(3) Rutherford's theory was incomplete because it did not mention anything about the arrangement of electrons in the orbit. This was one of the major drawbacks of Rutherford atomic model.

Bohr’s Atomic Model:

In 1913 Niels Bohr, an eminent scientist of Denmark successfully explained the stability of the atom and the reason behind the appearance of line spectra with the help of Plank’s quantum theory. The theory, put forward by Bohr regarding the structure of H-atom, is based on three revolutionary postulates-

Postulate 1: When an electron revolves in any selected orbits, it neither emits nor absorbs energy. The energy of an electron in a particular orbit is constant. These orbits are therefore, called stationary orbits. Depending on the distance of from the nucleus, these orbits are divided into energy levels such as K, L, M, N … etc. and these are designated respectively by the numbers 1, 2, 3, 4…etc.

Postulate 2: The electron in the hydrogen atom revolves around the nucleus only in certain selected circular paths (called orbit) which are associated with definite energies. Only those orbits are permitted for the revolving electron in which the angular momentum of the electron is a whole number multiple of $h/2\pi$
angular momentum of electron,

$$mvr = n \times \frac{h}{2\pi}$$

Where, n = 1, 2, 3, 4…etc.

m = mass of the electron

v = velocity of the electron

r = radius of the orbit

h = Plank’s constant

Thus the angular momentum of electrons in an atom is quantized.

Postulate 3: As long as an electron remains in a particular orbit, it neither emits (i.e., radiates or losses) nor absorbs energy. But when the electron is excited from a lower energy level to a higher energy level, it absorbs energy. On the other hand when it comes back from a higher energy level to a lower energy level, it emits energy. Now if ν the frequency of the radiation absorbed by the electron, then, according to Plank’s quantum theory of radiation, energy absorbed by the electron will be

$$\Delta E = E_2 - E_1 = h\nu$$

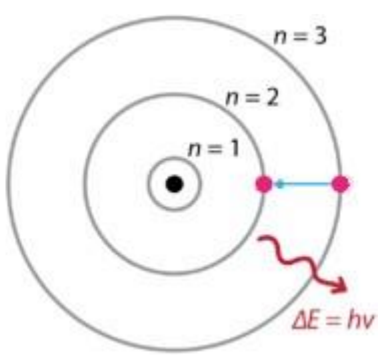


Figure: Bohr’s Atom Model

Merits of Bohr’s Atomic Model

1. Stability of atom
2. Line spectra of H-atom
3. Radius of the first orbit of H-atom
4. Principal quantum number
5. Energy of an electron

(Note: Here only the key points have been highlighted, you have to describe the details.)

Limitation of Bohr’s Atomic Model

1. Spectra of atoms or ions having two or more electrons (i.e., multi-electron system) cannot be explained with the help of Bohr’s theory.
2. Bohr’s theory cannot give any explanation for the splitting of spectral lines under the influence of magnetic or electric field. i.e., for the formation of fine structure of atomic spectra.
3. Bohr’s atomic model is two-dimensional and hence fails to give any idea about the actual three-dimensional electronic model of atom.
4. According to de-Broglie (1923), a tiny particle like electron has dual character i.e., electron has particle as well as wave nature. Bohr treated electron only as a particle.
5. According to Bohr’s atomic model, an electron moves around the nucleus along a fixed circular path with a definite velocity. But according to Heisenberg’s uncertainty principal, it is impossible to measure simultaneously both the position and velocity (or momentum) of a sub-atomic particle like electron with absolute accuracy at a particular instant.

Dual Nature of Electrons and de-Broglie’s Equation

De Broglie derived his equation using well established theories through the following series of substitutions:

De Broglie first used Einstein’s famous equation relating matter and energy:

$$E = mc^2 \qquad (1)$$

Where,

E = energy
m = mass and
c = speed of light

According to Plank’s equation:

$$E = h\nu \qquad (2)$$

Where,

h = Plank’s constant
ν = frequency

Since de Broglie believed particles and wave have the same traits, he hypothesized that the two energies would be equal:

$$mc^2 = h\nu \qquad (3)$$

Because real particles do not travel at the speed of light, De Broglie submitted velocity (v) for the speed of light (c)

From the wave equation, De Broglie substituted $\frac{v}{\lambda}$ for ν and arrived at the final expression that relates wavelength and particle with speed.

$$mv^2 = \frac{hv}{\lambda}$$

Hence

$$\lambda = \frac{h}{mv}$$

Thus this equation expresses the dual nature of electrons.

Heisenberg's uncertainty principle:

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than h/4π.

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

where Δx = uncertainty in position,

Δp = uncertainty in momentum

Heisenberg's uncertainty principle rules out the existence of definite paths or trajectories of electrons and other similar particles.

Spectrum:

When a white light is passed through a prism, it splits into a series of colored bands known as spectrum.

Spectrum is of two types:

a) **Continuous and line spectrum**: The spectrum which consists of all the wavelengths is called continuous spectrum.
b) **Line spectrum**: A spectrum in which only specific wavelengths are present is known as a line spectrum. It has bright lines with dark spaces between them.

Electromagnetic spectrum is a continuous spectrum. It consists of a range of electromagnetic radiations arranged in the order of increasing wavelengths or decreasing frequencies. It extends from radio waves to gamma rays.

Spectrum is also classified as emission and line spectrum.

a) **Emission spectrum**: The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.
b) **Absorption spectrum:** is the spectrum obtained when radiation is passed through a sample of material. The sample absorbs radiation of certain wavelengths. The wavelengths which are absorbed are missing and come as dark lines.

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, 4, 5 ...	Ultraviolet
Balmer	2	3, 4, 5 ...	Visible
Paschen	3	4, 5 ...	Infrared
Brackett	4	5, 6 ...	Infrared
Pfund	5	6, 7...	Infrared

The study of emission or absorption spectra is referred as spectroscopy.

Spectral Lines for atomic hydrogen: Rydberg equation

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

R_H = Rydberg's constant = 109677 cm^{-1}

(Note: Here only formulae has been highlighted, you have to solve mathematical problems.)

Significance of the negative sign of E_n:

When an electron is at infinite distance (n = ∞) from the nucleus, it experiences no force of attraction by the nucleus. Hence, the energy of the electron at infinite distance from the nucleus is taken as zero. When the electron moves towards the nucleus and it comes under the influences of nucleus, it experiences a force of attraction by the nucleus. As a result some energy is given out and the energy of the electron becomes less than zero, i.e., it becomes negative. Due to release of energy the stability of the electron, occupying a closer to the nucleus, it experiences greater force of attraction and hence more energy is released, thereby causing the electronic energy to be more negative.

Atomic Orbital: The three-dimensional region or space round the nucleus of an atom where the probability of finding an electron having a certain energy is maximum.

Difference between orbit and orbital

Orbit	Orbital
As postulated by Bohr, an orbit is a definite circular path at a definite distance from the nucleus in which the electron revolves round the nucleus.	As postulated by wave nature of an electron, an orbital is defined as a three-dimensional region or space around the nucleus within which the probability of finding an electron with a certain energy is maximum.
It represents the planar motion of the electrons.	It represents the three-dimensional motion of the electron round the nucleus.
Orbits are circular in shape.	Orbitals have different shapes, e.g., s-orbital is spherically symmetrical, p-orbitals are dumb-bell shaped etc.

Quantum Numbers

Quantum numbers: Certain identification numbers which are necessary to give complete information about any revolving electron in an atom are quantum numbers.

There are four quantum numbers used to describe the exact position and the nature of an electron. They are:

Principal quantum number: Different energy levels in an atom according to Bohr theory have been represented by ***n*** which can have non-zero positive integer values upto infinity i.e.,

$$n = 1, 2, 3, 4 \ldots \infty$$

Thus **n** can have infinite values and it has been called **principal quantum number**.

Azimuthal quantum number: In order to explain the formation of fine structure, **Sommerfeld** proposed the existence of elliptical orbits, besides the circular orbits of Bohr. In order to specify the shape of the elliptical orbit, another supplementary quantum number is necessary. This supplementary quantum number which indicates the ellipticity of the electronic orbit (sub-shell) is **called azimuthal or subsidiary quantum number** denoted by **'l'**. i.e., $\boldsymbol{l = \text{'0'} \rightarrow (n\text{-}1)}$

Values of *l* → **0** **1** **2** **3**

Designation of sub-shell → **s** **p** **d** **f**

Magnetic quantum number: Due to the angular motion of electron around the nucleus, a magnetic field is produced which interacts with the external magnetic field. As a result sub-shell of definite energy split into three dimensional spatial regions which can be expressed by magnetic quantum number. It is denoted by '***m***'. i.e., $\boldsymbol{m = -l \rightarrow +l}$

Spin quantum number: It is observed that the electron in an atom is not only revolved around the nucleus but is also spinning around its own axis like the earth. As this quantum number describes the spin motion of the electron. It is designated by 's'. Since the electron can spin only clockwise and therefore the spin quantum number can take only two values be +1/2 or -1/2.

Table: Information given by quantum numbers

Principal quantum number (n)	Azimuthal quantum number (l)	Magnetic quantum number (m)	Number of orbitals in a sub-shell	Number of electrons in a sub-shell	Total number of electrons
1 (K-shell)	0 (s)	0	1	1×2=2	2
2 (L-shell)	0 (s) 1 (p)	0 -1, 0, +1	1 3	1×2=2 3×2=6	8
3 (M-shell)	0 (s) 1 (p) 2 (d)	0 -1, 0, +1 -2, -1, 0, +1, +2	1 3 5	1×2=2 3×2=6 5×2=10	18
4 (N-shell)	0 (s) 1 (p) 2 (d) 3 (f)	0 -1, 0, +1 -2, -1, 0, +1, +2 -3, -2, -1, 0 +1, +2, +3	1 3 5 7	1×2=2 3×2=6 5×2=10 7×2=14	32

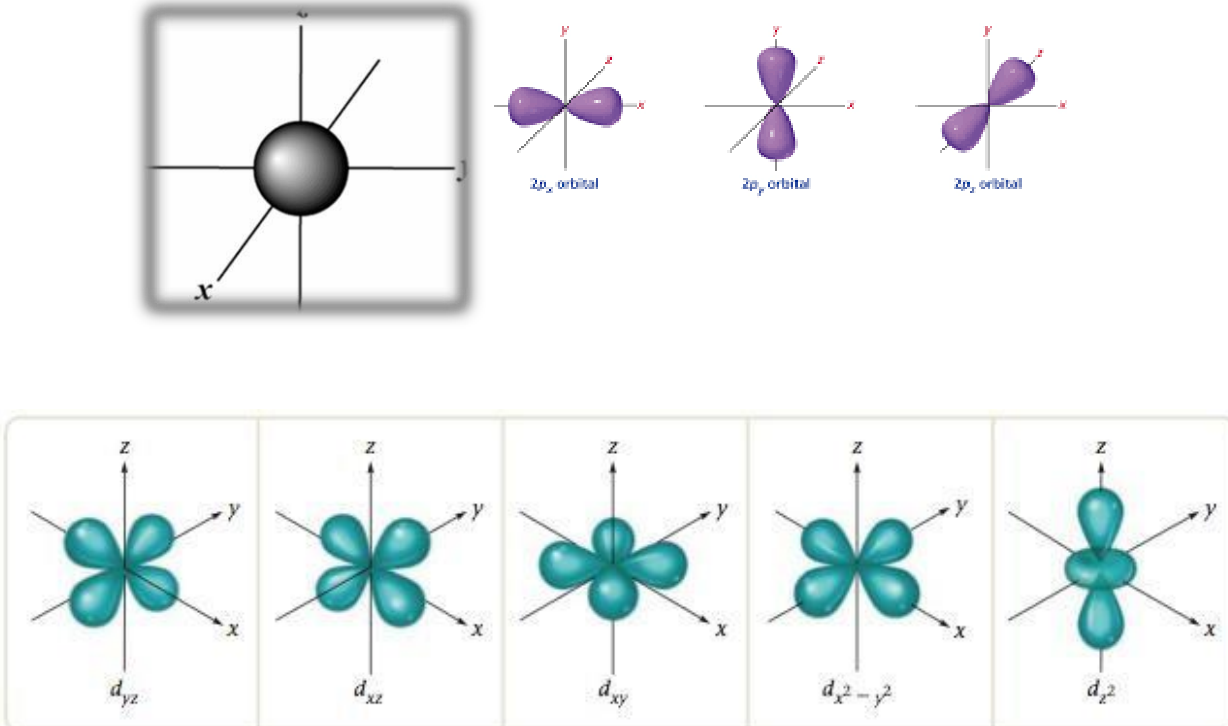


Figure: Spatial arrangement of atomic (s, p & d) orbitals

Aufbau, Hund’s and Pauli’s Exclusion Principle

According to quantum mechanics, a certain number of electrons in an atom are arranged in the orbitals of the various subshells obeying certain rules. These arrangements of electrons in different orbitals is called electronic configuration of atom. The filling of orbitals are governed by the following principles:

1. Pauli’s Exclusion Principle
2. Aufbau Principle
3. Hund’s Rule

Pauli’s Exclusion Principle: No two electrons in an atom can have same values for all the four quantum numbers.

For example, consider He atom having K-shell (n=1). It will have one value of l (as l=0) and one value of m (as m=0) but it can have either two values of s, as +1/2 or -1/2 i.e.,

n=1	l=0	m=0	s=+1/2
n=1	l=0	m=0	s=-1/2

This leads to the conclusion that an orbital can have maximum of two electrons. Moreover, if an orbital has two electrons they must be of opposite spins.

Aufbau Principle: Electrons first enter into lower energy orbital and subsequent electrons enter into higher energy orbital gradually.

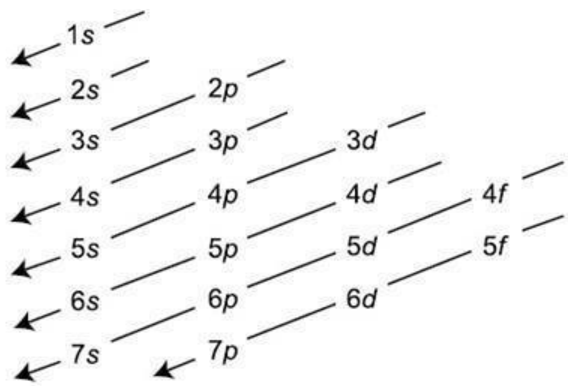


Figure: Energy increases diagram

Hund's Rule: Electrons pairing will not take place in orbital of same energy (same sub-shell) until each orbital is singly occupied.