# THE STRUCTURE OF ATOM
# CHEM-101

## Radioactivity and Atomic Structure

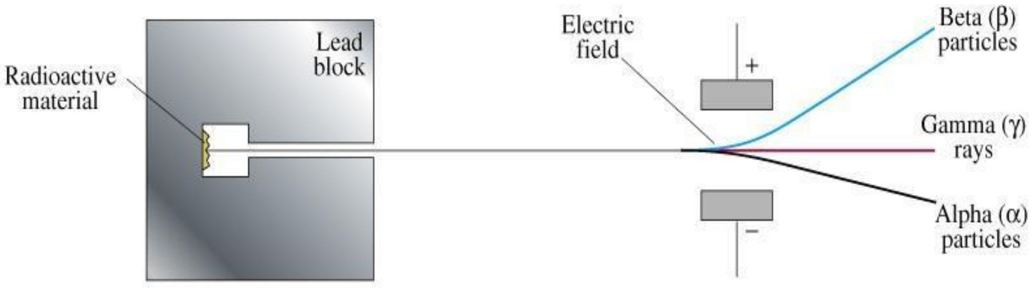
The idea of the structure of atom was provided by the discover of radioactivity.

Radioactivity is the spontaneous disintegration of atoms of certain elements, such as radium and uranium, into simpler elements with the simultaneous production of one or more of the three kinds of radiations emitted during the process.

These types of rays are known as alpha(α) rays, beta(β) rays and gamma(γ) rays.
The α-rays are deflected towards the negative pole of the electric field and consist of positively charged particles subsequently found to be double charged helium ion (He+2).

The β-rays are attracted towards the positive pole of the electric field.

The γ-rays are not affected by the electric field but are more penetrating having very short wavelengths similar to xrays and affect photographic plate or film.

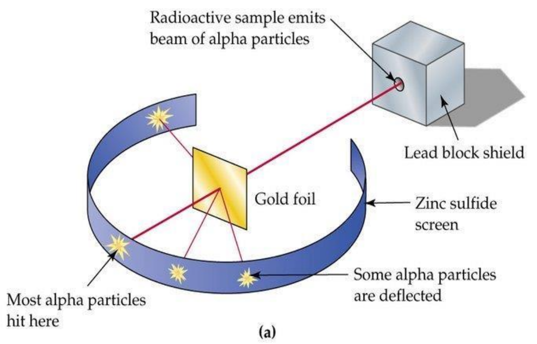



## Scattering of α-rays and the Idea of Nulceus

Rutherford in 1911 projected a beam of α-particles from a radioactive source upon a very thin gold foil.

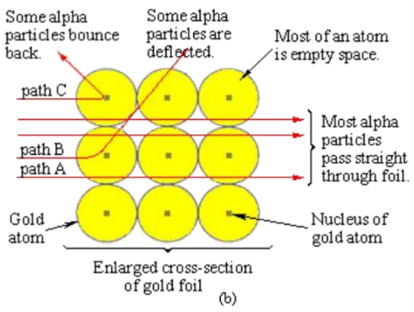
He found that most of the particles passed through the gold foil without deflection, and only a few of them turn back as if, the α-particles have met with some obstacles in their onward journey. From this experiment Rutherford assumed that the mass of an atom is concentrated in a central body called the Nucleus which is exceedingly small as compered to the total size of the atom.

The nucleus also carry the entire positive charge of the atom.



(a)

α-particles can only turn back by hitting the nucleus not only because of their obstacle but also due to repulsion by the positive charges on the nucleus as encounter with a massive shown in fig



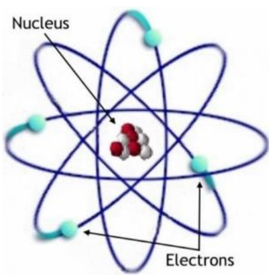

The electrons can be easily knocked out from the atoms and therefore constitute the external structure of the atom. When α-particles come in contact with such a system, there is little or no deflection of α-particles by the tiny electrons because of the mass and size of the particles.

Rutherford measured the nuclear charges of a large number of atoms and proved that the number of positive charges on the nucleus is, in many cases, approximately one-half the atomic weight of the element and also equal to the number of free electrons in the atom.

## Rutherford's Atom Model

Rutherford's solar system atom model may be described as follows:

- An atom consists of a small nucleus containing all the positive charges of the atom and practically the whole of its mass.
- The nucleus is surrounded by a number of electrons equal to the number of positive charges on the nucleus.
- The electrons are in constant motion round the nucleus like that of planets round the sun in such a way that the electrostatic force of attraction between the electrons and positive nucleus is counterbalanced by the centrifugal force.




Pictorial representation of the Rutherford (or planetary) model of an atom, in which the positively charged nucleus, which contains the majority of the atomic mass, is surrounded by orbiting electrons.

## Fundamental Particles of Atom

### Electron

An electron is the smallest of the subatomic particles. It has the unit electrical charge with negative sign. Its masses is about 1/1840 times less than that of a hydrogen atom or proton.
Electrons constitute the outer structure of atoms.
The chemical properties of elements and their compounds are mostly dependent upon the arrangement of the electrons in their atoms.

### Proton

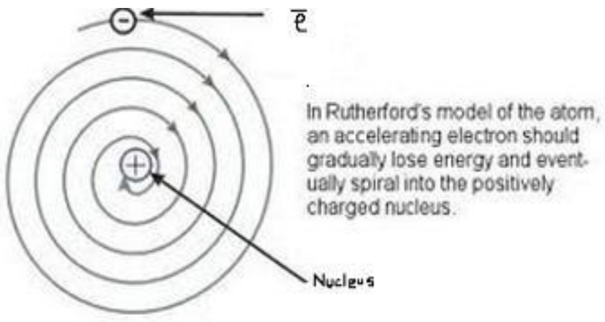
A proton is a subatomic particle, with a unit positive charge( i.e., $1.602\times10^{-20}$ emu) and a mass slightly less than that of a neutron. Protons and neutrons, each with masses of approximately one atomic mass unit, are jointly referred to as "nucleons" (particles present in atomic nuclei).

### Neutron

The neutron is a subatomic particle, which has a neutral (not positive or negative) charge, and a mass slightly greater than that of a proton. Protons and neutrons constitute the nuclei of atoms.

## Limitations of Rutherford Atom Model

- Newton's Laws of motion and gravitation can only be applied to neutral bodies such as planets and not to charged bodies such as tiny electrons moving round a positive nucleus.
- The analogy does not hold good since the electrons in an atom repel one another, where as planets attract each other because of gravitational forces. Beside there is electrostatic attraction in a nuclear atom model.
- According to Maxwell's theory, any charged body such as electrons rotating in an orbit must radiate energy continuously, thereby losing kinetic energy. Hence the electron must gradually spiral in towards the nucleus. The radius of the electron will gradually decrease and it will ultimately fall into the nucleus, thus annihilating the atom model.




- Since the process of radiating energy would go on continuously, the atomic spectra should also be continuous and should not give sharp and well-defined lines.

## Bohr's Atom Model

### Postulate of Energy Levels

- An atom has a number of stable orbits in which an electron can revolve without the radiation of energy. These orbits are referred to as "Energy Levels".

- The electrons in these orbits posses an integral multiple of the quantum of energy i.e., $h\gamma$, but do not radiate it.
- The electron moves in a circular orbit. The angular momentum of the electron in such orbit must be an integral multiple of $h/2\pi$, that is,

$$mvr=n.h/2\pi$$

- Where m is the mass of the electron, v is its velocity, r is the radius of the orbit and n is 1,2,3,4,5 etc. (h is the Planck's constant).

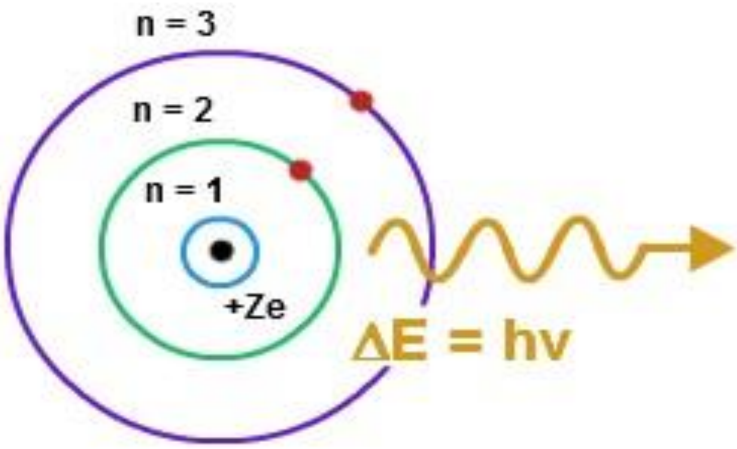
### Postulate of Frequency or Radiation

An electron can, jump from one orbit to another. An atom radiates energy when an electron passes from a higher energy level to another of lower energy. The jump of an electron from a lower energy level to that of a higher energy level is associated with absorption of energy.

If $E_1$ and $E_2$ are the energies of the electron in the initial and final levels respectively, the difference of energy radiated when the electron passes from the higher to the lower energy level is given the relation:

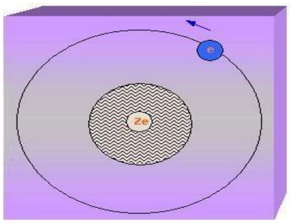
$$E_2-E_1=h\gamma$$

Where h is the Planck's constants and $\gamma$ is the frequency of radiation.




A single electron with a charge e, rotating in a circular orbit of radius r about a nucleus of charge Z.e (where Z is the atomic number). According to Coulomb's law, the electrostatic force of attraction $F_{e,}$ between the charges may be evaluated mathematically as

$F_e = Ze^2/r^2$ (using Gaussian units)



By definition, the magnitude of the centrifugal force Fc, for an electron of mass m, with a velocity in its orbit v, and with an orbital radius of r, is given as

$$F_c = mv^2/r$$

It is assume that the two forces, electrostatic and centrifugal, are equal and opposite to each other.

So, $mv^2/r = Ze^2/r^2$

or $v^2 = Ze^2/mr$ …………..(1)

From Bohr's postulate we know

$mvr = n.h/2\pi$

or, $v = nh/2\pi mr$

or, $v^2 = n^2h^2 /4\pi^2m^2r^2$ ……….(2)

Combining the equ (1) and (2),

$n^2h^2/4\pi^2m^2r^2 = Z.e^2/mr$

or, $r = n^2h^2/4\pi^2mZe^2$ ………(3)

The total energy of an electron is equal to the sum of the kinetic energy (K.E.) and the potential energy (P.E.).

Now,

And the potential energy of an electron of charge Z.e at a distance r from the nucleus is given by the equation: Potential energy = $-Ze^2/r$

The total energy E of an electron in any orbit is given by the equation:

E = K.E.+P.E.

$E = mv^2 /2 - Ze^2 /r$

since, $mv^2 /r = Ze^2 /r^2$

$mv^2 = Ze^2 /r$

therefore,

E = K.E.+P.E.

$E = mv^2/2 - Ze^2/r$

Substituting the value of r from (3) we get,

$$E = -2\pi^2 Z^2 e4m/n^2h^2 \quad \ldots\ldots (4)$$

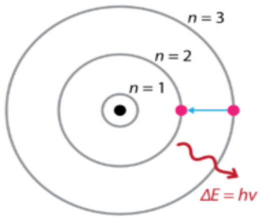
## Limitations of Bohr Theory

- Bohr theory was eminently successful in explaining the spectrum of hydrogen but failed to predict the energy state of more complicated atom in which there are more than one electron.
- Periodic motion around a central body usually follows an elliptic path rather than a circular path which has been assumed in the case of Bohr theory. If electrons follow elliptical path, the velocity along the path does not remain constant.
- High resolving power spectroscopy shows multiple lines in the atomic spectra and the multiplicity of lines has not been explained by Bohr theory.

## Origin of emission spectra of Hydrogen

While the electron of the atom remains in the ground state, its energy is unchanged. When the atom absorbs one or more quanta of energy, the electron moves from the ground state orbit to an excited state orbit that is further away.

The energy that is gained by the atom is equal to the difference in energy between the two energy levels From this it will tend to drop back to the lowest energy level in the stable position if not ionized. When the atom relaxes back to a lower energy state, it releases energy that is again equal to the difference in energy of the two orbits.




• Figure 1. Bohr model of the atom: electron is shown transitioning from the *n* = 3 energy level to the *n* = 2 energy level. The photon of light that is emitted has a frequency that corresponds to the difference in energy between the two levels.

The change in energy, Δ*E*, then translates to light of a particular frequency being emitted according to the equation *E* = *hv*. The atomic emission spectrum of hydrogen had spectral lines consisting of different frequencies.
The spectral series is broken into corresponding series based on the electron transition to lower energy state.

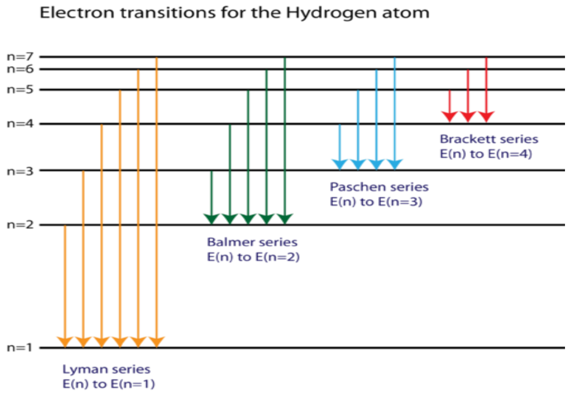



Figure 2. The electron energy level diagram for the hydrogen atom

**The spectral series of Hydrogen are:**

**Lyman series ($n_l$=1)**
According to Bohr's model,Lyman series is displayed when electron transition takes place from higher energy states($n_h$=2,3,4,5,6,…) to $n_l$=1 energy state. All the wavelength of Lyman series falls in Ultraviolet band.

**Balmer series ($n_l$=2)**
Balmer series is displayed when electron transition takes place from higher energy states($n_h$=3,4,5,6,7,…) to $n_l$=2 energy state. All the wavelength of Balmer series falls in visible part of electromagnetic spectrum.

**Paschen series ($n_l$=3)**
Paschen series is displayed when electron transition takes place from higher energy states($n_h$=4,5,6,7,8,…) to $n_l$=3 energy state. All the wavelength of Paschen series falls in the Infrared region of the electromagnetic spectrum.

**Brackett series ($n_l$=4)**
Brackett series is displayed when electron transition takes place from higher energy states($n_h$=5,6,7,8,9…) to $n_l$=4 energy state. All the wavelength of Brackett series falls in Infrared region of the electromagnetic spectrum.

Bohr's model was a tremendous success in explaining the spectrum of the hydrogen atom. Unfortunately, when the mathematics of the model was applied to atoms with more than one electron, it was not able to correctly predict the frequencies of the spectral lines.

## Quantum Numbers

To provide a complete description of an electron in an atom, four quantum numbers are needed. Moreover these quantum numbers describe the whole atomic state rather than particular orbits.

### The Principle Quantum Number

The nuclei of the more complex atoms are surrounded by electrons which are arranged in a series of energy levels or spherical shells.

The angular momentum of electron of this circular orbit is equal to a simple multiple of $h/2\pi$, i.e., $mvr = n.h/2\pi$ The integer n is designated as the Principle Quantum number and represents any particular circular orbit.

The value of n gives roughly the binding force and distance between the nucleus and the electron.

This quantum number represents the size of the electron orbit. When n=1, it represents the first energy level; n=2 represents the second energy level and so on.

### The Subsidiary Quantum Number

According to Sommerfeld modification the electrons in any particular energy level could have either a circular orbit or a number of elliptical orbits about the nucleus.

The angular momentum of this elliptical orbit is given by the equation

$$mvr = h.\sqrt{l(l+1)}/2\pi$$

Where l stands for subsidiary or azimuthal or orbital quantum number.

Thus the subsidiary quantum numbers describe the shapes of the electron's orbit.

The main energy level (or shells) of electron may be considered as being made up of one or more sub-levels (sub shells).

The number of sub-levels are limited by quantum condition, so that, if n is the principal quantum number, then the number of sub-levels will be equal to n. l may have value from 0 to n-1.

Hence for the first energy level where n=1, l can have only a value of 0. This means that energy level and sub-level coincide with each other.

For n=2, l can have values 0 and 1. Thus second energy level has two sub-levels.

## The Magnetic Quantum Number

Zeeman in 1896 observed the splitting of spectral lines in magnetic field. This is known as Zeeman effect.

The third quantum number was introduced to explain the orientation of electronic orbit in space particularly under the influence of an applied magnetic field.

This is known as the magnetic quantum number and is designated by m.

Mathematically, the magnetic quantum number may be expressed by the equation:

$$\text{Total angular momentum} = mh/2\pi$$

m can have values from $-l$ to $+l$ including 0. Thus, when n=1, then l=0 and m can have only one value of 0. When n=2, l can have values 0 and 1, and therefore, when l=0, m is also 0 and for l=1, m can have value -1,0 and +1.

## The spin Quantum Number

The spin quantum number represents the direction of the electron spin and is denoted by s. Mathematically, the spin quantum number is defined by the equation: $mvr = h\sqrt{s(s+1)}/2\pi$

The spin quantum numbers can have values +1/2 or -1/2 which are the mathematical notations for the spin direction of the electrons.

## The Physical Significance of Quantum Number

Four quantum numbers are necessary to describe an electron in an atom. These quantum numbers describe the electron orbit in terms of

(1) Size

(2) Shape

(3) Orientation in space and

(4) Direction of spin of electron in its axis.

The principle quantum number, n determines the size of the orbit and also gives a measure of the energy of the electron.

The subsidiary quantum number, l, determines the shape of the orbit and indicates weather the orbit is circular or elliptical.

The magnetic quantum number, m, determines the number of possible orientations in space or the number of plane in which the orbits are situated.

The spin quantum number s stands for spin directions and the symbols +1/2 and -1/2 are mathematical notations of spin rather than that of physical rotation.

## Palui Exclusion Principle

- No two electrons in the same atom can have the same values for the four quantum numbers.
- No two electrons in the same atom can have identical sets of four quantum numbers.
- No more than one electron can have given values for the four quantum numbers.

**Types of Electrons**

| Value of l | Electron symbol | Maximum No. of electrons of each type |
|---|---|---|
| **0** | s | 2 |
| **1** | p | 6 |
| **2** | d | 10 |
| **3** | f | 14 |

The maximum no of electrons in the various energy levels permitted by Palui Exclusion principle have been shown in Table:

| Quantum Numbers → Values ↓ | Principal Quantum Numbers(n) {1,2,3,4,...} | Azimuthal Quantum Numbers(l) [0 to(n-1)] | Magnetic Orbital Quantum($m_l$) {-l to +l} | Electron Spin Quantum Numbers($m_s$) {-1/2,+1/2} | Total |
|---|---|---|---|---|---|
| n | 1 | 0 s | 0 | (-1/2, +1/2) | 2 |
| n | 2 | 0 s<br>1 p | 0<br>-1, 0 ,+1 | 2(-1/2, +1/2)<br>6(-1/2, +1/2) | 8 |
| n | 3 | 0 s<br>1 p<br>2 d | 0<br>-1, 0 ,+1<br>-2, -1, 0 +1+2 | 2(-1/2, +1/2)<br>6(-1/2, +1/2)<br>10(-1/2, +1/2) | 18 |
| n | 4 | 0 s<br>1 p<br>2 d<br>3 f | 0<br>-1, 0 ,+1<br>-2, -1, 0 +1+2<br>-3, -2, -1, 0, +1, +2, +3 | 2(-1/2, +1/2)<br>6(-1/2, +1/2)<br>10(-1/2, +1/2)<br>14(-1/2, +1/2) | 32 |

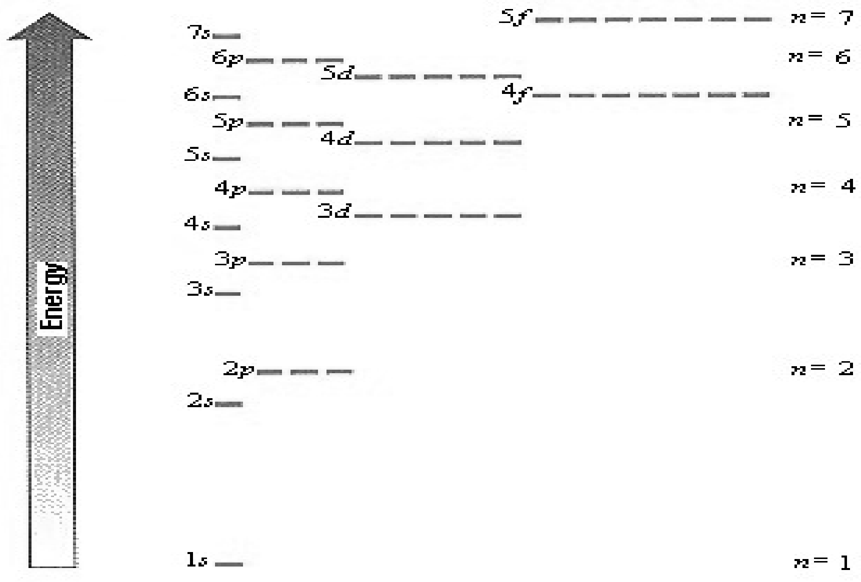
**Distribution of Electrons in the Atoms of Elements**

Electron distribution in orbitals

| Principle quantum number | Maximum number of electrons | Number of electrons distributed in orbitals |
|---|---|---|
| **1** | 2 | $1s^2$ |
| **2** | 8 | $2s^2 2p^6$ |
| **3** | 18 | 3s23p63d10 |
| **4** | 32 | 4s24p64d104f14 |
| **5** | 32 | 5s25P65d105f14 |

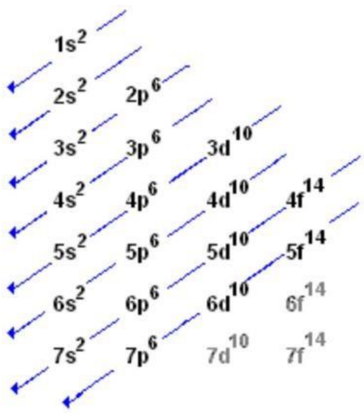
## Energy Level Diagram

A diagram representing roughly the energies of the electrons in the atoms is given Fig




The above diagram may also be represented as follows to indicate the increasing energies of the atomic orbitals:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p




## Aufbau Principle

- Electrons will first occupy orbitals of the lowest energy level.
- electrons will fill orbitals by the sum of the quantum numbers *n* and *l*. Orbitals with equal values of (*n*+*l*) will fill with the lower *n* values first.

### Aufbau Principle Exceptions

• Like most rules, there are exceptions. Half-filled and completely filled d and f subshells add stability to atoms, so the d and f block elements don't always follow the principal.

The electron configurations of
Cr(24)-$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ and Cu(29)-$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ occur because of the irregularities due to extra stabilities of filled and half-filled orbitals.

## Hund's Rules

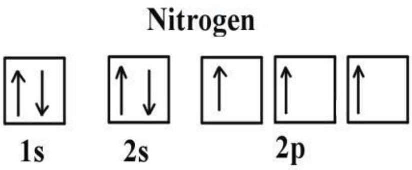
Hund's rule states that:

1. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.

2. All of the electrons in singly occupied orbitals have the same spin.

### Example 1: Nitrogen Atoms

Electron configuration of the nitrogen (Z = 7) atom: $1s^2\ 2s^2\ 2p^3$




### Example 2: Oxygen Atoms

Electronic configuration of oxygen (Z = 8) atom is: $1s^2\ 2s^2\ 2p^4$