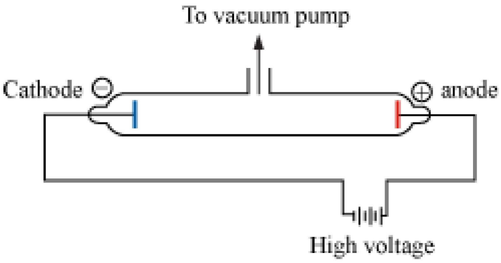
3. Structure of atom

Sub-atomic particles:

Name	**Symbol**	**Charge/C**	**Relative charge**	**Mass/kg**
Electron	e	-1.6022×10^{-19}	–1	9.1094×10^{-31}
Proton	p	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}
Neutron	n	0	0	1.6749×10^{-27}

Discovery of Electron



- Glass tube is partially evacuated (Low pressure inside the tube)
- Very high voltage is applied across the electrodes

Results:

- Cathode rays move from the cathode to the anode.
- Cathode rays are not visible.
- These rays travel in a straight line in the absence of electric and magnetic fields.
- The behaviour of cathode rays is similar to negatively charged particles (electrons) in the presence of an electrical or a magnetic field.
- Characteristics of cathode rays do not depend upon: the material of the electrodes and the nature of the gas present in the tube

Charge to Mass Ratio of Electron:

$$\frac{e}{m} = 1.7558820 \times 10^{11} \text{ Ckg}^{-1}$$

- **Atomic number** of an element is equal to the number of protons present in the atom and atomic mass is equal to the sum of the number of protons and neutrons present in it.

- **Isotopes** are atoms having the same atomic number and different atomic masses.

- **Isobars** are atoms having the same atomic mass and different atomic numbers.

Bohr's model of hydrogen atom

- The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy called orbit (stationary states or allowed energy states).
- Energy of an electron in the orbit does not change with time.

$\text{Angular momentum} = \mathrm{I} \times \omega$

$\mathrm{I} = \text{Moment of inertia} = m_e r^2$

$\omega = \text{Angular velocity} = \frac{v}{r} (v \text{ islinear velocity})$

Bohr's frequency rule

$$\boxed{\nu = \frac{\Delta E}{\mathrm{h}} = \frac{E_2 - E_1}{\mathrm{h}}}$$

Angular momentum $= \boxed{m_e vr}$

$$\boxed{m_e vr = n\frac{\mathrm{h}}{2\pi}}, n = 1, 2, 3.....$$

- ➢ $n = 1, 2, 3......$are principal quantum numbers

- ➢ $\boxed{r_n = n^2 a_0 ; a_0 = 529 \text{ pm}}$

  $\boxed{r_n}$ is the radii of the stationary states.

- ➢ $\boxed{E_n = -\mathrm{R}_H \left(\frac{1}{n^2}\right) n = 1,2,3.....}$

  R_H is Rydberg's constant.

Energy associated with ions such as He^+, Li^{2+}, etc. (hydrogen-like species) is –

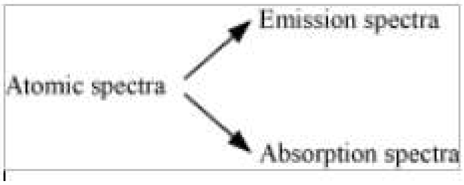
$$E_a = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right)J$$

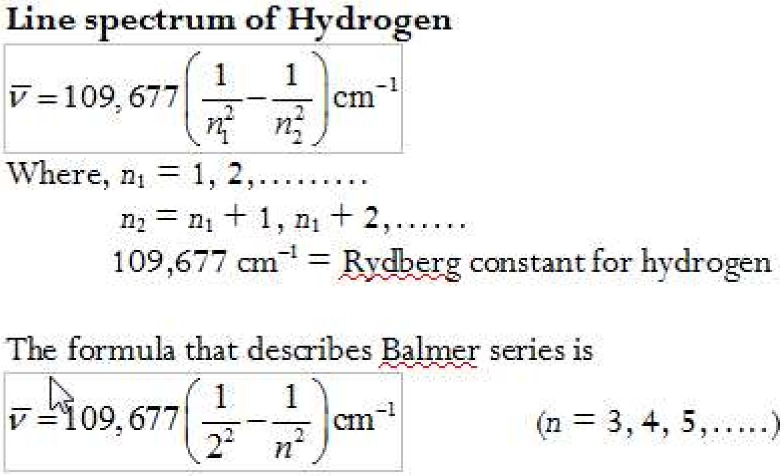
$$\text{Andradii}, r_n = \frac{52.9(n^2)}{Z}\text{pm}$$

Limitations of Bohr's model

- It was unable to explain the finer details of the hydrogen atom spectrum. It was also unable to explain the splitting of spectral lines in presence of magnetic and electric field.
- Could not explain the ability of atoms to form molecules by chemical bonds

Evidence for the quantized electronic energy levels:





Line spectrum of Hydrogen

$$\bar{\nu} = 109,677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1}$$

Where, $n_1 = 1, 2, \ldots\ldots\ldots$

$n_2 = n_1 + 1, n_1 + 2, \ldots\ldots$

109,677 cm^{-1} = Rydberg constant for hydrogen

The formula that describes Balmer series is

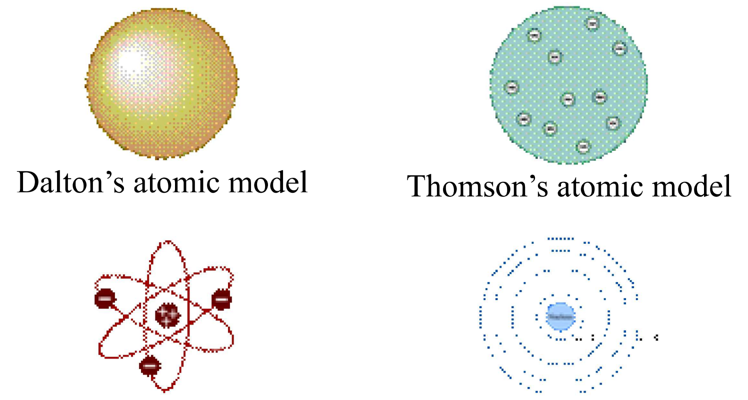
$$\bar{\nu} = 109,677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^{-1} \qquad (n = 3, 4, 5, \ldots\ldots)$$

Spectral lines for atomic hydrogen:

Series	n_1	n_2	**Spectral region**
Lyman	1	2, 3,….	UV
Balmer	2	3, 4,….	Visible
Paschen	3	4, 5,….	IR
Brackett	4	5, 6,….	IR
Pfund	5	6, 7,….	IR

- **Bohr's atomic model**:

- Neils Bohr proposed that the electrons present around the nucleus revolve in specific orbits called energy levels.
- He also stated that the electrons do not release energy while revolving. Thus, the resulting atom is a stable one.
- The shells in which the electrons are present are known as K, L, M, N, and so on (or 1, 2, 3, 4, and so on), as proposed by Bohr and Bury.
- Each shell contains a specific number of electrons, which can be calculated using the formula $2n^2$.



Atomic Models

Dalton’s atomic model

Thomson’s atomic model

Rutherford’s atomic model

Bohr’s atomic model

- Valency is defined as the combining capacity of the atom of an element. Valency of an element depends upon the number of electrons present in the outermost shell of its atom.

Dual behaviour of matter (de Broglie equation):

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

Heisenberg’s Uncertainty Principle:

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

$$\text{Or, } \Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

Where,

Δx = uncertainty in position

Δp = uncertainty in momentum

Quantum mechanical model of atom:

Schrodinger equation:

$$\widehat{H}\psi = E\psi$$

$\widehat{H}$ is Hamiltonian operator.

Orbitals and Quantum numbers:

- **Principal quantum number (*n*)**

n = 1 2 3 4….

Shell = K L M N….

- **Azimuthal quantum number (*l*)**

For a given value of n, possible values of ‘l’ are: 0, 1, 2, 3, …….(n – 1)

L	0	1	2	3	4	5…
Notation for sub-shell	*s*	*p*	*d*	*f*	*g*	*h*...

- **Magnetic quantum number (m_l)**

For any sub-shell,

$$m_l = -l, -(l-1), -(l-2).....0, 1, ...(l-2), (l-1), l$$

Value of *l*	0	1	2	3	4	5
Sub-shell notation	*s*	*p*	*d*	*f*	*g*	*h*
No. of orbitals	1	3	5	7	9	11

- **Electron spin:**

$m_s = +\frac{1}{2}(\uparrow)$ or $-\frac{1}{2}(\downarrow)$

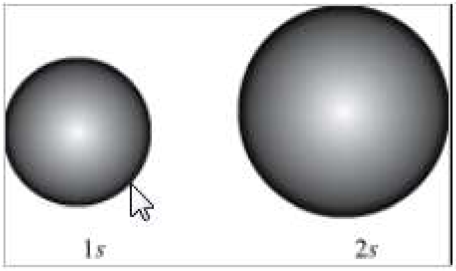
Five d – orbitals: d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}

Three p – orbitals: p_x, p_y, p_z

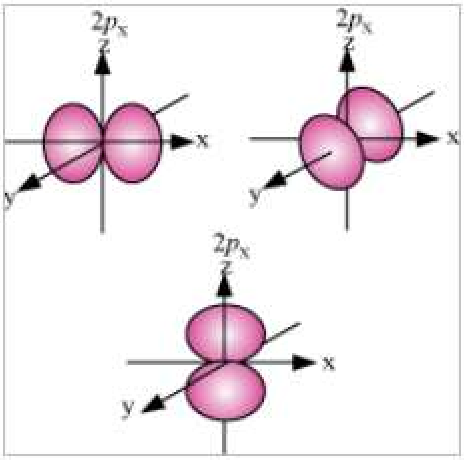
And, there are seven *f* orbitals.

Shapes of Atomic Orbitals

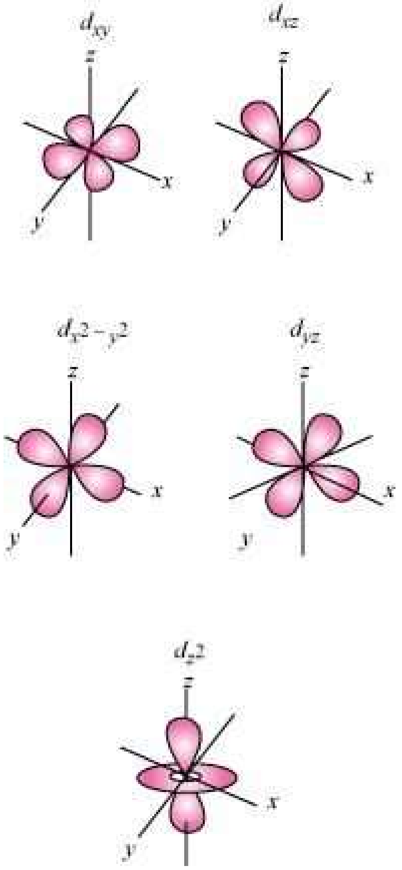
- Boundary surface diagrams for 1*s* and 2*s* orbitals are:



- Boundary surface diagram for three 2p orbitals



- Boundary diagrams for the five 3*d* orbitals are shown in the figure below.



- The total number of nodes is given by (*n*-1) i.e, sum of *l* angular nodes and (*n*-*l*-1) radial nodes.

Energies of Orbitals

Energy of the orbitals in a hydrogen atom increases as

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \ldots$$

Energy of the orbitals in a multi-electron atom follows the following rules:

- Lower the value of $(n + l)$ of an orbital, lower is its energy.
- When the two orbitals have same $(n + l)$ value, the orbital with lower value of 'n' will have lower energy.

Aufbau's principle:

- The orbitals are filled in order of their increasing energies (in the ground state).
- Increasing order of the energy of the orbitals and hence, the order of the filling of orbitals: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 4*f*, 5*d*, 6*p*, 7*s*, …

Pauli Exclusion Principle:

No two electrons in an atom can have the same set of four quantum numbers.

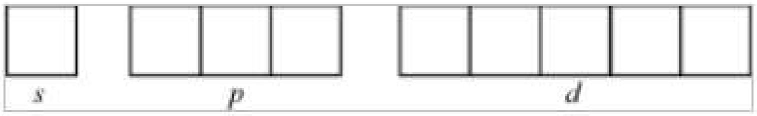
Hund's Rule of maximum Multiplicity:

Pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

- Electronic configuration of different atoms can be represented as:

(i) $s^a \; p^b \; d^c$............ notation

(ii) Orbital diagram



- Fully-filled and half-filled orbitals are the stable orbitals.

Exceptional cases in electronic configuration

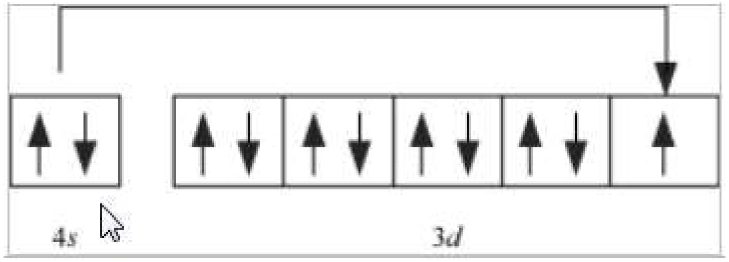
Configurations where the outer sub-shells are half-filled or completely filled provide extra stability to the atom. This is owing to the following reasons:

- Greater symmetry
- Greater exchange energy

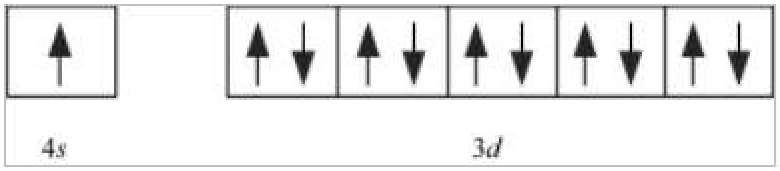
Elements such as Chromium (Cr) and Copper (Cu) deviate from the general rule of electronic configuration to attain half-filled and completely filled configuration respectively ensuring extra stability.

Copper (Z=29)

The expected configuration of Cu (Z=29) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$
But the actual configuration is obtained by promoting one electron from 4*s* to 3*d* as shown below:



The actual outer configuration of Cu then becomes:



The above configuration is preferred by copper because it has fully filled '*d*' sub-shell which is more stable.

Hence the actual configuration of Copper is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$