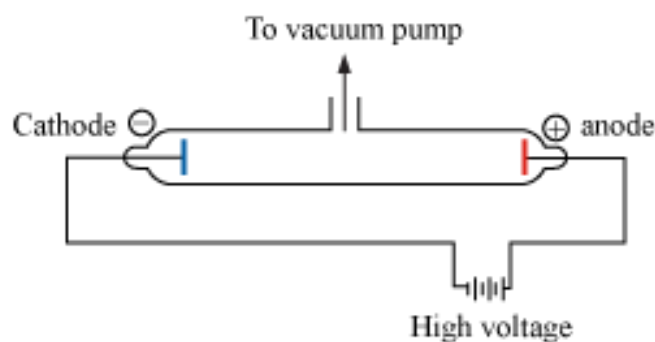


Structure of Atom

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:

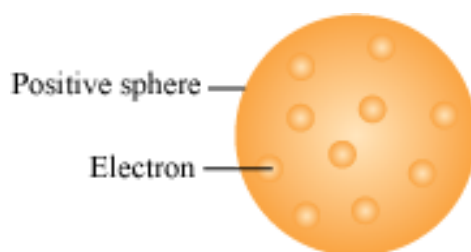
- Cathode rays move from the cathode to the anode.
- Cathode rays are not visible.
- These rays travel in a straight line in the absence of electric and magnetic fields.

- 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:

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

- Atoms are not indivisible and are composed of three fundamental particles. These particles are electrons, protons, and neutrons.
- **Charged particles in Matter**
 - Electrons are negatively-charged particles. They were discovered by J. J. Thomson, by cathode ray experiment.
 - Canal rays are positively charged radiation consisting of protons. Protons are positively-charged particles and were discovered by E. Goldstein.
 - The third fundamental particles present in an atom are neutrons. They are electrically-neutral and were discovered by J. Chadwick.
 - Various models were given to explain the structure of atom.
- **Thomson's atomic model:**
 - Thomson thought that an atom is a sphere of positive charge in which electrons are embedded.
 - An atom as a whole is electrically neutral because the negative and positive charges are equal in magnitude.



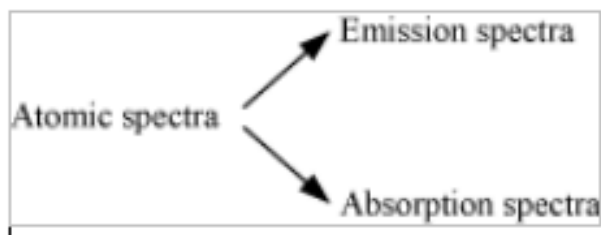
- **Rutherford's atomic model:**

- On the basis of his experiments with alpha rays and gold foil, Rutherford concluded that Thomson's atomic model was incorrect.
- He proposed an atomic model based on the results of his experiments.
- In this model, all the positive charges (i.e., protons) were present at the centre of the atom, inside the nucleus, and the electrons were present in circular orbits around the nucleus.
- He said that the electrons are not at rest and keep moving continuously in these circular orbits.
- He also said that the size of the nucleus is very small as compared to that of the atom.

- **Drawbacks of Rutherford's Model**

- It cannot explain the stability of an atom on the basis of classical mechanics and electromagnetic theory.
- If the electrons were stationary, then the strong electrostatic force of attraction between the dense nucleus and the electrons would pull the electrons towards the nucleus. Thus, it cannot explain the stability of an atom.
- Rutherford's model does not give any idea about the distribution of electrons around the nucleus (i.e., the electronic structure of the atom), and about their energy.
- It cannot explain the atomic spectra.

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, $n_1 = 1, 2, \dots$

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

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

The formula that describes Balmer series is

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

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 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.

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

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

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

Bohr's frequency rule

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

$$\text{Angular momentum} = m_e v r$$

$$m_e v r = n \frac{h}{2\pi}, n = 1, 2, 3, \dots$$

➤ $n = 1, 2, 3, \dots$ are principal quantum numbers

$$\text{➤ } r_n = n^2 a_0; a_0 = 529 \text{ pm}$$

r_n is the radii of the stationary states.

$$\text{➤ } E_n = -R_H \left(\frac{1}{n^2} \right) n = 1, 2, 3, \dots$$

R_H is Rydberg's constant.

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

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

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

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

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:

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

\hat{H} is Hamiltonian operator.

Orbitals and Quantum numbers:

- Principal quantum number (n)

$$n = 1 \ 2 \ 3 \ 4 \dots$$

$$\text{Shell} = K \ L \ M \ N \dots$$

- **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 | <i>s</i> | <i>p</i> | <i>d</i> | <i>f</i> | <i>g</i> | <i>h</i> ... |

- **Magnetic quantum number (m_l)**

For any sub-shell,

$$m_l = -l, -(l-1), -(l-2), \dots, 0, 1, \dots, (l-2), (l-1), l$$

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

- **Electron spin:**

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

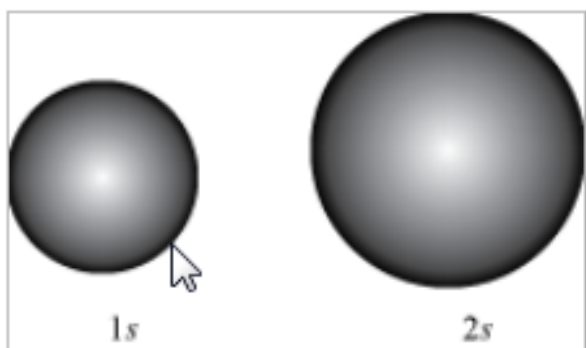
Five d – orbitals: d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2}

Three p – orbitals: p_x , p_y , p_z

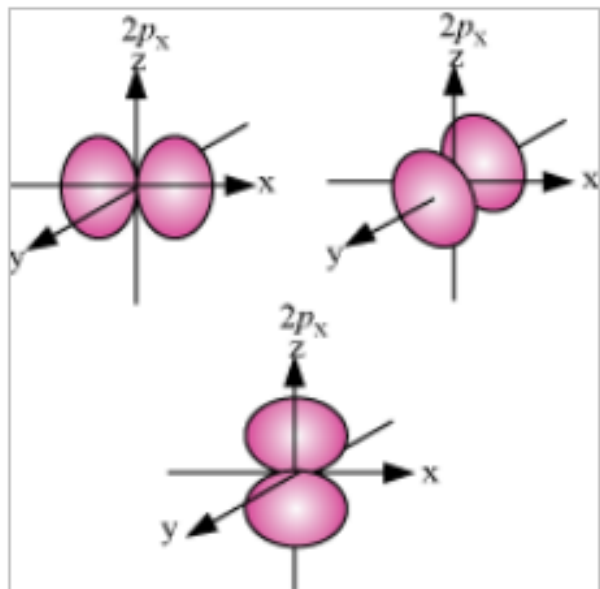
And, there are seven *f* orbitals.

Shapes of Atomic Orbitals

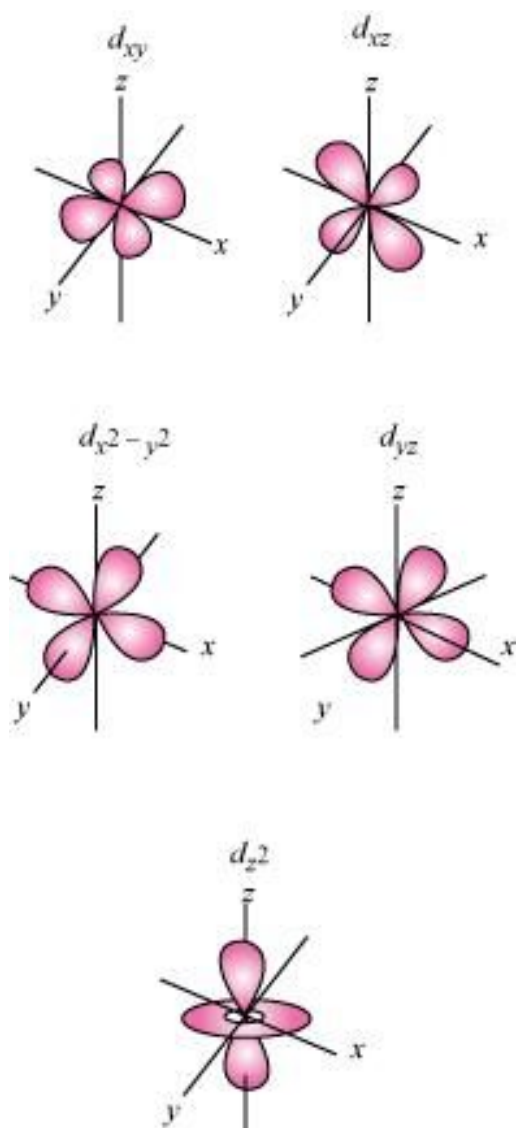
- Boundary surface diagrams for 1s and 2s orbitals are:



- Boundary surface diagram for three $2p$ orbitals



- Boundary diagrams for the five $3d$ 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

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

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: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s, \dots$

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) $s^a p^b d^c \dots\dots\dots$ notation

(ii) Orbital diagram



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

Exceptional cases in electronic configuration

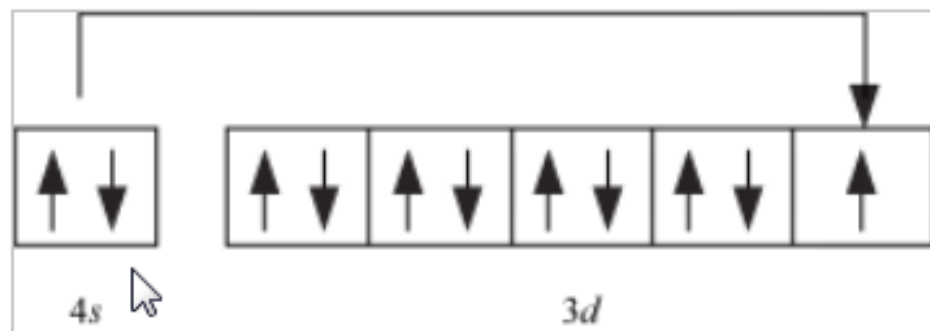
Configurations where the outer sub-shells are half-filled or completely filled provide extra stability to the atom. This is owing to the following reasons:

- Greater symmetry
- Greater exchange energy

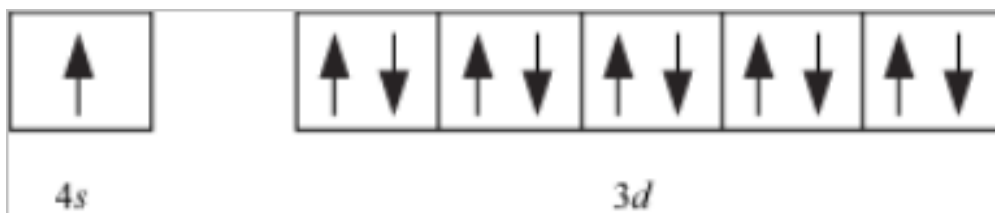
Elements such as Chromium (Cr) and Copper (Cu) deviate from the general rule of electronic configuration to attain half-filled and completely filled configuration respectively ensuring extra stability.

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 4s to 3d 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 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$