3. ATOMIC STRUCTURE

🎯 Learning outcomes

After the completion of the chapter, the students should be able to:

- ✓ Describe the Rutherford alpha ray scattering experiment and the nuclear atomic model
- ✓ Explain the limitations of Rutherford's atomic model.
- ✓ Summarise the postulates of Bohr's atomic theory and its importance.
- ✓ List the defects of Bohr's atomic theory
- ✓ Explain the origin of the hydrogen spectra with the help of Bohr's model.
- ✓ Explain the general idea about de Broglie's wave equation and probability.
- ✓ Explain quantum numbers and Planck's quantum theory.
- ✓ Explain the concept and general shapes of s, p, d, and f orbitals.
- ✓ Use the Aufbau principle, Pauli Exclusion Principle, and Hund's rule to write the electronic configuration of the atoms and ions.

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Rutherford's α-rays (α-particles) Scattering Experiment and Nuclear Model of the Atom

The Experiment (1911):

Ernest Rutherford bombarded a very thin **gold foil** (thickness ~10^{-5} cm) with **α-particles** (helium nuclei, **He^{2+}**) from a radioactive source. Scattered particles were detected on a circular **ZnS screen** that produced tiny flashes of light (scintillations).

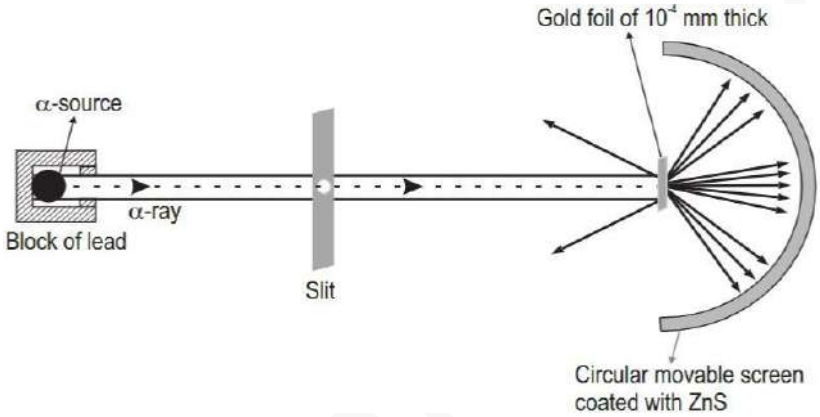

Fig: α-particles scattering experiment of Rutherford

Key Observations:

Observation	What This Tells Us
≥99% of α-particles passed straight through	An atom is mostly empty space
Some deflected at small angles	A small, dense positive region exists inside
Very few (~1 in 100,000) bounced back	The nucleus is extremely small but very massive

Based on the above conclusions, Rutherford put forward the following postulates for his model of the atom, called the Nuclear Model.

1) **Positive nucleus:** A very small, dense, positively charged nucleus sits at the centre and carries almost all the mass.
2) **Mostly empty:** The rest of the atom is largely empty space.
3) **Neutral atom:** The number of electrons outside equals the positive charge of the nucleus.
4) **Revolving electrons:** Electrons revolve around the nucleus, dispersed in the space around it.
5) **Force balance:** Electrostatic attraction between the nucleus and electrons is balanced by the centrifugal force of revolution.

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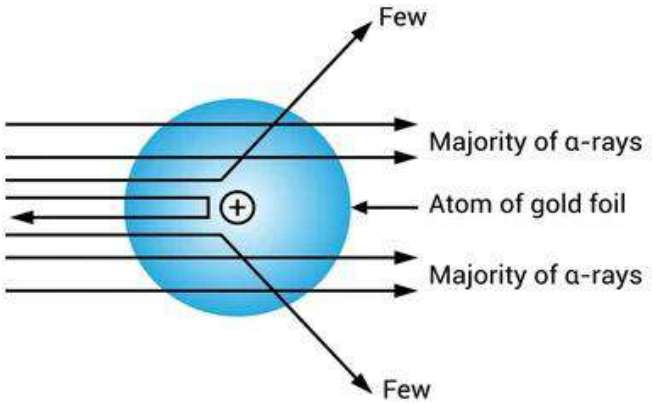
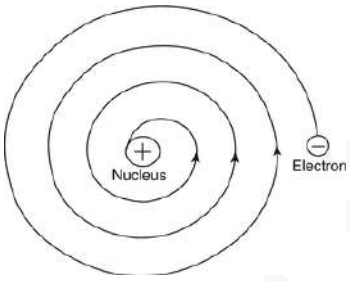


Figure: Explanation of α-particles scattering experiment.

Drawbacks of Rutherford's Atomic model

1. ⚠ **The stability of the atom**: According to classical electrodynamics, a moving charged body (electron) loses energy continuously in the field of another charge. If so, the electron should spiral inward and crash into the nucleus — but atoms are stable! Rutherford's model could not explain why atoms don't collapse.



2. ⚠ **Atomic spectra**: Classical physics predicts a continuous spectrum as the electron loses energy gradually. However, hydrogen (and other atoms) produces only **discrete lines** of specific wavelengths. Rutherford's model had no explanation for this

phet.colorado.edu/en/simulations/rutherford-scattering

Bohr's Atomic Model

Niels Bohr (1913), proposed the following postulates based upon Planck's quantum theory to overcome the shortcomings of Rutherford's atomic model.

The main postulates:

1. Electrons revolve around the nucleus in fixed concentric paths called orbits, shells, or energy levels.
2. As long as an electron remains in a particular shell, it neither loses nor gains energy. It means the energy of the electrons is constant; hence, these orbits are also called **stationary orbits**.
   The energies of electrons increase with increasing distance from the nucleus.

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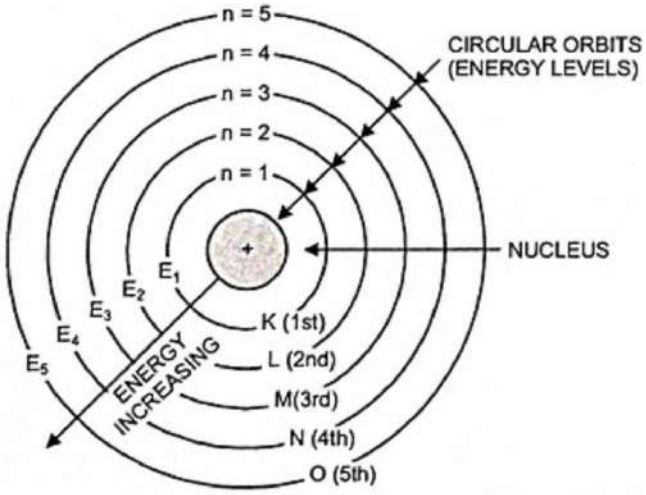
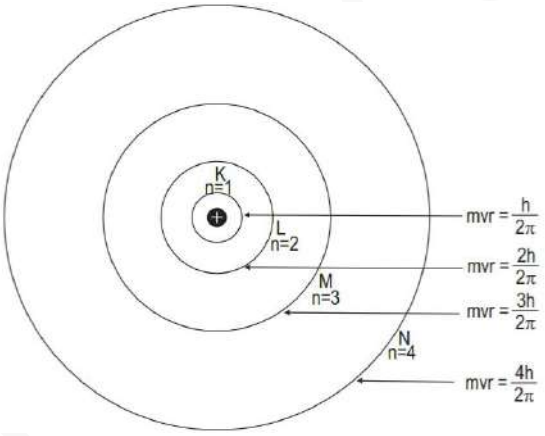


3. Only those orbits are possible where the **angular momentum** of the electrons is an integral multiple of h/2π. Or the angular momentum of the electrons is ***quantized***.

   i.e., angular momentum **(mvr) =** $\frac{nh}{2\pi}$ ……. (1)

   where, m = mass of electron
   r = radius of orbit
   v = linear velocity of the electron
   n = an integer representing the orbits
   (n = 1, 2, 3, ……∞)
   h = Plank's constant (6.624×10^{-34} Js)



This postulate explains the stability of atoms under ordinary conditions.

4. The electrostatic force of attraction between the nucleus and an electron is equal to the centrifugal force of the electrons. Due to this balance, the electron keeps revolving around the nucleus.

   Mathematically, $\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = \frac{mv^2}{r}$ ……(2)

   here, ε_0 = permittivity of the vacuum
   e = charge of electron (1.602×10^{-19} C)
   m = mass of an electron v = velocity of the electron
   r = radius of the orbit (distance from the nucleus)

5. The electrons emit or absorb the energy in the form of photons (or quanta) only when they jump from one energy level to another.

The energy absorbed or radiated equals the difference between the energy of an atom's lower and higher energy levels.

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

Where ΔE = difference in energy between the higher and the lower energy levels ΔE = energy of radiation emitted or absorbed

Hυ = energy of radiation
h = Planck's constant
υ = frequency of radiation (pronounced as 'neu')

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E_2 and E_1 = energy of an electron in a higher and lower orbit

The energy is absorbed when an electron jumps from a lower orbit to a higher orbit, and it is radiated when an electron jumps from a higher orbit to a lower orbit.

This postulate explains the origin of atomic spectra.

Successes of Bohr's atomic model

1. It overcame the defects of Rutherford's nuclear model of the atom, i.e., it explained the stability of an atom and the origin of atomic spectra in a one-electron system. (e.g., H, He^+, etc.)
2. It successfully calculated the radius and energy of an electron in an orbit. By using equations (1) and (2), it was derived,

$$r_n = \frac{\varepsilon_o n^2 h^2}{\pi m e^2} \quad \text{and} \quad E_n = \frac{-me^4}{8\varepsilon_0^2 n^2 h^2}$$

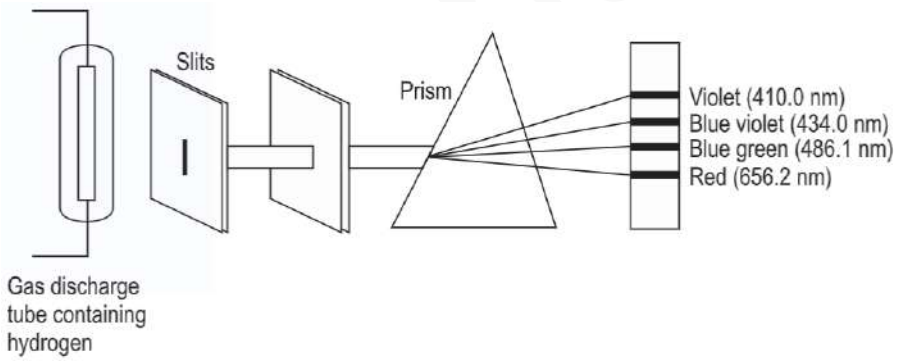
where, $r_n \rightarrow$ radius in n^{th} orbit & $E_n \rightarrow$ energy of electron in n^{th} orbit
and other symbols have the usual meanings.

Explanation of the stability of an atom by Bohr's atomic theory

According to Bohr's postulates, an electron cannot lose energy continuously, unlike explained by classical electrodynamics; instead, it may lose or gain energy only in the form of a packet called a ***quanta.*** On the other hand, the electron cannot fall from the first energy level to the nucleus since the angular momentum of an electron is quantized, and the value of mvr cannot be smaller than $h/2\pi$. Hence, electrons cannot be nearer to the nucleus than the first orbit.

Explanation of Hydrogen Spectra

When electrical energy is supplied through hydrogen gas filled in a discharge tube at very low pressure, the hydrogen molecules break into atoms. On supplying further energy, the electrons in these atoms, originally in the first shell, absorb energy and move to higher levels, i.e., n = 2, 3, 4, … etc. But an **excited electron**, being unstable, tends to jump back to lower energy levels and finally to the **ground state**, i.e., n = 1, after a very short interval of time. While returning to the lower energy level, the electrons emit energy in the form of radiation, which forms the atomic spectra.



On the jumping of the electron in different energy levels, different wavelength of radiation is produced as given by the following equation; this gives spectral lines of different series.

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

Where λ = wavelength of radiation
R = Rydberg's constant (R = 109700 cm^{-1})
n_1 & n_2 = lower and higher energy levels, respectively

Different scientists discovered different spectral series, so they got their names accordingly. Being in the visible part of the electromagnetic spectrum, the Balmer series was discovered first.

1. Lyman series:

These spectral lines are obtained when the electron returns from a higher energy level **($n_2 = 2, 3, 4 \ldots \infty$) to a ground state energy level ($n_1 = 1$)**. It lies in the ultraviolet region (λ = 912-1215A˚)

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2. Balmer series:

The spectral lines are obtained when the electron jumps to the second orbit **($n_1 = 2$) from higher orbits ($n_2 = 3, 4, 5, \ldots\infty$)**. It is in the visible part (λ = 3636-6563 A˚)

3. Paschen series:

These spectral lines are obtained when the electron jumps to the third shell **($n_1 = 3$) from higher energy levels ($n_2 = 4, 5, 6, \ldots\infty$).** It lies in the infrared region (λ = 9500-18750 A˚).

4. Brackett series:

The various spectral lines of this series are obtained on the jumping of electrons **from the fifth, sixth, seventh orbits, etc., to the fourth orbit**. It lies in the infrared region (IR).

5. Pfund series:

This is obtained when electrons return to **$n_1 = 5$ from $n_2 = 6, 7, 8\ldots$ etc**. It also lies in the IR region (λ = 37400-74000 A˚).

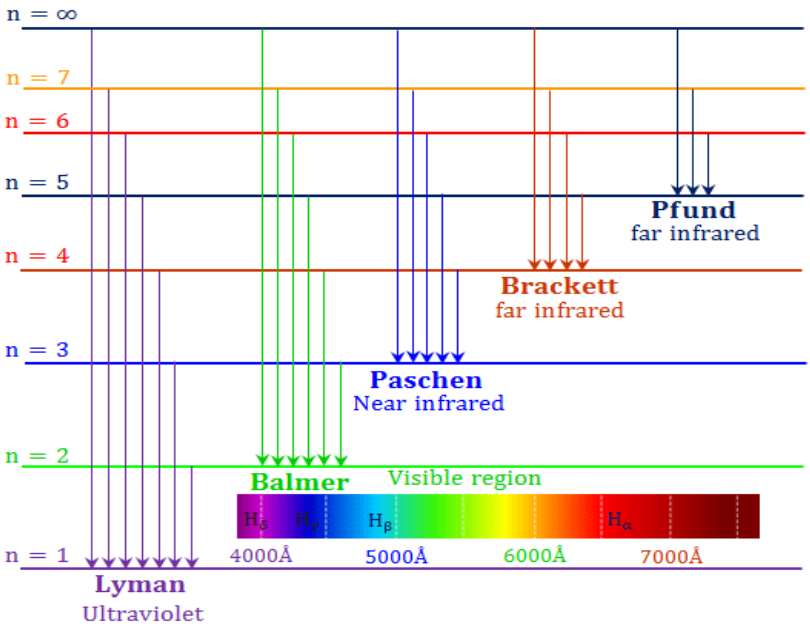

Figure: Origin of different spectral series obtained from different hydrogen atoms shown in a single diagram.

Spectral Series of Hydrogen:

Series	Transition ($n_2 \rightarrow n_1$)	Region	Wavelength Range
Lyman	n_1 = 1 from (n_2 = 2, 3, 4...)	Ultraviolet (UV)	912–1215 Å
Balmer	n_1 = 2 from (n_2 = 3, 4, 5...)	Visible	3636–6563 Å
Paschen	n_1 = 3 from (n_2 = 4, 5, 6...)	Infrared (IR)	9500–18750 Å
Brackett	n_1 = 4 from (n_2 = 5, 6, 7...)	Infrared (IR)	IR region
Pfund	n_1 = 5 from (n_2 = 6, 7, 8...)	Infrared (IR)	37400–74000 Å

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Defects of Bohr's Theory

1. **2D vs 3D:** Bohr's atomic model limits the electron's motion in a single plane (circular orbit). But atoms being **3-dimensional**, the electrons move in 3 dimensions.
2. **Multi-electron failure:** Bohr's theory could explain the spectral lines of single-electron systems like He^{+}, H, Li^{++}, etc., but **could not explain the multi-electron systems.**
3. **Fine structure:** The hydrogen spectrum under a high-resolution spectroscope shows several closely spaced **fine lines inside each line**. Bohr's model could not explain the origin of these fine structures.
4. **Zeeman & Stark effects:** The splitting of spectral lines into still thinner lines in the presence of magnetic and electric fields, called the **Zeeman and Stark effect**, respectively, could not be explained by Bohr's theory.
5. **Ignores wave nature:** According to **de-Broglie**, the electron behaves as a matter particle as well as a wave. According to **Heisenberg's Uncertainty Principle,** accurate measurement of the position and velocity of very small particles like an electron is not possible simultaneously. No such assumptions are in Bohr's theory.

Elementary Idea of Quantum Mechanical Model

The idea of only the particle nature of electrons and the concept of stationary orbits given by Bohr's theory are completely discarded by the de Broglie equation and Heisenberg's uncertainty principle. Later on, Schrodinger gave a more advanced model of atoms in the form of a wave equation, which takes into account electrons as particles as well as waves. Under this model, three different concepts are under consideration: 1. de-Broglie equation 2. Heisenberg's uncertainty principle 3. Probability concept.

de-Broglie Equation (Dual nature of matter)

de-Broglie(1924) suggested that, as light has dual character (particle and wave) all material particles in motion have dual character. He derived an equation for that, which was later verified experimentally.

Derivation of de Broglie's Equation:

From Planck's quantum theory (wave nature): $E = h\nu = hc/\lambda$ ...(1)

From Einstein's mass-energy equation (particle nature): $E = mc^2$ ...(2)

Combining (1) and (2): $hc/\lambda = mc^2 \Rightarrow \lambda = h/mc$

For an electron with mass m and velocity v:

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

λ = wavelength of electron | m = mass of electron | v = velocity | h = Planck's constant

This equation (3) is the de-Broglie equation.

Key Point:

For large objects (like a cricket ball), λ is negligibly small and unmeasurable. For tiny electrons, λ is significant and measurable. This is why **wave nature matters only for microscopic particles.**

It tells us that electrons can behave as particles as well as waves.

Heisenberg's Uncertainty Principle

A direct consequence of wave-particle duality: it is **impossible to simultaneously measure** both the **exact position** and **exact momentum** of a microscopic particle.

Mathematically, it is stated as follows;

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$\Delta p \times \Delta x \geq h/4\pi$

Where, Δp = Uncertainty in momentum; Δx = Uncertainty in position

The meaning of the above equation may be explained as follows;

1. If we measure the position accurately, its uncertainty becomes 0, then,
   $\Delta p.0 \geq \frac{h}{4\pi}$ or $\Delta p \geq \frac{h}{4\pi \times 0}$ or $\Delta p \geq \infty$

It means the uncertainty in momentum becomes infinitely large.

2. Similarly, if we measure the momentum accurately, the uncertainty in the position becomes infinite.

Probability Concept

Heisenberg's Uncertainty principle, de-Broglie equation, and wave mechanical model suggest that, as an electron can behave as a particle as well as a wave, its position and velocity cannot be measured accurately at the same time. So, it is evident that only the probability of locating an electron with a probable velocity in the particular region of space around the nucleus is possible. This leads to the concept of atomic orbitals.

Atomic Orbitals

The ***three-dimensional space*** in an atom around the nucleus ***where the probability of finding an electron is maximum*** is an atomic orbital.

Differences between an orbit and an orbital

Orbit (Bohr's model)	Orbital (Quantum model)
Circular path in a plane (2D)	3D region of space
Exact position of electron is known	Only probability of finding electron is given
Cannot explain molecular shapes	Can explain molecular shapes (directional)
Max electrons = $2n^2$	Max electrons per orbital = 2
Fixed, definite path	No fixed path; defined by probability

The shape of s - orbital

- Shape: **spherical** and symmetrical in all directions.
- 1s is a single sphere; 2s, 3s are **larger concentric spheres** with a node (zero probability region) between them.

The shape of p- orbitals

p-orbitals have a dumbbell shape with two lobes on the opposite side of the nucleus, as shown in the figure. There are three mutually perpendicular orbitals. These 3 p-orbitals have *equal energies* but *different orientations*; such orbitals are called ***degenerate orbitals***.

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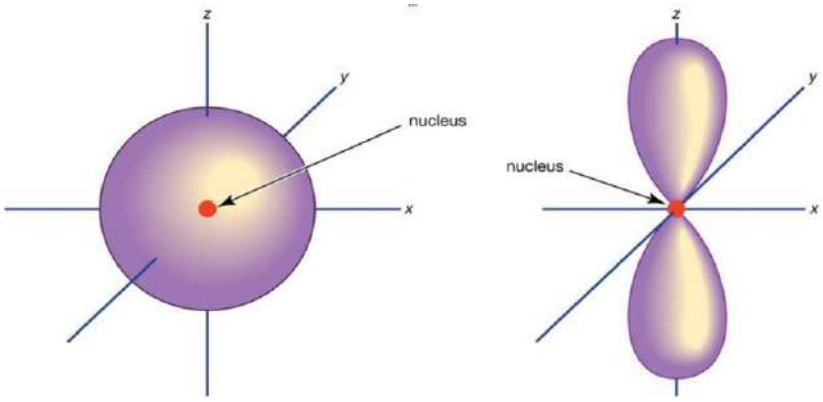

Figure: the shape of the orbital and p_z orbital

Quantum Numbers

Electrons are distributed in atoms in different shells represented by n = 1, 2, 3, 4, etc. These are called principal quantum numbers. Bohr had introduced them. Sommerfield introduced another quantum number called the azimuthal or Subsidiary quantum numbers. The wave mechanical treatment of atoms reveals that these numbers are not arbitrary. Now, it is clear that 4 sets of quantum numbers are needed to characterize an electron completely.

Quantum numbers can be defined as a set of numbers that give the energy, size, shape, and orientation of orbitals of electrons in an atom, as well as the spin of an electron.

1. Principal Quantum number (n)

- Introduced by Bohr's atomic model to ***represent the orbits.***
- has positive integer values n = 1, 2, 3, etc., which represent K, L, and M shells, respectively
- Determines the average ***distance of the electron from the nucleus*** and the average ***energy of an electron.***
- Helps to determine the maximum number of electrons that can be accommodated in a shell by *the $2n^2$ rule.*

n value	Shell	Max electrons ($2n^2$)	Subshells present
1	K	2	1s
2	L	8	2s, 2p
3	M	18	3s, 3p, 3d
4	N	32	4s, 4p, 4d, 4f

2. Azimuthal quantum number (l)

- Also called a **Subsidiary quantum number**.
- Mainly determines the ***orbital angular momentum of an electron.***
- ***Signifies the subshell*** to which the electron belongs.
- Helps to find the number of subshells in a given shell.
- Helps to determine the maximum number of electrons that can be accommodated in the given subshell by the ***2(2l+1) rule.***
- The Azimuthal quantum number may vary from ***0 to (n-1) for a given principal quantum number.***

n	1		2			3			4			
l	0	0	1	0	1	2		0	1	2	3	
subshell	s	s	p	s	p	d		s	p	d	f	

The azimuthal quantum number represents the relative energies of subshells and their shapes.
The energies of the subshell are in the following order: s < p < d < f

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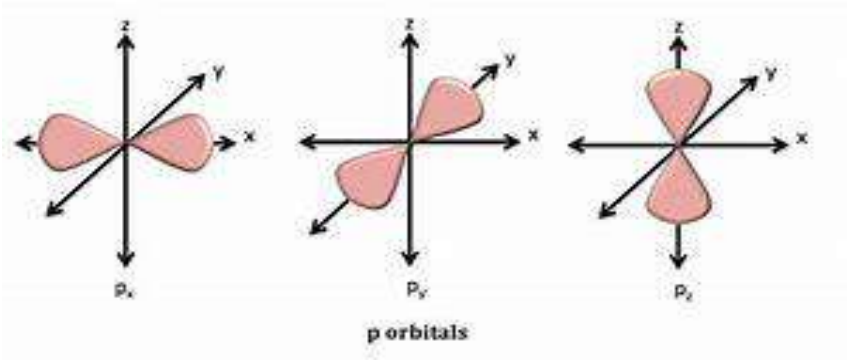
3. Magnetic Quantum Number (m)

- Describes the *behaviour of electrons in a magnetic field*.
- Signifies the ***orientation of the orbital*** in space in the presence of an external magnetic field.
- Or it *specifies the orbital* in which an electron lies.
- This successfully explains the ***Zeeman effect***.



p orbitals

For a given Azimuthal quantum number, l, the magnetic quantum number ranges from –l to 0 to +l.

l value	m values	No. of orbitals	Subshell
0	0	1	s (1 orbital)
1	−1, 0, +1	3	p (p_x, p_y, p_z)
2	−2, −1, 0, +1, +2	5	d (5 orbitals)
3	−3 to +3	7	f (7 orbitals)

4. Spin quantum numbers (s)

- determines the spin angular momentum or the direction of the spin of an electron around its axis.
- It can have only two values, +1/2 and -1/2, representing the electrons' clockwise and anticlockwise rotation.
- Two electrons in an orbital always have opposite spins. These are also represented by ↑ & ↓ or ↿ & ⇂.

Shell	**Principal quantum number(n)**	**Azimuthal quantum number(l) [0- (n-1)]**	**Magnetic quantum number(m) (-l to +l)**
K shell	n=1	0 (s-subshell)	0 (s-orbital)
L shell	n=2	0 (s-subshell) 1 (p-subshell)	0 (s- orbital) -1 (p_x-orbital) 0 (p_y-orbital) +1 (p_z-orbital)

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M shell	n=3	0 (s-subshell) 1(p-subshell 2 (d-subshell)	0 (s orbital) -1 (p_x-orbital) 0 (p_y-orbital) +1 (p_z-orbital) +2 (d_{xy} orbital) +1 (d_{yz} orbital) 0 (d_{xz} orbital) -1($d_{x^2-y^2}$ orbital) -2(d_{z^2}-orbital)

Pauli's Exclusion Principle

Pauli's exclusion principle states, ***"No two electrons* in an atom can have the same set of *four quantum numbers*."**

If two electrons in an atom are in different shells, their n values are different.
If two electrons of an atom are in the same shell, they might be in different subshells or have different l values.
If two electrons of an atom are in the same subshell, they can be in different orbitals or have different m values.
If two electrons of an atom are in the same orbital, they have different spin values.

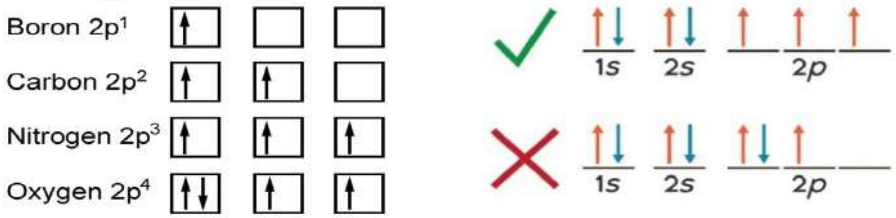
(Study the examples and explanations from the book and copy.)

Hund's Rule of Maximum Multiplicity

It states- **The pairing of electrons will not occur in any orbital until and unless all the available *degenerate orbitals* have one electron each with *parallel spin.***

This rule is based on the fact that negatively charged electrons repel each other. If two electrons move in the same region of space, e.g., $2p_x$ orbital, they will repel each other more strongly than if they move in different regions of space (e.g., $2p_x$ and $2p_y$ orbital). Thus, energetically, it is more favourable for them to go into different orbitals.

Illustration with examples:



Aufbau Principle

Aufbau is a German word meaning building up or construction. This principle states, "The orbitals are filled with electrons in increasing order of their energy."

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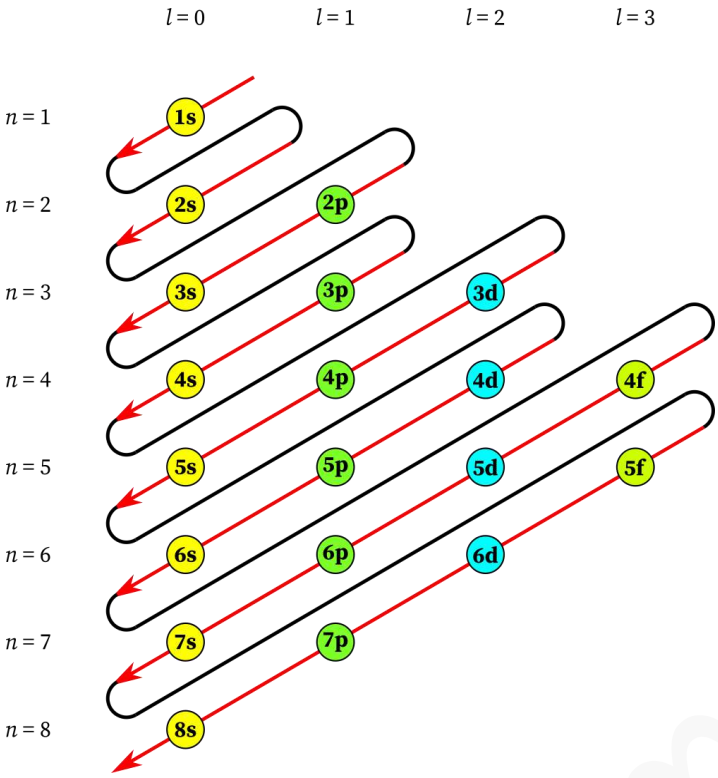
The principle may also be explained by the (n+l) rule. According to this rule,

1. The orbitals with the lower value of n+l are filled first.
2. When two orbitals have the same value of n+l, the orbital with a lower value of n is filled first.

The following device diagram can represent the sequence of filling of various subshells according to the Aufbau principle.



So, the electrons are filled in the following order;
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d,……..

Limitations of the Aufbau Principle (Exceptions)

Cr (chromium) (atomic number 24) has an electronic configuration of $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^5\,4s^1$ instead of $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^4\,4s^2$ because the half-filled d orbital is relatively more stable due to symmetry.

Similarly, Copper (29) has E.C. $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^{10}\,4s^1$ instead of $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^9\,4s^2$, because fully filled d-orbital is relatively more stable.

Bohr's Bury Rule

The maximum number of electrons a shell can hold equals the $2n^2$ rule, where n is the number of shells or principal quantum number.

The outermost shell cannot have more than 8 electrons, and the next to the outermost shell cannot have more than 18 electrons.

An orbit doesn't need to be completely filled before the next orbit starts filling. In fact, a new orbit begins when the outermost orbit gets 8 electrons.

Electronic Configurations of Atoms and Ions

The Nature of the Electron SIMPLIFIED in 5 Minutes!

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***** This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****

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