

2

Structure of Atom

—Wave Mechanical Approach

CHAPTER

CONTENTS

WAVE MECHANICAL CONCEPT OF ATOM

de BROGLIE'S EQUATION

HEISENBERG'S UNCERTAINTY PRINCIPLE

SCHRÖDINGER'S WAVE EQUATION

CHARGE CLOUD CONCEPT AND ORBITALS

QUANTUM NUMBERS

PAULI'S EXCLUSION PRINCIPLE

ENERGY DISTRIBUTION AND ORBITALS

DISTRIBUTION OF ELECTRONS IN ORBITALS

REPRESENTATION OF ELECTRON CONFIGURATION

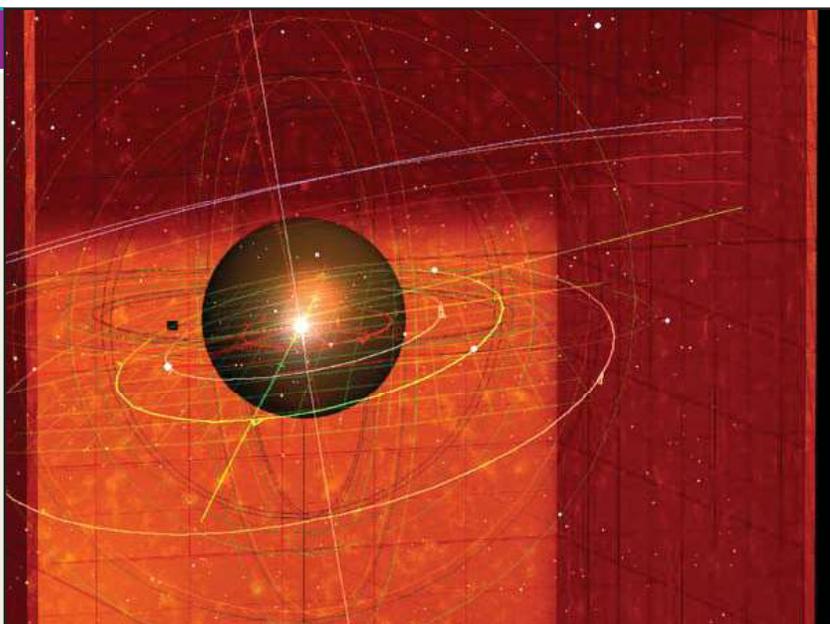
GROUND-STATE ELECTRON CONFIGURATION OF ELEMENTS

IONISATION ENERGY

MEASUREMENT OF IONISATION ENERGIES

ELECTRON AFFINITY

ELECTRONEGATIVITY



WAVE MECHANICAL CONCEPT OF ATOM

Bohr, undoubtedly, gave the first quantitative successful model of the atom. But now it has been superseded completely by the modern *Wave Mechanical Theory*. The new theory rejects the view that electrons move in closed orbits, as was visualised by Bohr. The Wave mechanical theory gave a major breakthrough by suggesting that the electron motion is of a complex nature best described by its wave properties and probabilities.

While the classical 'mechanical theory' of matter considered matter to be made of discrete particles (atoms, electrons, protons etc.), another theory called the 'Wave theory' was necessary to interpret the nature of radiations like X-rays and light. According to the wave theory, radiations as X-rays and light, consisted of continuous collection of waves travelling in space.

The wave nature of light, however, failed completely to explain the photoelectric effect *i.e.* the emission of electron from metal surfaces by the action of light. In their attempt to find a plausible explanation of radiations from heated bodies as also the photoelectric effect, Planck and Einstein (1905) proposed that energy radiations, including those of heat and light, are emitted

discontinuously as little ‘bursts’, quanta, or photons. This view is directly opposed to the wave theory of light and it gives particle-like properties to waves. **According to it, light exhibits both a wave and a particle nature, under suitable conditions.** This theory which applies to all radiations, is often referred to as the ‘**Wave Mechanical Theory**’.

With Planck’s contention of light having wave and particle nature, the distinction between particles and waves became very hazy. In 1924 Louis de Broglie advanced a complimentary hypothesis for material particles. According to it, the dual character—the wave and particle—may not be confined to radiations alone but should be extended to matter as well. In other words, matter also possessed particle as well as wave character. This gave birth to the ‘**Wave mechanical theory of matter**’. This theory postulates that electrons, protons and even atoms, when in motion, possessed wave properties and could also be associated with other characteristics of waves such as wavelength, wave-amplitude and frequency. **The new quantum mechanics, which takes into account the particulate and wave nature of matter, is termed the Wave mechanics.**

de BROGLIE’S EQUATION

de Broglie had arrived at his hypothesis with the help of Planck’s Quantum Theory and Einstein’s Theory of Relativity. He derived a relationship between the magnitude of the wavelength associated with the mass ‘ m ’ of a moving body and its velocity. According to Planck, the photon energy ‘ E ’ is given by the equation

$$E = h\nu \quad \dots(i)$$

where h is Planck’s constant and ν the frequency of radiation. By applying Einstein’s mass-energy relationship, the energy associated with photon of mass ‘ m ’ is given as

$$E = mc^2 \quad \dots(ii)$$

where c is the velocity of radiation

Comparing equations (i) and (ii)

$$mc^2 = h\nu = h \frac{c}{\lambda} \quad \left(\because \nu = \frac{c}{\lambda} \right)$$

$$\text{or} \quad mc = \frac{h}{\lambda} \quad \dots(iii)$$

$$\text{or} \quad \text{mass} \times \text{velocity} = \frac{h}{\text{wavelength}}$$

$$\text{or} \quad \text{momentum } (p) = \frac{h}{\text{wavelength}}$$

$$\text{or} \quad \text{momentum} \propto \frac{1}{\text{wavelength}}$$

The equation (iii) is called **de Broglie’s equation** and may be put in words as : **The momentum of a particle in motion is inversely proportional to wavelength, Planck’s constant ‘ h ’ being the constant of proportionality.**

The wavelength of waves associated with a moving material particle (matter waves) is called **de Broglie’s wavelength**. The de Broglie’s equation is true for all particles, but it is only with very small particles, such as electrons, that the wave-like aspect is of any significance. Large particles in motion though possess wavelength, but it is not measurable or observable. Let us, for instance consider de Broglie’s wavelengths associated with two bodies and compare their values.

(a) For a large mass

Let us consider a stone of mass 100 g moving with a velocity of 1000 cm/sec. The de Broglie’s wavelength λ will be given as follows :

$$\lambda = \frac{6.6256 \times 10^{-27}}{100 \times 1000} \quad \left(\lambda = \frac{h}{\text{momentum}} \right)$$

$$= 6.6256 \times 10^{-32} \text{ cm}$$

This is too small to be measurable by any instrument and hence no significance.

(b) For a small mass

Let us now consider an electron in a hydrogen atom. It has a mass = 9.1091×10^{-28} g and moves with a velocity 2.188×10^{-8} cm/sec. The de Broglie's wavelength λ is given as

$$\lambda = \frac{6.6256 \times 10^{-27}}{9.1091 \times 10^{-28} \times 2.188 \times 10^{-8}}$$

$$= 3.32 \times 10^{-8} \text{ cm}$$

This value is quite comparable to the wavelength of X-rays and hence detectable.

It is, therefore, reasonable to expect from the above discussion that **everything in nature possesses both the properties of particles (or discrete units) and also the properties of waves (or continuity)**. The properties of large objects are best described by considering the particulate aspect while properties of waves are utilized in describing the essential characteristics of extremely small objects beyond the realm of our perception, such as electrons.

THE WAVE NATURE OF ELECTRON

de Broglie's revolutionary suggestion that moving electrons had waves of definite wavelength associated with them, was put to the acid test by Davison and Germer (1927). They demonstrated the physical reality of the wave nature of electrons by showing that a beam of electrons could also be *diffracted* by crystals just like light or X-rays. They observed that the diffraction patterns thus obtained were just similar to those in case of X-rays. It was possible that electrons by their passage through crystals may produce secondary X-rays, which would show diffraction effects on the screen. Thomson ruled out this possibility, showing that the electron beam as it emerged from the crystals, underwent deflection in the electric field towards the positively charged plate.

Davison and Germers Experiment

In their actual experiment, Davison and Germer studied the scattering of slow moving electrons by reflection from the surface of nickel crystal. They obtained electrons from a heated filament and passed the stream of electrons through charged plates kept at a potential difference of V esu. Due to the electric field of strength $V \times e$ acting on the electron of charge e , the electrons emerge out with a uniform velocity v units. The kinetic energy $\frac{1}{2}mv^2$ acquired by an electron due to the electric field shall be equal to the electrical force. Thus,

$$\frac{1}{2}mv^2 = Ve$$

or
$$v = \sqrt{\frac{2Ve}{m}}$$

Multiplying by m on both sides,

$$mv = m\sqrt{\frac{2Ve}{m}} = \sqrt{2mVe} \quad \dots(i)$$

But according to de Broglie's relationship

$$mv = \frac{h}{\lambda} \quad \dots(ii)$$

Comparing (i) and (ii)

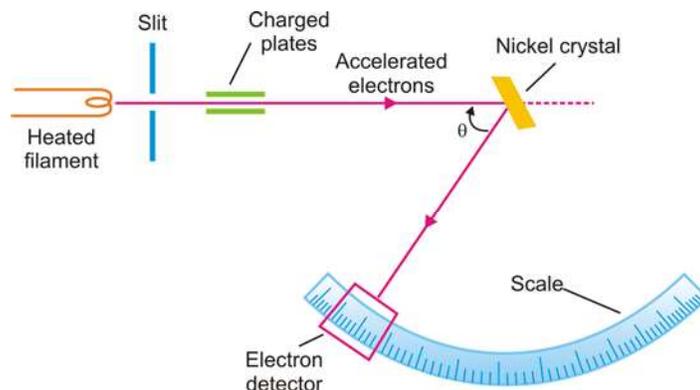
$$\frac{h}{\lambda} = \sqrt{2mVe}$$

$$\therefore \lambda = \frac{h}{\sqrt{2mVe}} = \sqrt{\frac{h^2}{2mVe}}$$

Substituting for $h = 6.6256 \times 10^{-27}$ erg-sec, $m = 9.1091 \times 10^{-28}$ g, $e = 4.803 \times 10^{-10}$ esu, and changing V esu to V volts by using the conversion factor $\frac{1}{3} \times 10^{-2}$, we have

$$\begin{aligned} \lambda &= \sqrt{\frac{(6.6256 \times 10^{-27})^2 \times 0.33 \times 10^{-2}}{2 \times 9.1091 \times 10^{-28} \times 4.803 \times 10^{-10} V \text{ volts}}} \\ &= \sqrt{\frac{150}{V \text{ volts}}} \times 10^{-8} \text{ cm} = \sqrt{\frac{150}{V \text{ volts}}} \text{ \AA} \quad \dots(iii) \end{aligned}$$

If a potential difference of 150 volts be applied, the wavelength of electrons emerging out is $\lambda = 1 \text{ \AA}$. Similarly if a potential difference of 1500 volts be created, the electrons coming out shall have a wavelength 0.1 \AA . It is clear, therefore, that electrons of different wavelengths can be obtained by changing the potential drop. These wavelengths are comparable with those of X-rays and can undergo diffraction.



■ **Figure 2.1**
Schematic representation of the apparatus
used by Davison and Germer.

The electrons when they fall upon the nickel crystal, get diffracted. Electrons of a definite wavelength get diffracted along definite directions. The electron detector measures the angle of diffraction (say θ) on the graduated circular scale. According to Bragg's diffraction equation, the wavelength λ of the diffracted radiation is given by $\lambda = d \sin \theta$, where d is a constant ($= 2.15$ for Ni crystal) and θ the angle of diffraction. By substituting the experimental value of θ in Bragg's equation ($\lambda = d \sin \theta$), the wavelength of electrons may be determined. This wavelength would be found to agree with the value of λ , as obtained from equation (iii).

Since diffraction is a property exclusively of wave motion, Davison and Germer's 'electron diffraction' experiment established beyond doubt the wave nature of electrons. We have described earlier in this chapter that electrons behave like particles and cause mechanical motion in a paddle

wheel placed in their path in the discharge tube. This proves, therefore, that electrons not only behave like ‘particles’ in motion but also have ‘wave properties’ associated with them. It is not easy at this stage to obtain a pictorial idea of this new conception of the motion of an electron. But the application of de Broglie’s equation to Bohr’s theory produces an important result. The quantum restriction of Bohr’s theory for an electron in motion in the circular orbit is that the angular momentum (mvr) is an integral multiple (n) of $h/2\pi$. That is,

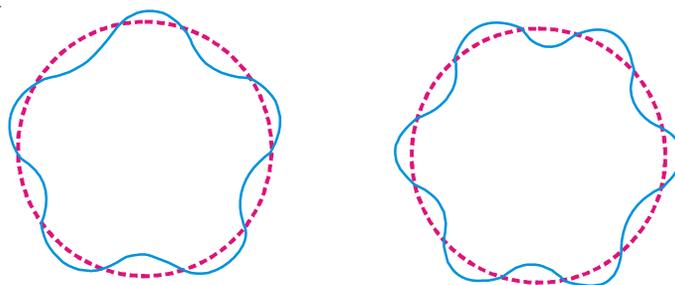
$$mvr = n \frac{h}{2\pi} \quad \dots \text{Bohr Theory}$$

On rearranging, we get

$$2\pi r = n \frac{h}{mv}$$

Putting the value of $\frac{h}{mv}$ from equation (i), we have

$$2\pi r = n\lambda \quad \left(\because \lambda = \frac{h}{mv} \right)$$



■ **Figure 2.2**

**de Broglie's wave accommodated in Bohr's orbits.
For these two wave trains the value of n is different.**

Now the electron wave of wavelength λ can be accommodated in Bohr's orbit only if the circumference of the orbit, $2\pi r$, is an integral multiple of its wavelength. Thus de Broglie's idea of standing electron waves stands vindicated. However, if the circumference is bigger, or smaller than $n\lambda$, the wave train will go out of phase and the destructive interference of waves causes radiation of energy.

SOLVED PROBLEM. Calculate the wavelength of an electron having kinetic energy equal to 4.55×10^{-25} J. ($h = 6.6 \times 10^{-34}$ kg m² sec⁻¹ and mass of electron = 9.1×10^{-31} kg).

SOLUTION

$$\begin{aligned} \text{Kinetic energy of an electron} &= \frac{1}{2} mv^2 \\ &= 4.55 \times 10^{-25} \text{ J (given)} \\ &= 4.55 \times 10^{-25} \text{ kg m}^2 \text{ sec}^{-2} \end{aligned}$$

$$\begin{aligned} \text{or} \quad v^2 &= \frac{2 \times 4.55 \times 10^{-25}}{m} \\ &= \frac{2 \times 4.55 \times 10^{-25} \text{ kg m}^2 \text{ sec}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \end{aligned}$$

$$\text{or} \quad v^2 = 1 \times 10^6 \text{ m}^2 \text{ sec}^{-2}$$

or $v = 1 \times 10^3 \text{ m sec}^{-1}$

We know $\lambda = \frac{h}{m \times v}$ (de Broglie equation)

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (1 \times 10^3 \text{ m sec}^{-1})}$$

$$= 7.25 \times 10^{-7} \text{ m}$$

$$= 7.25 \times 10^{-7} \times 10^9 \text{ nm}$$

$$= \mathbf{725 \text{ nm}}$$

SOLVED PROBLEM. Calculate the wavelength of an α particle having mass $6.6 \times 10^{-27} \text{ kg}$ moving with a speed of 10^5 cm sec^{-1} ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$)

SOLUTION. We know $\lambda = \frac{h}{mv}$ (de Broglie equation)

Given $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$

$$m = 6.6 \times 10^{-27} \text{ kg}$$

$$v = 1 \times 10^5 \text{ cm sec}^{-1}$$

$$= 1 \times 10^3 \text{ m sec}^{-1}$$

On substitution, we get

$$\lambda = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{6.6 \times 10^{-27} \text{ kg} \times 10^3 \text{ m sec}^{-1}}$$

$$= \mathbf{1 \times 10^{-10} \text{ m}}$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

One of the most important consequences of the dual nature of matter is the uncertainty principle developed by Werner Heisenberg in 1927. This principle is an important feature of wave mechanics and discusses the relationship between a pair of *conjugate properties* (those properties that are independent) of a substance. According to the uncertainty principle, it is impossible to know simultaneously both the conjugate properties accurately. For example, the position and momentum of a moving particle are interdependent and thus conjugate properties also. Both the position and the momentum of the particle at any instant cannot be determined with absolute exactness or certainty. If the momentum (or velocity) be measured very accurately, a measurement of the position of the particle correspondingly becomes less precise. On the other hand if position is determined with accuracy or precision, the momentum becomes less accurately known or uncertain. **Thus certainty of determination of one property introduces uncertainty of determination of the other.** The uncertainty in measurement of position, Δx , and the uncertainty of determination of momentum, Δp (or Δmv), are related by Heisenberg's relationship as

$$\Delta x \times \Delta p \geq \frac{h}{2\pi}$$

or $\Delta x \times m \Delta v \geq \frac{h}{2\pi}$

where h is Planck's constant.

It may be pointed out here that there exists a clear difference between the behaviour of large objects like a stone and small particles such as electrons. **The uncertainty product is negligible in case of large objects.**

For a moving ball of iron weighing 500 g, the uncertainty expression assumes the form

$$\Delta x \times m \Delta v \geq \frac{h}{2\pi}$$

or

$$\Delta x \times \Delta v \geq \frac{h}{2\pi m}$$

$$\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 500} \approx 5 \times 10^{-31} \text{ erg sec g}^{-1}$$

which is very small and thus negligible. Therefore for large objects, the uncertainty of measurements is practically nil.

But for an electron of mass $m = 9.109 \times 10^{-28}$ g, the product of the uncertainty of measurements is quite large as

$$\Delta x \times \Delta v \geq \frac{h}{2\pi m}$$

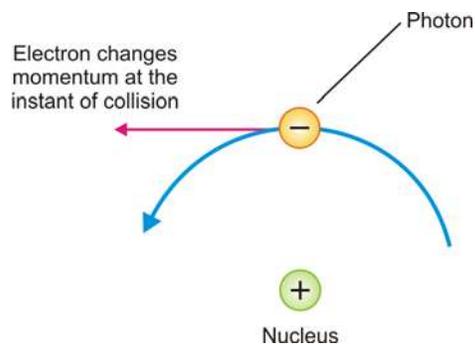
$$\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.109 \times 10^{-28}} \approx 0.3 \text{ erg sec g}^{-1}$$

This value is large enough in comparison with the size of the electron and is thus in no way negligible. If position is known quite accurately *i.e.*, Δx is very small, the uncertainty regarding velocity Δv becomes immensely large and *vice versa*. It is therefore very clear that **the uncertainty principle is only important in considering measurements of small particles comprising an atomic system.**

Physical Concept of Uncertainty Principle

The physical concept of uncertainty principle becomes illustrated by considering an attempt to measure the position and momentum of an electron moving in Bohr's orbit. To locate the position of the electron, we should devise an instrument 'supermicroscope' to see the electron. A substance is said to be seen only if it could reflect light or any other radiation from its surface. Because the size of the electron is too small, its position at any instant may be determined by a supermicroscope employing light of very small wavelength (such as X-rays or γ -rays). A photon of such a radiation of small λ , has a great energy and therefore has quite large momentum. As one such photon strikes the electron and is reflected, it instantly changes the momentum of electron. Now the momentum gets changed and becomes more uncertain as the position of the electron is being determined (Fig. 2.3). Thus it is impossible to determine the exact position of an electron moving with a definite velocity (or possessing definite energy). It appears clear that the Bohr's picture of an electron as moving in an orbit with fixed velocity (or energy) is completely untenable.

As it is impossible to know the position and the velocity of any one electron on account of its small size, the best we can do is to speak of the probability or *relative chance* of finding an electron with a probable velocity. **The old classical concept of Bohr has now been discarded in favour of the probability approach.**



■ **Figure 2.3**

The momentum of the electron changes when a photon of light strikes it, so does its position.

SOLVED PROBLEM. Calculate the uncertainty in position of an electron if the uncertainty in velocity is $5.7 \times 10^5 \text{ m sec}^{-1}$.

SOLUTION. According to Heisenberg's uncertainty principle

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

or
$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or
$$\Delta x = \frac{h}{4\pi m \times \Delta v}$$

Here
$$\Delta v = 5.7 \times 10^5 \text{ m sec}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

On substitution we get

$$\begin{aligned} \Delta x &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.14 \times (9.1 \times 10^{-31} \text{ kg}) (5.7 \times 10^5 \text{ m sec}^{-1})} \\ &= \frac{6.6 \times 10^{-8}}{4 \times 3.14 \times 9.1 \times 5.7} \text{ m} \\ &= 1 \times 10^{-10} \text{ m} \end{aligned}$$

SOLVED PROBLEM. The uncertainty in the position and velocity of a particle are 10^{-10} m and $5.27 \times 10^{-24} \text{ m sec}^{-1}$ respectively. Calculate the mass of the particle.

SOLUTION. We know
$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

or
$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or
$$m = \frac{h}{4\pi \times \Delta x \times \Delta v}$$

Here
$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$\Delta x = 1 \times 10^{-10} \text{ m}$$

$$\Delta v = 5.27 \times 10^{-24} \text{ m sec}^{-1}$$

Substituting the values, we get

$$\begin{aligned} m &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.14 \times (1 \times 10^{-10} \text{ m}) (5.27 \times 10^{-24} \text{ m sec}^{-1})} \\ &= 0.10 \text{ kg} \\ &= 100 \text{ g} \end{aligned}$$

SCHRÖDINGER'S WAVE EQUATION

In order to provide sense and meaning to the probability approach, Schrödinger derived an equation known after his name as **Schrödinger's Wave Equation**. Calculation of the probability of finding the electron at various points in an atom was the main problem before Schrödinger. **His equation is the keynote of wave mechanics and is based upon the idea of the electron as 'standing wave' around the nucleus.** The equation for the standing wave*, comparable with that of a stretched string is

* For the derivation of equation for a 'standing wave' in a stretched string, the reader may refer to a book on Physics (Sound).

$$\psi = A \sin 2\pi \frac{x}{\lambda} \quad \dots(a)$$

where ψ (pronounced as *sigh*) is a mathematical function representing the amplitude of wave (called *wave function*) x , the displacement in a given direction, and λ , the wavelength and A is a constant.

By differentiating equation (a) twice with respect to x , we get

$$\frac{d\psi}{dx} = A \frac{2\pi}{\lambda} \cos 2\pi \frac{x}{\lambda} \quad \dots(1)$$

and
$$\frac{d^2\psi}{dx^2} = -A \frac{4\pi^2}{\lambda^2} \sin 2\pi \frac{x}{\lambda} \quad \dots(2)$$

But
$$A \sin 2\pi \frac{x}{\lambda} = \psi$$

\therefore
$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \dots(3)$$

The K.E. of the particle of mass m and velocity v is given by the relation

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2} \frac{m^2 v^2}{m} \quad \dots(4)$$

According to Broglie's equation

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

or
$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

or
$$m^2 v^2 = \frac{h^2}{\lambda^2}$$

Substituting the value of $m^2 v^2$, we have

$$\text{K.E.} = \frac{1}{2} \times \frac{h^2}{m\lambda^2} \quad \dots(5)$$

From equation (3), we have

$$\lambda^2 = -\frac{4\pi^2\psi}{\frac{d^2\psi}{dx^2}} \quad \dots(6)$$

Substituting the value of λ^2 in equation (5)

$$\begin{aligned} \text{K.E.} &= -\frac{1}{2m} \cdot \frac{h^2}{4\pi^2\psi} \cdot \frac{d^2\psi}{dx^2} \\ &= -\frac{h^2}{8\pi^2 m\psi} \cdot \frac{d^2\psi}{dx^2} \end{aligned}$$

The total energy E of a particle is the sum of kinetic energy and the potential energy

i.e.,
$$E = \text{K.E.} + \text{P.E.}$$

or
$$\text{K.E.} = E - \text{P.E.}$$

$$= -\frac{h^2}{8\pi^2 m\psi} \cdot \frac{d^2\psi}{dx^2}$$

or
$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E - \text{P.E.}) \psi$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

This is Schrödinger's equation in one dimension. It need be generalised for a particle whose motion is described by three space coordinates x , y and z . Thus,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

This equation is called the **Schrödinger's Wave Equation**. The first three terms on the left-hand side are represented by $\Delta^2\psi$ (pronounced as del-square sigh).

$$\Delta^2 \psi + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \psi = 0$$

Δ^2 is known as **Laplacian Operator**.

The Schrödinger's wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and are not valid. If the potential energy term is known, the total energy E and the corresponding wave function ψ can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible if E is given certain characteristic values called **Eigen-values**. Corresponding to these values of E , we have several characteristic values of wavefunction ψ and are called **Eigen-functions**. As the eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr's model may be considered as a direct consequence of wave mechanical approach.

Significance of ψ and ψ^2

In Schrödinger's wave equation ψ represents the amplitude of the spherical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of the sound or light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function ψ . This may be stated as the probability of finding an electron in an extremely small volume around a point. It is proportional to the square of the function ψ^2 at that point. If wave function ψ is imaginary, $\psi\psi^*$ becomes a real quantity where ψ^* is a complex conjugate of ψ . This quantity represents the probability ψ^2 as a function of x , y and z coordinates of the system, and it varies from one space region to another. Thus the probability of finding the electron in different regions is different. This is in agreement with the uncertainty principle and gave a death blow to Bohr's concept.

In Schrödinger's Wave Equation, **the symbol ψ represents the amplitude of the spherical wave**. For hydrogen atom, Schrödinger's Wave Equation gives the wave function of the electron (with energy = -2.18×10^{-11} ergs) situated at a distance ' r ',

$$\psi = C_1 e - C_2 r$$

where C_1 and C_2 are constants. The square of the amplitude ψ^2 is proportional to the density of the wave. **The wave of energy or the cloud of negative charge is denser in some parts than in others**. Max Born interpreted the wave equations on the basis of probabilities. Even if an electron be considered as a particle in motion around the nucleus, the wave equation may be interpreted in terms of probability or relative chance of finding the electron at any given distance from the nucleus. The space characteristic of an electron is best described in terms of distribution function given by

$$D = 4\pi r^2 \psi^2$$

The numerical value of ' D ' denotes the probability or chance of finding the electron in a shell of radius r and thickness dr , or of volume $4\pi r^2 dr$. Substituting for ψ we have,

$$D = 4\pi r^2 (C_1 e - C_2 r)^2$$

The probability of finding the electron is clearly a function of ' r '. When $r = 0$ or ∞ , the probability function D becomes equal to zero. In other words, there is no probability of finding the electron at the nucleus or at infinity. However, it is possible to choose a value of r such that there is 90-95 percent chance of finding the electron at this distance. For the hydrogen atom, this distance is equal to 0.53×10^{-8} cm or 0.53 \AA . If the probability distribution be plotted against the distance r from the nucleus, the curve obtained is shown in Fig. 2.4. The probability distribution is maximum at the distance 0.53 \AA and spherically symmetrical. This distance corresponds to Bohr's first radius a_0 . The graph can be interpreted as representing a contour that encloses a high-percentage of charge.

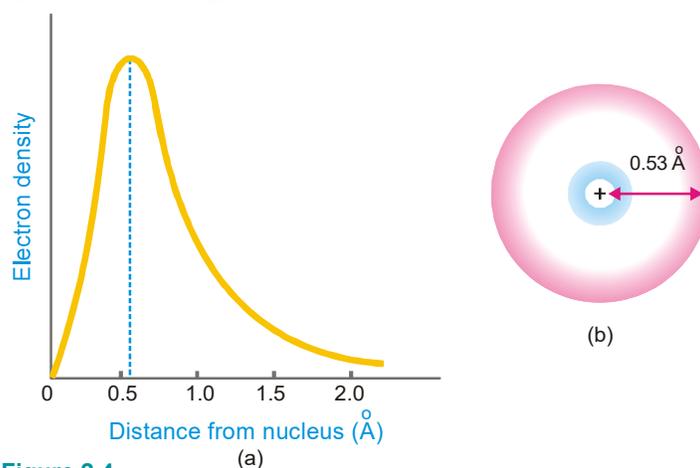
When the electron gets excited and it is raised from n to higher energy levels (say $n = 2$ or $n = 3$), the solution of wave equation gives sets of value of ψ^2 which give different shapes to the space distribution of the electron.

CHARGE CLOUD CONCEPT AND ORBITALS

The Charge Cloud Concept finds its birth from wave mechanical theory of the atom. The wave equation for a given electron, on solving gives a three-dimensional arrangement of points where it can possibly lie. There are regions where the chances of finding the electron are relatively greater. Such regions are expressed in terms of '**cloud of negative charge**'. We need not know the specific location of the electrons in space but are concerned with the negative charge density regions. Electrons in atoms are assumed to be vibrating in space, moving haphazardly but at the same time are constrained to lie in regions of highest probability for most of the time. **The charge cloud concept simply describes the high probability region.**

The three-dimensional region within which there is higher probability that an electron having a certain energy will be found, is called an orbital.

An orbital is the most probable space in which the electron spends most of its time while in constant motion. In other words, it is the spatial description of the motion of an electron corresponding to a particular energy level. **The energy of electron in an atomic orbital is always the same.**



■ **Figure 2.4**
Shows the probability distribution of electron cloud :
(a) gives the graphical representation while
(b) depicts cross-section of the cloud.

Each energy level corresponds to a three-dimensional electron wave which envelopes the nucleus. This wave possesses a definite 'size', 'shape' and 'orientation' and thus can be represented pictorially.

QUANTUM NUMBERS

Bohr's electronic energy shells or levels, designated as Principal Quantum Numbers ' n ', could

hardly explain the hydrogen spectrum adequately. Spectra of other elements that are quite complex, also remained unexplained by this concept. Many single lines of the spectra are found to consist of a number of closely related lines when studied with the help of sophisticated instruments of high resolving power. Also the spectral lines split up when the source of radiation is placed in a magnetic field (**Zeeman Effect**) or in an electrical field (**Stark Effect**).

To explain these facts, it is necessary to increase the number of ‘possible orbits’ where an electron can be said to exist within an atom. In other words, it is necessary to allow more possible energy changes within an atom (or a larger number of energy states) to account for the existence of a larger number of such observed spectral lines. Wave mechanics makes a provision for three more states of an electron in addition to the one proposed by Bohr. Like the energy states of Bohr, designated by $n = 1, 2, 3, \dots$, these states are also identified by numbers and specify the position and energy of the electron. Thus there are in all four such identification numbers called **quantum numbers** which fully describe an electron in an atom. Each one of these refers to a particular character.

Principal Quantum Number ‘ n ’

This quantum number denotes the principal shell to which the electron belongs. This is also referred to as **major energy level**. It represents the average size of the electron cloud *i.e.*, the average distance of the electron from the nucleus. This is, therefore, the main factor that determines the values of nucleus-electron attraction, or the energy of the electron. In our earlier discussion, we have found that the energy of the electron and its distance from the nucleus for hydrogen atom are given by

$$E_n = -\frac{313.3}{n^2} \text{ kcal}$$

$$\text{and} \quad r_n = 0.529 n^2 \text{ \AA}$$

where n is the principal quantum number of the shell.

The principal quantum number ‘ n ’ can have non-zero, positive, integral values $n = 1, 2, 3, \dots$ increasing by integral numbers to infinity. Although the quantum number ‘ n ’ may theoretically assume any integral value from 1 to ∞ , only values from 1 to 7 have so far been established for the atoms of the known elements in their ground states. In a polyelectron atom or ion, the electron that has a higher principal quantum number is at a higher energy level. An electron with $n = 1$ has the lowest energy and is bound most firmly to the nucleus.

The letters K, L, M, N, O, P and Q are also used to designate the energy levels or shells of electrons with a n value of 1, 2, 3, 4, 5, 6, 7 respectively. There is a limited number of electrons in an atom which can have the same principal quantum number and is given by $2n^2$, where n is the principal quantum number concerned. Thus,

Principal quantum number ($n =$)	1	2	3	4
Letter designation	K	L	M	N
Maximum number of electrons ($2n^2 =$)	2	8	18	32

Azimuthal Quantum number ‘ l ’

This is also called secondary or subsidiary quantum number. It defines the spatial distribution of the electron cloud about the nucleus and describes the angular momentum of the electron. In other words, **the quantum number l defines the shape of the orbital occupied by the electron and the angular momentum of the electron.** It is for this reason that ‘ l ’ is sometimes referred to as *orbital* or *angular quantum* number. For any given value of the principal quantum number n , the azimuthal quantum number l may have all integral values from 0 to $n - 1$, each of which refers to an *Energy sublevel* or *Sub-shell*. **The total number of such possible sublevels in each principal level is numerically equal to the principal quantum number of the level under consideration.** These sublevels

are also symbolised by letters s, p, d, f etc. For example, for principal quantum number $n = 1$, the only possible value for l is 0 *i.e.*, there is only one possible subshell *i.e.* s -subshell ($n = 1, l = 0$). For $n = 2$, there are two possible values of $l, l = 0$ and $l = 2 - 1 = 1$.

This means that there are two subshells in the second energy shell with $n = 2$. These subshells are designated as $2s$ and $2p$. Similarly, when $n = 3, l$ can have three values *i.e.* 0, 1 and 2. Thus there are three subshells in third energy shell with designations $3s, 3p$ and $3d$ respectively. For $n = 4$, there are four possible values of azimuthal quantum number l ($= 0, 1, 2$, and 3) each representing a different sublevel. In other words, the fourth energy level consists of four subshells which are designated as $4s, 4p, 4d$ and $4f$. Thus for different values of principal quantum numbers we have

$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$l = 0 (1s)$	$l = 0 (2s)$	$l = 0 (3s)$	$l = 0 (4s)$	$l = 0 (5s)$
	$l = 1 (2p)$	$l = 1 (3p)$	$l = 1 (4p)$	$l = 1 (5p)$
		$l = 2 (3d)$	$l = 2 (4d)$	$l = 2 (5d)$
			$l = 3 (4f)$	$l = 3 (5f)$
				$l = 4 (5g)$

For a given value of principal quantum number the order of increasing energy for different subshells is

$$s < p < d < f \quad (\text{except for H atom})$$

Magnetic Quantum Number ‘ m ’

This quantum number has been proposed to account for the splitting up of spectral lines (Zeeman Effect). An application of a strong magnetic field to an atom reveals that electrons with the same values of principal quantum number ‘ n ’ and of azimuthal quantum number ‘ l ’, may still differ in their behaviour. They must, therefore, be differentiated by introducing a new quantum number, the magnetic quantum number m . This is also called **Orientation Quantum Number** because it gives the orientation or distribution of the electron cloud. For each value of the azimuthal quantum number ‘ l ’, the magnetic quantum number m , may assume all the integral values between $+l$ to $-l$ through zero *i.e.*, $+l, (+l-1), \dots, 0, \dots, (-l+1), -l$. Therefore for each value of l there will be $(2l+1)$ values of m_l . Thus when $l=0, m=0$ and no other value. This means that **for each value of principal quantum number ‘ n ’, there is only one orientation for $l=0$ (s orbital) or there is only one s orbital.** For s orbital, there being only one orientation, it must be spherically symmetrical about the nucleus. There is only one spherically symmetrical orbital for each value of n whose radius depends upon the value of n .

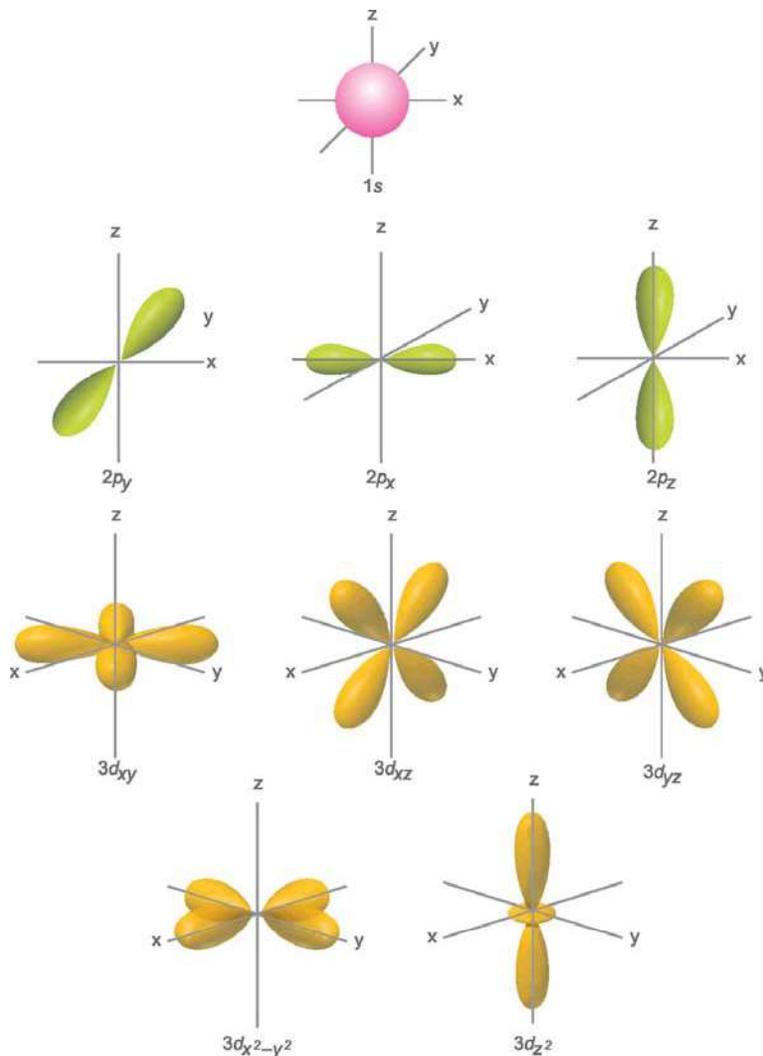


■ **Figure 2.5**
Spherical s orbitals, symmetrically disposed about the nucleus.

For $l = 1$ (p orbital), the magnetic quantum number m will have *three* values: $+1, 0$ and -1 ; so there are *three* orientations for p orbitals. These *three* types of p orbitals differ only in the value of magnetic quantum number and are designated as p_x, p_y, p_z depending upon the axis of orientation. The subscripts x, y and z refer to the coordinate axes. In the absence of a magnetic field, these three p orbitals are equivalent in energy and are said to be **three-fold degenerate** or **triply degenerate***. In

*Different orbitals of equivalent energy are called degenerate orbitals and are grouped together.

presence of an external magnetic field the relative energies of the three p orbitals vary depending upon their orientation or magnetic quantum number. This probably accounts for the existence of more spectral lines under the influence of an external magnetic field. The p orbitals are of dumb-bell shape consisting of two lobes. The two lobes of a p orbital extend outwards and away from the nucleus along the axial line. Thus the two lobes of a p orbital may be separated by a plane that contains the nucleus and is perpendicular to the corresponding axis. Such plane is called a **nodal plane**. **There is no likelihood of finding the electron on this plane.** For a p_x orbital, the yz plane is the nodal plane. The shapes and orientations of the p orbitals are given in Fig. 2.6.



■ **Figure 2.6**
Shapes and orientation of s , p and d orbitals.

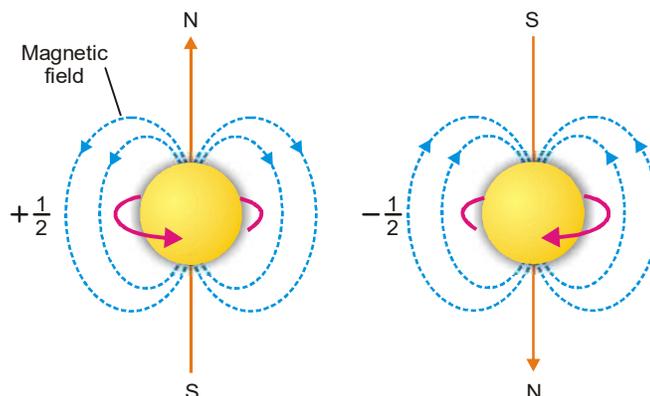
For $l = 2$ (d orbital), the magnetic quantum number are *five* ($2 \times 2 + 1$); $+2, +1, 0, -1, -2$. Thus there are five possible orientations for d orbitals which are equivalent in energy so long as the atom is not under the influence of a magnetic field and are said to be **five-fold degenerate** (Different orbitals of equivalent energy are called degenerate orbitals and are grouped together). The *five* d orbitals are

designated as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2} . These orbitals have complex geometrical shapes as compared to p orbitals. The conventional boundary surfaces or shapes of five d_{z^2} orbitals are shown in Fig. 2.6. The shape of the d_{z^2} orbitals is different from others.

When $l = 3$ (f orbital) the magnetic quantum number m can have *seven* ($2 \times 3 + 1$) values as $+3$, $+2$, $+1$, 0 , -1 , -2 and -3 . These *seven* orientations give rise to a set of **seven-fold degenerate orbitals**. These seven orbitals possess very complicated shapes and orientation in space. The shapes of s , p and d orbitals only are of interest to chemists.

Spin Quantum Number 's'

This quantum number has been introduced to account for the spin of electrons about their own axis. Since an electron can spin clockwise or anticlockwise (in two opposite directions), there are two possible values of s that are equal and opposite. As quantum numbers can differ only by unity from each other, there are two values given to s ; $+\frac{1}{2}$ and $-\frac{1}{2}$ depending upon whether the electron spins in one direction or the other. These spins are also designated by arrows pointing upwards and downward as $\downarrow\uparrow$. **Two electrons with the same sign of the spin quantum numbers are said to have parallel spins** while those having opposite signs of the spin quantum numbers are said to have **opposite spin** or **antiparallel spin** or **paired-up spin**.



■ **Figure 2.7**
Clockwise and anticlockwise spins of electrons about their own axis produce opposite magnetic fields.

Since a spinning charge is associated with a magnetic field, an electron must have a magnetic moment associated with it.

The permitted values for each of these quantum numbers are given in the Table 2.1.

SOLVED PROBLEM. List all possible values of l and m for $n = 2$.

SOLUTION. Here, the principal quantum number $n = 2$. The azimuthal quantum number can have only two values. These are 0 and 1

When	$l = 0$	$m = 0$
and	$l = 1$	$m = +1, 0, -1$

SOLVED PROBLEM. Which of the following sets of quantum numbers are not allowable and why?

- | | | | | |
|-----|---------|---------|---------|--------------------|
| (a) | $n = 2$ | $l = 2$ | $m = 0$ | $s = +\frac{1}{2}$ |
| (b) | $n = 3$ | $l = 1$ | $m = 0$ | $s = -\frac{1}{2}$ |

(c)	$n = 1$	$l = 1$	$m = +1$	$s = +\frac{1}{2}$
(d)	$n = 2$	$l = 0$	$m = -1$	$s = 0$
(e)	$n = 3$	$l = 2$	$m = +2$	$s = -\frac{1}{2}$

SOLUTION

- (a) Not allowable as l cannot have value equal to 2 when $n = 2$.
 (b) Allowable
 (c) Not allowable as l cannot have value equal to 1 when $n = 1$
 (d) Not allowable as s cannot have value equal to 0.
 (e) Allowable

SOLVED PROBLEM. What designation are given to the orbitals having

(a)	$n = 2$	$l = 1$
(b)	$n = 1$	$l = 0$
(c)	$n = 3$	$l = 2$
(d)	$n = 4$	$l = 3$

SOLUTION

(a)	when $n = 2$	and $l = 1$	the orbital is $2p$
(b)	when $n = 1$	and $l = 0$	the orbital is $1s$
(c)	when $n = 3$	and $l = 2$	the orbital is $3d$
(d)	when $n = 4$	and $l = 3$	the orbital is $4f$

PAULI'S EXCLUSION PRINCIPLE

The nature of an electron, its position and energy, is fully implied only by mentioning the values of four quantum numbers ascribed to it. Each electron is, therefore, fully characterised by a set of four quantum numbers 'n' – giving the size of electron orbital, l – its shape, and m – the orientation or disposition of the orbital and s the spin of the electron. Electrons having the same value of n , the principal quantum number, are said to belong to the same major energy level. However, the energies possessed by these electrons may yet be different owing to the different values of other quantum numbers assigned to them. In fact, the major energy levels are made of sublevels, given by the value of azimuthal quantum number ' l '. A particular energy sublevel may be designated by s , p , d and f . Within each energy level, the various sublevels have slightly different energies which increase in the same order as the value of the azimuthal quantum number l . Therefore, for the major energy level $n = 4$, which has an s orbital ($l = 0$), p orbitals ($l = 1$), d orbitals ($l = 2$) and f orbitals ($l = 3$), the energy increases in the order $s < p < d < f$. An electron with the principal quantum number n and azimuthal quantum number l has always lesser energy than that of an electron with principal quantum number $(n + 1)$ and the same azimuthal quantum number l *i.e.*, the energy of a $3s$ orbital is less than that of $4s$ orbital and energy of $4p$ orbitals is always more than the energy of $3p$ orbitals, and so on. The other two quantum numbers namely magnetic and spin quantum numbers determine the maximum number of electrons that can be accommodated in orbitals of a sublevel. It is, therefore, the assignment of the four quantum numbers to the electrons which ultimately count to determine its energy and location in space within an atom.

TABLE 2.1. QUANTUM NUMBERS AND ELECTRON ACCOMMODATION

Principal Q-number n	Azimuthal Q-number l	Magnetic Quantum Number m	Spin Quantum Number s	Number of Electrons accommodated		
1	K	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2	L	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
3	M	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
		2	d	$+2, +1, 0, -1, -2,$	$+\frac{1}{2}, -\frac{1}{2}$	10
4	N	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6
		2	d	$+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$	10
		3	f	$+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$	14

Wolfgang Pauli put forward an ingenious principle which controls the assignment of values of four quantum numbers of an electron. It applies certain restrictions on the values of electrons in an atom and hence the name ‘**exclusion principle**’. It is stated as : **No two electrons in an atom can have the same set of four identical quantum numbers.**

Even if two electrons have the same values for n , l and m , they must have different values of s . Thus every electron in an atom differs from every other electron in total energy and, therefore, there can be as many electrons in a shell as there are possible arrangements of different quantum numbers. The arrangements of electrons using permitted quantum numbers n , l , m and s are given in the Table 2.1. Let us find out the maximum number of electrons that can be accommodated in an orbital. We have seen that the first shell ($n = 1$) has only one orbital *i.e.*, $1s$. The possible arrangements for the quantum numbers are only two in accordance with Pauli’s exclusion principle.

n	l	m	s
1	0	0	$+\frac{1}{2}$ (1st electron)
1	0	0	$-\frac{1}{2}$ (2nd electron)

It follows, therefore, that a maximum of two electrons can be accommodated in an orbital and they must possess opposite spins.

Consider the second shell ($n = 2$), there being four orbitals, one s orbital ($l = 0$) and three p orbitals ($l = 1$), the possible number of electrons having different set of quantum numbers can be as follows :

n	l	m	s
2	0	0	$+\frac{1}{2}$
2	0	0	$-\frac{1}{2}$

Two electrons accommodated in $2s$ orbital ($l = 0$)

2	1	+1	$+\frac{1}{2}$	}	Six electrons in all the three $2p$ orbitals ($l = 1$), two electrons each in $2p_x$ ($m = +1$), $2p_y$ ($m = -1$) and $2p_z$ ($m = 0$) orbitals.
2	1	+1	$-\frac{1}{2}$		
2	1	-1	$+\frac{1}{2}$	}	
2	1	-1	$-\frac{1}{2}$		
2	1	0	$+\frac{1}{2}$	}	
2	1	0	$-\frac{1}{2}$		

The total number of electrons that can be accommodated in second shell is equal to $2 + 6 = 8$. Similarly it can be shown that the maximum number of electrons in the third and fourth shells is equal to 18 and 32 respectively. On the basis of the above direction and the Table 2.1 it follows that s sublevel may contain upto *two* electrons, p sublevel upto *six*, d sublevel upto *ten* and f sublevel may have upto *fourteen* electrons. Each sublevel can accommodate at the most twice the number of available orbitals at that sublevel.

Pauli's exclusion principle is of immense value in telling the maximum number of electrons accommodated in any shell.

ENERGY DISTRIBUTION AND ORBITALS

In our earlier discussion we have seen that the energy of an electron is determined by the first two quantum numbers n and l , while the other two specify the orientation of the electron orbital in space and the spin. As we discuss the distribution of energy of the orbitals, the following two cases may arise :

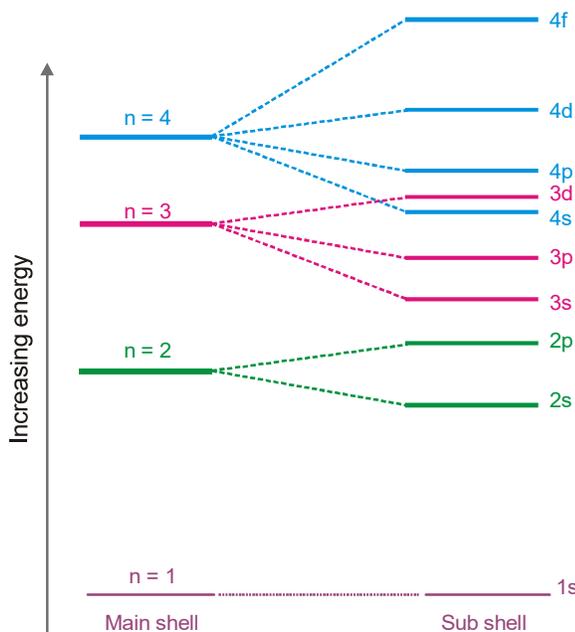
(a) Hydrogen and Hydrogen-like atoms

Hydrogen is the simplest of all atoms since there is only one electron in it. This single electron is expected normally to be present in the lowest energy state $n = 1$. The values of l and m are both zero and spin quantum numbers can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. When it absorbs energy, it may jump to higher energy levels given by n or a subshell thereon (represented by l values). The spectral study of hydrogen has revealed that its spectral lines correspond to the major energy levels only. Thus the energy value of an electron having a particular quantum is fixed, irrespective of the orbital to which it may belong. In other words, the energy associated with electrons in s , p , d and f orbitals of a particular principal quantum number is the same. For example, the energy level of $3s$, $3p$ and $3d$ orbitals is equal (Fig. 2.8).

(b) Polyelectron atoms

Let us first consider a two electron atom. The second electron which may differ from the first electron in spin only, is also accommodated in the $1s$ orbital, thereby completing the K shell. Unlike hydrogen, where there is no such completed shell, the energies of the subsequent electrons coming in various levels and sublevels will be affected. Thus it is this completed K shell that affects the energy of the electrons occupying subsequent energy levels. For atoms having more than two electrons, the nuclear charge is shielded from the outer electrons by the two K shell electrons. The effect of the completed K shell of electrons is to make the energy level of any orbital in a principal level n dependent upon the value of orbital quantum number l . The dependence of energy of orbitals of a shell on l ($l = 0$ or s , $l = 1$ or p etc.) is because of the fact that s orbital electrons ($l = 0$), for example, penetrate near the nucleus and are, therefore, less effectively shielded from the nuclear charge. The s electrons ($l = 0$) being less shielded are drawn inwards and possess lesser energy than p orbital ($l = 1$) electrons. The same argument can be extended for other values of l . Thus within each energy

level 'n', the various sublevels (different l values orbitals) exhibit slightly different energies. The orbitals at a principal level n get split up and come to possess different energies, which increase in the same order as the various values of l . Thus for a particular principal level, the energy of the sublevels is in the order $s < p < d < f$.



■ **Figure 2.8**
Energy level schemes of Hydrogen atom.

The energy levels of $3s$, $3p$ and $3d$ orbitals are different even though they belong to the same shell $n = 3$. However, **it may be noted that the energy of electrons in the same orbital is the same.** Thus all $3d$ orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{z^2}$, $3d_{x^2-y^2}$) or $4p$ orbitals ($4p_x$, $4p_y$, $4p_z$) are at the same level of energy, irrespective of their orientation. It is also noteworthy from the above diagram that the order of increase of energy values of various orbitals approximately follows the sequence given below :

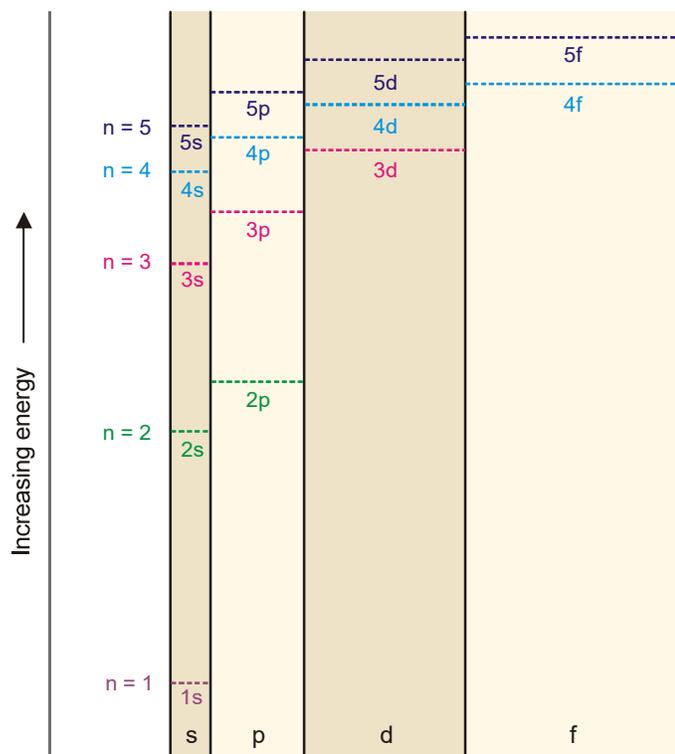
$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d$$

It is, therefore, clear that the $3d$ orbital electrons belonging to a lower shell ($n = 3$) possess more energy than $4s$ orbital electrons which belong to higher shell ($n = 4$). The $3d$ orbitals lie at a higher energy level than $4s$ orbital.

DISTRIBUTION OF ELECTRONS IN ORBITALS

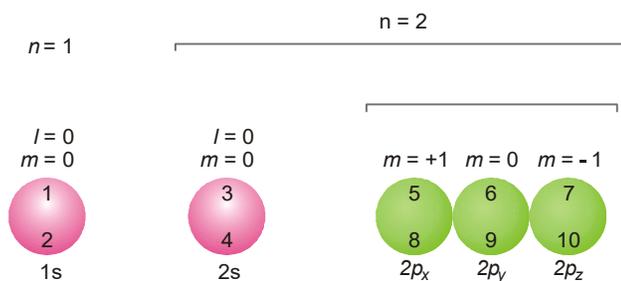
In passing along the periodic table of the elements from one element to the other, we find that one electron is added every time to the next atom. Where should the incoming electron go? The answer is provided by the possible values of the quantum numbers that can be assigned to the electron in accordance with Pauli's exclusion principle—prohibiting an orbital to accommodate two electrons with the same set of quantum numbers.

On the basis of magnetic measurements, which also help to determine the electronic configuration of elements, Hund put forward another empirical rule, popularly known after his name as **Hund's Rule of Maximum Multiplicity**. It states that : **Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.**



■ **Figure 2.9**
Energy level scheme of polyelectron atoms.

Thus the orbitals available at a subshell are first filled singly before they begin to pair. The following illustration shows the order of filling of electrons in the orbitals of $n=1$ and $n=2$ shells. The orbitals are shown by circles and the order of filling for the first ten electrons is indicated by the numbers entered in them.



■ **Figure 2.10**
Order of filling of electrons in orbitals of $n=1$ and $n=2$ shells.

It is also clear from the illustration that no two electrons in an orbital have the same values of all four quantum numbers. In fact, three are identical while the fourth quantum number *i.e.*, the spin quantum number is invariably different. The electrons in the p orbitals are arranged and accommodated such that they have all obtained one electron first (5th in $2p_x$, 6th in $2p_y$, 7th in $2p_z$) and now they begin to pair up getting the 8th, 9th and 10th electrons respectively.

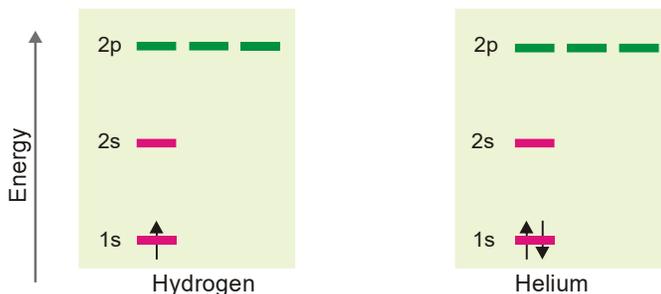
SCHEMATIC REPRESENTATION OF ELECTRON CONFIGURATION

We have seen above that to define completely the state of an atom it is obligatory to refer to all the four quantum numbers (n , l , m and s) of every electron in it. Since a simultaneous representation of all quantum numbers of each electron in a single symbolic notation seems quite difficult, it is customary to take into account the first two quantum numbers only while the other two can be inferred indirectly. The general symbolic notation employed for the purpose is nl^a where the numerical value of $n = 1, 2, 3$ etc., represents the principal quantum number, the letter designate of l (s for $l = 0$, p for $l = 1$ and so on) stands for the orbital and the superscript a gives the number of electrons in the orbital. Thus $3s^2$ indicates that two electrons are present in the first subshell s ($l = 0$) of the third shell ($n = 3$). For instance, the distribution of seven electrons (of N atom) may be schematically represented as $1s^2; 2s^2, 2p^3$ or more elaborately as $1s^2; 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$. By using the various designates of orbitals at a sublevel such as $2p_x, 2p_y$ etc., the third quantum number m is also indicated (e.g., $2p_x$, for $m = +1$, $2p_y$ for $m = 0$ and $2p_z$ for $m = -1$). Spin quantum numbers are indirectly inferred. Whenever there are two electrons in an orbital, one of these has $+\frac{1}{2}$ and the other $-\frac{1}{2}$ as their spin quantum number.

It is a common practice to denote an orbital by a horizontal line or a circle or square and an electron by an arrow over it. The direction of the arrow indicates the spin, an upward arrow representing a clockwise spin while the downward arrow stands for the anticlockwise direction of spin. When there are more than one orbitals in a subshell (**degenerate orbitals**), they are shown by an equivalent number of horizontal lines at the same energy level. Let us now describe the electron configuration of first ten elements.

(a) Hydrogen and Helium

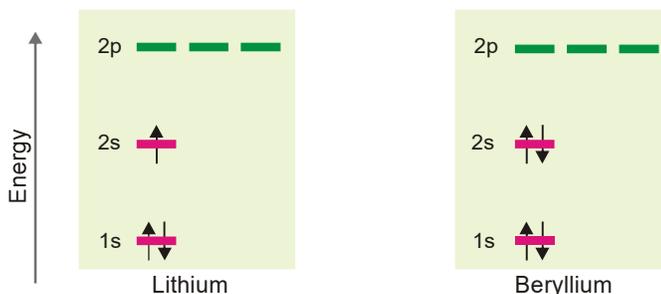
These have one and two electrons respectively which are accommodated in $1s$ orbital while others remain vacant. The lone electron of hydrogen is filled in $1s$ orbital and for helium the second electron would also go in $1s$ orbital, since it could accommodate another electron with opposite spin.



■ **Figure 2.11**
Electron configuration of Hydrogen and Helium.

(b) Lithium and Beryllium

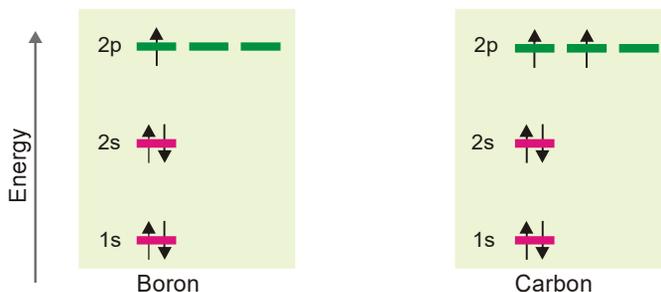
These have three and four electrons respectively. The third electron of Li enters in the $2s$ orbital and the fourth electron of Be also enters in the same orbital, but has an opposite direction of spin.



■ **Figure 2.12**
Electron configuration of Lithium and Beryllium.

(c) Boron and Carbon

These atoms have five and six electrons respectively. $1s$ and $2s$ orbitals being completely filled with four electrons, the fifth electron of boron would go in one of the $2p$ orbitals say $2p_x$. The sixth electron in carbon would prefer to be accommodated in another vacant $2p$ orbital say ($2p_y$) rather than going to $2p_z$ orbital (Hund's rule). The two unpaired electrons shall have similar spins as indicated.

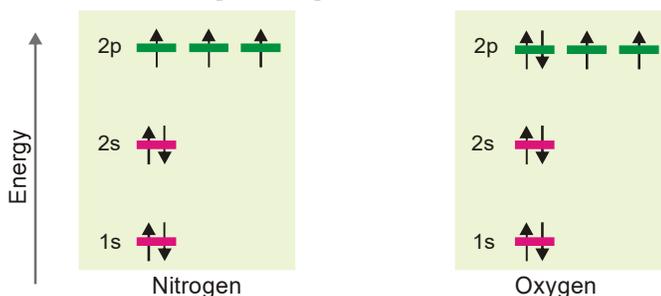


■ **Figure 2.13**

Electron configuration of Boron and Carbon.

(d) Nitrogen and Oxygen

These atoms have seven and eight electrons respectively. After six electrons have been accommodated as above, there is a vacant $2p_z$ orbital which will be the seat of the seventh electron possessing the same direction of spin. The eighth electron of the next element oxygen will go to pair up with the $2p_x$ electron and has an antiparallel spin as shown below.

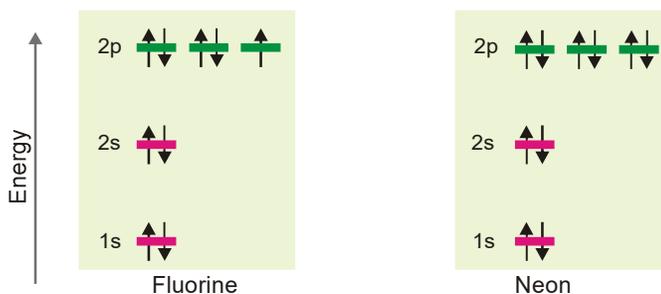


■ **Figure 2.14**

Electron configuration of Nitrogen and Oxygen.

(e) Fluorine and Neon

These atoms possess nine and ten electrons respectively which go to complete the other $2p$ orbitals as shown in Fig. 2.15.



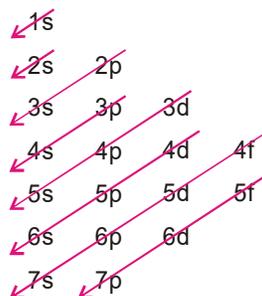
■ **Figure 2.15**

Electron configuration of Fluorine and Neon.

GROUND-STATE ELECTRON CONFIGURATION OF ELEMENTS

So far we have considered the electron configuration of simple atoms. For complicated atoms which may contain many electrons and have many energy levels or orbitals, the ‘building up’ process for the electrons is governed by the following rules :

- Rule 1.** Each electron shell can hold a maximum of $2n^2$ electrons where n is the shell number.
- Rule 2.** These electrons are accommodated in s , p , d and f orbitals, the maximum number of electrons in each type of orbitals being determined by its electron-holding capacity (for $s = 2$, $p = 6$, $d = 10$ and $f = 14$).
- Rule 3.** In the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first. This is called ‘building up principle’ or **Aufbau Principle** (*Aufbau* is a German expression meaning *building up or construction*). Lower energy orbitals are, therefore, better seats for electrons and better seats are occupied first. Fig 2.9 shows the energy level scheme of orbitals and this order can conveniently be remembered by the simple device given below.



■ **Figure 2.16**
Aufbau order of orbitals for feeding in electrons.

The increasing order of energy of various orbitals is as follows :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \dots\dots$$

The energy of an orbital is determined by the sum of principal quantum number (n) and the azimuthal quantum number (l). This rule is called **($n + l$) rule**. There are two parts of this rule :

- The orbitals with the lower value of $(n + l)$ has lower energy than the orbitals of higher $(n + l)$ value.
- When two orbitals have same $(n + l)$ value, the orbital with lower value of n has lower energy. For example, let us compare the $(n + l)$ value for $3d$ and $4s$ orbitals.

For $3d$ orbital $n = 3$, $l = 2$ and $n + l = 5$ and for $4s$ orbital $n = 4$, $l = 0$ and $n + l = 4$.

Therefore, $4s$ orbital is filled before $3d$ orbital. Similarly, for $4p$ and $5s$ orbitals, the $(n + l)$ values are $(4 + 1)$ and $(5 + 0)$ respectively. In this case $4p$ orbital has lesser value of n and hence it has lower energy than $5d$ orbital and is filled first.

It is, therefore, clear from above that $4s$ orbital would be filled before $3d$ orbitals (belonging to a lower shell *i.e.*, third) are filled because the latter have higher energy than the former.

- Rule 4.** Any orbital may have one or two electrons at the most. Two electrons can occupy the same orbital only if they have opposite spins (Pauli’s exclusion principle).
- Rule 5.** When several orbitals of equal energy (degenerate orbitals) are available, electrons prefer to occupy separate orbitals rather than getting paired in the same orbital. Such electrons tend to have same spins (Hund’s rule).

Actual electron configuration of atoms of all elements of the periodic table is given in Table 2.3. We find that these configurations are by and large the same as predicted by the Aufbau procedure. However, there are quite a few elements which exhibit slight variations from the standard pattern. Some anomalies are tabled below showing only the concerned orbitals.

TABLE 2.2. ANOMALOUS ELECTRON CONFIGURATION OF SOME ELEMENTS

Element	At. No.	Expected Configuration	Actual Configuration
Cr	24	$4d^4 4s^2$	$3d^5 4s^1$
Cu	29	$3d^9 4s^2$	$3d^{10} 4s^1$
Mo	42	$4d^4 5s^2$	$4d^5 5s^1$
Pd	46	$4d^8 5s^2$	$4d^{10} 5s^0$
Ag	47	$4d^9 5s^2$	$4d^{10} 5s^1$
Pt	78	$5d^8 6s^2$	$5d^9 6s^1$
Au	79	$5d^9 6s^2$	$5d^{10} 6s^1$

TABLE 2.3. GROUND STATE ELECTRON CONFIGURATION OF ELEMENTS

Z	Element	Electron configuration	Z	Element	Electron configuration
1	H	$1s^1$	21	Sc	$[\text{Ar}]3d^14s^2$
2	He	$1s^2$	22	Ti	$[\text{Ar}]3d^24s^2$
3	Li	$[\text{He}]2s^1$	23	V	$[\text{Ar}]3d^34s^2$
4	Be	$[\text{He}]2s^2$	24	Cr	$[\text{Ar}]3d^54s^1$
5	B	$[\text{He}]2s^22p^1$	25	Mn	$[\text{Ar}]3d^54s^2$
6	C	$[\text{He}]2s^22p^2$	26	Fe	$[\text{Ar}]3d^64s^2$
7	N	$[\text{He}]2s^22p^3$	27	Co	$[\text{Ar}]3d^74s^2$
8	O	$[\text{He}]2s^22p^4$	28	Ni	$[\text{Ar}]3d^84s^2$
9	F	$[\text{He}]2s^22p^5$	29	Cu	$[\text{Ar}]3d^{10}4s^1$
10	Ne	$[\text{He}]2s^22p^6$	30	Zn	$[\text{Ar}]3d^{10}4s^2$
11	Na	$[\text{Ne}]3s^1$	31	Ga	$[\text{Ar}]3d^{10}4s^24p^1$
12	Mg	$[\text{Ne}]3s^2$	32	Ge	$[\text{Ar}]3d^{10}4s^24p^2$
13	Al	$[\text{Ne}]3s^23p^1$	33	As	$[\text{Ar}]3d^{10}4s^24p^3$
14	Si	$[\text{Ne}]3s^23p^2$	34	Se	$[\text{Ar}]3d^{10}4s^24p^4$
15	P	$[\text{Ne}]3s^23p^3$	35	Br	$[\text{Ar}]3d^{10}4s^24p^5$
16	S	$[\text{Ne}]3s^23p^4$	36	Kr	$[\text{Ar}]3d^{10}4s^24p^6$
17	Cl	$[\text{Ne}]3s^23p^5$	37	Rb	$[\text{Kr}]5s^1$
18	Ar	$[\text{Ne}]3s^23p^6$	38	Sr	$[\text{Kr}]5s^2$
19	K	$[\text{Ar}]4s^1$	39	Y	$[\text{Kr}]4d^15s^2$
20	Ca	$[\text{Ar}]4s^2$	40	Zr	$[\text{Kr}]4d^25s^2$

Z	Element	Electron configuration	Z	Element	Electron configuration
41	Nb	[Kr]4d ⁴ 5s ¹	73	Ta	[Xe]4f ¹⁴ 5d ³ 6s ²
42	Mo	[Kr]4d ⁵ 5s ¹	74	W	[Xe]4f ¹⁴ 5d ⁴ 6s ²
43	Tc	[Kr]4d ⁵ 5s ²	75	Re	[Xe]4f ¹⁴ 5d ⁵ 6s ²
44	Ru	[Kr]4d ⁷ 5s ¹	76	Os	[Xe]4f ¹⁴ 5d ⁶ 6s ²
45	Rh	[Kr]4d ⁸ 5s ¹	77	Ir	[Xe]4f ¹⁴ 5d ⁷ 6s ²
46	Pd	[Kr]4d ¹⁰	78	Pt	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
47	Ag	[Kr]4d ¹⁰ 5s ¹	79	Au	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
48	Cd	[Kr]4d ¹⁰ 5s ²	80	Hg	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
49	In	[Kr]4d ¹⁰ 5s ² 5p ¹	81	Tl	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹
50	Sn	[Kr]4d ¹⁰ 5s ² 5p ²	82	Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
51	Sb	[Kr]4d ¹⁰ 5s ² 5p ³	83	Bi	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
52	Te	[Kr]4d ¹⁰ 5s ² 5p ⁴	84	Po	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
53	I	[Kr] 4d ¹⁰ 5s ² 5p ⁵	85	At	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
54	Xe	[Kr] 4d ¹⁰ 5s ² 5p ⁶	86	Rn	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
55	Cs	[Xe]6s ¹	87	Fr	[Rn]7s ¹
56	Ba	[Xe]6s ²	88	Ra	[Rn]7s ²
57	La	[Xe]5d ¹ 6s ²	89	Ac	[Rn]6d ¹ 7s ²
58	Ce	[Xe]4f ¹ 5d ¹ 6s ²	90	Th	[Rn]6d ² 7s ²
59	Pr	[Xe]4f ³ 6s ²	91	Pa	[Rn]5f ² 6d ¹ 7s ²
60	Nd	[Xe]4f ⁴ 6s ²	92	U	[Rn]5f ³ 6d ¹ 7s ²
61	Pm	[Xe]4f ⁵ 6s ²	93	Np	[Rn]5f ⁴ 6d ¹ 7s ²
62	Sm	[Xe]4f ⁶ 6s ²	94	Pu	[Rn]5f ⁶ 7s ²
63	Eu	[Xe]4f ⁷ 6s ²	95	Am	[Rn]5f ⁷ 7s ²
64	Gd	[Xe]4f ⁷ 5d ¹ 6s ²	96	Cm	[Rn]5f ⁷ 6d ¹ 7s ²
65	Tb	[Xe]4f ⁹ 6s ²	97	Bk	[Rn]5f ⁹ 7s ²
66	Dy	[Xe]4f ¹⁰ 6s ²	98	Cf	[Rn]5f ¹⁰ 7s ²
67	Ho	[Xe]4f ¹¹ 6s ²	99	Es	[Rn]5f ¹¹ 7s ²
68	Er	[Xe]4f ¹² 6s ²	100	Fm	[Rn]5f ¹² 7s ²
69	Tm	[Xe]4f ¹³ 6s ²	101	Md	[Rn]5f ¹³ 7s ²
70	Yb	[Xe]4f ¹⁴ 6s ²	102	No	[Rn]5f ¹⁴ 7s ²
71	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	103	Lr	[Rn]5f ¹⁴ 6d ¹ 7s ²
72	Hf	[Xe]4f ¹⁴ 5d ² 6s ²	104	Rf	[Rn]5f ¹⁴ 6d ² 7s ²

Note : The symbol in brackets indicates the electron core of the Noble gas.

**PERIODIC TABLE OF ELEMENTS
(ELECTRON CONFIGURATIONS)**

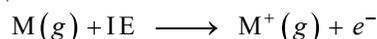
Group number	Periods																													
	1	2	3										13	14	15	16	17	18												
	1A	2A	3B	4B	5B	6B	7B	8	9	10	11	12	3A	4A	5A	6A	7A	8A												
1	1 H $1s^1$	2 He $1s^2$																												
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$												
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$												
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$												
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$												
6	55 Cs $6s^1$	56 Ba $6s^2$	57 *La $5d^1 6s^2$	72 Hf $5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$												
7	87 Fr $7s^1$	88 Ra $7s^2$	89 †Ac $6d^1 7s^2$	104 Rf $6d^2 7s^2$	105 Db $6d^3 7s^2$	106 Sg $6d^4 7s^2$	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	114 Fl	116 Lv	(285)	(289)	(289)	(289)												
			Lanthanides										Actinides																	
			58 Ce $4f^2 6s^2$	59 Pr $4f^3 6s^2$	60 Nd $4f^4 6s^2$	61 Pm $4f^5 6s^2$	62 Sm $4f^6 6s^2$	63 Eu $4f^7 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 6s^2$	66 Dy $4f^{10} 6s^2$	67 Ho $4f^{11} 6s^2$	68 Er $4f^{12} 6s^2$	69 Tm $4f^{13} 6s^2$	70 Yb $4f^{14} 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$	90 Th $6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^4 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 7s^2$	95 Am $5f^7 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 7s^2$	98 Cf $5f^{10} 7s^2$	99 Es $5f^{11} 7s^2$	100 Fm $5f^{12} 7s^2$	101 Md $5f^{13} 7s^2$	102 No $5f^{14} 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

We find from the table that irregularities involve the placing of one or two electrons from ns orbital in $(n-1)d$ orbitals. There is very little energy difference between such s and d orbitals so that there is very little to choose from energy point of view. The deviations occur when d level orbitals are either almost full (e.g., Cu, Pd, Ag, Pt and Au) or half-full (Cr and Mo). The explanation for this deviation lies in the superior stability of completely filled or all half-filled orbitals than nearly filled or nearly half-filled orbitals. Thus d^5 and d^{10} configurations are much more stable than d^4 or d^8 or d^9 . Spectroscopic data and magnetic properties of elements justify the statement that **half-filled and completely filled subshells contribute to the stability.**

IONISATION ENERGY

The process of removing an electron from an isolated atom to form a positive ion is called ionisation. Energy will be required to remove an electron from the atom against the force of attraction of the nucleus.

The ionisation energy (IE) of an element is defined as the energy needed to remove a single electron from an atom of the element in the gaseous state. That is,

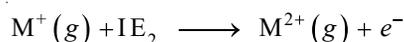


Since one, two or more electrons may be removed from the same atom, one after the other, we have as many ionisation energies of the element.

The **First ionisation energy (IE₁)**, is the energy needed to remove the first electron from the gaseous atom M to form M⁺ ion.

The **Second ionisation energy (IE₂)**, is the energy needed to remove a second electron, from the gaseous M⁺ ion to form M²⁺ ion.

Higher ionisation energies can be defined in the same way. We can depict the first, second and third ionisation energies in the form of equations as :



Ionisation energies are sometimes called **Ionisation potentials**. Ionisation energies are usually expressed in electron volts (eV) per atom, or in kilojoules per mole of atoms (kJ mol⁻¹). For conversion, 1eV atom⁻¹ = 96.48 kJ mol⁻¹.

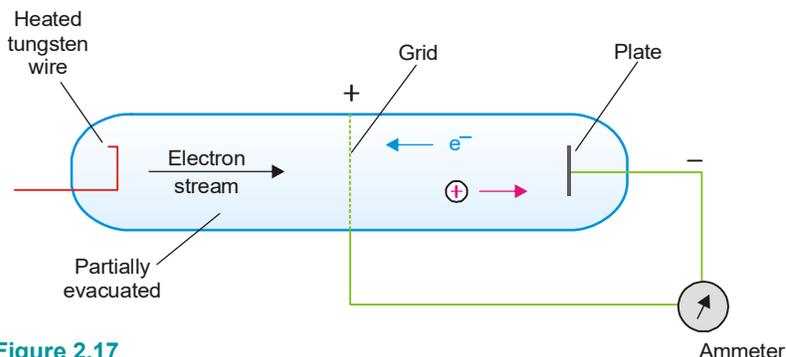
MEASUREMENT OF IONISATION ENERGIES

The amount of energy required to detach an electron from an atom can be measured by supplying the required energy as thermal energy, electrical energy, or radiant energy. Thus ionisation energies can be determined from the spectrum of the element or by any of the two methods detailed below.

(1) The Electrical method

The apparatus used is shown in Fig. 2.17. The electrically heated tungsten wire emits electrons. The grid can be charged positively to different voltages which we read with a voltmeter. The plate opposite the grid has a small negative charge. When the potential to the grid is zero, no current flows between the grid and the plate. However if we give sufficient potential to the grid, the electrons emitted by the tungsten wire are accelerated towards the grid, pass through it and ionise the atoms between grid and plate. The electron ejected by each atom is attracted to grid and positive ion is attracted to plate. A current thus passes between grid and plate which is shown up by an ammeter.

The minimum grid voltage that just produces a current is called ionization potential.



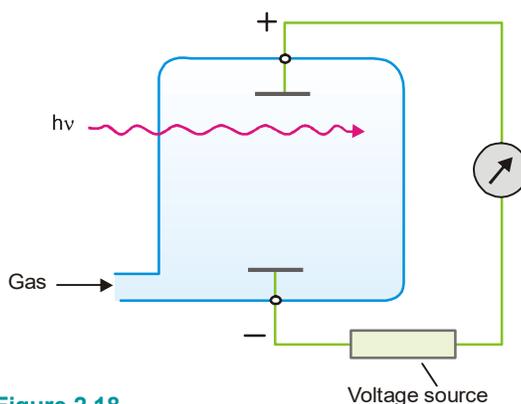
■ **Figure 2.17**
Measurement of ionisation energy.

If V be the ionization potential, the ionization energy (IE) is calculated as :

$$\begin{aligned} \text{IE} &= V \times \text{charge of electron} \times \text{Avogadro No} \\ &= V \times 1.60 \times 10^{-19} \times 6.02 \times 10^{23} \\ &= V \times 96.3 \text{ kJ mol}^{-1} \end{aligned}$$

(2) Photo-ionisation Method

The gaseous atoms are introduced into a chamber containing two electrically charged plates (Fig. 2.18). As neutral atoms, they do not conduct electricity and no current flows between the plates. When radiant energy ($h\nu$) is supplied to the gaseous atoms, ionisation will occur and electric current will flow. The frequency of the radiation used is gradually increased. The minimum frequency necessary to cause ionisation of the gaseous atoms, as shown by the flow of an electric current is noted. From this frequency the ionisation energy is calculated.



■ **Figure 2.18**
Measurement of ionisation energy
by photo-ionisation method.

Order of Successive Ionisation Energies

The second ionisation energy (IE_2) is larger than the first ionisation energy (IE_1) because it is more difficult to detach an electron from a +ve ion than a neutral atom. The third ionisation energy (IE_3) is still larger as the third electron has to be detached from a 2+ ion. Thus in general successive ionisation energies increase in magnitude. That is,

$$IE_1 < IE_2 < IE_3 < IE_4, \text{ and so on.}$$

For illustration, the first four ionisation energies for sodium and magnesium are listed below:

TABLE 2.4. IONISATION ENERGIES IN KILO JOULE PER MOLE (KJ mol^{-1})

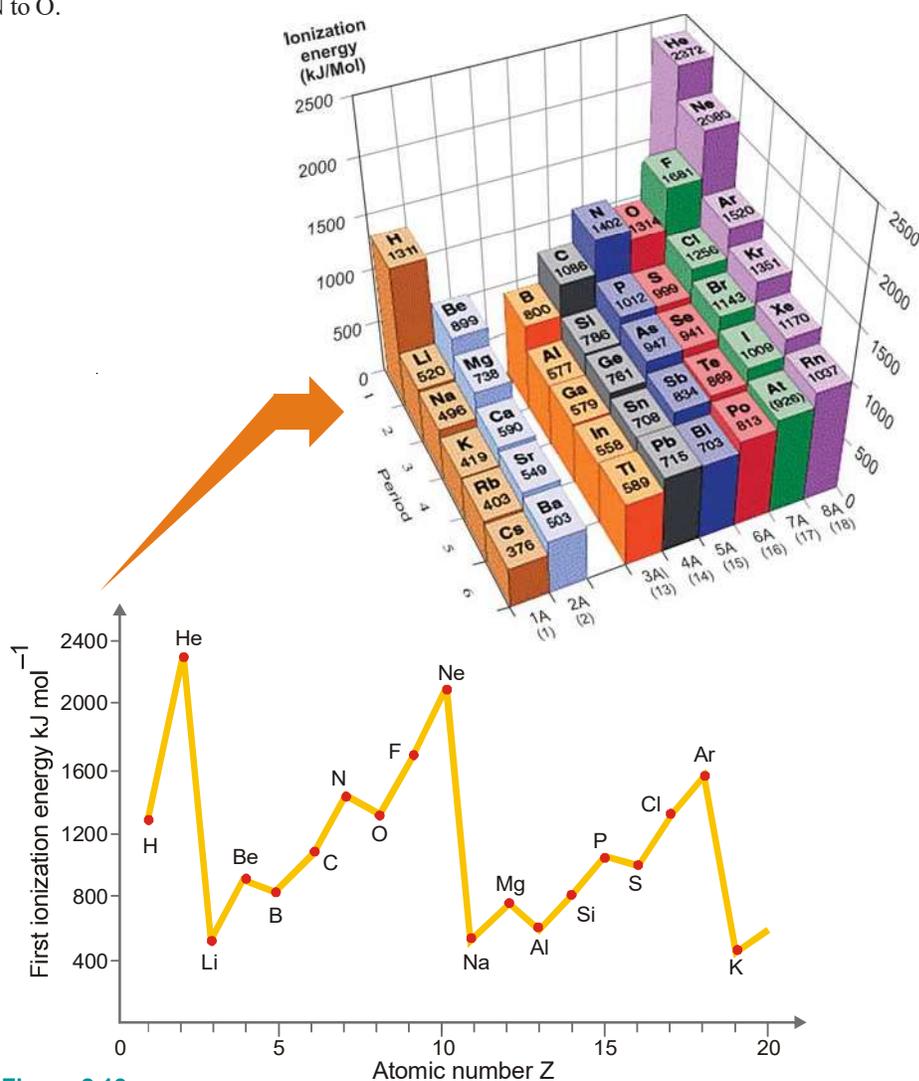
	IE_1	IE_2	IE_3	IE_4
Sodium	500	4600	6900	9500
Magnesium	740	1500	7700	10500

Principal Trends in Ionisation Energies

A graph of the first ionisation energies against atomic number (Z) for the first 18 elements of the Periodic Table is shown in Fig. 2.19.

The important trends as illustrated by the graph are:

- (1) **Ionisation energies increase across a period.** *e.g.*, Li to Ne.
- (2) **Ionisation energies decrease down a group** *e.g.*, Li, Na, K.
- (3) **There are regular discontinuities in the increase trend across a period** *e.g.*, Be to B, and N to O.



■ **Figure 2.19**
Graph showing the variation of first ionisation energies with increase of atomic number.

Increase across a Period

As we pass from left to right in a period, the first ionisation energy shows a steady increase. Thus in Period 2 from Li to N, we have

	Li	Be	B	C	N
IE_1 (kJ mol ⁻¹)	525	906	805	1090	1400

Explanation

The outer-shell electrons in the elements of the same period are arranged in the same shell. For example, the build up of electrons in Period 2 from Li to B is shown in Fig. 2.20.

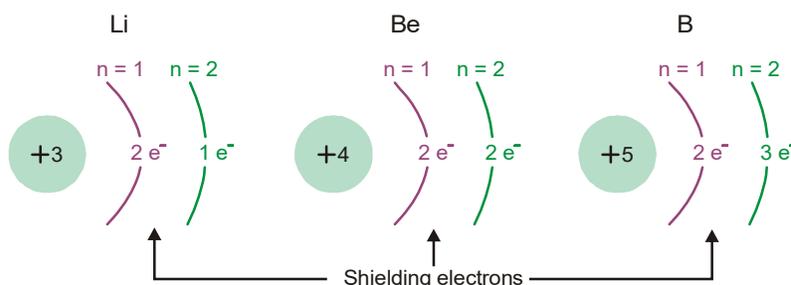


Figure 2.20
Build up of atoms of elements for Li, Be, B.

Moving from Li to B, the positive charge on the nucleus increases whereas the distance between the nucleus and valence electrons decreases. Therefore more energy is required to remove an electron as we go from left to right in the Period. Since the number of screening electrons remains the same, they do not upset the increase trend.

Decrease down a Group

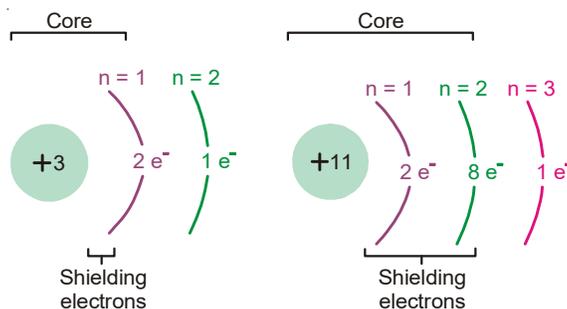
In the elements of a vertical Group of the Periodic table, the number of outer shell electrons is the same. But the following changes are noted from top to bottom.

- (1) The principal quantum number n containing the valence electrons increases.
- (2) The nuclear charge (At. No.) increases.
- (3) The number of electrons in the inner shells (shielding electrons) increases.

The net result of these changes is that the first ionisation energies down a group record a progressive decrease. Thus for Group IA we have

	Li	Na	K	Rb	Cs
IE_1 (kJ mol ⁻¹)	525	500	424	408	382

Let us explain the above decrease trend by taking example of lithium and sodium. They have the atomic structures.



Lithium and sodium both have one outer-shell electron. The number of shielding electrons in sodium is 10 while in lithium it is 2. If we assume that the inner shell electrons provide hundred percent screening, the core charge attracting the outer-shell electron would be :

	Nuclear charge	Shielding electrons	Core charge attracting outer-shell electron
Li	3	2	$3 - 2 = +1$
Na	11	2, 8	$11 - 10 = +1$

Thus the same net charge (+ 1) attracts the outer-shell electrons to the core. But the distance of the outer electron from the nucleus is greater in Na ($n = 3$) than in Li ($n = 1$). Therefore the force of attraction between the outer electron and the core will be less in Na than in Li. That explains the lower I E of Na compared to Li. By the same line of argument, the decrease trend in I E from element to element while going down a Group can be justified.

Regular Discontinuities

As already discussed, the first ionisation energies increase across a period. But this increase trend is upset at the third and sixth element in a period. As clear from graph in Fig. 2.19, there are breaks at B and O which occupy the third and fifth positions respectively in the 2nd period. The I E₁ of B is less than that of Be and the I E₁ of O is less than that of N.

Explanation

(a) The electronic configuration of Be and B are :



The 2p orbital electron of B is already higher in energy than the 2s orbital electron. Therefore the removal of electron from B requires less energy and its I E₁ is lower.

(b) The electronic configuration of N and O is :



The 2p orbitals may be represented as

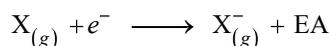


Whenever two electrons occupy a particular orbital, they repel each other. As a result it is easier to remove one of the paired 2p electrons from O than it is to remove an unpaired electron from N atom. Thus I E₁ of O is lower than that of N.

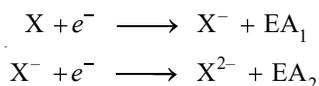
ELECTRON AFFINITY

A neutral atom can accept an electron to form negative ion. In this process, in general, energy is released.

Electron affinity (EA) of an element is the amount of energy released when an electron is added to a gaseous atom to form an anion.



The energy involved in the addition of the first electron is called **first-electron affinity**; the energy involved in the addition of a second electron is called **second-electron affinity**; and so on. Thus,

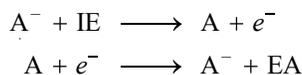


The electron affinity of an element measures the ease with which it forms an anion in the gas phase.

Electron affinities are difficult to measure and accurate values are not known for all elements. They are expressed in kJ mol^{-1} .

Trends in Electron Affinities

The factors that determine the magnitude and sign of electron affinities are similar to those used to explain ionisation energies of elements. In fact, the electron affinity of a neutral atom may be thought of simply as equivalent to the ionisation energy of the singly charged negative ion of the atom.



The first-electron affinities of elements in the Periodic table are expected to show trends analogous to those of ionisation energies.

(a) Increase across a Period

The values of electron affinities for Period 2 are listed below.

Be	B	C	N	O	F	Ne
-240	23	123	0.00	142	323	-29 k J mol ⁻¹

As we proceed from left to right, the general trend is the increase of electron affinities. Be, N and Ne are exceptions.

Explanation

Elements having relatively stable electronic configurations find it difficult to accept an electron readily. The atom of Be has the configuration $1s^2 2s^2$. The $1s$ subshell is completely filled and, therefore, the electron being added must go to a subshell of considerably higher energy. This gives rise to negative electron affinity for Be.

The atom of N ($1s^2 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$) has half-filled $2p$ subshells, a condition of extra stability. Therefore the electron affinity of N would be less than expected.

The electron affinity of Neon is low because it has a stable outer-shell octet. Its atom shows little tendency to start a new shell.

(b) Decrease down a Group

The values of electron affinities for halogens (Group VII) are given below.

F	Cl	Br	I
332.6	349	324.7	296 k J mol ⁻¹

The electron affinities show a general decrease from top to bottom. This is so because the valence shell is progressively farther from the nucleus. The value for fluorine, however, is out of line as it has a smaller atomic size than that of chlorine.

(c) Second electron affinity negative

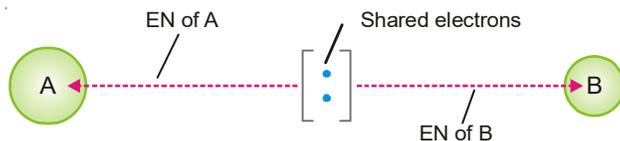
The second electron affinity of an element is always negative. This is on account of repulsion between the electron being added and the already negatively charged atom. For example,



ELECTRONEGATIVITY

In a molecule A–B the electrons forming the covalent bond are attracted by atom A as well as by B. This attraction is measured in terms of what we call **electronegativity, EN**. It may be defined as :

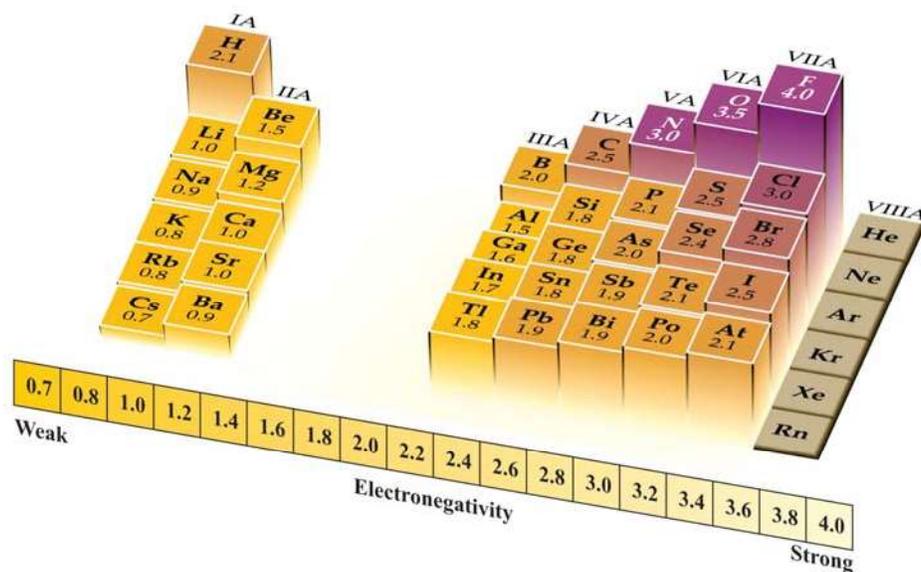
The attraction exerted by an atom on the electron pair bonding it to another atom by a covalent bond.



It is evident that an atom of high electronegativity will attract the shared electron pair away from one of lower electronegativity. Thus the former atom will acquire a partial negative charge while the other atom will get a partial positive charge.

Electronegativity Values

Using measured values of bond energies, Pauling devised a set of electronegativity values. He allotted a value of 4 to the most electronegative atom, namely fluorine, and assigned values to the atoms of other elements.



Trend in Electronegativities

The variations in electronegativities of elements in the Periodic table are similar to those of ionisation energies and electron affinities.

(1) Increase across a Period

The values of electronegativities increase as we pass from left to right in a Period. Thus for Period 2 we have

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0

This is so because the attraction of bonding electrons by an atom increases with increase of nuclear charge (At. No.) and decrease of atomic radius. Both these factors operate as we move to the right in a Period.

(2) Decrease down a Group

The electronegativities of elements decrease from top to bottom in a Group. Thus for Group VII

we have

F	Cl	Br	I
4.0	3.0	2.8	2.5

The decrease trend is explained by more shielding electrons and larger atomic radius as we travel down a Group.

Importance of Electronegativity

The electronegativities of elements are widely used throughout the study of Chemistry. Their usefulness will be discussed at appropriate places. The important applications of electronegativities are listed below.

- (1) **In predicting the polarity of a particular bond.** The polarity of a bond, in turn, shows the way how the bond would break when attacked by an organic reagent.
- (2) **In predicting the degree of ionic character of a covalent bond.**
- (3) **In predicting of inductive effects in organic chemistry.**
- (4) **In understanding the shapes of molecules.**

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(a) Planck's constant	(b) de Broglie equation
(c) Heisenberg's uncertainty principle	(d) Schrödinger's wave equation
(e) Principal quantum number	(f) Azimuthal quantum number
(g) Magnetic quantum number	(h) Zeeman effect
(i) Spin quantum number	(j) Pauli's exclusion principle
(k) Aufbau principle	(l) Hund's rule
2. What do you mean by the 'ionization potential' of an element? Why the first ionization potential of an element is less than the second ionization potential? How does the ionization potential of an element vary with atomic volume?
3. (a) What do you understand by the dual character of matter? Derive de Broglie's equation. How was it verified?
 (b) A particle having a wavelength 6.6×10^{-4} cm is moving with a velocity of 10^6 cm sec⁻¹. Find the mass of the particle. Planck's constant = 6.62×10^{-27} erg sec.
Answer. (b) 1.003×10^{-29} g
4. (a) State and discuss Heisenberg's uncertainty principle.
 (b) Draw energy level diagram valid for hydrogen and multi-electron atoms.
 (c) Write Schrödinger wave equation.
5. Discuss the following :
 - (a) Hund's Rule of Maximum multiplicity.
 - (b) Pauli's Exclusion Principle.
6. What is the wavelength associated with a particle of mass 0.1 g moving with a speed of 1×10^5 cm sec⁻¹ ($h = 6.6 \times 10^{-27}$ erg sec)
Answer. 6.6×10^{-31} cm
7. State Pauli's exclusion principle. Based on this principle show that the maximum number of electrons that can be accommodated in an orbit is 8 when $n = 20$.
8. The velocity of a ball being bowled by Kapil Dev is 25 m sec⁻¹. Calculate the wavelength of the matter-