BOOK
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SYLLABUS

INORGANIC CHEMISTRY UNIT – I

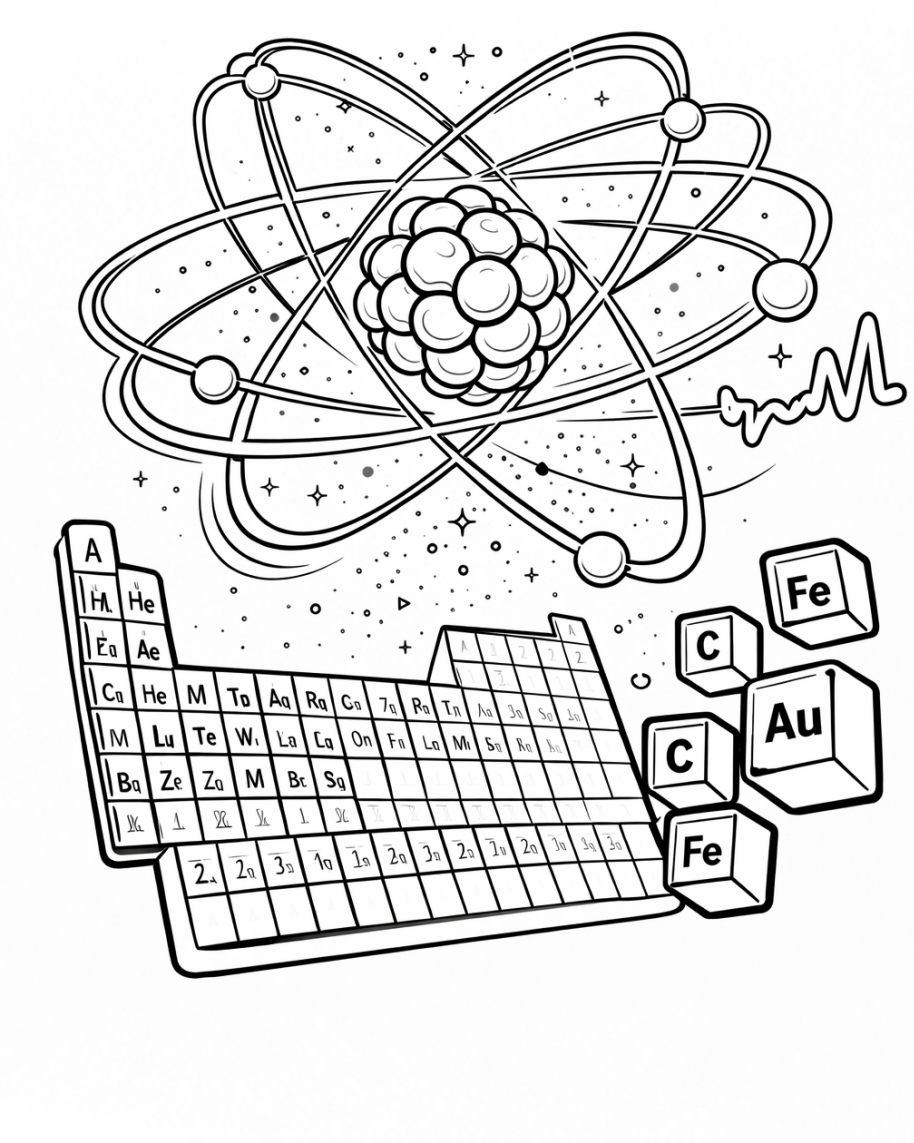
A. ATOMIC STRUCTURE AND PERIODIC CLASSIFICATION

- Atomic models: Rutherford, Bohr and Sommerfield-Origin of hydrogen spectrum-Electromagnetic radiation- Dualism of light-Black body radiation- Planck's quantum theory-Phtoelectric effect-Compton effect-de Broglie equation-Heisenberg uncertainty principle.
- Periodic properties of elements: Atomic ionic radii, Ionization potential, electron affinity, electronegativity (Pauling and Mulliken's scale) of elements along period and groups, -Effective nuclear charge, screening effect, Slater rule
- Postulates of quantum mechanics-operators: linear, non-linear, commutator- Schrodinger wave equation and derivation)-6LJQLILFDQFHRIįDQGį2 , wave mechanical concept of atomic orbitals.

B. CHEMICAL BONDING

- Ionic bond-Factors influencing the ionic bond-Lattice energy- Inert pair effect-Fajan's rules-Born-Haber cycle-Born-Lande equation (derivation not required)
- Covalent bond-Lewis theory-VSEPR theory-Shapes of BeF2, BCl3,SnCl2, CCl4, PF5, Valence bond theory- Coordinate bond-Hybridization: sp3 ,dsp2 , sp3 d2 , d2 sp3
- Shapes of orbitals,-quantum numbers-Zeeman effect-Pauling's exclusion principle, Hund, rule, Aufbau Principle, Electronic configuration of elements- MO theory, MO diagrams of O2, N2
- Intermolecular forces: hydrogen bond, van der Waals forces
- Dipole moment

A. ATOMIC STRUCTURE AND PERIODIC CLASSIFICATION



1. Atomic Models

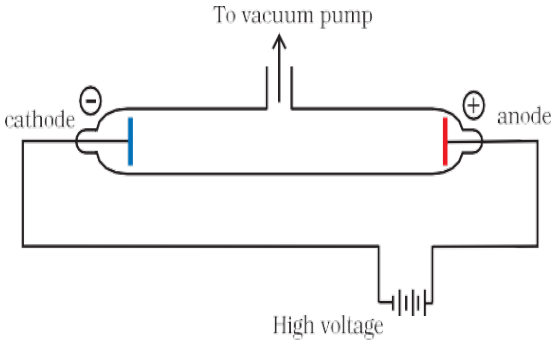
The word 'atom' has been derived from the Greek word *'a-tomio'* which means 'uncutable' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century. The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter. Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

Discovery of Sub-atomic Particles

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other".

1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. These results suggested the particulate nature of electricity. In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes. It is depicted in the figure given below.



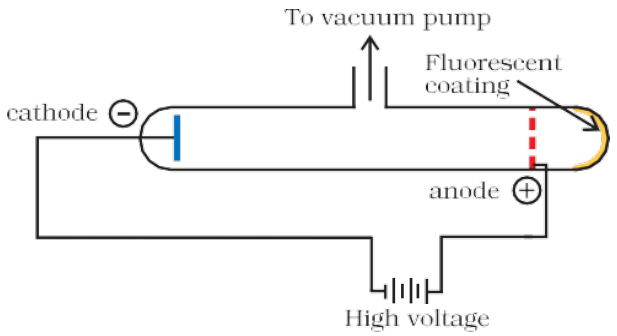
(A cathode ray discharge tube)

A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called cathode rays or cathode ray particles. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating.

Do you know?

We Didn't "See" Atoms Until 1981

Atoms were first imaged using a scanning tunneling microscope invented by Gerd Binnig and Heinrich Rohrer. They later won a Nobel Prize for this invention



(A cathode ray discharge tube with perforated anode)

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called electrons.

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube. Thus, we can conclude that electrons are basic constituent of all the atoms.

Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of canal rays carrying positively charged particles. The characteristics of these positively charged particles are listed below.

i) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

ii) The charge to mass ratio of the particles depends on the gas from which these originate.

iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as neutrons.

Table: Properties of Fundamental Particles

Name	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron (e)	-1.602176×10^{-19}	−1	9.109382×10^{-31}	0.00054	0
Proton (p)	$+1.602176\times10^{-19}$	+1	1.6726216×10^{-27}	1.00727	1
Neutron (n)	0	0	1.674927×10^{-27}	1.00867	1

2. ATOMIC MODELS

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is

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composed of sub-atomic particles carrying positive and negative charges.

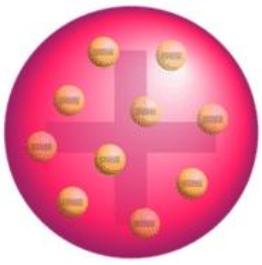
The major problems before the scientists after the discovery of sub-atomic particles were:

- to account for the stability of atom,
- to compare the behaviour of elements in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms, and
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, one proposed by J.J. Thomson and the other proposed by Ernest Rutherford are discussed below.

2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. Many different names are given to this model, for example, plum pudding, raisin pudding or watermelon.

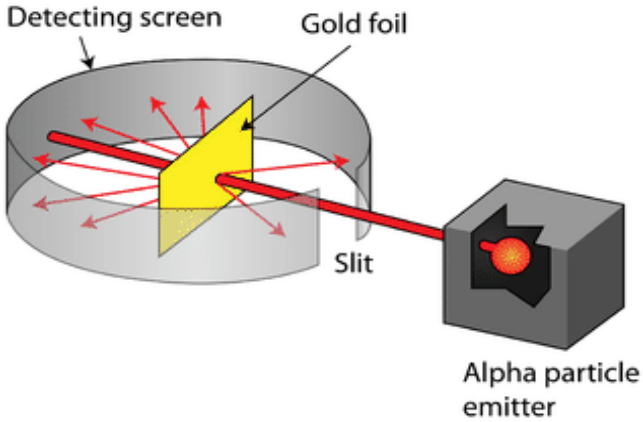


(Thomson model of atom)

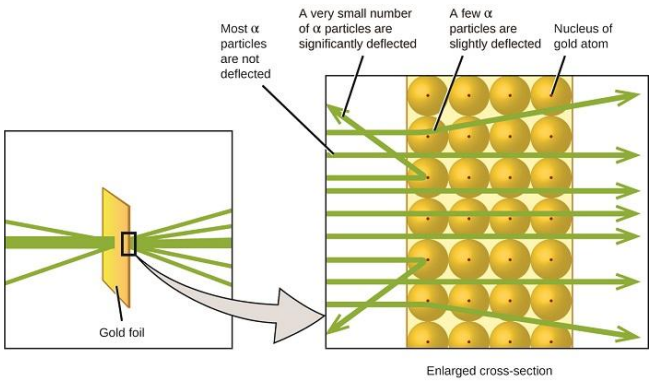
This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous –particle scattering experiment is represented in the following figure.



(Rutherford's scattering experiment)



(Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.)

A stream of high energy α –particles from a radioactive source was directed at a thin foil (thickness ~100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α –particles struck the screen, a tiny flash of light was produced at that point. The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α –particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil.

It was observed that:

i) most of the α –particles passed through the gold foil undeflected.

ii) a small fraction of the α –particles was deflected by small angles.

iii) a very few α –particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom:

Most of the space in the atom is empty as most of the α –particles passed through the foil undeflected.

A few positively charged α –particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α –particles.

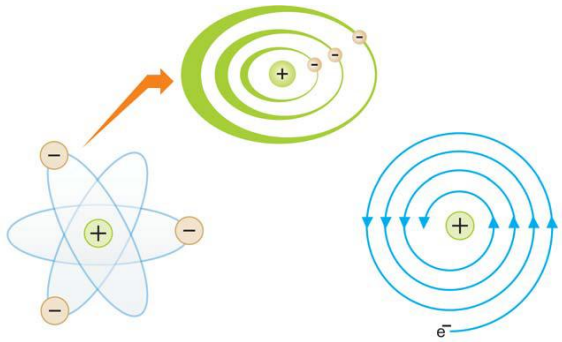
Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford.

ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

iii) Electrons and the nucleus are held together by electrostatic forces of attraction.



(Rutherford's model of atom : electrons orbiting around nucleus. And Orbiting electron would radiate energy and spiral into the nucleus.)

Drawbacks of Rutherford Model

Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the

electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the $\left(G.\frac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements.

The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force $\left(k.\frac{q_1q_2}{r^2}\right)$ where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink.

Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom. Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

2.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra.

Fact : Bohr's Model Was "Wrong" - But Essential

Modern quantum mechanics (developed by scientists like Werner Heisenberg and Erwin Schrödinger) showed that electrons don't travel in neat circular orbits.

Instead, they exist in probability clouds (orbitals).

Yet Bohr's model remains:

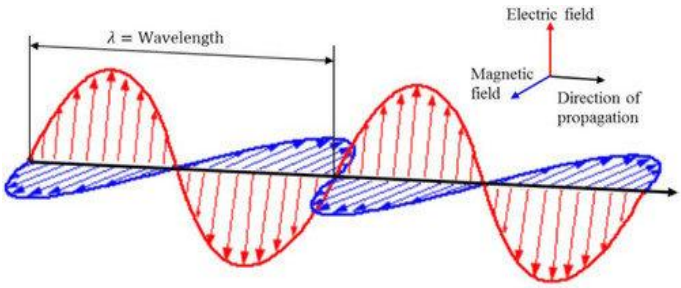
- Extremely useful for teaching
- Accurate for hydrogen
- A key stepping stone toward modern

2.3.1 Wave Nature of Electromagnetic Radiation

In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occurred in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed in the early **1870's by James Clerk Maxwell,** which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century when wave nature of light was established. Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character.



(The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.)

Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.

(ii) Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called electromagnetic spectrum. Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called visible light. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

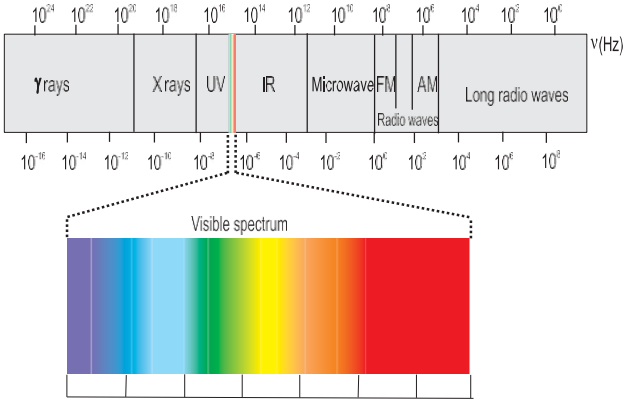
(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ).

The SI unit for frequency (ν) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. The figure given below shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vacuum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925×10^8 ms^{-1}, to be precise). This is called speed of light and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation $c = \nu\lambda$



(a) The spectrum of electromagnetic radiation.

(b) Visible spectrum. The visible region is only a small part of the entire spectrum.)

The other commonly used quantity specially in spectroscopy, is the wavenumber ($\bar{\nu}$). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1} (not SI unit).

2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black-body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

(iv) Line spectra of atoms with special reference to hydrogen.

These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below:

Why was the Planck's Quantum Theory considered Revolutionary?

Before Planck:

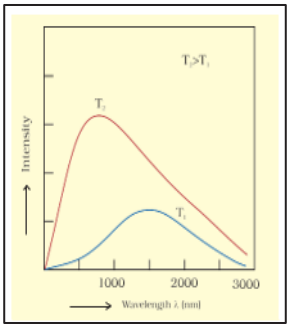
- Energy was believed to be continuous (like water flowing).

After Planck:

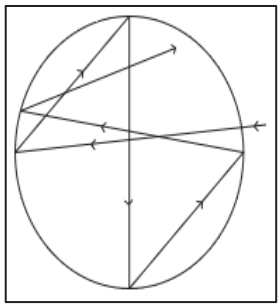
- Energy behaves more like coins - exchanged in fixed amounts.

Even Planck himself initially thought this was just a mathematical trick!

Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation. In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength.



(a. Wavelength-intensity relationship)



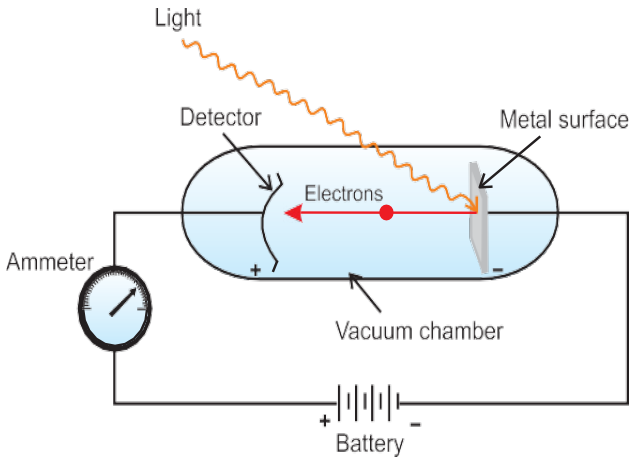
(b. Black body)

Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength. But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck arrived at a satisfactory relationship by making an assumption that absorption and emission of radiation arises from oscillator i.e., atoms in the wall of black body.

Their frequency of oscillation is changed by interaction with oscillators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name quantum to

the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation E = hν. The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} Js.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures. Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them. E= 0, hν, 2hν, 3hν, nhν



(Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.)

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in the above figure. The phenomenon is called Photoelectric effect. The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light. (Content Developed by Pro.fessor Ac.ademy)

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [$\nu = (4.3 \text{ to } 4.6) \times 10^{14}$ Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light (ν = 5.1–5.2 × 10^{14} Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν_0) for potassium metal is 5.0×10^{14} Hz.

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Who Discovered photoelectric effect?

- First observed in 1887 by Heinrich Hertz.
- Explained in 1905 by Albert Einstein.

Einstein later won the Nobel Prize in Physics in 1921 for explaining it — **not** for relativity.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Table : Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

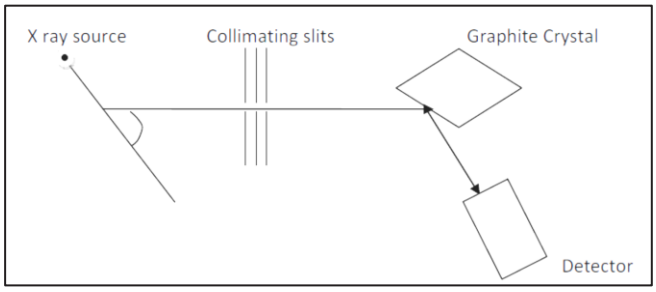
Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to h ν and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0), then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation $h\nu = h\nu_0 + \frac{1}{2}m_e v^2$ where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Key Terms

- Threshold frequency – Minimum frequency needed to eject electrons.
- Work function – Minimum energy required to remove an electron.
- Kinetic energy of electron – Extra energy after

COMPTON EFFECT

In 1924, Arthur Compton discovered that when a beam of monochromatic X-rays or γ rays (of shorter wavelength) are scattered by atoms of an element of low atomic number (such as graphite), the scattered radiation contains not only the original wavelength but also but also another new modified radiation of slightly longer wavelength – the satellite line. Scattering leading to a modified wavelength is called incoherent scattering. This type of incoherent X-Ray scattering is called Compton effect. The difference between the wavelength of original wave and the scattered modified wave is called Compton shift.



(Compton's experimental arrangement)

Applying momentum conservation in Y direction

$$0 = \left(\frac{hv'}{c}\right) sin\theta - mvsin\phi$$

Applying energy conservation

$$hv + m_0c^2 = hv' + mc^2$$

$$\boldsymbol{mvccos\phi = h(v - v'cos\theta)\ and\ mvcsin\phi = hv'sin\theta})$$

Squaring and adding

$$m^2v^2c^2 = h^2(v^2 + v'^2 - 2vv'cos\theta)$$

$$mc^2 = m_0c^2 + h(v - v')$$

Squaring

$$m^2c^4 = {m_0}^2c^4 + h^2(v^2 + v'^2 - 2vv') + 2m_0c^2 + h(v - v')$$

From the above equations,

$$\boldsymbol{m^2c^2(c^2 - v^2) = {m_0}^2c^4 - 2h^2vv'(1 - cos\theta) + 2m_0c^2h(v - v')}$$

Or

$$\boldsymbol{m^2c^2\left(1 - \frac{v^2}{c^2}\right) = {m_0}^2c^4 - 2h^2vv'(1 - cos\theta) + 2m_0c^2h(v - v')}$$

Now the relativistic mass

$$m = \frac{m_0}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}}$$

Hence $m_0 = m\sqrt{\left(1 - \frac{v^2}{c^2}\right)}$ and ${m_0}^2 = m^2\sqrt{\left(1 - \frac{v^2}{c^2}\right)}$

From the above equations,

$${m_0}^2c^4 = {m_0}^2c^4 - 2h^2vv'(1 - cos\theta) + 2m_0c^2h(v - v')$$

Or

$$0 = -2h^2vv'(1 - cos\theta) + 2m_0c^2h(v - v')$$

Or

$$2h^2vv'(1 - cos\theta) = 2m_0c^2h(v - v')$$

Or

$$hvv'(1 - cos\theta) = m_0c^2(v - v')$$

Or

$$2hvv'sin^2\left(\frac{\theta}{2}\right) = m_0c^2(v - v')$$

Or

$$2hsin^2\left(\frac{\theta}{2}\right) = m_0c^2\left(\frac{v - v'}{vv'}\right)$$

Or

$$2hsin^2\left(\frac{\theta}{2}\right) = m_0c^2\left(\frac{1}{v'} - \frac{1}{v}\right)$$

Or

$$2hsin^2\left(\frac{\theta}{2}\right) = m_0c\left(\frac{1}{v'} - \frac{1}{v}\right)$$

Or

$$2hsin^2\left(\frac{\theta}{2}\right) = m_0c(\lambda - \lambda')$$

Or

$2hsin^2\left(\frac{\theta}{2}\right) = m_0c(d\lambda)$ where $d\lambda = (\lambda - \lambda')$= Compton shift

Or

$$d\lambda = \frac{2hsin^2\left(\frac{\theta}{2}\right)}{m_0c} = 2\lambda_0sin^2\left(\frac{\theta}{2}\right)$$

This equation gives the expression for Compton shift.

$\lambda_0 = \frac{2h}{m_0c}$; m_0 = rest mass of electron, c = velocity of light and h = Planck's constant.

All these quantities are universal constants. So λ_0 is also an universal constant which has a dimension of length and is called **Compton wavelength of an electron** . The value of $\lambda_0$is 0.024Å. This shows that the Compton shift

depends only on the angle of scattering but independent of the frequency of incident radiation and nature of target.

Energy of scattered photon.

Energy of scattered photon is E'= hν'.

Now, it has been shown earlier that :

$$2hsin^2\left(\frac{\theta}{2}\right) = m_0c^2\left(\frac{1}{\nu'} - \frac{1}{\nu}\right)$$

Or

$$h(1 - cos\theta) = m_0c^2\left(\frac{1}{\nu'} - \frac{1}{\nu}\right)$$

Or

$$\frac{1}{\nu'} = \frac{1}{\nu} + \frac{h(1 - cos\theta)}{m_0c^2}$$

Hence

$$\nu' = \frac{1}{\frac{1}{\nu} + \frac{h(1 - cos\theta)}{m_0c^2}}$$

Or

$$E^{'} = h\nu' = \frac{h\nu}{\frac{1}{\nu} + \frac{h(1 - cos\theta)}{m_0c^2}}$$

Energy of scattered photon in terms of scattering angle θ and energy hν of incident photon and energy hν of incident photon.

Kinetic energy of recoil electron.

Since the kinetic energy is supplied by a part of the energy of the incident photon, hence gain in electron energy is equal to the loss in photon energy. So the kinetic energy of the recoil electron is obtained by simply subtracting the energy of the scattered photon from the energy of incident photon.

$$E_k = h\nu - \frac{h\nu}{1 + \frac{h\nu(1 - cos\theta)}{m_0c^2}}$$

$$E_k = h\nu\left(1 - \frac{1}{1 + \frac{h\nu(1 - cos\theta)}{m_0c^2}}\right)$$

$$E_k = h\nu\left(1 - \frac{\frac{h\nu(1 - cos\theta)}{m_0c^2}}{1 + \frac{h\nu(1 - cos\theta)}{m_0c^2}}\right)$$

$$E_k = h\nu\left(\frac{a(1 - cos\theta)}{1 + a(1 - cos\theta)}\right)$$

where $a = \frac{h\nu}{m_0c^2}$;

Relation between the angle of scattering of the photon 'θ', and the angle of deviation 'ϕ' of the recoil electron.

From equations given above,

$$tan\phi = \frac{\nu' sin\theta}{\nu - \nu' cos\theta}$$

Also from it has been deduced earlier that:

$$\frac{1}{\nu'} = \frac{1}{\nu} + \frac{h(1 - cos\theta)}{m_0c^2}$$

Or

$$\frac{1}{\nu'} = \frac{1}{\nu}\left\{1 + \frac{h(1 - cos\theta)}{m_0c^2}\right\}$$

$$= \frac{1}{\nu}\left(1 + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)\right) \text{ Where a} = \frac{\text{h}\nu}{m_0c^2}$$

Hence $\nu' = \frac{\nu}{1+2a\text{Sin}^2\left(\frac{\theta}{2}\right)}$

Substituting the value of $\nu^{'}$

$$\tan\ \phi = \frac{\frac{\nu}{1 + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)}\text{Sin}\theta}{\nu - \frac{\nu}{1 + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)}\text{Cos}\theta}$$

$$= \frac{\frac{\nu}{1 + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)}\text{Sin}\theta}{\frac{\nu(1 - \text{Cos}\theta) + 2a\nu\text{Sin}^2\left(\frac{\theta}{2}\right)}{1 + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)}}$$

$$= \frac{\nu\text{Sin}\theta}{\nu\left\{((1 - \text{Cos}\theta)) + 2a\text{Sin}^2\left(\frac{\theta}{2}\right)\right\}}$$

$$= \frac{2v\text{Sin}\left(\frac{\theta}{2}\right)\text{Cos}\left(\frac{\theta}{2}\right)}{2v\text{Sin}^2\left(\frac{\theta}{2}\right)\{1+\text{a}\}}$$

$$= \frac{\text{Cot}\left(\frac{\theta}{2}\right)}{1+a}$$

Or

$$\text{Cot}\phi = \tan\left(\frac{\theta}{2}\right)(1+a) = \left(1+\frac{\text{h}\nu}{m_0c^2}\right)\tan\left(\frac{\theta}{2}\right)$$

Equation gives the Relation between the angle of scattering of the photon $'\theta'$, and the angle of deviation $'\phi'$ of the recoil electron.

Why It Matters Today

Compton scattering is used in:

- Medical imaging
- Radiation therapy
- Astrophysics
- Particle physics experiments

Comparison between Compton scattering and photoelectric effect.

S.No	Compton scattering	Photoelectric effect
1	The energy of the incident light quantum should be greater than the binding energy of the electron, so that the electron recoils and a scattered photon of lower energy appears.	The energy of the incident light quantum should be of the same order of the binding energy of the electron. As the photon is absorbed, the binding energy is overcome by the acquired energy, and the electron as well as the resulting ion recoil with a certain energy and momentum.
2	A part of the energy of the incident photon is absorbed by the electron.	The energy of incident photon is either completely absorbed by the electron or no energy is absorbed at all.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Lesser-Known Facts

1. Visible light is only a tiny part of the EM spectrum.
2. The Sun emits all types of electromagnetic radiation.
3. Gamma rays and radio waves are fundamentally the same - only energy differs.
4. Moving electric charges produce electromagnetic waves.

2.3.3 Evidence for the quantized Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since

ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called continuous spectrum. Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation. When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum. The study of emission or absorption spectra is referred to as spectroscopy. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra because the emitted radiation is identified by the appearance of bright lines in the spectra.

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements. Elements like rubidium (Rb), caesium (Cs), thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of

discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula:

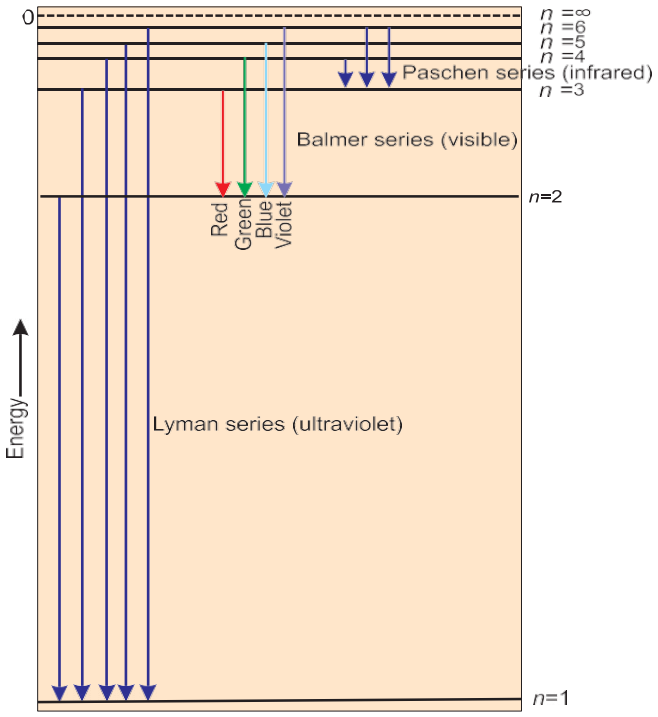
$\bar{\nu} = 109{,}677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^{-1}$

The series of lines described by this formula are called the Balmer series. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression

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

The value 109,677 cm^{-1} is called the Rydberg constant for hydrogen. The first five series of lines that correspond to n_1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively. These series of transitions in the hydrogen spectrum.

Series	n_1	n_2	Region	Wavelength λ(Å)
Lyman	1	2, 3, 4, 5, etc.	ultraviolet	920-1200
Balmer	2	3, 4, 5, 6, etc.	visible	4000-6500
Paschen	3	4, 5, 6, 7, etc.	infrared	9500-18750
Brackett	4	5, 6, 7	infrared	19450-40500
Pfund	5	6, 7	infrared	37800-75000



(The diagram shows the Lyman, Balmer and Paschen series of transitions)

Figure shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e.,

(i) line spectrum of element is unique and

(ii) there is regularity in the line spectrum of each element.

2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra.

Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.

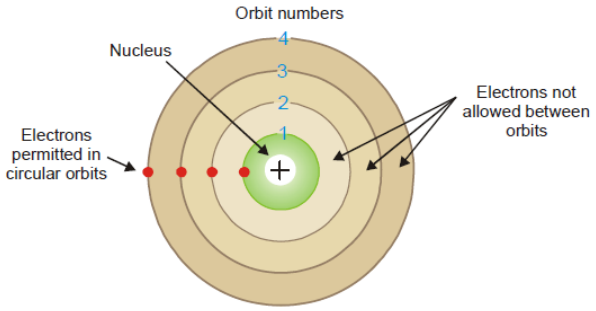
iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by:

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

where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv) The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation $m_e vr = n\frac{h}{2\pi}$ where n = 1,2,3..... where m_e is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. That means angular momentum is quantized. Radiation is emitted or absorbed only when transition of electron takes place from one quantized value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.



(Circular electron orbits or stationary energy levels in an atom)

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered n = 1,2,3.These integral numbers are known as Principal quantum numbers.

b) The radii of the stationary states are expressed as $r_n = n^2 a_0$ where a_0 = 52.9 pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

The most important property associated with the electron, is the energy of its stationary state. It is given by the expression $E_n = -R_H\left(\frac{1}{n^2}\right)\text{cm}^{-1}$. n = 1,2,3..where R_H is called Rydberg constant and its value is 2.18×10^{-18}J. The energy of the lowest state, also called as the ground state, is E_1

$= -2.18\times10^{-18}\left(\frac{1}{1^2}\right) = -2.18\times10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2 = 2.18\times10^{-18}\left(\frac{1}{2^2}\right) = -0.545\times10^{-18}$ J.

c) This energy level diagram depicts the energies of different stationary states or energy levels of hydrogen atom. When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number = n = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation and depicts its stability relative to the reference state of zero energy and n = ∞.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+, Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression $E_n = -2.18\times10^{-18}\left(\frac{z^2}{n^2}\right)$J and radii by the expression $r_n = \frac{52.9\,n^2}{Z}$pm where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits. What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation so that $E_\infty = 0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by n =1 which corresponds to the most stable orbit. We call this the ground state.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation $\Delta E = E_f - E_i$.

On combining the equations,

$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_1^2}\right)$ (where n_i and n_f stand for initial orbit and final orbits)

LEARNER TESTIMONIALS

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குழந்தைகளுக்காகத் தனியார் பள்ளி வேலையை விட்டுவிட்டு, முழு நேர தயாரிப்பில் இறங்கினேன். Professor Academy–யின் லைவ் மற்றும் ரெக்கார்டட் வீடியோக்கள் என் தயாரிப்பை எளிதாக்கியது. இன்று என் வீட்டிற்கு 5 கி.மீ அருகிலேயே அரசுப் பள்ளி ஆசிரியையாகப் பணியாற்றுகிறேன். கனவு நனவானது!

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டிஆர்பி அறிவிப்பு வந்த பிறகு ஒரு வாரம் கழித்தே படிக்கத் தொடங்கினேன். இது என் முதல் முயற்சி! மிகக் குறைந்த காலத்தில் நான் வெற்றி பெற Professor Academy ஆசிரியர்களின் துல்லியமான வழிகாட்டுதலே காரணம். இன்று சிவகங்கை அரசுப் பள்ளியில் ஆசிரியராகப் பணியாற்றுவது மட்டற்ற மகிழ்ச்சி!

Shanthi Priya. N
TRB Chemistry

வேலை, இரண்டு குழந்தைகள் எனப் பல பொறுப்புகளுக்கு இடையே UG TRB தேர்வில் 31–வது ரேங்க் பெற்றது மகிழ்ச்சி! Professor Academy – இன் வீடியோ வகுப்புகள் & தேர்வுகள் என் வெற்றிக்கு அடித்தளம். இல்லத்தரசிகளும் வேலைக்குச் செல்பவர்களும் சரியான வழிகாட்டுதலுடன் சாதிக்க முடியும் என நிரூபித்துவிட்டேன்!

Sumiya Parveen
TRB Chemistry - GHSS Veppalodai - Thoothukudi

ஒரே Courseல் சேர்ந்து SET, PG TRB (Dist 1st), TET என 3 தேர்வுகளில் வெற்றி! இல்லத்தரசியான எனக்கு அகாடமியின் ஆழமான பயிற்சியும், சலிக்காத சந்தேகத் தீர்வும் மிகப்பெரிய பலம். சோர்வடைந்த நேரத்தில் மென்டர்களின் ஆதரவு என்னை ஜெயிக்க வைத்தது. சாதிக்கத் துடிக்கும் பெண்களுக்கு ProfessorAcademy ஒரு வரப்பிரசாதம்!

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3 வயது குழந்தையைப் பராமரித்துக்கொண்டு, இரவு நேரங்களில் படித்து அரசுப் பணி பெற்றேன். Educational Methodology மற்றும் GK–வில் அதிக மதிப்பெண் பெறத் தேர்வுகளை எழுதிப் பார்த்ததே என் TRB வெற்றியின் ரகசியம்! குறைந்த கட்டணத்தில் முழு பாடத்திட்டத்தையும் கவர் செய்த Professor Academy எனக்குப் பெரும் பலம்.

$$\Delta E = \mathrm{R_H}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

The frequency (v) associated with the absorption and emission of the photon can be evaluated by using equation

$$v = \frac{\Delta E}{h} = \frac{\mathrm{R_H}}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
$$= \frac{2.18 \times 10^{-18}\ \mathrm{J}}{6.626 \times 10^{-34}\mathrm{Js}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
$$= 3.29 \times 10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\mathrm{Hz}$$

and in terms of wavenumbers ($\bar{V}$)

$$\bar{v} = \frac{v}{\mathrm{c}} = \frac{\mathrm{R_H}}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
$$= \frac{3.29 \times 10^{15}\ \mathrm{s^{-1}}}{3 \times 10^{8}\ \mathrm{m\ s^{-s}}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
$$= 1.09677 \times 10^{7}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\mathrm{m^{-1}}$$

In case of absorption spectrum, $n_f > n_1$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_1 > n_f, \Delta E$ is negative and energy is released.

The expression is similar to that used by Rydberg derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+}, Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds. In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

SOMMERFELD'S MODIFICATION OF BOHR ATOM

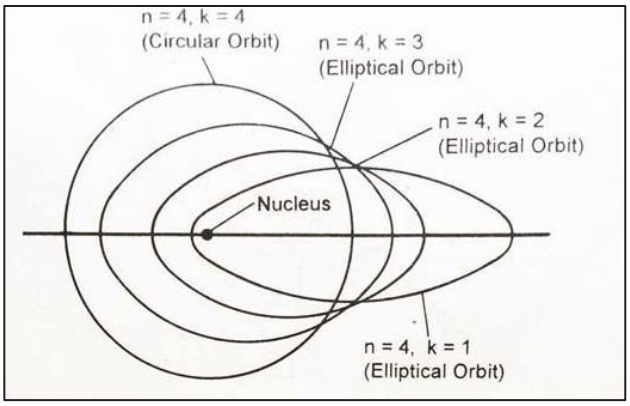
When spectra were examined with spectrometers, each line was found to consist of several closely packed lines. The existence of these multiple spectral lines could not be explained on the basis of Bohr's theory. Sommerfeld modified Bohr's theory as follows. **Bohr considered electron orbits as circular but Sommerfeld postulated the presence of elliptic orbits** also. An ellipse has a major and minor axis. A circle is a special case of an ellipse with equal major and minor axis. The angular momentum of an electron moving in an elliptic orbit is also supposed to be quantized. Thus only a definite set of values is permissible. It is

further assumed that the angular momentum can be an integral part of $h/2\pi$ units, where h is Planck's constant. Or that,

$$\text{angular momentum } = \frac{kh}{2\pi}$$

where k is called the azimuthal quantum number, whereas the quantum number used in Bohr's theory is called the principal quantum number. The two quantum numbers n and k are related by the expression:

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$



(Sommerfeld's atomic model)

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

(i) According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

(ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

(i) The varying distance of the electron from the nucleus (r).

(ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal angle φ.

To deal with these two variables, two quantum numbers are introduced (i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and

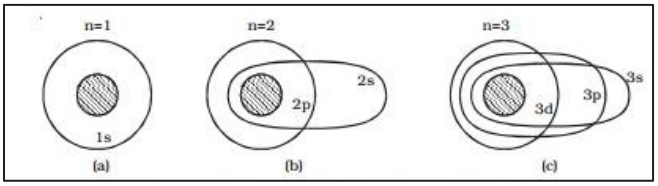
(ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity.

This orbital quantum number (l) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that b/a = l+1/n where a and b are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number n, there are n possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of n subshells, one is circular and the remaining (i.e., n-1) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level (n=1). When n = 1, l = 0 i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when $a = b$, the two axes of the ellipse are equal. As a result of this, the orbit corresponding to n=1 is circular. This subshell is designated as s sub-shell. Since, this sub-shell belongs to n=1, it is designated as 1s.



Various sub-shells for the electrons

Similarly, for the second energy level *n*=2, there are two permissible sub-shells for the electrons. For *n*=2, *l* can take two values, 0 and 1.

When *n* = 2, *l* = 0, b/a= 0+1/2 =1/2 or b=a/2

This subshell corresponding to *l* = 0 is elliptical in shape and is designated as 2s.

when *n* = 2, *l* = 1, b/a= 1+1/2 =2/2 =1 or b=a.

This sub-shell corresponding to *l* = 1 is circular in shape and is designated as 2*p*.

For n = 3, *l* has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when n = 3, *l* = 0, b/a= (0+1)/3 =1/3 =1 or b=a/3

when n = 3, *l* = 1, b/a= (1+1)/3 =2/3 =1 or b=2a/3

and when n = 3, *l* = 2, b/a= (2+1)/3 =3/3 =1 or b=a

The sub-shells corresponding to *l* = 0, 1 and 2 are designated as 3s, 3*p* and 3*d* respectively. The circular shell is designated as 3*d* and the other two are elliptical in shape. It is common practice to assign letters to *l*-values as given below:

Orbital quantum number l : 0 1 2 3 4

electron state : s p d f g

Hence, electrons in the *l* = 0, 1, 2, 3 states are said to be in the *s, p, d, f* states.

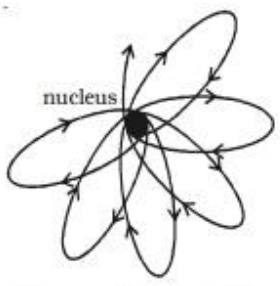
Fine structure of spectral line

Based on Sommerfeld atom model, the total energy of an electron in the elliptical orbit can be shown as,

$$E_n = \frac{(-me^4Z^2)}{8\varepsilon_0 h^2 n^2}$$

This expression is the same as that obtained by Bohr. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. In this way, the attempt of Sommerfeld to explain the fine structure of spectral lines failed. But soon, on the basis of variation of mass of electron with velocity, Sommerfeld could find the solution for the problem of the fine structure of the spectral lines.

According to Sommerfeld, the velocity of the electron is maximum when the electron is nearest to the nucleus and minimum when it is farthest from the nucleus, since the orbit of the electron is elliptical. This implies that the effective mass of the electron will be different at different parts of its orbit. Taking into account the relativistic variation of the mass of the electron, Sommerfeld modified his theory and showed that the path of electron is not a simple ellipse but a precessing ellipse called a rosette.



(Rosette path of an electron)

Based on this idea, Sommerfeld successfully explained the fine structure of spectral lines of hydrogen atom.

Drawbacks

(i) Though Sommerfeld's modification gave a theoretical background of the fine structure of spectral lines of hydrogen, it could not predict the correct number of observed fine structure of these lines.

(ii) It could not explain the distribution and arrangement of electrons in atoms.

(iii) Sommerfeld's model was unable to explain the spectra of alkali metals such as sodium, potassium etc.

(iv) It could not explain Zeeman and Stark effect.

(v) This model does not give any explanation for the intensities of the spectral lines.

2.5 QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

1. Dual behaviour of matter,

2. Heisenberg uncertainty principle

2.5.1 De-Broglie's Matter Waves: Dual Nature Of Matter

This is based on wave mechanical concept of an electron in an atom. Albert Einstein proposed dual character of electromagnetic radiation in 1905, *viz*. wave character based on Maxwell's concept evidenced by diffraction, interference, polarisation kinds of phenomena and particle character based on Planck's quantum theory witnessed by quantization of energy and hence photoelectric effect, i.e. the ejection of photoelectrons from metal surface on striking electromagnetic radiation.

On the basis of above analogy, French Physicist Louis de Broglie (1924) postulated that not only light but all material objects (both micro and macroscopic) in motion such as electrons, protons, atoms, molecules etc. possess both, wave and the particle properties and thus have dual character, i.e. the wave character and particle (corpuscular) character. He called the waves associated with material particles as matter waves which are now named de Broglie's wave. These waves differ from electromagnetic or light waves in a sense that these are unable to travel through empty space and their speed is different form light waves.

De-Broglie's relation

De-Broglie deduced a fundamental relation between the wave length of moving particle and its momentum by making use of Einstein's mass energy relationship and Planck's quantum theory. The material particle as a wave satisfies the Planck's relation for a photon, i.e. E = hν where h is Planck's constant and ν is the frequency of the wave. The frequency for light wave, $\nu = \frac{c}{\lambda}$ and for particle wave, $\nu = \frac{v}{\lambda}$ (c = speed of light wave and v = speed of particle wave). At the same time, Einstein's mass energy relationship is applicable to it, i.e. $E = mc^2$ (for a photon) or $E = mv^2$ (for a particle where $v \neq c$) where m is the mass and v the speed/velocity of the particle.

From the equations, we have

$h\nu = mc^2$; (or)

$h\frac{c}{\lambda} = mv^2$; (or)

$\frac{h}{\lambda} = mv = p$ (momentum) (or)

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

Here, λ corresponds to the wave character of matter and p its particle character. This is known as de Broglie's relation. From this relationship, it is concluded that "the momentum of a moving particle is inversely proportional to the wavelength of the wave associated with it".

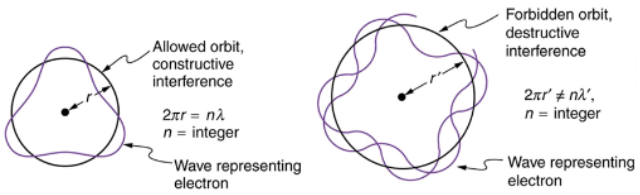
It is important to note here from above discussion that de Broglie's relation is applicable to material particles of all sizes and dimensions but the wave character is significant only for micro objects like electrons and is negligible for macro objects hence cannot be measured properly. This infers that de Broglie's relation is more useful for smaller particles.

de Broglie's relation has been applied to a moving electron around a nucleus in a circular path in an atom to justify Bohr's postulate which states that elections can move only in those orbits for which the angular momentum is equal to an integral multiple of $\frac{h}{2\pi}$.

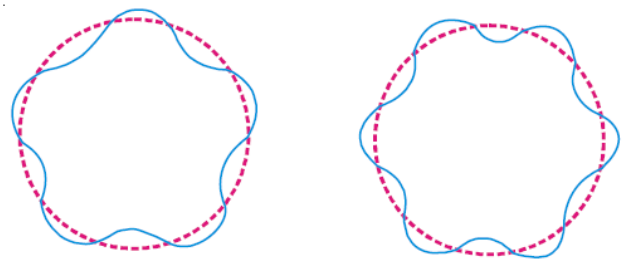
$$mvr = \frac{nh}{2\pi}.$$

This moving electron is considered as a standing wave extended around the nucleus in circular path and not as a mass particle. If the circumference of the orbit is an integral multiple of the wave length, λ, i.e. 2πr = n λ where r is the radius of the orbit and n is the whole number, the wave remains continually in phase, i.e. is a merging wave

Putting the value of λ, in equation, we get $2\pi r = n\frac{h}{mv}$



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.



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

2.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.** Mathematically, it can be given as in equation.

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

$$\text{or } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

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

where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron

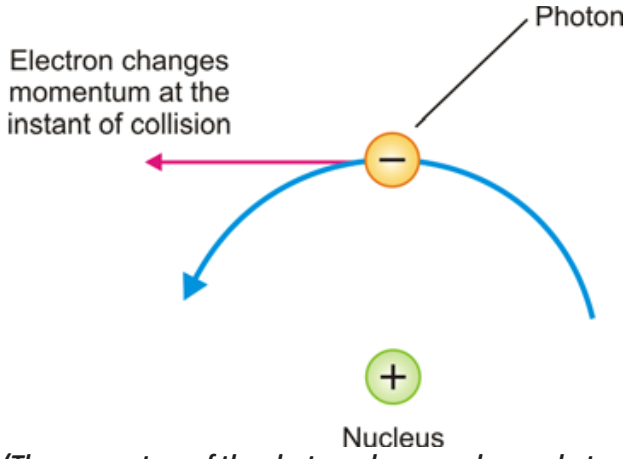
will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$ would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

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.**



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

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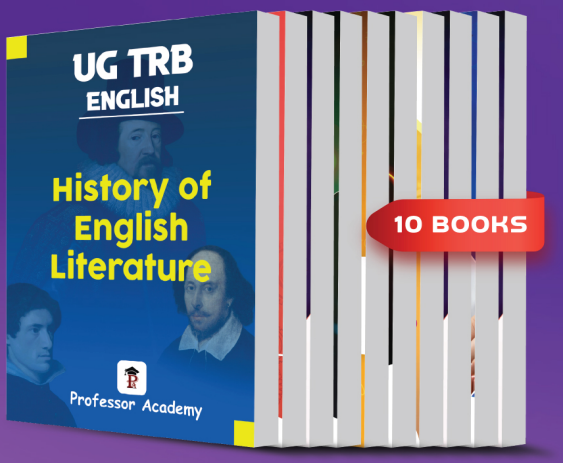

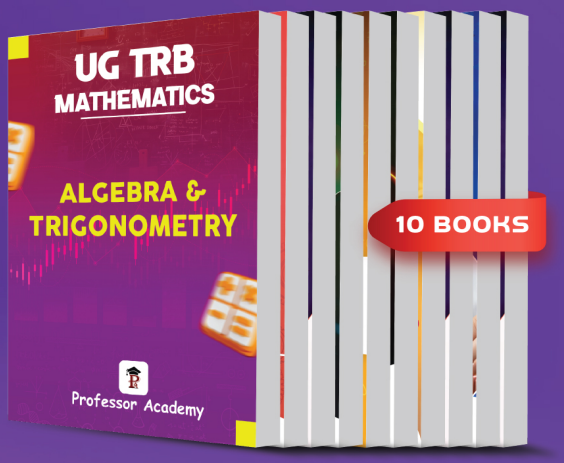

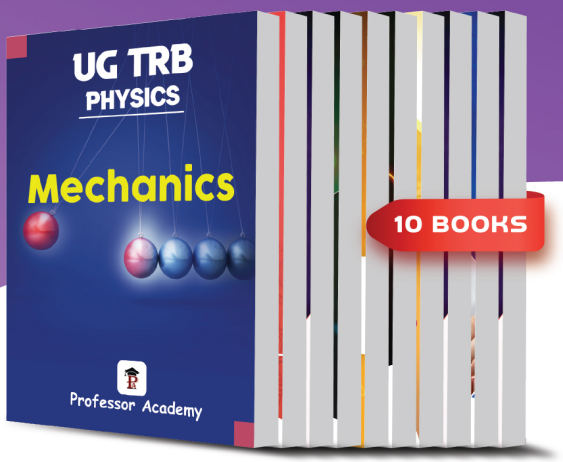

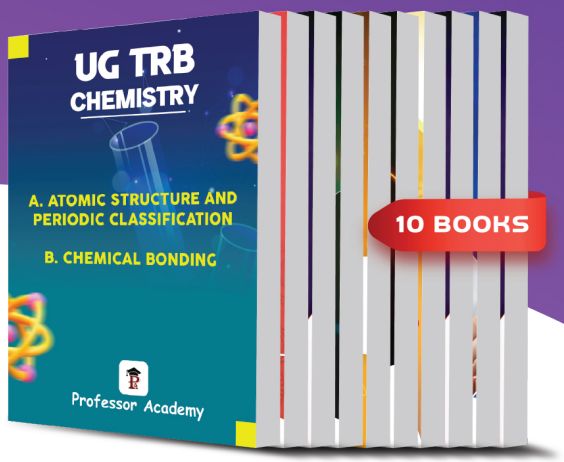

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Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that it rules out existence of definite paths or trajectories of electrons and other similar particles. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

$$\Delta v \cdot \Delta x = \frac{h}{4\pi \cdot m}$$
$$= \frac{6.626 \times 10^{-34}\text{Js}}{4 \times 3.1416 \times 10^{-6}\text{ kg}} \approx 10^{-28}\text{ m}^{-2}\text{ s}^{-1}$$

The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that in dealing with milligramsized or heavier objects, the associated uncertainties are hardly of any real consequence.

In the case of a microscopic object like an electron on the other hand. $\Delta v \cdot \Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg., according to Heisenberg uncertainty principle

$$\Delta v.\, \Delta x = \frac{h}{4\pi m}$$
$$= \frac{6.626 \times 10^{-34}\text{Js}}{4 \times 3.1416 \times 9.11 \times 10^{-31}\text{ kg}}$$
$$= 10^{-4}\text{ m}^{-2}\text{ s}^{-1}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be

$$\frac{10^{-4}\text{ m}^2\text{ s}^{-1}}{10^{-8}\text{ m}} \approx 10^4\text{ ms}^{-1}$$

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.

Reasons for the Failure of the Bohr Model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

2.6 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called quantum mechanics.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave- particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

Major Achievements of Schrodinger equation

- Correctly explained hydrogen atom spectrum
- Predicted atomic orbitals (s, p, d, f shapes)
- Replaced Bohr's circular orbits with probability clouds
- Became the foundation of quantum mechanics

For a system (such as an atom or a molecule whose energy does not change with time) the **Schrödinger equation** is written as $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and λ.

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

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

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 twice with respect to x, we get

$$\frac{d\psi}{dx} = A\frac{2\pi}{\lambda}\cos\ 2\pi\frac{x}{\lambda}$$
$$\frac{d^2\psi}{dx^2} = -A\frac{4\pi^2}{\lambda^2}\sin\ 2\pi\frac{x}{\lambda}$$

But

$$A\sin\ 2\pi\frac{x}{\lambda} = \Psi$$
$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\Psi$$

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

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2}\frac{m^2v^2}{m}$$

According to Broglie's equation

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

or

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

or

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

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

$$\text{K.E.} = \frac{1}{2}\times\frac{h^2}{m\lambda^2}$$

We have

$$\lambda^2 = -\frac{4\pi^2\psi}{\frac{d^2\psi}{dx^2}}$$

Substituting the value of λ^2 in equation

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

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

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

or

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

This is Schrödinger's equation in one dimension. It need be generalized 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.

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning.

Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

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 $= -2.18 \times 10^{-11}$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 ' $\propto$, 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 0.53Å. If the probability distribution be plotted against the distance r from the nucleus, the curve obtained. The probability distribution is maximum at the distance 0.53Å 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.

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.

2. The existence of quantised electronic energy levels is a direct result of the wave like

properties of electrons and are allowed solutions of Schrödinger wave equation.

3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.

4. An atomic orbital is the wave function ψ for an electron in an atom. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.

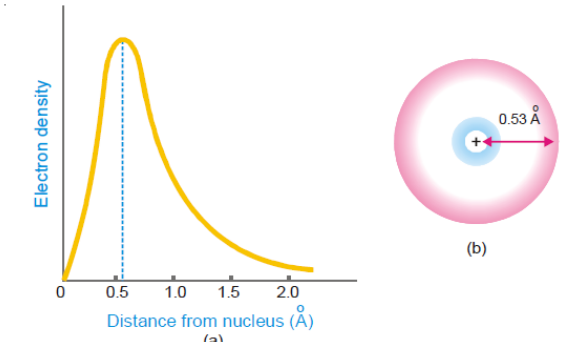
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as probability density and is always positive. From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.

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.



(a) gives the graphical representation
(b) 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 $n = 1,2,3$ ..., 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

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

$$r_n = 0.529n^2\text{Å}$$

and where n is the principal quantum number of the shell.

The principal quantum number ' n ' can have non-zero, positive, integral values $n = 1,2,3$ ... increasing by integral numbers to infinity. Although the quantum number ' n ' may theoretically assume any integral value from 1 to $\propto$, 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

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

For a given value of principal quantum number the order of increasing energy for different subshells is $s<p<d<f$ (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., $+l,\ (+l-l), \ldots 0 \ldots, (-l+1), -l$.

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 ' $\boldsymbol{n}$ ', 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.

LEARNER TESTIMONIALS

Sajini

Chemistry | Rank 25

10 வருட இடைவெளிக்குப் பின் அகாடமியில் இணைந்தேன். OMR பயிற்சி, தவறுகளை ஆய்வு செய்தல் மற்றும் முறையான Revision என் மதிப்பெண்ணை உயர்த்தியது. அகாடமியின் Structured Classes மற்றும் Mentor Guidance எனக்குப் பெரும் நம்பிக்கையை அளித்தது. இலக்கை நோக்கி உழையுங்கள், வெற்றி நிச்சயம் உங்களுக்கே.

Leelavathi

TRB Chemistry achiever Government higher secondary school , Ariyalur

நெட்வொர்க் பிரச்சினையால் ஆன்லைன் வகுப்புகளையும் டெஸ்ட் சீரிஸையும் எழுத சிக்னல் தேடி அலைந்தேன். தெருவிளக்கு வெளிச்சத்தில் அமர்ந்து Professor Academy வகுப்புகளைக் கவனித்த என் விடாமுயற்சி, இன்று என்னை அரியலூர் அரசுப் பள்ளியில் ஆசிரியராக அமர்த்தியுள்ளது!

Komathi A

PG Assistant Chemistry in GBHSS- Pennadam, Cuddalore district

'பாடத்திட்ட மாற்றம், தமிழ் தகுதித் தேர்வு எனப் பல சவால்களை Professor Academy–யின் ஸ்டேட் ரேங்க் இலக்கோடு எதிர்கொண்டேன். அந்தத் தெளிவான பயிற்சிதான் என்னை இன்று பெண்ணாடம் அரசுப் பள்ளியில் முதுகலை வேதியியல் ஆசிரியராக மாற்றியுள்ளது. அந்த கௌரவம் என் வெற்றி!

Nirmal Kumar C

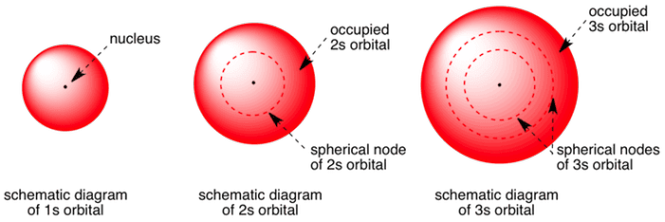
GHSS Kilambakkam, Chennai TRB Chemistry Achiever

சிலபஸ் மாறியபோது பாடங்களை முடிப்பார்களா என்ற பயம் இருந்தது. ஆனால், யூனிட் 1 முதல் 10 வரை அகாடமி காட்டிய அக்கறையும் விரிவான கற்பித்தலும் என் பயத்தைப் போக்கியது. தினசரி தேர்வுகள் மற்றும் ரிவிஷன் வகுப்புகளே என்னை இன்று கிளாம்பாக்கம் அரசுப் பள்ளியில் ஆசிரியராக்கியுள்ளது!

Sanjeevkumar K

TRB Chemistry Achiever GHSS Tirupathur

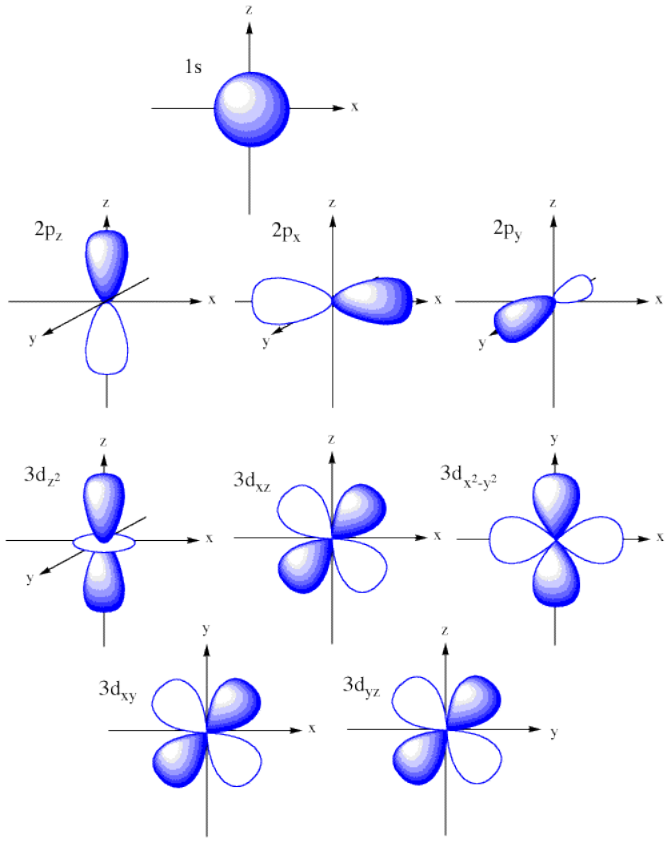
காலை 7:30 முதல் மாலை 7:30 வரை வேலை, இரவு 3 மணி நேர உறக்கம் – இதுதான் என் 4 மாத கால வாழ்க்கை. என் குடும்பத்தின் தியாகமும், Professor Academy–யின் வழிகாட்டுதலுமே இன்று என்னை திருப்பத்தூர் அரசுப் பள்ளியில் ஆசிரியராக்கியுள்ளது. விடாமுயற்சி இருந்தால் வெற்றி நிச்சயம்!



(Spherical 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 the 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 orbital 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 the figure given below.



(Shapes and orientation of s, p and d orbitals)

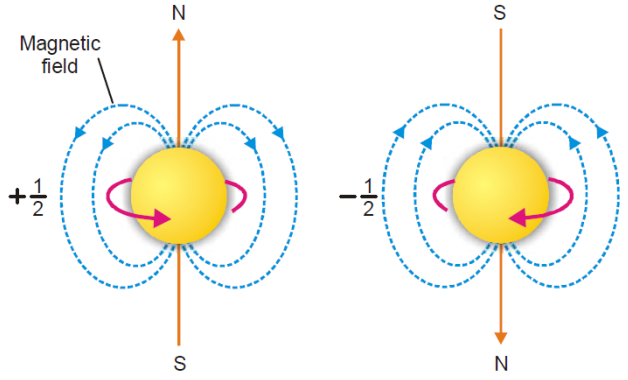
For l = 2 (d orbital), the magnetic quantum number are *five* (2 × 2 + 1); + 2, + 1, 0, – 1, – 2. Thus there are five possible orientations for d orbitals which are equivalent in energy so long as the atom is not under the influence of a magnetic field and are said to be **five-fold degenerate** (Different 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 above. The shape of the d_z orbitals is different from others.

When $l = 3$ (forbital) the magnetic quantum number m can have seven (2 × 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 ↓↑. 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.



(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.

To sum up, the four quantum numbers provide the following information :

i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

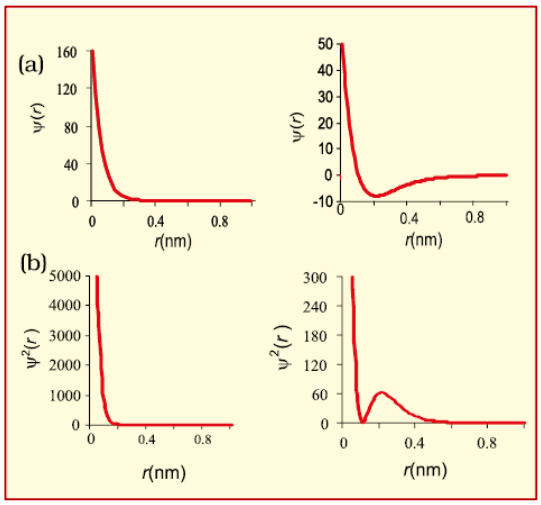
ii) There are n subshells in the nth shell. l identifies the subshell and determines the shape of the orbital. There are (2l+1) orbitals of each type in a subshell, that is, one s orbital (l = 0), three p orbitals (l = 1) and five d orbitals (l = 2) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) m_l designates the orientation of the orbital. For a given value of l, m_l has (2l+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) m_s refers to orientation of the spin of the electron.

Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of *r* (the distance from the nucleus) are different. Figure given such plots for 1*s* (*n* = 1, *l* = 0) and 2*s* (*n* = 2, *l* = 0) orbitals.



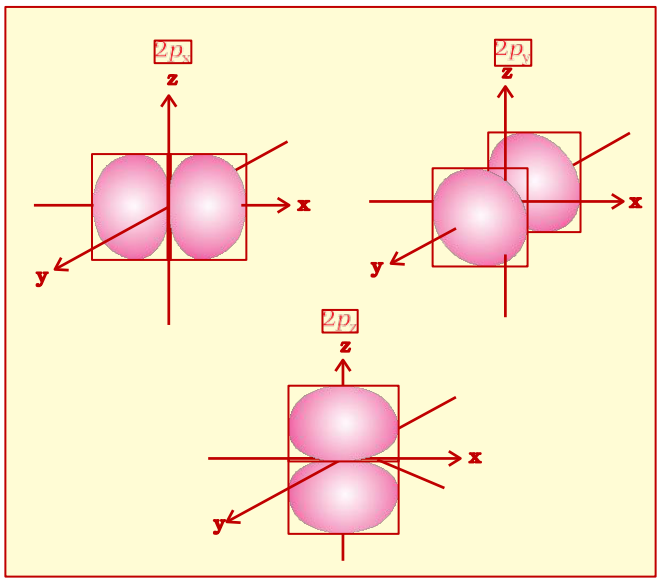
(The plots of (a) the orbital wave function ψ(r); (b) the variation of probability density ψ²(r) as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.)

According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of *r* for 1*s* and 2*s* orbitals is given in Figure. Here again, you may note that the curves for 1*s* and 2*s* orbitals are different.

It may be noted that for 1*s* orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2*s* orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of *r* increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that *ns*-orbital has (*n* – 1) nodes, that is, number of nodes increases with increase of principal quantum number *n*. In other words, number of nodes for 2*s* orbital is one, two for 3*s* and so on. These probability density variation can be visualized in terms of charge cloud diagrams. In these diagrams, the density of the dots in a region represents electron probability density in that region.

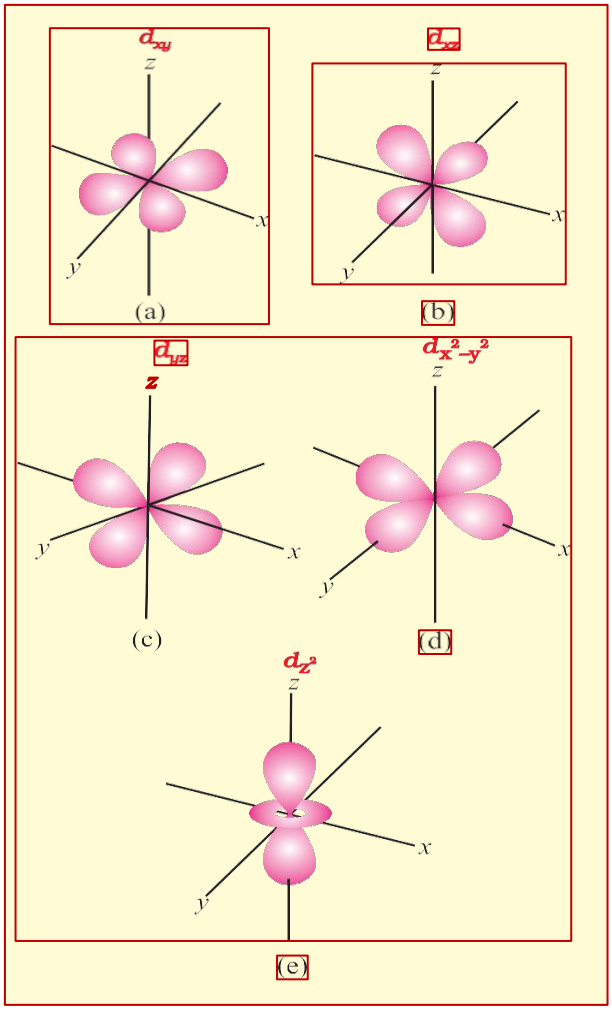
Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in figure. The probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus.

It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%. Thus, we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, that is, 4s > 3s > 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases. Boundary surface diagrams for three 2p orbitals (l = 1) are shown.



(Boundary surface diagrams of the three 2p orbitals.)

In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of ml (–1, 0 and +1) and the x, y and z directions.



(Boundary surface diagrams of the five 3d orbitals)

It is sufficient to remember that, because there are three possible values of ml, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases.

The number of nodes are given by the n –2, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than n–1. There are five ml values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in figure.

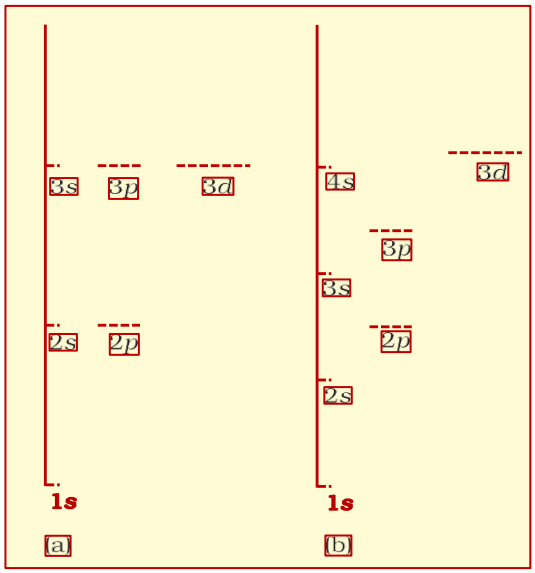
The five d-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} and d_{z2}. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z2}, is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size. Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and n_d orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis.

These are called angular nodes and number of angular nodes are given by 'l', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. The total number of nodes are given by (n–1), i.e., sum of l angular nodes and (n – l – 1) radial nodes.

2.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals in hydrogen atom increases as follows :

1s < 2s = 2p < 3s = 3p = 3d <4s = 4p = 4d= 4f < and etc... is depicted in Fig. given below. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present in 2p orbital. The orbitals having the same energy are called degenerate. The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the ground state and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in excited state.



(Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers)

The energy of an electron in a multi- electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, *s*, *p*, *d*, *f* ... all have different energies. Within a given principal quantum number, the energy of orbitals increases in the order *s*<*p*<*d*<*f*. For higher energy levels, these differences are sufficiently pronounced and staggering of orbital energy may result, e.g., 4*s*<3*d* and 6*s*<5*d*; 4*f*<6*p*. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in multi-electron atoms. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom.

Thus the stability of an electron in a multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (Z_e) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Z_e). The effect will be lowered due to

the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding of the outer shell electrons from the nucleus by the inner shell electrons,** and the net positive charge experienced by the outer electrons is known as effective nuclear charge (Z_{eff} *e*).

Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with increase of nuclear charge. In other words, the energy of interaction between, the nucleus and electron (that is orbital energy) decreases (that is more negative) with the increase of atomic number (***Z***). Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present.

For example electrons present in spherical shaped, *s* orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in *p* orbital. Similarly electrons present in *p* orbitals shield the outer electrons from the nucleus more than the electrons present in *d* orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of *s* orbital, the *s* orbital electron spends more time close to the nucleus in comparison to *p* orbital electron which spends more time in the vicinity of nucleus in comparison to *d* orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (*l*), that is, **the *s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron*.**

The energy of electrons in *s* orbital will be lower (more negative) than that of *p* orbital electron which will have less energy than that of *d* orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an orbital, as mentioned earlier, depends upon the values of *n* and *l*. Mathematically, the dependence of energies of the orbitals on *n* and *l* are quite complicated but one simple rule is that, the **lower the value of (*n* + *l*) for an orbital, the lower is its energy. If two orbitals have the same value of (*n* + *l*), the orbital with lower value of *n* will have the lower energy.**

Table: Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule

Orbital	Value of n	Value of l	Value of (n+l)	
1s	1	0	1+0=1	
2s	2	0	2+0=2	
2p	2	1	2+1=3	2p (n=2) has lower energy than
3s	3	0	3+0=3	3s (n=3)
3p	3	1	3+1=4	3p (n=3) has lower energy than
4s	4	0	4+0=4	4s (n=4)
3d	3	2	3+2=5	3d (n=3) has lower energy than
4p	4	1	4+1=5	4p (n=4)

The Table illustrates the $(n + l)$ rule and same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number (Zeff)**. For example, energy of 2*s* orbital of hydrogen atom is greater than that of 2*s* orbital of lithium and that of lithium is greater than that of sodium and so on, that is, E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K).

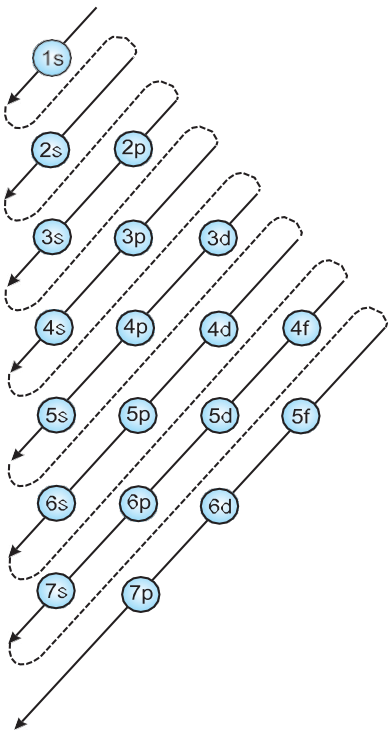
2.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the *aufbau* principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle

The word *'aufbau'* in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states : In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms. However, following order of energies of the orbitals is extremely useful:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s... The order may be remembered by using the method given in below the Figure.



(Order of filling of orbitals)

Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. For example, valence electron in potassium must choose between 3*d* and 4*s* orbitals and as predicted by this sequence, it is found in 4*s* orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur.

Pauli's Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist

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Kalaiyarasi
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Josephine Dheepika L
- Commerce -

2 STATE SECOND

Kokila P
- Geography -

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Sangeetha A
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- Computer Science -

"Once a dream — now State Rankers, even from failed students."

Wolfgang Pauli (1926). According to this principle : **No two electrons in an atom can have the same set of four quantum numbers.** Pauli exclusion principle can also be stated as : **"Only two electrons may exist in the same orbital and these electrons must have opposite spin."** This means that the two electrons can have the same value of three quantum numbers n, l and m_l, but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as : **the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.**

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called **degenerate orbitals**). It states : **pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.** Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry.

Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example :

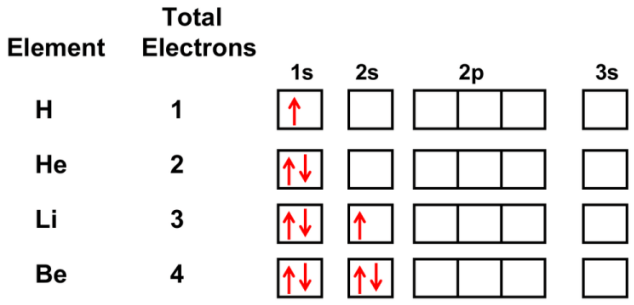
(i) $s^a p^b d^c$ ..... notation

(ii) Orbital diagram

In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c, ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.

The third electron of lithium (Li) is not allowed in the 1*s* orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2*s* orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2*s* orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2\ 2s^2$.



In the next six elements—boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the 2*p* orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :

The electronic configuration of the elements sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar,$1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be

Atom	Symbol	Atomic number	Sub-level Electronic configuration						
			1s	2s	2p	3s	3p	4s	
Hydrogen	H	1	$1s^1$						1^{st} shell Full
Helium	He	2	$1s^2$						
Lithium	Li	3	$1s^2$	$2s^1$					
Beryllium	Be	4	$1s^2$	$2s^2$					
Boron	B	5	$1s^2$	$2s^2$	$2p^1$				2^{nd} shell full
Carbon	C	6	$1s^2$	$2s^2$	$2p^2$				
Nitrogen	N	7	$1s^2$	$2s^2$	$2p^3$				
Oxygen	O	8	$1s^2$	$2s^2$	$2p^4$				
Fluorine	F	9	$1s^2$	$2s^2$	$2p^5$				
Neon	Ne	10	$1s^2$	$2s^2$	$2p^5$				
Sodium	Na	11	$1s^2$	$2s^2$	$2p^6$	$3s^1$			
Magnesium	Mg	12	$1s^2$	$2s^2$	$2p^6$	$3s^2$			
Aluminium	Al	13	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^1$		
Silicon	Si	14	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^2$		3^{rd} shell full
Phosphorus	P	15	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$		
Sulphur	S	16	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^4$		
Chlorine	Cl	17	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$		
Argon	Ar	18	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$		
Potassium	K	19	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^1$	
Calcium	Ca	20	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	

simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.** For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4*s* orbital, being lower in energy than the 3*d* orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3*d* orbital, being lower in energy than the 4*p* orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3*d* orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3*d* orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half- filled orbitals have extra stability (that is, lower energy). Thus p^3, p^6, d^5, d^{10},f^7, f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration.

With the saturation of the 3*d* orbitals, the filling of the 4*p* orbital starts at gallium (Ga) and is complete at krypton (Kr).

In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the 5*s*, 4*d* and 5*p* orbitals are similar to that of 4*s*, 3*d* and 4*p* orbitals as discussed above. Then comes the turn of the 6*s* orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4*f* and 5*d* orbitals.

After this, filling of 6*p*, then 7*s* and finally 5*f* and 6*d* orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic methods) are tabulated in Table.

The modern approach to the chemistry, in fact, depends almost entirely on electronic distribution to understand and explain chemical behavior. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge.

Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. However, in certain elements such as Cu, or Cr, where the two subshells (4*s* and 3*d*) differ slightly in their energies, an electron shifts from a subshell of lower energy (4*s*) to a subshell of

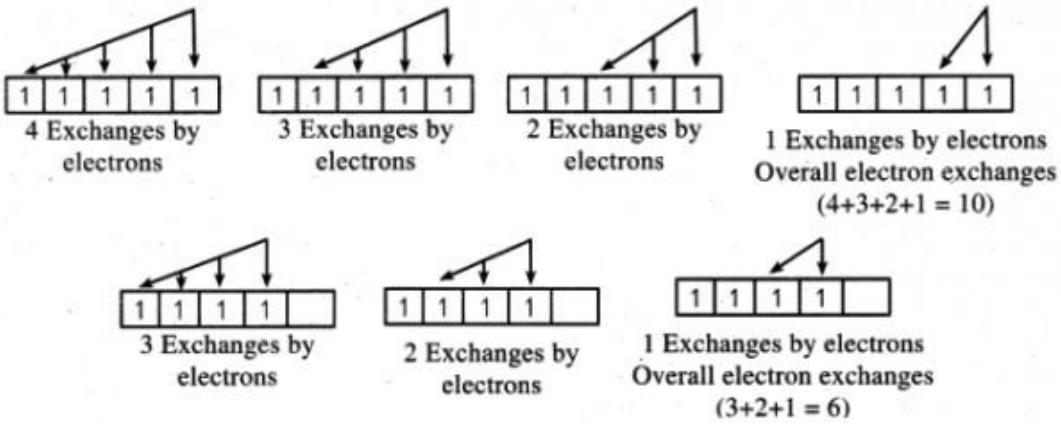
higher energy (3*d*), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5\ 4s^1$ and $3d^{10}\ 4s^1$ respectively and not $3d^4\ 4s^2$ and $3d^9\ 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half-filled Subshells

The completely filled and completely half-filled subshells are stable due to the following reasons:

1. Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here *3d*) have equal energy but different spatial distribution. Consequently, their shielding of one- another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy : The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability. You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy.



(Possible exchange for a d^5 configuration)

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Practice Questions

1. The de Broglie wavelength of a particle is inversely proportional to:

A) Its kinetic energy B) Its momentum
C) Its velocity D) Its mass

2. The Compton shift depends on:

A) Wavelength of incident radiation
B) Nature of the target material
C) Scattering angle
D) Intensity of radiation

3. The threshold frequency in photoelectric effect depends on:

A) Intensity of incident light
B) Nature of the metal
C) Temperature of metal
D) Work done function only

4. The operator corresponding to linear momentum in quantum mechanics is:

A) $-i\hbar\frac{d}{dx}$ B) $i\hbar\frac{d}{dx}$
C) $\hbar\frac{d}{dx}$ D) $-\hbar\frac{d}{dx}$

5. For a hydrogen atom, energy of n^{th} orbit is proportional to:

A) n B) n^2 C) $1/n$ D) $1/n^2$

6. The Balmer series lies in:

A) Infrared region B) Ultraviolet region
C) Visible region D) X-ray region

7. In Rutherford scattering experiment, most α-particles passed undeflected because:

A) Nucleus is negatively charged
B) Atom is electrically neutral
C) Atom is mostly empty space
D) α-particles have low energy

8. The Heisenberg uncertainty principle is mathematically expressed as:

A) $\Delta x\Delta p = h$ B) $\Delta x\Delta p \geq \hbar/2$
C) $\Delta x\Delta p \leq h$ D) $\Delta x\Delta p = \hbar$

9. The Rydberg constant for hydrogen is approximately:

A) $1.097 \times 10^7\ m^{-1}$ B) $3.0 \times 10^8\ m^{-1}$
C) $6.626 \times 10^{-34}\ m^{-1}$ D) $9.11 \times 10^{-31}\ m^{-1}$

10. The shape of BeF_2 according to VSEPR theory is:

A) Bent B) Linear
C) Trigonal planar D) Tetrahedral

11. In MO theory, O_2 is:

A) Diamagnetic B) Paramagnetic
C) Ferromagnetic D) Antiferromagnetic

12. The angular momentum of electron in Bohr model is quantized as:

A) $mvr = nh$ B) $mvr = n\hbar/4\pi$
C) $mvr = \frac{nh}{2\pi}$ D) $mvr = \frac{h}{n}$

13. The principal quantum number determines:

A) Shape of orbital B) Orientation of orbital
C) Spin of electron D) Energy and size of orbital

14. The Compton wavelength of electron is:

A) 0.0024 Å B) 0.024 Å C) 2.4 Å D) 24 Å

15. In photoelectric effect, kinetic energy of emitted electron depends on:

A) Intensity B) Frequency
C) Surface area D) Metal thickness

16. The nodal planes in p-orbital are:

A) 0 B) 1 C) 2 D) 3

17. The number of orbitals in d-subshell is:

A) 3 B) 5 C) 7 D) 10

18. For hydrogen-like species, energy is proportional to:

A) Z B) Z^2 C) 1/Z D) $1/Z^2$

19. Effective nuclear charge increases across a period because:

A) Shielding increases
B) Atomic size increases
C) Nuclear charge increases
D) Ionization decreases

20. The number of radial nodes in 3p orbital is:

A) 0 B) 1 C) 2 D) 3

21. The relation between wavelength and frequency is:

A) $c = \lambda/\nu$ B) $c = \nu\lambda$
C) $c = \nu/\lambda$ D) $c = \lambda - \nu$

22. The spin quantum number has values:

A) 0, 1 B) ±1 C) ±1/2 D) 0, ±1

23. Hydrogen bonding is strongest in:

A) NH_3 B) H_2O C) HF D) HCl

24. The inert pair effect is significant in:

A) Group 1 B) Group 2
C) Heavier p-block elements D) Transition metals

25. The degeneracy of 3d orbitals is:

A) 3 B) 5 C) 7 D) 10

26. Sommerfeld introduced which quantum number?

A) Spin quantum number
B) Magnetic quantum number
C) Azimuthal quantum number
D) Principal quantum number

27. Born-Haber cycle is used to calculate:

A) Ionization energy B) Lattice energy
C) Electron affinity D) Bond energy

28. The Zeeman effect refers to splitting of spectral lines in:

A) Electric field B) Magnetic field
C) Gravitational field D) Thermal field

29. For n = 4, maximum value of l is:

A) 2 B) 3 C) 4 D) 5

30. The wavefunction ψ has physical significance in terms of:

A) ψ B) ψ^2 C) ∇ψ D) dψ/dx

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
B	C	B	A	D	C	C	B	A	B	B	C	D	B	B

16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
B	B	B	C	B	B	C	C	C	B	C	B	B	B	B

ANSWERS

TRB 2025

Achiever's Testimonials

As a student preparing under the newly revised syllabus, I faced a lot of uncertainty. But the guidance I received from Professor Academy—especially in Education Methodology and General Knowledge—gave me the exact pathway I needed. Their support didn't end with classes; they prepared us strategically even after the syllabus change. The YouTube 'One Day – Two Points' session was a major booster and played a crucial role in helping me secure State 1st Rank."

SHRI JANANAI S | STATE 1ST RANK

"Simple habits made a big difference in my PG TRB prep — sticky notes, daily tests, and reviewing mistakes. I trusted only my class notes and Professor Academy materials to create clear, focused notes. These practices, along with Professor Academy's guidance, helped me secure State 1st Rank in PG TRB Computer Science."

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