UNIT: 1 ATOMIC STRUCTURE AND INTRODUCTION TO WAVE MECHANICAL CONCEPT (12 hrs)

Bohr theory of atom – calculation of Bohr radius, velocity and energy of an electron. Atomic spectra of hydrogen . Limitations of Bohr theory- Classical mechanics – concept, failure. Black body radiation- Planck's law of radiation. Photoelectric effect- Heisensberg's uncertainty principle and its significance, dual nature of electrons – Davisson and Germer's experiment. - de Broglie hypothesis - Schrodinger wave equation (derivation not expected), - Postulates of quantum mechanics (brief study). Application of Schrodinger wave equation to particle in one dimensional box. – normalization of wave function. Quantum numbers - Shapes of orbitals - Aufbau, Pauli's and Hunds rule - Electronic configuration of atoms.

Structure of Atoms

The first model of the atom to include the concept of quantization was proposed by Niels Bohr in 1913. Before this time, the prevailing notion was that the atom consisted of a dense, positively charged nucleus, about which the electrons orbited much like the planets orbit around the sun. One of the inherent contradictions with the planetary model was that the negatively charged electrons should undergo a constant acceleration by virtue of their electrostatic attraction to the nucleus. At the same time, Maxwell's theory of electromagnetism requires that any charged particle undergoing acceleration must continuously emit light. In fact, classical calculations predicted that the electron in a hydrogen atom should rapidly collapse into the nucleus in a matter of several nanoseconds. This, of course, does not occur. Furthermore, the gradual loss of energy as the electron's orbit spirals in closer and closer to the nucleus should lead to an emission spectrum that resembles a continuum of many different wavelengths.

Metal cations are heated in a Bunsen burner, they will emit light of a characteristic color. These are the common flame tests of a qualitative general chemistry laboratory and that form the basis for the different colors in fireworks. For instance, Li^+ and Sr^{2+} are red, Na^+ is yellow-orange, and Ba^{2+} is green. Instead of a continuum, as would have been predicted by classical theory, each ion emitted light with a characteristic fingerprint of narrow wavelengths (or lines) when passed through a prism. The line spectrum of hydrogen was well established at the time and is shown in Figure 1. In 1885, a Swiss math teacher named Johann Balmer noticed the mathematical pattern in the spectral lines of hydrogen in the visible spectrum and derived an empirical equation to explain them. Then, in 1888, the Swedish physicist Johannes Rydberg generalized the Balmer equation to include several other series of lines that were discovered in the UV and near-IR regions of the hydrogen line spectrum

(shown in Figure 2) The Rydberg formula, shown in Equation (1), can be used to calculate the wavenumber $(1/\lambda)$ of any line in the emission spectrum of hydrogen, where RH is the Rydberg constant and n_f and n_i are both positive integers (with $n_f < n_i$).

Figure 1. The line spectrum of hydrogen in the visible region.
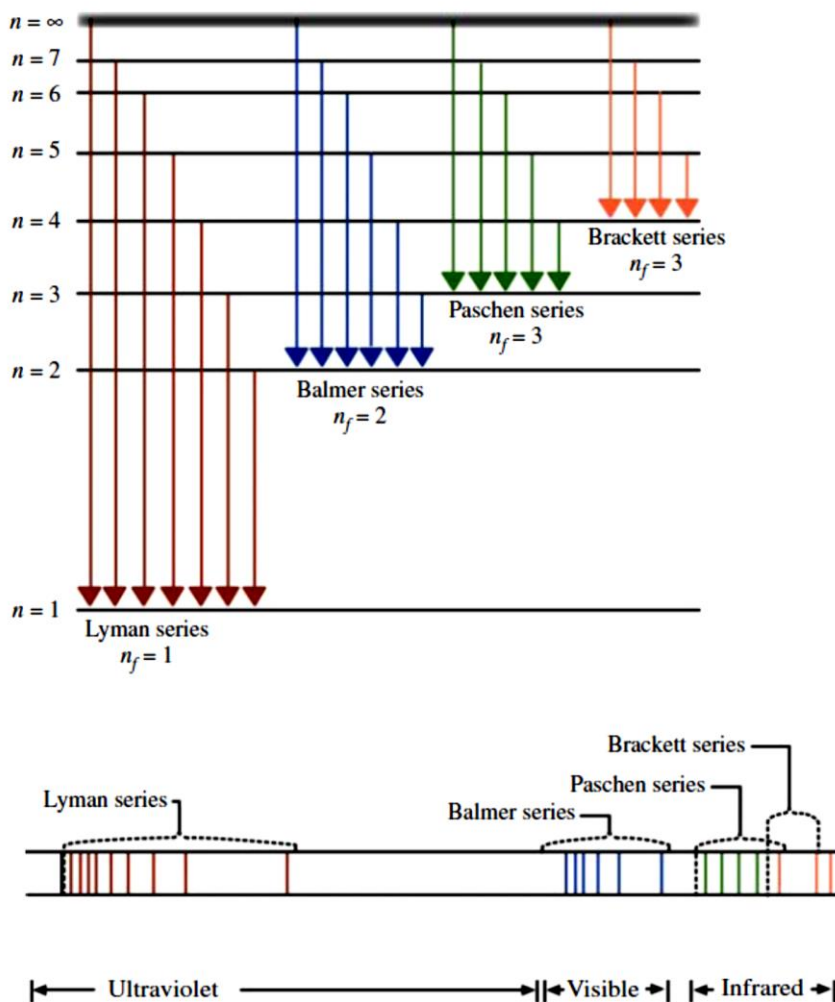
Figure 1. The complete line spectrum of hydrogen from the ultraviolet to the infrared. Transitions from the $n_i = \infty$ energy level to the lowest energy level in each series correspond with the series limit, where the individual energy levels all start to blur together.

Dr. Biju A R

Each series of lines converges at short wavelengths on what is known as the **series limit**. Because the series limit occurs at the shortest wavelength in each series (or the largest wavenumber), the value of n_i for the series limit is always taken as infinity. While mathematically convenient, the Rydberg equation was entirely an empirical equation in desperate need of a more theoretical explanation.

$$\bar{\vartheta} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad (1)$$

Where $R_H = 109{,}678 \; cm^{-1}$ and $n_f < n_i$

The Bohr model of atom

In the summer of 1912, Niels Bohr wrote to his older brother Harald: "Perhaps I have found out a little about the structure of atoms." His revolutionary model of the atom was published the following year. In an attempt to develop a theoretical model of the hydrogen atom that was consistent with the lines predicted by the Rydberg formula, Bohr proposed the following:

(1)   The electron moves around the nucleus in circular orbits, where the centripetal and centrifugal forces are exactly balanced. The centrifugal force results from the electrostatic attraction of the negatively charged electron for the positively charged proton in the nucleus and can be calculated according to Coulomb's law. The electron's centripetal motion is governed by Newton's second law. The two forces are set equal in Equation (2), where F is the force, e is the electronic charge = 1.602×10^{-19} C, r is the radius, $4\pi\varepsilon_0$ is the permittivity of free space = 1.113×10^{-12} C²/Nm², and r is the radius of the orbit.

$$F = \frac{e^2}{4\pi\varepsilon_0 r^2} \;\; (\text{Coulombic law}) \;\; = ma \quad (\text{Newton's second law}) = \frac{mv^2}{r} \quad (2)$$

(2)   The stationary state assumption: In a given orbit, the total energy (kinetic + potential) will be a constant. The kinetic energy KE is equal to $(1/2)mv^2$, while the potential energy V can be obtained by integrating Coulomb's law with respect to distance. While this assumption was in opposition to the classical prediction that the electron will spiral into the nucleus, it was necessary in order to explain the experimental observations.

$$E = K.E + V \;\; = \frac{1}{2}mv^2 + \int \frac{e^2}{4\pi\varepsilon_0 r^2} \, dr = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

From equation 2 it is clear that $\frac{e^2}{4\pi\varepsilon_0 r} = mv^2$

So

$$E = \frac{1}{2}mv^2 - mv^2$$

$$E = -\frac{1}{2}mv^2$$

$$E = -\frac{e^2}{8\pi\varepsilon_0 r} \qquad (3)$$

(3)   The quantum restriction postulate: Only certain quantized orbits will be allowed.
These orbits are restricted to the condition where the angular momentum (l) is an
integral multiple of h/2π:

$$l = mvr = \frac{nh}{2\pi} \text{ where } n = 1, 2, 3 \text{ etc.}$$

$$\text{Since } E = -\frac{1}{2}mv^2 = -\frac{e^2}{8\pi\varepsilon_0 r}$$

$$mvr = \frac{e^2}{4\pi\varepsilon_0 v}$$

$$\frac{e^2}{4\pi\varepsilon_0 v} = \frac{nh}{2\pi}$$

$$v = \frac{2\pi e^2}{4\pi\varepsilon_0 nh}$$

$$E = -\frac{1}{2}mv^2$$

$$E = -\frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 n^2 h^2}$$

(4)   When an electron jumps from a higher to a lower energy orbit, the energy difference
(ΔE) will be emitted as a photon:

$$E_f - E_i = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (4)$$

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) joules$$

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

$$\bar{\vartheta} = \frac{2.18 \times 10^{-18}}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) cm^{-1} = 109{,}678\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) cm^{-1}$$

n_i is the initial Bohr orbit (the one farther from the nucleus, or the excited state) and n_f is the final Bohr orbit, as shown in Figure 3. For absorption ΔE is positive and for emission it is negative.

The following values of n_f correspond with the listed series: $n_f = 1$ (Lyman), $n_f = 2$ (Balmer), $n_f = 3$ (Paschen), $n_f = 4$ (Brackett), and $n_f = 5$ (Pfund). Thus, for example, the first four lines for the Balmer series originate in the $n_i = 3, 4, 5$, and 6 energy levels and terminate in the $n_f = 2$ level, as shown in Figure 3.

We know that

$$E = -\frac{1}{2}mv^2 = -\frac{e^2}{8\pi\varepsilon_0 r}$$

$$r = -\frac{e^2}{8\pi\varepsilon_0 E} = \frac{(4\pi\varepsilon_0)^2 n^2 h^2 e^2}{2\pi^2 m e^4 \, 8\pi\varepsilon_0} = \frac{4\pi\varepsilon_0(\hbar)^2}{me^2} \qquad (5)$$

Here n =1 the value is called a_0, the other allowed orbital's are obtained from the relation $a_0\, n^2$.
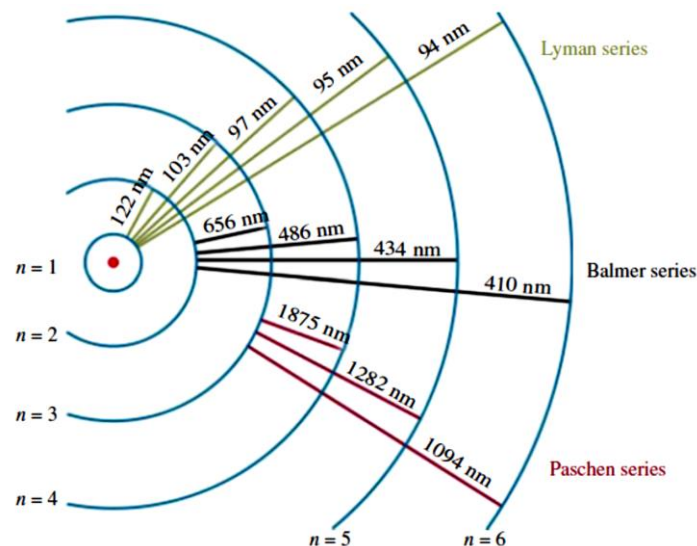
Figure 3. According to the Bohr model of the atom, the lines in the emission spectrum of hydrogen result from transitions between stationary orbits that exhibit quantization of angular momentum. The first several transitions and their corresponding wavelengths are shown for each series of lines in the line spectrum of hydrogen.
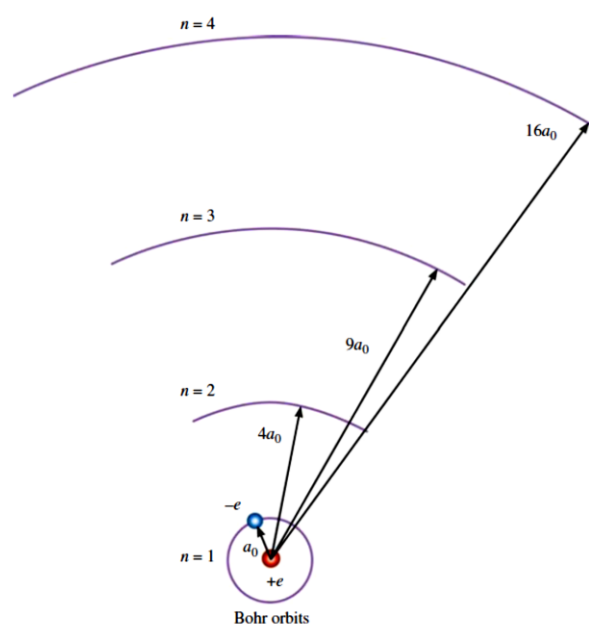
Figure 4. The allowed orbital radii in the Bohr model of the atom.

Limitations of Bohr's model

1. The model only applies to atoms with one electron, such as hydrogen, and does not work for atoms with multiple electrons.

2. The model assumes that the electrons in an atom move in circular orbits, but in reality, their motion is more complex and can involve elliptical or more complicated paths.

3. The model does not accurately predict the energy levels of the electrons in an atom, particularly for larger atoms.

4. The model does not take into account the concept of electron spin, which is an important aspect of quantum mechanics.

5. The model does not explain the formation of chemical bonds between atoms, which is essential to understanding the behavior of molecules.

6. It cannot explain Zeeman effect

7. It cannot explain Stark effect

Blackbody radiation

By 1900 the success of Maxwell's electromagnetic theory had firmly established the wave nature of light. A hot body emits electromagnetic radiation. The rate of production of energy by a hot surface depends on its temperature and its surface area. For the same area and temperature, a black surface radiates more energy per second than a polished surface. The blacker the surface, the surface the greater the radiation. A blackbody is one that is a perfect absorber of radiation: it absorbs all the radiation falling on it, without reflecting any. A perfect black body may be defined as a cavity within a box with a pinhole in one of the walls. Such a cavity is called hohlraum. Black bodies are good emitters and absorbers of radiation. When such a black body is heated, it absorbs the radiation and at the same time emits it through the orifice. Soon absorption and emission occur at the equal rates. A state of equilibrium is set up. The radiation coming out in this condition is called equilibrium black body radiation.
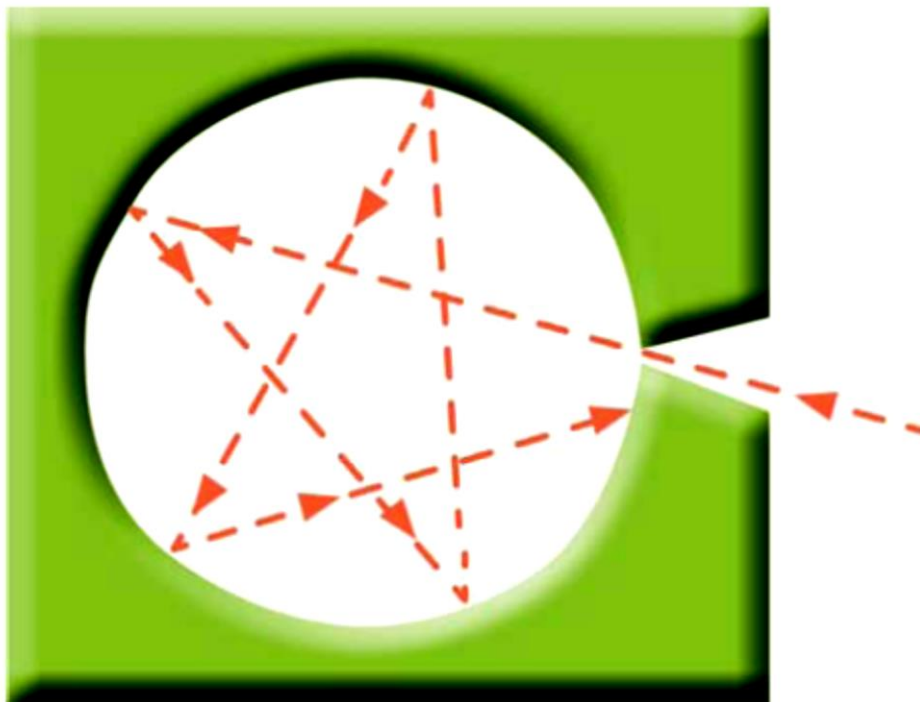

Figure 4. Analogy of a perfect blackbody with a hollow metal cavity having a tiny pinhole

The radiation from a hohlraun can be dispersed into a spectrum of different wavelengths by passing it though a fluorite prism. A bolometer can be placed at different positions of the spectrum and energy emitted/cm^2/sec, called the emissive power for a given wavelengths and

denoted as intensity, may be determined by various wavelengths. The plot of intensity against λ shown in figure 5 and reveals the following

1. At a particular wavelngth intensity depends on λ

2. At particular λ, intensity depends on temperature.

3. Only small amount of energy are emitted at short and long wavelengths. The curve passes through a maximum at any given temperature. The wavelengths corresponding to this maximum is denoted λ_{max}

4. As the temperature is raised λ_{max} shifts to shorter wavelengths.
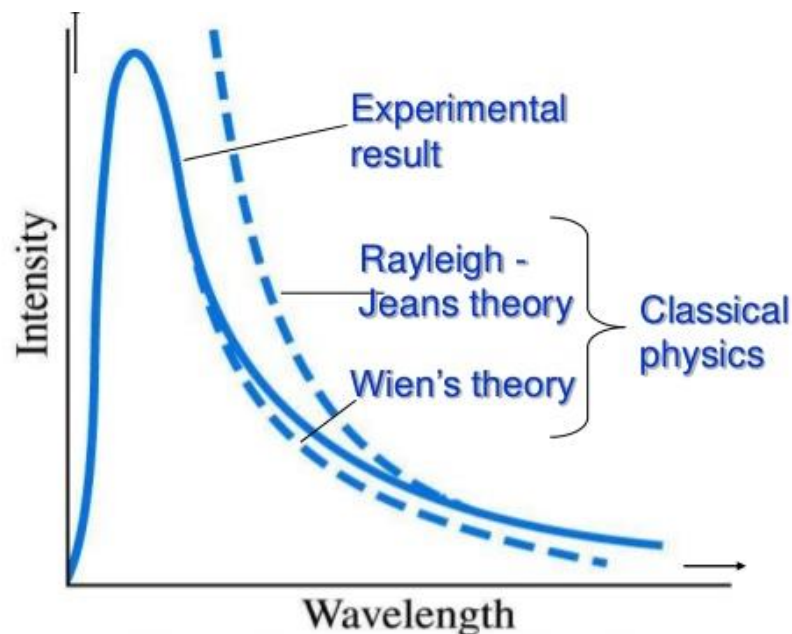
Figure 5. Curve fitting of various theories with black body radiation

Experimentally it has been shown that the wavelength at the maximum of this spectral distribution is inversely proportional to the temperature:

$\lambda_m T = 2.8979 \times 10^{-3}$ m K

This is **Wien's displacement law**. From the diagram it is seen that Wein's equation gives good results at shorter wavelengths.

The total energy distribution by Rayleigh- Jeans formula is given as

$$\rho_v(T)dv = \frac{8\pi v^2}{c^3} kT dv \qquad (6)$$

$$\rho_\lambda(T)d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda \qquad (7)$$

Rayleigh and Jeans equation gives good results at longer wavelength only. It predicts an infinite energy density as $\lambda \to 0$; hence an infinite value of the total energy density in the cavity is not possible and it is called ultraviolet catastrophe.

Max Planck made the bold suggestion that an oscillator can emit or absorb radiation only in certain discrete amounts called quanta, each quantum being a unit of energy. The size of quantum energy depends up on the fundamental frequency ϑ of the oscillator. The value of the energy quantum $\varepsilon = h\vartheta$ where h is Planck's constant. Its value is give 6.626 x $10^{-34} Js$. As the dimension of h is equal to energy multiplied by time, it is often referred to as the action constant. According to Planck, an oscillator can have energies only as integral multiplies of this energy quantum namely 0, 1ε, 2ε, 3ε,…etc. Making use of this quantum hypothesis, Planck derived an expression for the mean energy of an oscillator.

$$\rho(v)dv = \frac{8\pi hv^3}{c^3}\frac{1}{e^{hv/kT}-1}dv \qquad (8)$$

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. 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.

(iii)   For each metal, there is a characteristic minimum frequency, v_0 (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $v > v_0$, 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 [υ = (4.3 to 4.6 x 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 (υ = 5.1–5.2 × 10^{14} Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (υ_0) for potassium metal is 5.0×10^{14} Hz.

These facts were explained by Einstein in 1905 in a way that now appears very simple, but in fact relies on concepts that were at the time revolutionary. Einstein went beyond Planck and postulated that not only was the *process* of absorption and emission of light quantized, but that light itself was quantized, consisting of in effect of particles of energy

$$E_{particle} = h\upsilon$$

where υ is the frequency of the light. These particles were given the name *photons.* If the energy of the photon before it removes an electron from the metal is equal to the energy required to tear the electron free of the metal, plus the kinetic energy of the free electron, then

$$h\upsilon = W + \frac{1}{2} m_e \upsilon^2$$

where W is the work function of the metal, energy needed to remove an electron (with no energy left over), m_e is the mass of an electron, is the velocity of electron ejected by the photon and $\frac{1}{2} m_e \upsilon^2$ is the kinetic energy of free electron. On rearranging we get

$$\frac{1}{2} m_e \upsilon^2 = h\upsilon - W \qquad (9)$$

Thus a plot of the kinetic energies of the electrons ($\frac{1}{2} m_e \upsilon^2$) vs. the frequency υ of the light should be a straight line of positive slope (*h*; this is one way to find Planck's constant) intersecting υ the axis at a positive value ($\upsilon = \frac{W}{h}$)as experiment indeed showed in the following figure

$$1/2\, mv^2 = h\upsilon - W$$
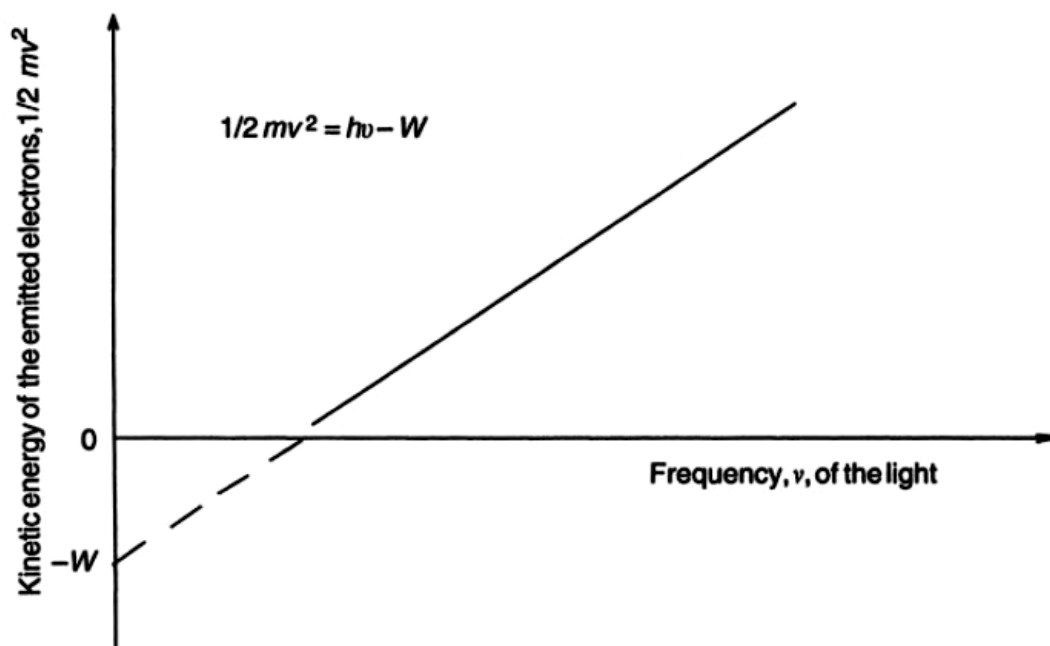
Table 2.2 Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

Planck's explanation of the blackbody radiation curves (1900) and Einstein's explanation of the facts of the photoelectric effect (1905) indicated that the flow of energy in physical processes did not take place continuously, as had been believed, but rather jerkily, in discrete jumps, quantum by quantum. The contributions of Planck and Einstein were the signal developments marking the birth of quantum theory and the transition from classical to modern physics. One of the significant points in the interpretation of the photoelectric effect is that light is considered to be particulate in nature. In other experiments, such as the diffraction experiment of T. Young, it was necessary to assume that light behaved as a wave. Many photovoltaic devices in common use today (light meters, optical counters, etc.) are based on the photoelectric effect.

Particle wave duality

Because light behaved as both waves (diffraction, as proved by Young in 1803) and particles (the photoelectric effect shown by Einstein in 1905), the nature of light was debated for many years. Of course, light has characteristics of both a wave and a particle, the so-called *particle–wave duality*. In 1924, Louis de Broglie, a young French doctoral student, investigated some of the consequences of relativity theory. For electromagnetic radiation

$$E = hv = \frac{hc}{\lambda}$$

where c, v, and λ are the velocity, frequency, and wavelength, respectively, for the radiation. The photon also has an energy given by the relationship from relativity theory,

$$E = mc^2$$

A particular photon has only one energy, so

$$mc^2 = \frac{hc}{\lambda}$$

This does not mean that light has a mass, but because mass and energy can be interconverted, it has an energy that is equivalent to some mass. The quantity represented as mass times velocity is the momentum, so above equation predicts a wavelength that is Planck constant divided by the momentum

De Broglie reasoned that if a particle had a wave character, the wavelength would be given by

$$\lambda = \frac{h}{mv} \qquad (10)$$

where the velocity is written as υ rather than c because the particle will not be traveling at the speed of light.

Experimental verification of matter waves

The wave nature of waves was verified in 1927 by **C. J. Davisson** and **L. H. Germer** working at Bell Laboratories in Murray Hill, New Jersey. The schematic drawing of the experiments are shown below.
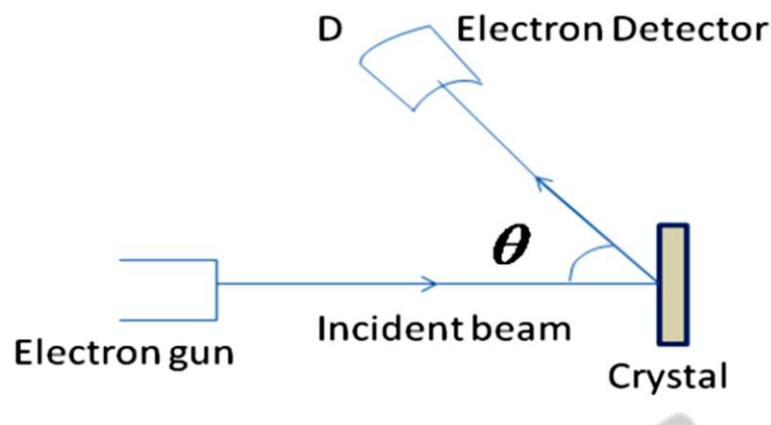
Electrons emitted by a tungsen filament are accelerated to a desired velocity by applying suitable voltage. This collimated beam is made to fall on the surface of nickel crystal. The electrons are scattered in all directions by the atoms of the crystal. The intensity of the electron beam, scattered in a given direction is measured by the electron detector. The detector can be moved on a circular scale and is connected to a sensitive galvanometer to

record the current. The whole apparatus is enclosed in an evacuated chamber. The intensity of the scattered beam is measured for different values of angle of scattering θ. The variation of the intensity I of the scattered electrons with the angle of scattering θ is obtained for different accelerating voltages.

It was noticed that a strong peak appeared in the intensity I of the scattered electrons for an accelerating voltage was of 54 V at a scattering angle θ = 50. The appearance of the peak in a particular direction is due to the constructive interference from different layers of the regularly spaced atoms of the crystal.

The de Broglie wavelength associated with the electrons is given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}} = \frac{1.227}{\sqrt{V}} \, nm$$

$$\lambda = \frac{1.227}{\sqrt{54}} \, nm = 0.167 \, nm \qquad (11)$$

This is found to be in rather good agreement between the theoretical value and the experimentally observed value of the de-Broglie wavelength.

Uncertainty Principle

In 1927, the German physicist Werner Heisenberg proposed a principle that has utmost importance in the philosophical groundwork for quantum mechanics. He deduced that when the uncertainties in the simultaneous measurements of momentum and position for a particle are multiplied together, the product is approximately equal to Planck's constant divided by 4π. Mathematically, this can be expressed as

$$\Delta x \, \Delta p \geq \frac{h}{4\pi} \qquad (12)$$

where Δ means "uncertainty of." Thus, Δx is the uncertainty of position and Δp is the uncertainty of momentum. If the measured uncertainties of position and momentum are large, their product can be substantially greater than $h/4\pi$. The significance of Equation 12, which is the mathematical statement of the Heisenberg uncertainty principle, is that even in the most favorable conditions for measuring position and momentum, the lower limit of uncertainty is always given by $h/4\pi$. Conceptually, we can see why the uncertainty principle should exist. Any measurement of a system must, by necessity, result in some disturbance on the system. Suppose that we want to determine the position of a quantum-mechanical object, say an electron. To locate the electron within a distance Δx, we might employ light with a wavelength on the order of $\lambda \approx \Delta x$. During the interaction collision between the photon and the electron, part of the photon's momentum $(p = \frac{h}{\lambda})$ will be transferred to the electron. Thus,

the very act of trying to "see" the electron has changed its momentum. If we want to locate the electron more accurately, then we must use light of a shorter wavelength. Consequently, the photons of the light will possess greater momentum, resulting in a correspondingly larger change in the momentum of the electron. In essence, to make Δx as small as possible, the uncertainty in the momentum (Δp) will become correspondingly large at the same time. Similarly, if we design an experiment to determine the momentum of an electron as accurately as we can, then the uncertainty in its position will simultaneously become large. Keep in mind that this uncertainty is not the result of poor measurements or experimental techniques— it is a fundamental property of the act of measurement itself.

Finally, we note that the Heisenberg uncertainty principle can be expressed also in terms of energy and time, as follows. Because

$$
\begin{aligned}
\text{momentum} &= \text{mass} \times \text{speed} \\
&= \text{mass} \times \frac{\text{speed}}{\text{time}} \text{time} \\
\\
&= \text{force} \times \text{time}
\end{aligned}
$$

Thus,

$$
\begin{aligned}
\text{momentum} \times \text{distance} &= \text{force} \times \text{distance} \times \text{time} \\
&= \text{energy} \times \text{time}
\end{aligned}
$$

where ΔE is the uncertainty in energy when the system is in a certain state, and Δt is the time interval during which the system is in the state. Equation 12 can now be written as.

$$
\Delta E \times \Delta t = \frac{h}{4\pi}
$$

Thus, we cannot measure the kinetic energy of a particle with absolute precision (i.e., to have $\Delta E = 0$) in a finite span of time. In quantum-mechanical language, momentum and position form a *conjugate pair*, as do energy and time.

Dual nature of electron

The dual nature of an electron is a concept that is central to the field of quantum mechanics, which is the theory that describes the behavior of particles at the atomic and subatomic scale. This dual nature refers to the fact that electrons can exhibit both wave-like and particle-like properties, depending on how they are observed or measured. When the electrons are not

being directly observed, they behave like waves and exhibit wave-like properties. However, when the position of the electrons is measured, they behave like particles and exhibit particle-like properties. This dual nature of electrons has been confirmed by numerous experiments and is an important aspect of our understanding of the quantum world.

Light's particle-like traits are best explained by the **photoelectric effect**, the theory that Albert Einstein won his Nobel Prize for. The photoelectric effect refers to the emission (or ejection) of electrons from the surface of a metal in response to incident light. Energy contained by the incident light is absorbed by the electrons in the metal; this gives the electrons enough energy to be emitted from the surface of the metal. Here is where Einstein's theory provided an explanation. Einstein argued that this could be explained if light was composed of "bundles", or photons; when a photon strikes the metal's surface, its energy was transferred to the electron - much like when two billiard balls collide. This was the ultimate evidence for light's **particle nature**.

According to de-Broglie, the wavelength of a particle of mass m traveling at velocity v is given by the ratio $\lambda = \frac{h}{mv}$, where h= Planck's constant. Davisson and Germer experimentally confirmed this by observing diffraction effects with an electron beam.

Postulates of quantum mechanics

Postulate 1

The state function of a quantum mechanical system is completely specified by a function $\Psi(r, t)$, that depends on the coordinates of the particle and on the time. This function is called wave function or the state function, has an important property that $\Psi^*(r, t)\Psi(r, t)dxdydz$ is the probability that the particle lies in the volume element dxdydz located at r at the time t. The wave function should be normalizable, square integrable, and single valued, continuous and finite.

Postulate 2

To every observable in a classical mechanics there corresponds to a operator in quantum mechanics.

NO	Observable	Classical notation	Operator	Quantum mechanical operation
1	Position	x	$\hat{x}$	Multiplied by x
	Position	r	$\hat{r}$	Multiplied by r
2	Momentum	p_x	$\hat{p}_x$	$-i\hbar\dfrac{\partial}{\partial x}$
3	Kinetic energy	K_x	$\hat{K}_x$	$\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$

Postulate 3

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvlaues a, which satisfy the eigenvalue equation.

$$\hat{A}\Psi = a\Psi$$

Postulate 4

If a system is in a state described by a normalized wave function Ψ, then the average value of the observable corresponding to $\hat{A}$ is given by

$$< a >= \int_{-\infty}^{+\infty} \Psi^* \hat{A}\, \Psi d\tau$$

Postulate 5

The wave function or state function of a system evolves in time according to the time dependent Schrodinger equation.

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$$

Schrodinger equation

Time dependent Schrodinger

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$$

Time independent Schrodinger equation

The Schrodinger equation for the matter wave propagating in three dimensional space associated with the motion of the particle of mass m is given as

$$\frac{-\hbar^2}{2m}\left\{\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right\} + V(x,y,z)\psi = E\psi$$

Here E is the total energy of the particle, $V(x, y, z)$ is the potential energy, $\hbar = \frac{h}{2\pi}$ where h is the Planck's constant and ψ is the wave function of the particle.

Particle in one-dimensional box

Consider a particle moving in one-dimensional box of length L with infinity high walls at two ends. Inside the box the potential energy is zero and outside the box potential energy is infinite. In other words particle is confined to move in the length L.

Region I	Region II	Region III
V(x)=∞	V(x)=0	V(x)=∞

0   L   x
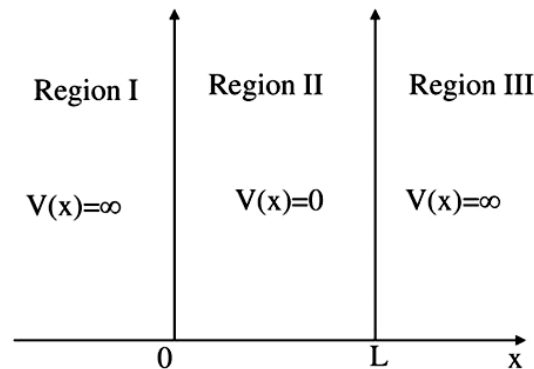
V(x)=0   for L>x>0
V(x)=∞   for x≥L, x≤0

The Schrödinger equation of the particle inside the box can be written as

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

Let assume $\frac{2mE}{\hbar^2} = K^2$

$$\frac{d^2\psi(x)}{dx^2} + K^2\psi(x) = 0 \qquad (1)$$

The general solution for this second order homogenous equation can be given as follows

$$\psi(x) = A\, Sin(Kx) + B\, Cos(Kx) \qquad (2)$$

To find the value of A and B

1. At x= 0, $\psi(x) = 0$

Equation 2 becomes

$$A\,Sin(0) + B\,Cos(0) = 0$$

$$B\,Cos(0) = 0$$

Since Cos0 is 1 B should be zero

$$\psi(x) = A\,Sin(Kx)$$

2. At x = L, $\psi(x) = 0$

$$0 = A\,Sin(KL)$$

If A= 0 it is trivial solution. So $Sin(KL)$ should be zero and we know that $Sin(n\pi) = 0$

$$\text{So} \quad n\pi = KL$$

$$K = \frac{n\pi}{L}$$

$$K^2 = \frac{n^2\pi^2}{L^2}$$
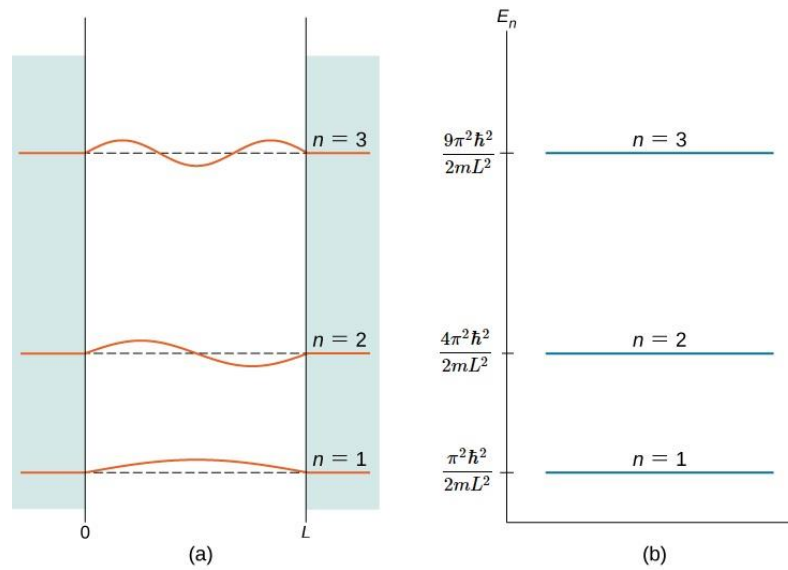
And we know that $\frac{2mE}{\hbar^2} = K^2$

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$E = \frac{\hbar^2 n^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

Where n is an integer 1,2,3 etc but not zero. If n = 0, K would be zero and $\psi(x)$ would be zero everywhere.

$$\psi(x) = A\,Sin\left(\frac{n\pi}{L}\right)x$$

$$E = \frac{n^2h^2}{8mL^2}$$

(a)   (b)

Normalization of the wave function

$$\int_0^L \psi(x)^* \, \psi(x) dx = 1$$

$$\int_0^L A^2 \, Sin\left(\frac{n\pi x}{L}\right)^2 dx = 1$$

$$A^2 \int_0^L \frac{1 - Cos\left(\frac{2n\pi x}{L}\right)}{2} dx = 1$$

$$\frac{A^2}{2}\int_0^L dx - \int_0^L \frac{Cos\left(\frac{2n\pi x}{L}\right)}{2} dx = 1$$

$$\frac{A^2}{2}[x]_0^L - \left[\frac{Sin\left(\frac{2n\pi x}{L}\right)}{\frac{4n\pi x}{L}}\right]_0^L$$

$$\frac{A^2 L}{2} = 0$$

$$A = \sqrt{\frac{2}{L}}$$

The normalized wave function is thus

$$\psi(x) = \sqrt{\frac{2}{L}} \, Sin\left(\frac{n\pi}{L}\right) x$$

Quantum numbers

Quantum numbers are a set of numbers which specify the location and energy of an electron in an atom. Each electron in an atom is characterized by a set of four quantum numbers and each set acts as a label to describe the state of the electron in the atom.

(i) Principle quantum number (n)

It specifies the average distance of the electron for the nucleus and determines a large extent the energy associated with it. n can have any positive values like 1,2, 3 etc. In general the greater the value of n the higher the energy associated with the electron.

The principal quantum number also identifies the shell. All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters.

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

Shell $= K\ L\ M\ N$ ....

Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus.

(ii) **Azimuthal quantum number or Angular momentum quantum number (l)**

It signified the orbital angular momentum of the electron. It can have integral values from 0 to n-1. Each shell consists of one or more subshells or sub-levels. The number of subshells in a principal shell is equal to the value of n. For example in the first shell ($n = 1$), there is only one sub-shell which corresponds to $l = 0$. There are two sub-shells ($l = 0, 1$) in the second shell ($n = 2$), three ($l = 0, 1, 2$) in third shell ($n = 3$) and so on. Each sub-shell is assigned an azimuthal quantum number.

Principal Quantum Number, n	Angular Momentum Quantum Number, ℓ $\ell = 0, 1, 2... n\text{-}1$	Subshells
1	$\ell = 0$	s (1 subshell)
2	$\ell = 0$ $\ell = 1$	s p (2 subshells)
3	$\ell = 0$ $\ell = 1$ $\ell = 2$	s p d (3 subshells)
4	$\ell = 0$ $\ell = 1$ $\ell = 2$ $\ell = 3$	s p d f (4 subshells)

l denotes the subshell in which the electron is present and is thus linked to the geometrical shape of the spatial region in which it is most probably found.

(iii) **Magnetic quantum number**

Magnetic orbital quantum number m_l gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by 'l' value) $2l+1$ values of m_l are possible and these values are given by :

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

Thus for l = 0, the only permitted value of m_l = 0, . For l = 1, m_l can be –1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For l = 2, m_l = –2, –1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of ml are derived from l and that the value of l are derived from n. Each orbital in an atom, therefore, is defined by a set of values for n, l and ml. An orbital described by the quantum numbers n = 2, l = 1, m_l = 0 is an orbital in the p subshell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Angular Momentum Quantum Number ℓ	Number of Orbitals $2\ell +1$	Values of m_l $m_l = -\ell$ to $+\ell$
0 (s subshell)	1	0
1 (p subshell)	3	-1, 0, +1
2 (d subshell)	5	-2, -1, 0, +1, +2
3 (f subshell)	7	-3, -2, -1, 0, +1, +2, +3

(iv) Spin quantum number

The three quantum numbers labeling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers. In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the electron spin quantum number (m_s). An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can

have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers ms which can take the values of +½ or –½. These are called the two spin states of the electron and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different ms values (one +½ and the other –½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

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's. 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, ml has (2l+1) values, the same as the number of orbital's 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.

Shape of orbital's

Since orbital's are probability distribution regions for the electron around the nucleus each of them should possess a characteristic geometrical shape. In order to know what an orbital look like, a consideration of the solution of Schrodinger equation in terms of spherical polar coordinate and making plots in terms of certain functions. mAn s orbital is spherically symmetrical about the nucleus. P orbitals are dumb-bell shaped and oriented about symmetrically about x, y and z axis.

$3d_{xy}$

$3d_{xz}$

Nodal planes

$3d_{z^2}$

$3d_{yz}$

$3d_{x^2-y^2}$