



Study material for Physics

Semester:5th

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*The material is intended to help the learner
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Unit 1

Historical note

At the end of the nineteenth century, physics consisted essentially of classical mechanics, the theory of electromagnetism, and thermodynamics. Classical mechanics was used to predict the dynamics of material bodies, and Maxwell's electromagnetism provided the proper framework to study radiation; matter and radiation were described in terms of particles and waves respectively. As for the interactions between matter and radiation, they were well explained by the Lorentz force or by thermodynamics. The overwhelming success of classical physics (classical mechanics, classical theory of electromagnetism, and thermodynamic) made people believe that the ultimate description of nature had been achieved. It seemed that all known physical phenomena could be explained within the framework of the general theories of matter and radiation. At the turn of the twentieth century, however, classical physics, which had been quite unassailable, was seriously challenged on two major fronts:

Relativistic domain: Einstein's 1905 theory of relativity showed that the validity of Newtonian mechanics ceases at very high speeds (i.e., at speeds comparable to that of light).

Microscopic domain: As soon as new experimental techniques were developed to the point of probing atomic and subatomic structures, it turned out that classical physics fails miserably in providing the proper explanation for several newly discovered phenomena. It thus became evident that the validity of classical physics



ceases at the microscopic level and those new concepts had to be invoked to describe, for instance, the structure of atoms and molecules and how light interacts with them.

The failure of classical physics to explain several microscopic phenomena—such as blackbody radiation, the photoelectric effect, atomic stability, and atomic spectroscopy—had cleared the way for seeking new ideas outside its purview.

The first real breakthrough came in 1900 when Max Planck introduced the concept of the quantum of energy. In his efforts to explain the phenomenon of blackbody radiation, he succeeded in reproducing the experimental results only after postulating that the energy exchange between radiation and its surroundings takes place in discrete, quantized, amounts. He argued that the energy exchange between an electromagnetic wave of frequency ν and matter occurs only in integer multiples of $h\nu$, which he called the energy of a quantum, where h is a fundamental constant called Planck's constant. The quantization of electromagnetic radiation turned out to be an idea with far-reaching consequences. Planck's idea, which gave an accurate explanation of blackbody radiation, prompted new thinking and triggered an avalanche of new discoveries that yielded solutions to the most outstanding problems of the time. In 1905 Einstein provided a powerful consolidation to Planck's quantum concept. In trying to understand the photoelectric effect, Einstein recognized that Planck's idea of the quantization of the electromagnetic waves must be valid for light as well. So, following Planck's approach, he posited that light itself is made of discrete bits of energy (or tiny particles), called photons, each of energy $h\nu$, ν being the frequency of the light. The introduction of the photon concept enabled Einstein to give an elegantly accurate explanation to the photoelectric problem, which had been waiting for a solution ever since its first experimental observation by Hertz in 1887.



Another seminal breakthrough was due to Niels Bohr. Right after Rutherford's experimental discovery of the atomic nucleus in 1911, and combining Rutherford's atomic model, Planck's quantum concept, and Einstein's photons, Bohr introduced in 1913 his model of the hydrogen atom. In this work, he argued that atoms can be found only in discrete states of energy and that the interaction of atoms with radiation, i.e., the emission or absorption of radiation by atoms, takes place only in discrete amounts of $h\nu$ because it results from transitions of the atom between its various discrete energy states. This work provided a satisfactory explanation to several outstanding problems such as atomic stability and atomic spectroscopy.

Then in 1923 Compton made an important discovery that gave the most conclusive confirmation for the corpuscular aspect of light. By scattering X-rays with electrons, he confirmed that the X-ray photons behave like particles with momenta $h\nu/c$; ν is the frequency of the X-rays.

This series of breakthroughs—due to Planck, Einstein, Bohr, and Compton—gave both the theoretical foundations as well as the conclusive experimental confirmation for the particle aspect of waves; that is, the concept that waves exhibit particle behavior at the microscopic scale. At this scale, classical physics fails not only quantitatively but even qualitatively and conceptually.

As if things were not bad enough for classical physics, de Broglie introduced in 1923 another powerful new concept that classical physics could not reconcile: he postulated that not only does radiation exhibit particle-like behavior but, conversely, material particles themselves display wave-like behavior. This concept was confirmed experimentally in 1927 by Davisson and Germer; they showed that interference patterns, a property of waves, can be obtained with material particles such as electrons.



Although Bohr's model for the atom produced results that agree well with experimental spectroscopy, it was criticized for lacking the ingredients of a theory. Like the "quantization" scheme introduced by Planck in 1900, the postulates and assumptions adopted by Bohr in 1913 were quite arbitrary and do not follow from the first principles of a theory. It was the dissatisfaction with the arbitrary nature of Planck's idea and Bohr's postulates as well as the need to fit them within the context of a consistent theory that had prompted Heisenberg and Schrödinger to search for the theoretical foundation underlying these new ideas. By 1925 their efforts paid off: they skillfully welded the various experimental findings as well as Bohr's postulates into a refined theory: quantum mechanics. In addition to providing an accurate reproduction of the existing experimental data, this theory turned out to possess an astonishingly reliable prediction power which enabled it to explore and unravel many uncharted areas of the microphysical world. This new theory had put an end to twenty five years (1900–1925) of patchwork which was dominated by the ideas of Planck and Bohr and which later became known as the old quantum theory.

Historically, there were two independent formulations of quantum mechanics. The first formulation, called matrix mechanics, was developed by Heisenberg (1925) to describe atomic structure starting from the observed spectral lines. Inspired by Planck's quantization of waves and by Bohr's model of the hydrogen atom, Heisenberg founded his theory on the notion that the only allowed values of energy exchange between microphysical systems are those that are discrete: quanta. Expressing dynamical quantities such as energy, position, momentum and angular momentum in terms of matrices, he obtained an eigen value problem that describes the dynamics of microscopic systems; the diagonalization of the Hamiltonian matrix yields the energy spectrum and the state vectors of the system. Matrix mechanics was



very successful in accounting for the discrete quanta of light emitted and absorbed by atoms.

The second formulation, called wave mechanics, was due to Schrödinger (1926); it is a generalization of the de Broglie postulate. This method, more intuitive than matrix mechanics, describes the dynamics of microscopic matter by means of a wave equation, called the Schrödinger equation; instead of the matrix eigenvalue problem of Heisenberg, Schrödinger obtained a differential equation. The solutions of this equation yield the energy spectrum and the wave function of the system under consideration. In 1927 Max Born proposed his probabilistic interpretation of wave mechanics: he took the square moduli of the wave functions that are solutions to the Schrödinger equation and he interpreted them as probability densities.

These two ostensibly different formulations—Schrödinger's wave formulation and Heisenberg's matrix approach—were shown to be equivalent. Dirac then suggested a more general formulation of quantum mechanics which deals with abstract objects such as kets (state vectors), bras, and operators. The representation of Dirac's formalism in a continuous basis—the position or momentum representations—gives back Schrödinger's wave mechanics. As for Heisenberg's matrix formulation, it can be obtained by representing Dirac's formalism in a discrete basis. In this context, the approaches of Schrödinger and Heisenberg represent, respectively, the wave formulation and the matrix formulation of the general theory of quantum mechanics.

Combining special relativity with quantum mechanics, Dirac derived in 1928 an equation which describes the motion of electrons. This equation, known as Dirac's equation, predicted the existence of an antiparticle, the positron, which has similar properties, but opposite charge, with the electron; the positron was discovered in 1932, four years after its prediction by quantum mechanics.



In summary, quantum mechanics is the theory that describes the dynamics of matter at the microscopic scale. Fine! But is it that important to learn? This is no less than an otiose question, for quantum mechanics is the only valid framework for describing the microphysical world. It is vital for understanding the physics of solids, lasers, semiconductor and superconductor devices, plasmas, etc. In short, quantum mechanics is the founding basis of all modern physics: solid state, molecular, atomic, nuclear, and particle physics, optics, thermodynamics, statistical mechanics, and so on. Not only that, it is also considered to be the foundation of chemistry and biology.

Particle Aspect of Radiation

According to classical physics, a particle is discrete entity, characterized by energy E and a momentum p , whereas a wave is extended physical entity characterized by an amplitude and a wave vector $\vec{k} = |\vec{k}| = 2\pi/\lambda$ that specifies the direction of propagation of the wave. Particles and waves exhibit entirely different behaviors. We should note that waves can exchange any (continuous) amount of energy with particles. But these rigid concepts of classical physics could not explain a number of microscopic phenomena such as blackbody radiation, the photoelectric effect, and the Compton Effect. As it turned out, these phenomena could only be explained by abandoning the rigid concepts of classical physics and introducing a new concept: the particle aspect of radiation.

Failure of classical theory

By the end of the nineteenth century, it was established that light was a wave and the entire phenomenon could be explained by using the wave nature of light. However, in the beginning of 20th century certain aspects between matter and energy were observed which could not be explained using the wave character of light. The

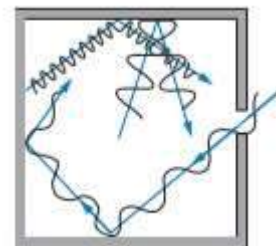


important phenomena unexplained by wave nature were: (a) photoelectric effect (b) black body radiation (c) Compton effect (d) optical spectra of substance

Blackbody Radiation

When heated, a solid object glows and emits thermal radiation having continuous distribution of frequencies ranging from infrared to ultraviolet. As the temperature increases, the object becomes red, then yellow, then white. The continuous pattern of the distribution spectrum is in sharp contrast to the radiation emitted by heated gases; the radiation emitted by gases has a discrete distribution spectrum: a few sharp (narrow), colored lines with no light (i.e., darkness) in between. Understanding the continuous character of the radiation emitted by a glowing solid object constituted one of the major unsolved problems during the second half of the nineteenth century.

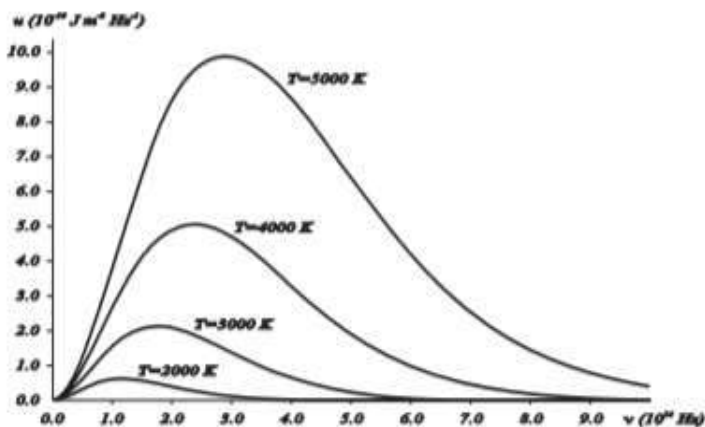
An idealized “blackbody” is a material object that absorbs all of the radiation falling on it, and hence appears as black under reflection when illuminated from outside. When an object is heated, it radiates electromagnetic energy as a result of the thermal agitation of the electrons in its surface. The intensity of this radiation depends on its frequency and on the temperature; the light it emits ranges over the entire spectrum. An object in thermal equilibrium with its surroundings radiates as much energy as it absorbs. It thus follows that a blackbody is a perfect absorber as well as a perfect emitter of radiation. A practical blackbody can be constructed by taking a hollow cavity with blackened walls and having a small hole as shown in figure acts as a black body. The radiation contained in the body and emitted from the hole produces a black body spectrum.



Birth of Quantum mechanics



In the last century, a number of experiments were carried out to measure the energy per unit volume contained by the black body, denoted by $u_T(\nu)$ at different temperatures. Some of the representative curves showing the variation of $u_T(\nu)$ as a function of ν at different temperatures are given.



Various investigations try to explain the nature of these curves using well established laws of classical physics, including thermodynamics. Till 1900 most of the measurements of the energy spectrum of the black body radiation were made at smaller wave lengths. These could be satisfactorily explained by Wein's formula give by

$$u_T(\lambda) d\lambda = a\lambda^{-5}e^{-b/\lambda kT} d\lambda$$

Where a and b were adjustable parameters.

Planck found empirically that by replacement of $\exp(-b/\lambda kT)$ by $\exp(b/\lambda kT - 1)^{-1}$. However, he found it extremely difficult to give a theoretical justification for above mentioned replacement. Ultimately out of depression, on 18th December, 1900, Planck declared that the only way to derive the correct formula was



to postulate that exchange of energy between matter (walls) and radiation (cavity) could take place only in bundles of certain size.

In classical physics, energy is regarded as an infinitely divisible quantity. Hence exchange of energy between matter and radiation can take place in infinite number of ways. However, through his postulate Planck reduced the number of ways to be finite. Planck further postulated that the unit or the quantum of energy is directly proportional to its frequency, i.e.

$$E = h\nu$$

Where h is Planck's constant.

This new idea gave birth to a new physics, known as quantum physics.

Planck's radiation law

The failure of R.J formula to explain the experimentally observed distribution of energy in the spectrum of a black body radiation showed that there was something wrong either with the equipartition law or with the classical electromagnetic theory or both.

Planck examined the whole situation critically and found an empirical formula to explain the experimentally observed distribution of energy in the spectrum of a black body. The formula may be deduced using following assumptions which may be called as Planck's hypothesis.

1. A black body radiation chamber is filled up not only with radiation, but also with simple harmonic oscillators or resonators of molecular dimensions which can vibrate with all possible frequencies. The vibration of the resonator entails one degree of freedom only.



2. The oscillator or resonators cannot radiate or absorb energy continuously, but an oscillator of frequency ν can only radiate or absorb energy in units or quanta of magnitude $h\nu$, where h is Planck's constant.

The number of oscillators in energy state $\epsilon_n = nh\nu$ is determined by the well-known Maxwell-Boltzmann distribution function:

$$N_n = N_0 e^{-\epsilon_n/kT} = N_0 e^{-nh\nu/kT}$$

The average energy per oscillator according to new ideas introduced by Plank is

$$\langle \epsilon \rangle = \frac{\sum_{n=0}^{\infty} N_n \epsilon_n}{\sum_{n=0}^{\infty} N_n}$$

or
$$\langle \epsilon \rangle = \frac{N_0 \epsilon_0 + N_1 \epsilon_1 + N_2 \epsilon_2 + N_3 \epsilon_3 + \dots}{N_0 + N_1 + N_2 + \dots}$$

or
$$\langle \epsilon \rangle = \frac{N_0 \times 0 + N_0 e^{-h\nu/kT} \times h\nu + N_0 e^{-2h\nu/kT} \times 2h\nu + N_0 e^{-3h\nu/kT} \times 3h\nu + \dots}{N_0 + N_0 e^{-h\nu/kT} + N_0 e^{-2h\nu/kT} + N_0 e^{-3h\nu/kT} + \dots}$$

Put $e^{-h\nu/kT} = x$

$$\therefore \langle \epsilon \rangle = \frac{N_0 h\nu x [1 + 2x + 3x^2 + \dots]}{N_0 [1 + x + x^2 + x^3 + \dots]} = \frac{h\nu x (1-x)^{-2}}{(1-x)^{-1}} = \frac{h\nu x}{1-x} = \frac{h\nu}{x^{-1} - 1}$$

$$\therefore \langle \epsilon \rangle = \frac{h\nu}{e^{h\nu/kT} - 1}$$

The number of modes of vibration per unit volume within frequency range ν and $\nu + d\nu$ is

$$\frac{4\pi\nu^2}{c^3} d\nu$$



Now the black body radiation travel with velocity of light c and transverse in character. As there are two possible polarisation states for each transverse wave, the number of modes of vibration of transverse is double as for longitudinal waves. Therefore the number of modes of vibration per unit volume within frequency range ν and $\nu + d\nu$ is

$$\frac{8\pi\nu^2}{c^3}d\nu$$

Now energy density belonging to the range $d\nu$ can be obtained by multiplying the average energy of Planck's oscillator by number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$ i.e

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu$$

Which is Planck's law in terms of frequency.

Photoelectric effect

The phenomenon of photoelectric emission was discovered in 1887 by Heinrich Hertz, during his electromagnetic wave experiments. In 1888, Hallwachs showed experimentally that electrons are emitted from Zn plate when ultraviolet falls on the plate.

This phenomenon of emission of electrons from a metallic surface when illuminated by light of appropriate wavelength or frequency is called photoelectric effect. The electrons emitted in this process are called photoelectrons and current so produced is called photoelectric current.

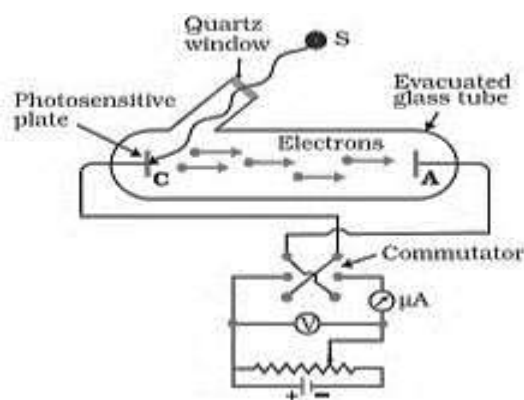
It was found that certain metals like zinc, cadmium, magnesium, etc., responded only to ultraviolet light, having short wavelength, to cause electron



emission from the surface. However, some alkali metals such as lithium, sodium, potassium, caesium and rubidium were sensitive even to visible light.

EXPERIMENTAL STUDY OF PHOTOELECTRIC EFFECT

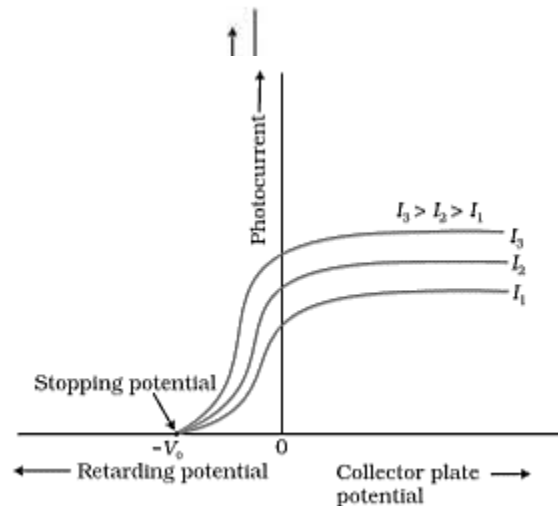
Figure depicts a schematic view of the arrangement used for the experimental study of the photoelectric effect. It consists of an evacuated glass/quartz tube having a photosensitive plate C and another metal plate A. Monochromatic light from the source S of sufficiently short wavelength passes through the window W and falls on the photosensitive plate C (emitter). A transparent quartz window is sealed on to the glass tube, which permits radiation to pass through it and irradiate the photosensitive plate C. The electrons are emitted by the plate C and are collected by the plate A (collector), by the electric field created by the battery. The battery maintains the potential difference between the plates C and A, that can be varied. The polarity of the plates C and A can be reversed by a commutator. The emission of electrons causes flow of electric current in the circuit. The potential difference between the emitter and collector plates is measured by a voltmeter (V) whereas the resulting photo current flowing in the circuit is measured by a microammeter (μA). The photoelectric current can be increased or decreased by varying the potential of collector plate A with respect to the emitter plate C. The intensity and frequency of the incident light can be varied, as can the potential difference V between the emitter C and the collector A.





Dependence of photoelectric current on intensity of light

The collector A is maintained at a positive potential with respect to emitter C so that electrons ejected from C are attracted towards collector A. Keeping the frequency of the incident radiation and the accelerating potential fixed, the intensity of light is varied and the resulting photoelectric current is measured each time. It is found that the photocurrent increases linearly with intensity of incident



light as shown graphically in Fig. The photocurrent is directly proportional to the number of photoelectrons emitted per second. This implies that the number of photoelectrons emitted per second is directly proportional to the intensity of incident radiation.

Effect of potential on photoelectric current

Keeping the intensity and frequency of incident light fixed. Increase the positive potential of plate A gradually and measure current each time. It is found that the photoelectric current increases with increase in accelerating (positive) potential. At some stage, for a certain positive potential of plate A, all the emitted electrons are collected by the plate A and the photoelectric current becomes maximum or saturates. If we increase the accelerating potential of plate A further, the photocurrent does not increase. This maximum value of the photoelectric current is called saturation current. Saturation current corresponds to the case when all the photoelectrons emitted by the emitter plate C reach the collector plate A. We now apply a negative (retarding) potential to the plate A with respect to the plate C and



make it increasingly negative gradually. When polarity is reversed, the electrons are repelled and only the most energetic electrons are able to reach the collector A. The photocurrent is found to decrease rapidly until it drops to zero at a certain sharply defined, critical value of the negative potential V_0 on the plate A. For a particular frequency of incident radiation, the minimum negative (retarding) potential V_0 given to the plate A for which the photocurrent stops or becomes zero is called the cut-off or stopping potential.

If the light of same frequency is used at higher intensity and above experiment is repeated, the saturation is found to be greater but stopping potential remains same. The interpretation of the observation in terms of photoelectrons is straightforward. All the photoelectrons emitted from the metal do not have the same energy.

Effect of frequency of incident radiation on stopping potential

Now suitably adjust the same intensity of light radiation at various frequencies and study the variation of photocurrent with collector plate potential. The resulting variation is shown in Fig. We obtain different values of stopping potential but the same value of the saturation current for incident radiation of different frequencies. The energy of the emitted electrons depends on the frequency of the incident radiations. The stopping potential is more negative for higher frequencies of incident radiation.

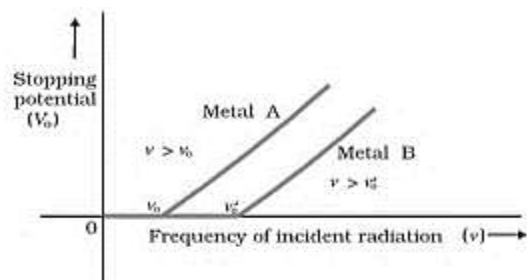
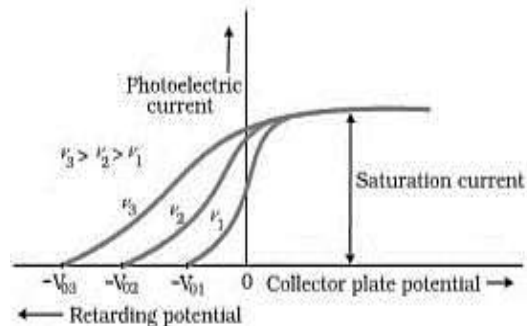




Fig. shows that the stopping potentials are in the order $V_{03} > V_{02} > V_{01}$ if the frequencies are in the order $\nu_3 > \nu_2 > \nu_1$. This implies that greater the frequency of incident light, greater is the maximum kinetic energy of the photoelectrons. Consequently, we need greater retarding potential to stop them completely. If we plot a graph between the frequency of incident radiation and the corresponding stopping potential for different metals we get a straight line, as shown in Fig. The graph shows that

- (a) Stopping potential is directly proportional to frequency of incident radiation.
- (b) There is minimum frequency ν_0 (threshold frequency) of incident radiation for which stopping potential is zero.

Laws of photoelectric effect

The experimental fact regarding photoelectric emission can be summarized in terms of the fundamental laws of photoelectric emission:

1. For a given photosensitive material and frequency of incident light, the photoelectric current is directly proportional to the intensity of incident light, provided frequency is above the threshold.
2. For a given photosensitive material, there is certain minimum frequency called the threshold frequency below which no photoelectrons are emitted, no matter how great is the intensity of the light.
3. Above the threshold frequency, the maximum kinetic of photoelectrons is found to increase with the increase in frequency of the incident light and is found to be independent on the intensity of light.
4. The process of photoelectric emission is instantaneous i.e. as soon as frequency of incident light exceeds the threshold limit, the emission starts immediately without



any apparent time lag (10^{-9} s), even when the incident radiation is made exceedingly dim.

EINSTEIN'S PHOTOELECTRIC EQUATION

In 1905, Albert Einstein proposed a radically new picture of electromagnetic radiation to explain photoelectric effect. Einstein applied Planck's quantum theory and proposed that the emission of photoelectrons was the result of the interaction of a single photon with only one electron, in which photon is completely absorbed by the electron.

Whenever a photon with energy $h\nu$ is incident on a photosensitive metallic surface. A part of energy of photon is used in liberating the electron from the metal surface which is equal to work function φ_0 of the metal. The rest of energy is used in imparting kinetic energy K_{max} to the photoelectron. Thus according to conservation of energy

$$h\nu = \varphi_0 + K_{max}$$

or
$$K_{max} = h\nu - \varphi_0 \quad (1)$$

If the incident photon is of threshold frequency ν_0 , then incident photon of energy $h\nu_0$ is just sufficient to eject electron from the metal surface without imparting it any kinetic energy. Hence

$$h\nu_0 = \varphi_0$$

From (1),
$$K_{max} = h\nu - h\nu_0$$

Or
$$K_{max} = h(\nu - \nu_0)$$

This equation is called Einstein's photoelectric equation.



Explanation of laws of photoelectric effect:

Einstein's theory leads to conclusion that one photon of incident light may eject one photoelectron from metal surface. Therefore if the intensity of incident light is increased, the number of incident photons increases, which results in an increase in the number of photoelectrons ejected. This is the first law of photoelectric effect.

From Einstein's photoelectric equation, it is evident that if frequency of incident light is less than threshold frequency. Kinetic energy is negative. Which means no emission of photoelectrons takes place whatever be the intensity of incident light. This is second law of photoelectric emission.

From Einstein's photoelectric equation, it is evident that if frequency of incident light is greater than the threshold frequency, kinetic energy of ejected photoelectrons is directly proportional to the frequency and is independent on the intensity. This is third law of photoelectric emission.

In photoelectric effect there is elastic collision between a photon and an electron. The electron absorbs energy of photon at once without any time lag and gets ejected instantaneously. This is the fourth law of photoelectric emission.

PHOTOELECTRIC EFFECT AND WAVE THEORY OF LIGHT

The phenomena of interference, diffraction and polarisation were explained in a natural and satisfactory way by the wave picture of light. According to this picture, light is an electromagnetic wave consisting of electric and magnetic fields with continuous distribution of energy over the region of space over which the wave is extended.



According to the wave picture of light, the free electrons at the surface of the metal (over which the beam of radiation falls) absorb the radiant energy continuously. The greater the intensity of radiation, the greater are the amplitude of electric and magnetic fields. Consequently, the greater the intensity, the greater should be the energy absorbed by each electron. In this picture, the maximum kinetic energy of the photoelectrons on the surface is then expected to increase with increase in intensity. Also, no matter what the frequency of radiation is, a sufficiently intense beam of radiation (over sufficient time) should be able to impart enough energy to the electrons, so that they exceed the minimum energy needed to escape from the metal surface. A threshold frequency, therefore, should not exist. These expectations of the wave theory directly contradict experimental observations.

Further, we should note that in the wave picture, the absorption of energy by electron takes place continuously over the entire wave front of the radiation. Since a large number of electrons absorb energy, the energy absorbed per electron per unit time turns out to be small. Explicit calculations estimate that it can take hours or more for a single electron to pick up sufficient energy to overcome the work function and come out of the metal. This conclusion is again in striking contrast to observation that the photoelectric emission is instantaneous. In short, the wave picture is unable to explain the most basic features of photoelectric effect.

Compton Effect

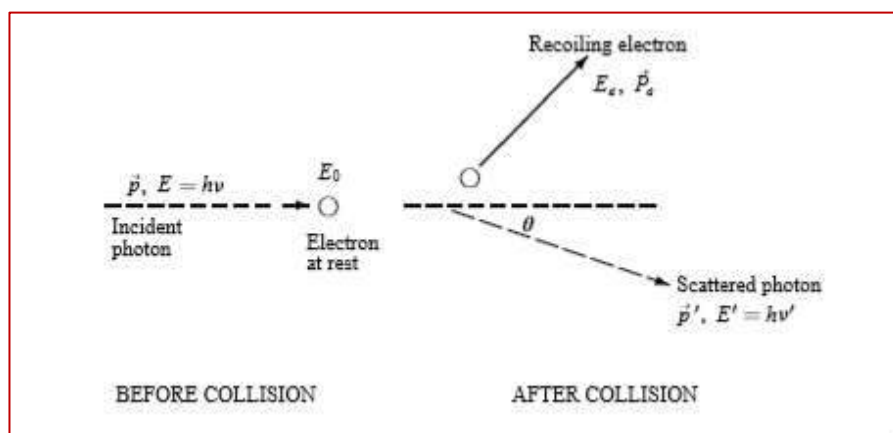
In his 1921 experiment, Compton provided the most conclusive confirmation of the particle aspect of radiation. By scattering X-rays off free electrons, he found that the wavelength of the scattered radiation is larger than the wavelength of the incident radiation. This can be explained only by assuming that the X-ray photons behave like particles.



Issue here is to study how X-rays scatter off free electrons. According to classical physics, the incident and scattered radiation should have the same wavelength. This can be viewed as follows. Classically, since the energy of the X-ray radiation is too high to be absorbed by a free electron, the incident X-ray would then provide an oscillatory electric field which sets the electron into oscillatory motion, hence making it radiate light with the same wavelength but with an intensity I that depends on the intensity of the incident radiation I_0 (i.e., $I \propto I_0$). Neither of these two predictions of classical physics is compatible with experiment. The experimental findings of Compton reveal that the wavelength of the scattered X-radiation increases by an amount $\Delta\lambda$, called the wavelength shift, and that $\Delta\lambda$ depends not on the intensity of the incident radiation, but only on the scattering angle.

Compton succeeded in explaining his experimental results only after treating the incident radiation as a stream of particles—photons—colliding elastically with individual electrons. In this scattering process, which can be illustrated by the elastic scattering of a photon from a free electron, the laws of elastic collisions can be invoked, notably the conservation of energy and momentum.

Consider that the incident photon, of energy $E = h\nu$ and



momentum $p = h\nu/c$, collides with an electron that is initially at rest. If the photon



scatters with a momentum p' at an angle θ , while the electron recoils with a momentum p'_e , the conservation of linear momentum yields

$$\vec{p} = \vec{p}_e + \vec{p}'$$

Which leads to

$$p'^2 = p^2 + p_e'^2 - 2pp' \cos \theta = \frac{h^2}{c^2}(v^2 + v'^2 - 2vv' \cos \theta)$$

Let us now turn to the energy conservation. The energies of the electron before and after the collision are given, respectively, by

$$E_0 = m_e c^2$$

$$E_e = \sqrt{p_e'^2 c^2 + m_e^2 c^4} = h \sqrt{\left(v^2 + v'^2 - 2vv' \cos \theta + \frac{m_e^2 c^4}{h^2}\right)}$$

Since the energies of the incident and scattered photons are given by $E = hv$ and $E' = hv'$, respectively, conservation of energy dictates that

$$E + E_0 = E' + E_e$$

or

$$hv + m_e c^2 = hv' + h \sqrt{\left(v^2 + v'^2 - 2vv' \cos \theta + \frac{m_e^2 c^4}{h^2}\right)}$$

Which in turn leads to

$$v - v' + \frac{m_e c^2}{h} = \sqrt{\left(v^2 + v'^2 - 2vv' \cos \theta + \frac{m_e^2 c^4}{h^2}\right)}$$

Squaring both sides



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

Hence the wavelength shift is given

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta)$$

Where $\frac{h}{m_e c} = 2.426 \times 10^{-12} m$ is called the Compton wavelength of the electron. This relation, which connects the initial and final wavelengths to the scattering angle, confirms Compton's experimental observation: the wavelength shift of the X-rays depends only on the angle at which they are scattered and not on the frequency (or wavelength) of the incident photons.

In summary, the Compton Effect confirms that photons behave like particles: they collide with electrons like material particles.

Dual nature of matter:

The universe is composed of matter and electromagnetic radiation. In 1924 Louis de Broglie said that the nature is symmetrical in many ways and as radiation possesses both wave and particle characteristics, so the material particle when in motion must have wave property as well.

De-Broglie hypothesis:

According to de-Broglie a moving material particle sometimes acts as a wave and sometimes acts as a particle. The wave associated with moving particle is



called matter wave or de-Broglie wave whose wavelength called de-Broglie wavelength, is given by

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

Where m is the mass of particle at velocity v and h is a Planck's constant.

Derivation of de-Broglie wavelength:

According to Planck's quantum theory the energy of photon of a radiation of frequency ν and wavelength λ is

$$E = h\nu = h\frac{c}{\lambda} \quad (1) \quad \because c = \nu\lambda$$

According to Einstein's theory of relativity energy E and rest mass m_0 are related as

$$E = \sqrt{P^2c^2 + m_0^2c^4}$$

For photons rest mass is zero, therefore

$$E = Pc \quad (2)$$

Comparing eq. (1) and (2), we get

$$Pc = h\frac{c}{\lambda}$$

$$\text{or} \quad \lambda = \frac{h}{P} \quad (3)$$



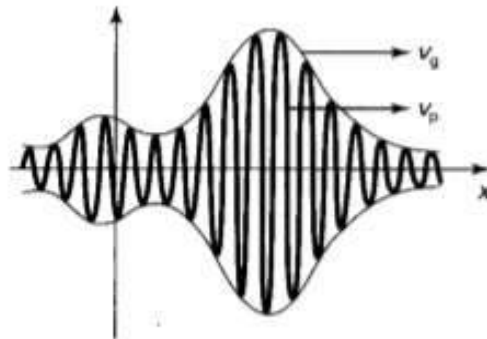
According to de-Broglie the equation (3) is equally applicable to both the photons of radiation and other material particles.

If a material particle of mass m is moving with velocity v . The de-Broglie wavelength associated with particle is

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

$$\text{or } \lambda = \frac{h}{p}$$

Where p is the momentum of particle. This relation is called de-Broglie



wavelength relation.

Phase velocity

A single (infinite) wave is described by the expression $\cos(\omega t - kx)$ or $\sin(\omega t - kx)$ or equivalent. The pattern travels with a velocity (actually a speed) $v_p = \lambda/T = v\lambda = \omega/k$ known as phase velocity. Thus phase velocity is the velocity with which a single (infinite) wave is propagating.



$$v_p = \frac{\omega}{k} = \frac{E}{p} = \frac{mc^2}{p} = \frac{c^2}{v}$$

Group velocity

An infinite wave is unrealistic. A real wave has to have beginning and end. The overall shape is called the envelope. Various shapes are possible - abrupt or gentle. Group velocity is the velocity with which a wave packet (envelope) propagates. A wave packet is a group of waves with slightly different wavelengths and frequencies interfering with one another in such a way that the amplitude of the group is non zero only in the neighbourhood of the particle.

Consider two travelling waves represented by

$$\Psi_1 = A \sin(\omega t - kx)$$

$$\Psi_2 = A \sin[(\omega + d\omega)t - (k + dk)x]$$

The superposition of these waves yields a resultant wave given by

$$\Psi = \Psi_1 + \Psi_2 = A \sin(\omega t - kx) + A \sin[(\omega + d\omega)t - (k + dk)x]$$

or
$$\Psi = 2A \left[\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \sin(\omega t - kx) \right]$$

Ψ has an envelope equal to $2A \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$ modulating the sine wave given by $\sin(\omega t - kx)$

The velocity of envelope is $d\omega/dk$ is known as group velocity (v_g)

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp}$$

Now from special theory of relativity

$$E^2 = p^2c^2 + m_0^2c^4$$



$$2EdE = 2pc^2 dp$$

$$\frac{dE}{dp} = \frac{pc^2}{E} = \frac{pc^2}{mc^2} = v$$

$$\therefore v_g = \frac{d\omega}{dk} = \frac{dE}{dp} = v$$

The phenomenon of pair production

Pair production is a phenomenon of nature where energy is converted to mass. It provides a conceptual framework for how our internal world gets translated into the physical reality we experience. The phenomenon of pair production can be viewed two different ways. One way is as a particle and antiparticle and the other is as a particle and a hole.

Basic process

In this phenomenon a photon interacts with a heavy nucleus to form an electron - positron pair. Pair production is observed to occur in nature when a photon of energy greater than 1.02 million electron volts passes near the electric field of heavy atom such as lead, uranium or other heavy material with a large number of protons.

Heisenberg's Uncertainty Principle

within the context of quantum mechanics a particle is represented by means of a wave function corresponding to the particle's wave, and since wave functions cannot be localized, then a microscopic particle is somewhat spread over space and, unlike classical particles, cannot be localized in space.. The classical concepts of exact position, exact momentum, and unique path of a particle therefore make no sense at the microscopic scale. This is the essence of Heisenberg's uncertainty principle. In its original form, Heisenberg's uncertainty principle states that: If the x-component of



the momentum of a particle is measured with an uncertainty Δp_x , then its x-component of position cannot, at the same time, be measured more accurately than $\Delta x = \hbar/2\Delta p_x$. The three-dimensional form of the uncertainty relations for position and momentum can be written as follows:

$$\Delta x \Delta p_x \geq \hbar/2 \quad \Delta y \Delta p_y \geq \hbar/2 \quad \Delta z \Delta p_z \geq \hbar/2$$

This principle indicates that, although it is possible to measure the momentum or position of a particle accurately, it is not possible to measure these two observables simultaneously to an arbitrary accuracy. That is, we cannot localize a microscopic particle without giving to it a rather large momentum. We cannot measure the position without disturbing it; there is no way to carry out such a measurement passively as it is bound to change the momentum. If a particle were localized, its wave function would become zero everywhere else and its wave would then have a very short wavelength. According to de Broglie's relation $p = h/\lambda$, the momentum of this particle will be rather high. Formally, this means that if a particle is accurately localized (i.e., $\Delta x \rightarrow 0$), there will be total uncertainty about its momentum (i.e. $\Delta p_x \rightarrow \infty$). To summarize, since all quantum phenomena are described by waves, we have no choice but to accept limits on our ability to measure simultaneously any two complementary variables. Heisenberg's uncertainty principle can be generalized to any pair of complementary, or canonically conjugate, dynamical variables: it is impossible to devise an experiment that can measure simultaneously two complementary variables to arbitrary accuracy (if this were ever achieved, the theory of quantum mechanics would collapse). Energy and time, for instance, form a pair of complementary variables. Their simultaneous measurement must obey the time–energy uncertainty relation:



$$\Delta E \Delta t \geq \hbar/2$$

Heisenberg's γ -ray microscope

A striking thought experiment illustrating uncertainty principle is Bohr's / Heisenberg's Gamma-ray microscope. To observe a particle, say an electron, we shine it with light ray of wavelength λ and collect the Compton scattered light in a microscope objective whose diameter subtends an angle 2θ with the electron as shown in the figure below.

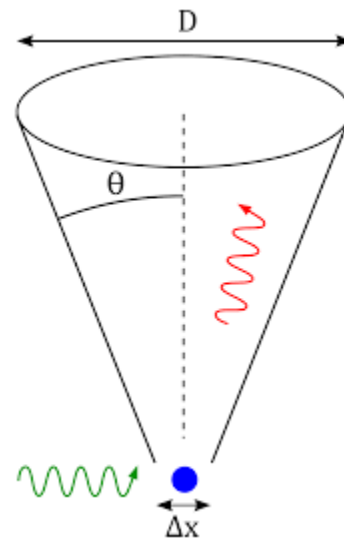
The precision with which the electron can be located, Δx , is defined by the resolving power of the microscope,

$$\Delta x = \frac{\lambda}{2 \sin \theta}$$

It appears that by making λ small, that is why we choose γ -ray and by making $\sin \theta$ large, Δx can be made as small as desired. But, according to uncertainty principle, we can do so only at the expense of our knowledge of x-component of electron momentum.

In order to record the Compton scattered photon by the microscope, the photon must stay in the cone of angle θ and hence its x-component of the momentum can vary within $\pm(h/\lambda \sin \theta)$. This implies, the magnitude of the recoil momentum of the electron is uncertain by $\Delta p_x = 2h/\lambda \sin \theta$. The product of the uncertainty yields,

$$\Delta x \times \Delta p_x = h > \frac{h}{2}$$



Application of uncertainty principle



(A) Non existence of electron inside the nucleus

The size of the nucleus is of the order of one Fermi. Therefore if the electrons are present inside the nucleus, the maximum uncertainty in their position is $\Delta x = 10^{-15}m$, hence Δp will be $\hbar/\Delta x \approx 10^{-19} jsm^{-1}$. If this is the uncertainty in momentum of the electron, the momentum of the electron must be at least comparable with its magnitude i.e. $p = 10^{-19} jsm^{-1}$. The total energy may be obtained from the relation $E^2 = p^2c^2 + m_0^2c^4$, or $E = pc$ as m_0c^2 is much smaller than pc . Thus we obtain

$$E = 3 \times 10^{-11}j \approx 200 MeV$$

However, experimentally we find that during β -decay of a nucleus, electrons of energies 2-3 MeV are ejected. Hence we conclude that electrons were present in the nucleus before the decay.

(B) Zero point energy

According to kinetic theory, the energies of atoms oscillating about their positions in crystals are proportional to the absolute temperature. Hence at absolute Zero, the atoms according to kinetic theory, would stop oscillating and would remain fixed in their lattice positions. But, according to uncertainty relation both position and momentum cannot be specified at the same time with complete accuracy. This means that the atomic oscillator even at absolute zero would retain a certain amount of oscillatory motion to obey enough the uncertainty relation. This energy possessed by the atomic oscillator at absolute zero is termed as zero point energy.

(C) The radius of the Bohr's first orbit

Suppose size of hydrogen atom to be " a " then the uncertainty in the position of the electron is about " a ". Hence according to uncertainty principle, the uncertainty in momentum is given by $\Delta p = \hbar/a$. The total (non-relativistic) energy of the electron is equal to



$$E = \frac{p^2}{2m} - \frac{1}{4\pi\epsilon_0} \times \frac{e^2}{a}$$

For stable atom, E will be minimum for that electron will be in first orbit. Hence we replace p by \hbar/a and equate $dE/da = 0$. This yield

$$a = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} \approx 0.5 \approx A^\circ$$

And corresponding value of energy E is

$$E = -\frac{1}{2} \frac{me^4}{(4\pi\epsilon_0)^2 \hbar^2} = -13.6 \text{ eV}$$



Unit 11

Postulates of Quantum Mechanics

First postulate: information about the properties of a system of particles is contained in a function Ψ of all coordinates and time. The function Ψ is called the wave function of the system. For this to be acceptable, the function should be single valued, continuous and finite everywhere, going over to zero at infinity.

Second postulate: information regarding any physical variable of a system can be extracted from the wave function by the use of corresponding operator for the variable.

If f is a physical variable and \hat{F} is its operator then $\hat{F}\Psi = f\Psi$. The L.H.S means the operator \hat{F} acting on the wave function Ψ , while R.H.S means f multiplied by Ψ .

Third Postulate: The expectation value $\langle f \rangle$ of a variable f for a system of wave function Ψ is

$$\langle f \rangle = \frac{\oint \Psi^* \hat{F} \Psi d\tau}{\oint \Psi^* \Psi d\tau}$$

Where Ψ^* is complex conjugate of Ψ and integration is over all the space variables.

Schrodinger's Equation

In 1926, a major step was taken by Erwin Schrodinger when he published his famous, wave equation, which was the beginning of the new quantum mechanics, and for which he received the Nobel Prize in 1933. Schrodinger also showed the equivalence between his wave mechanics and the matrix mechanics of Heisenberg,



which are thus different ways of expressing quantum mechanics. The fundamental assumptions made by Schrodinger, which led him to his final equation, can be outlined as follows. There exists an analogy among the basic equations of classical mechanics and those of geometrical optics (we recall the analogy between Hamilton's principle of least action and Fermat's principle in optics) .Then, if atomic particles have wave properties, they should be governed by a wave mechanics that must bear the same relation to classical mechanics as wave optics bears with regard to geometrical optics, according to the following scheme:

Wave Optics → Geometrical Optics

Wave Mechanics → Classical Mechanics

In essence, the mathematical way to get the Schrodinger equation is the following.

- (a) First write down the classical expression for the energy of the system under investigation. The kinetic energy is expressed in terms of the linear momentum:

$$\frac{1}{2m}[p_x^2 + p_y^2 + p_z^2] + U(r) = E \quad (1)$$

Where $p^2/2m$, $U(r)$ and E are the kinetic, potential, and total energies, respectively.,

- (b) Classical quantities are replaced by operators, denoted by hatted letters, according to the following rules:

$$p_x = \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$
$$p_y = \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \quad (2)$$



$$p_z = \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

$$E = \hat{E} = i\hbar \frac{\partial}{\partial t}$$

Coordinates are substituted by themselves as operators, $\hat{x} = x, \hat{y} = y, \hat{z} = z$
(c) A differential equation is built for the wave function, using the substitutions (1) in (2), and applying the result to the wave function $\Psi(r, t)$

$$-\left[\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(r) \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Where the quantity in squared brackets is named the Hamiltonian operator denoted by \hat{H} so that it is written simply as

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Time independent Schrodinger wave equation

Consider a system of stationary waves to be associated with a particle. Let $\Psi(\mathbf{r}, t)$ be wave displacement for the de-Broglie waves at any location $\mathbf{r} = x\hat{i} + y\hat{j} + z\hat{k}$ at time t . Then the differential equation of wave motion in three dimensions in accordance with Maxwell's wave equation can be written as

$$\nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} \quad (1)$$

Where v is wave velocity.

The solution of this equation gives Ψ as a periodic displacement in terms of time, i.e

$$\Psi(\mathbf{r}, t) = \Psi_0(\mathbf{r})e^{-i\omega t} \quad (2)$$



Differentiate this equation twice with respect to t , we get

$$\frac{\partial^2 \Psi}{\partial t^2} = -\omega^2 \Psi(\mathbf{r}, t)$$

Substituting this in equation (1), we get

$$\nabla^2 \Psi = -\frac{\omega^2}{v^2} \Psi(\mathbf{r}, t)$$

$$\text{now } \frac{\omega}{v} = \frac{2\pi\nu}{v} = \frac{2\pi}{\lambda}$$

$$\therefore \nabla^2 \Psi + \frac{4\pi^2}{\lambda^2} \Psi(\mathbf{r}, t) = 0$$

According to de-Broglie wavelength relation

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

$$\therefore \nabla^2 \Psi + \frac{4\pi^2 m^2 v^2}{h^2} \Psi(\mathbf{r}, t) = 0$$

If E and V are the total and potential energies of the particle respectively, then kinetic energy

$$\frac{1}{2}mv^2 = E - V \Rightarrow m^2v^2 = 2m(E - V)$$

$$\therefore \nabla^2 \Psi + \frac{8\pi^2 m(E - V)}{h^2} \Psi(\mathbf{r}, t) = 0$$

$$\text{or } \nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V) \Psi(\mathbf{r}, t) = 0$$

The above equation is called Schrodinger's time independent wave equation.



Probabilistic Interpretation

In quantum mechanics the state (or one of the states) of a quantum particle is described by a wave function $\Psi(\vec{r}, t)$ corresponding to the de Broglie wave of this particle; so $\Psi(\vec{r}, t)$ describes the wave properties of a particle. As a result, when discussing quantum effects, it is suitable to use the amplitude function, Ψ , whose square modulus, $|\Psi|^2$, is equal to the intensity of the wave associated with this quantum effect. The intensity of a wave at a given point in space is proportional to the probability of finding, at that point, the material particle that corresponds to the wave.

In 1927 Born interpreted, $|\Psi|^2$ as the probability density and $|\Psi(\vec{r}, t)|^2 d\tau$ as the probability, $dP(\vec{r}, t)$, of finding a particle at time t in the volume element $d\tau$ located between \vec{r} and $\vec{r} + d\vec{r}$

$$|\Psi(\vec{r}, t)|^2 d\tau = dP(\vec{r}, t),$$

If we integrate over the entire space, we are certain that the particle is somewhere in it. Thus, the total probability of finding the particle somewhere in space must be equal to one

$$\int_{\text{All space}} |\Psi(\vec{r}, t)|^2 d\tau = 1$$

Properties of wave functions

Mathematical properties of Ψ

- A. Ψ must be continuous and single-valued everywhere.
- B. $\frac{\partial \Psi}{\partial x}$, $\frac{\partial \Psi}{\partial y}$, $\frac{\partial \Psi}{\partial z}$ must be continuous and single-valued everywhere. (There may be exception in some special situations, we will discuss this later.)



C. Ψ must be normalizable. $|\Psi|^2$ must go to 0 fast enough as $x, y, \text{ or } z \rightarrow \pm\infty$ so that $\int |\Psi(\vec{r}, t)|^2 d\tau$ remains finite.

Linearity of quantum mechanics: linear superposition

The time-dependent Schrodinger equation is also linear in the wave function Ψ , just as the time-independent Schrodinger equation was. Again, no higher powers of Ψ appear anywhere in the equation. In the time-independent equation, this allowed us to say that, if Ψ was a solution, then so is $A\Psi$, where A is any constant and the same kind of behavior holds here for the solutions Ψ of the time-dependent Schrodinger equation. Another consequence of linearity is the possibility of linear superposition of solutions, which we can state as a linear combination of solutions of Schrodinger equation for a given system is also itself a solution i.e.

If $\Psi_a(r, t)$ and $\Psi_b(r, t)$ are solutions,

Then so also is $\Psi_{a+b}(r, t) = \Psi_a(r, t) + \Psi_b(r, t)$

This is easily verified by substitution into the time-dependent Schrodinger equation.

We can also multiply the individual solutions by arbitrary constants and still have a solution to the equation, i.e.

$$\Psi_c(r, t) = c_a \Psi_a(r, t) + c_b \Psi_b(r, t)$$

Where c_a and c_b are (complex) constants, is also a solution.

The concept of linear superposition solutions is, at first sight, a very strange one from a classical point of view. There is no classical precedent for saying that a particle or a system is in a linear superposition of two or more possible states. In classical mechanics, a particle simply has a "state" that is defined by its position and



momentum, for example. Here we are saying that a particle may exist in a superposition of states each of which may have different energies (or possibly positions or momenta). Actually, however, it will turn out that, to recover the kind of behavior we expect from particles in the classical picture of the world, we need to use linear superposition.

Expectation Values

In general, the outcome of a measurement in quantum mechanics is a random variable with many possible values. The average of these values is called the expectation value. In principle, the expectation value can be found by taking the average result of measurements on an infinite ensemble of identically prepared systems. Alternatively, we can calculate the expectation value using the probability distribution which governs the outcomes of the measurement.

Let us consider the measurement of a dynamical variable or observable f of a system. Keeping the system always in a particular state Ψ we measure f repeatedly. In general, each individual measurement will yield a different result. Hence we take average of these measurements $\langle f \rangle$ as the value of the dynamical variable for that particular state. Since we have always started same state Ψ , it is reasonable to assume that knowing Ψ we should be able to calculate $\langle f \rangle$. Such a relation between Ψ and $\langle f \rangle$ is provided by another postulate of the quantum mechanics. According to this postulate,

$$\langle f \rangle = \frac{\int \Psi^* \hat{f} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Particle in one dimensional box



Consider the Schrodinger equation for the 1D case where the potential (x) is defined to be a function with zero value for $0 < x < a$ (inside the box) and infinite value outside this range. The Schrodinger equation inside the box is given by

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2mE}{\hbar^2} \Psi(\mathbf{r}, t) = 0 \quad (1)$$

This equation is of the form

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi(\mathbf{r}, t) = 0$$

Hence the solution of equation (1) will be of the form

$$\Psi = A \sin \sqrt{\frac{2mE}{\hbar^2}} x + B \cos \sqrt{\frac{2mE}{\hbar^2}} x \quad (2)$$

Applying the boundary condition

$\Psi = 0$ at $x = 0$ $\Psi = 0$ at $x = a$ to equation(2), we get

$$0 = A \sin 0 + B \cos 0 \Rightarrow B = 0$$

$$\therefore \Psi = A \sin \sqrt{\frac{2mE}{\hbar^2}} x \quad (3)$$

Now apply other boundary condition

$\Psi = 0$ at $x = a$ to equation(3), we get

$$A \sin \sqrt{\frac{2mE}{\hbar^2}} a = 0$$

Now A can not be zero, which is meaningless. Therefore,



$$\sin \sqrt{\frac{2mE}{\hbar^2}} a = 0 \quad \text{which gives}$$

$$\sqrt{\frac{2mE}{\hbar^2}} a = n\pi \quad n = 1, 2, 3, 4, \dots \quad (4)$$

Replacing E by E_n for different values of n

$$\Rightarrow E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad (5)$$

Hence energy of particle is quantized and can have only discrete values. These values of energy are called eigen values.

The wave function of particle of energy E_n is given by putting equation (4) in equation (3), we get

$$\Psi_n = A \sin \frac{n\pi}{a} x$$

Where Ψ_n is the eigen function for energy eigen value E_n

As the particle is certainly within the box, we have the normalized condition

$$\int_0^a \Psi_n^* \Psi_n dx = 1$$

$$\int_0^a \left(A \sin \frac{n\pi}{a} x \right)^* \left(A \sin \frac{n\pi}{a} x \right) dx = 1$$

$$\int_0^a A^2 \sin^2 \frac{n\pi}{a} x dx = 1$$



$$\text{or } \int_0^a \frac{A^2}{2} \left(1 - \cos \frac{2n\pi}{a} x\right) dx = 1$$

$$\text{or } \frac{A^2}{2} \left[\int_0^a dx - \int_0^a \cos \frac{2n\pi}{a} x dx \right] = 1$$

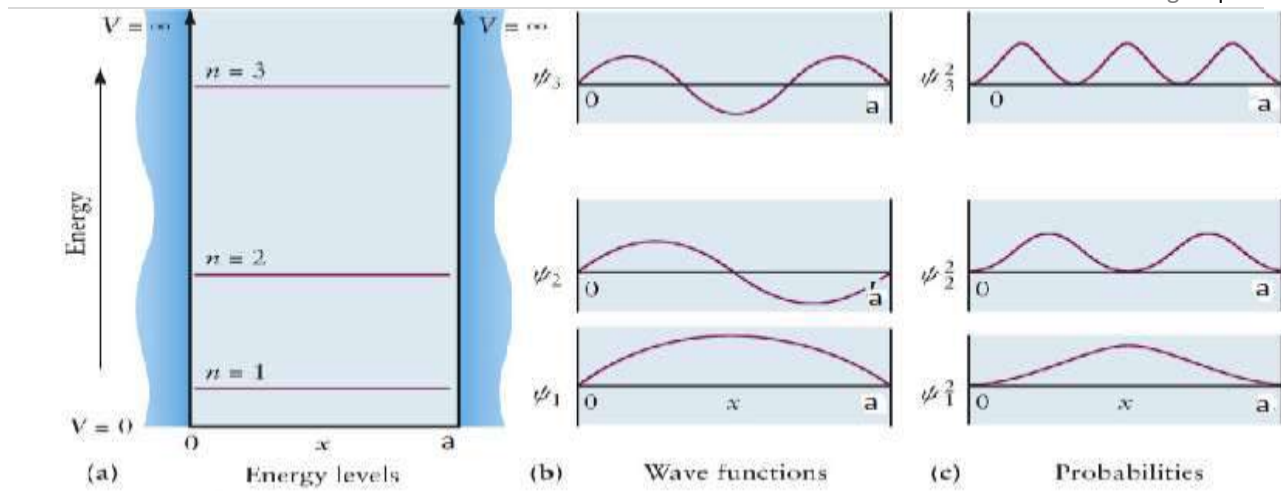
$$\text{or } \frac{A^2}{2} \left[|x|_0^a - \left| \frac{\sin \frac{2n\pi}{a} x}{\frac{2n\pi}{a}} \right|_0^a \right] = 1$$

$$\text{or } A = \sqrt{\frac{2}{a}}$$

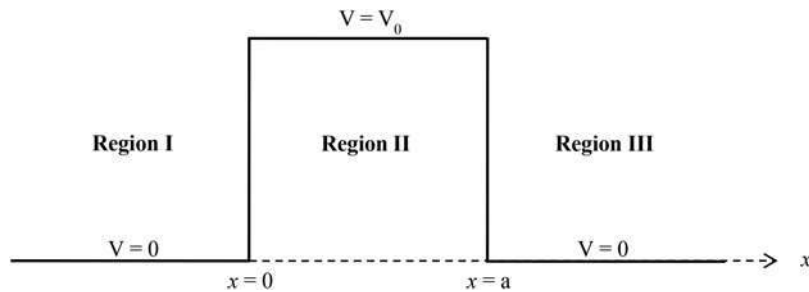
Therefore normalized wave function for a particles in one dimensional box is given by

$$\Psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x$$

The normalized wave function $\Psi_1, \Psi_2, \Psi_3 \dots etc$ and probability densities $|\Psi_1|^2, |\Psi_2|^2, |\Psi_3|^2 \dots etc$ are plotted as shown in figure.



One dimensional rectangular potential Barrier



Consider a particle of mass m incident on a potential barrier of height V_0 and width a as shown in figure.

Let the total energy E of the particle is less than the height of the potential barrier. Using the laws of classical mechanics there is zero probability for the electron to be present on the other side of the barrier. But in quantum mechanics, using the delocalized electron wave function it is possible to show that there is a finite probability for the electron to 'tunnel' through the barrier. This probability depends on the energy E , barrier height V_0 and width a . There are 3 regions marked I, II, and III, for which Schrödinger equation can be written as



$$\frac{\partial^2 \Psi_1}{\partial x^2} + \frac{2mE}{\hbar^2} \Psi_1 = 0$$

$$\frac{\partial^2 \Psi_2}{\partial x^2} - \frac{2m}{\hbar^2} (V_0 - E) \Psi_2 = 0$$

$$\frac{\partial^2 \Psi_3}{\partial x^2} + \frac{2mE}{\hbar^2} \Psi_3 = 0$$

The above equation can be written as

$$\frac{\partial^2 \Psi_1}{\partial x^2} + k_1^2 \Psi_1 = 0 \quad (1)$$

$$\frac{\partial^2 \Psi_2}{\partial x^2} - k_2^2 \Psi_2 = 0 \quad (2)$$

$$\frac{\partial^2 \Psi_3}{\partial x^2} + k_1^2 \Psi_3 = 0 \quad (3)$$

Where $k_1^2 = 2mE/\hbar^2$ and $k_2^2 = 2m(V_0 - E)/\hbar^2$

The solution of eq (1), (2) and (3) are

$$\Psi_1 = A e^{ik_1x} + B e^{-ik_1x} \quad (4)$$

$$\Psi_2 = C e^{-k_2x} + D e^{k_2x} \quad (5)$$

$$\Psi_3 = E e^{ik_1x} + F e^{-ik_1x} \quad (6)$$

Where A, B, C, D, E and F are arbitrary constants. The first term of equation (4) represents incident wave and second term represents reflected wave in region I. The first term of equation (6) represents transmitted wave. Since the particle cannot be reflected from region III, hence $F = 0$, hence eq (4), (5) and (6) can be written as



$$\Psi_1 = A e^{ik_1x} + B e^{-ik_1x}$$

$$\Psi_2 = C e^{-k_2x} + D e^{k_2x}$$

$$\Psi_3 = E e^{ik_1x} \quad (9)$$

The wave function must be continuous and continuously differentiable at the boundaries.

Continuity of wave function at $x = 0$ demands

$$\Psi_1(0) = \Psi_2(0)$$

$$\text{or } [A e^{ik_1x} + B e^{-ik_1x}]_{x=0} = [C e^{-k_2x} + D e^{k_2x}]_{x=0}$$

$$\text{or } A + B = C + D \quad (10)$$

Continuity of wave function at $x = a$ demands

$$\Psi_2(a) = \Psi_3(a)$$

$$\text{or } [C e^{-k_2x} + D e^{k_2x}]_{x=a} = [E e^{ik_1x}]_{x=a}$$

$$\text{or } C e^{-k_2a} + D e^{k_2a} = E e^{ik_1a} \quad (11)$$

Continuity of derivative of wave function at $x = 0$ demands

$$\left[\frac{\partial \Psi_1}{\partial x} \right]_{x=0} = \left[\frac{\partial \Psi_2}{\partial x} \right]_{x=0}$$

$$A - B = \frac{ik_2}{k_1} [C - D] \quad (12)$$

Continuity of derivative of wave function at $x = a$ demands



$$\left[\frac{\partial \Psi_2}{\partial x} \right]_{x=a} = \left[\frac{\partial \Psi_3}{\partial x} \right]_{x=a}$$

$$-k_2 C e^{-k_2 a} + k_2 D e^{k_2 a} = ik_1 E e^{ik_1 a} \quad (13)$$

Adding and subtracting eq(11) and (13) and solving further we get

$$C = \frac{E e^{ik_1 a}}{2} \left[1 - \frac{ik_1}{k_2} \right] e^{k_2 a} \quad (14)$$

$$D = \frac{E e^{ik_1 a}}{2} \left[1 + \frac{ik_1}{k_2} \right] e^{-k_2 a} \quad (15)$$

Putting these values in eq (10) and (11) and solving we get

$$A + B = E e^{ik_1 a} \left[\cosh(k_2 a) - \frac{ik_1}{k_2} \sinh(k_2 a) \right] \quad (16)$$

$$A - B = E e^{ik_1 a} \left[\cosh(k_2 a) + \frac{ik_2}{k_1} \sin(k_2 a) \right] \quad (17)$$

From eq (16) and (17) we get

$$A = E e^{ik_1 a} \left[\cosh(k_2 a) + \frac{i}{2} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \sinh(k_2 a) \right]$$

$$B = \frac{-i E e^{ik_1 a}}{2} \left[\left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \sin(k_2 a) \right]$$

Transmission coefficient: it is defined as the ratio of the transmitted probability flux to the incident probability flux i.e.

$$T = \frac{v_3 \Psi_t^* \Psi_t}{v_1 \Psi_i^* \Psi_i}$$



Since the velocity in regions *I* and *III* are equal, $v_1 = v_3$

$$\therefore T = \frac{\Psi_t^* \Psi_t}{\Psi_i^* \Psi_i} = \frac{E^* E}{A^* A}$$

$$T = \frac{1}{\cosh^2(k_2 a) + \frac{1}{4} \left[\frac{k_2}{k_1} - \frac{k_1}{k_2} \right]^2 \sinh^2(k_2 a)}$$

$$\text{or } T = \frac{1}{1 + \sinh^2(k_2 a) + \left[\frac{k_2^2 - k_1^2}{2k_1 k_2} \right]^2 \sinh^2(k_2 a)}$$

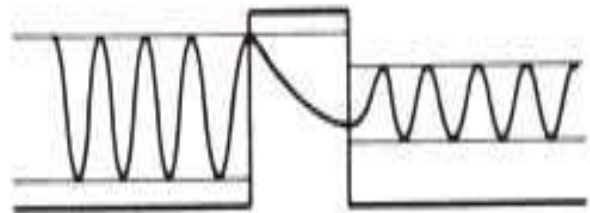
$$\text{or } T = \frac{1}{1 + \left[1 + \left(\frac{k_2^2 - k_1^2}{2k_1 k_2} \right)^2 \right] \sinh^2(k_2 a)} = \frac{1}{1 + \left[\left(\frac{k_1^2 + k_2^2}{2k_1 k_2} \right)^2 \right] \sinh^2(k_2 a)}$$

Substituting the value of k_1 and k_2 we get

$$T = \frac{1}{1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} a}$$

For wide and tall barrier

$$\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} a \gg 1$$



$$T = T_0 e^{-2 \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} a}$$

Where

$$T_0 = \frac{16E(V_0 - E)}{V_0^2}$$

Tunnel effect: The transmission coefficient T is a measure of the probability that the particle will be transmitted through the barrier. As T is not zero, there is some



probability that the particle may penetrate through the barrier and appear in the region *III* even when its energy E is less than V_0

This phenomenon of particle to cross over a barrier when its energy is less than the barrier height is called quantum mechanical tunneling as shown in figure.

The Schrodinger equation in spherical coordinates

The Schrodinger equation in three dimensions has the following form

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - V) \Psi(\mathbf{r}, t) = 0 \quad (1)$$

Where Ψ is function of x , y and z .

The Cartesian and spherical polar coordinates are related as given below

$$x = r \sin \theta \cos \phi \quad (2)$$

$$y = r \sin \theta \sin \phi \quad (3)$$

$$z = r \cos \theta \quad (4)$$

Squaring and adding eq (2), (3) and (4)

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}} \quad (5)$$

From eq (4)

$$\cos \theta = \frac{z}{r} \quad (6)$$

Divide eq (3) by (2)

$$\tan \phi = \frac{y}{x} \quad (7)$$



Differentiating eq (5) w.r.t x

$$\frac{\partial r}{\partial x} = \frac{1}{2} (x^2 + y^2 + z^2)^{-\frac{1}{2}} \times 2x = \frac{x}{r} = \sin \theta \cos \phi$$

Similarly

$$\frac{\partial r}{\partial y} = \sin \theta \sin \phi$$

Schrodinger's wave equation for hydrogen atom

Hydrogen atom consists of an electron and a proton. For convenience we assume proton is at rest and electron is revolving. The potential energy of the system as a function of distance is

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad (1)$$

Where $-e$ is the charge on the electron and $+e$ charge on the proton

Now reduced mass of electron proton system is

$$\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_p} \quad (2)$$

As $m_p \gg m_e$, therefore reduced mass m is nearly equal to the mass of the electron. Therefore, the three dimensional Schrodinger equation for hydrogen atom can be written as

$$\nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V) \Psi(\mathbf{r}, t) \quad (3)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian operator in cartesian coordinates



As V is function of r we use Schrodinger wave equation in spherical co-ordinates (r, θ, ϕ) due to spherical symmetry. ∇^2 in terms of spherical co-ordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Therefore Schrodinger wave equation for hydrogen atom in spherical co-ordinate system can be written as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \Psi \quad (4)$$

Separation of variable

Let us suppose that

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (4)$$

Where $R(r)$ Radial function of r , $\Theta(\theta)$ the polar function of θ and $\Phi(\phi)$ the azimuthal function ϕ

$$\therefore \frac{\partial \Psi}{\partial r} = \Theta\Phi \frac{dR}{dr}, \frac{\partial \Psi}{\partial \theta} = R\Phi \frac{d\Theta}{d\theta}, \frac{\partial \Psi}{\partial \phi} = R\Theta \frac{d\Phi}{d\phi} \text{ and } \frac{\partial^2 \Psi}{\partial \phi^2} = R\Theta \frac{d^2 \Phi}{d\phi^2} \quad (5)$$

Using these equations in Schrodinger wave equation for hydrogen atom

$$\frac{\Theta\Phi}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R\Phi}{r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{R\Theta}{r^2 \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R\Theta\Phi = 0 \quad (6)$$

Divide by $R\Theta\Phi$, we get

$$\frac{1}{Rr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{\Theta r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi r^2 \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = 0$$

Multiplying both sides by $r^2 \sin^2 \theta$ and rearranging, we get



$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2\theta = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} \quad (7)$$

The left hand side of above equation is a function of r and θ and right hand side is a function of ϕ . This equation can be satisfied only if both sides of the equation are equal to some constant say m_l^2

$$\therefore -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = m_l^2 \quad (8)$$

And

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2\theta = m_l^2 \quad (9)$$

Now divide both sides by $\sin^2\theta$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right)$$

Here left hand side is function of r and right hand side is a function of θ . This equation can be satisfied only if both sides of the equation are equal to same constant say $l(l+1)$ called separation constant.

$$\therefore \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = l(l+1) \quad (10)$$

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) = l(l+1) \quad (11)$$

Rearranging these equations we can write

$$\frac{d^2\Phi}{d\phi^2} + m_l^2 \Phi = 0 \quad (12)$$



$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (13)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right) R = 0 \quad (14)$$

Thus Schrodinger equation for H-atom had been splitted up into three equations involving three different variables.

Solution of azimuthal function Φ

The solution of equation (12) can be written as

$$\Phi_{ml}(\phi) = Ae^{\pm im_l \phi} \quad (15)$$

Where A is an arbitrary constant. Here

$$\int_0^{2\pi} \Phi^* \Phi d\phi = 1 \quad \text{or} \quad A^2 \int_0^{2\pi} d\phi = 1 \quad \text{or} \quad A = \frac{1}{\sqrt{2\pi}}$$

Thus from equation (15), we get

$$\Phi_{ml}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im_l \phi} \quad (16)$$

Since Ψ should be single valued hence Φ should also be single valued over the ϕ space. After every 2π rotation, we get the same point. Hence Φ should have the same value after every 2π rotation.

$$\therefore e^{\pm im_l \phi} = e^{\pm im_l (\phi + 2\pi)}$$

This is possible if $m_l = 0, \pm 1, \pm 2, \dots$ here m_l is magnetic quantum number.

Solution of polar function Θ



Polar equation for H-atom is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (17)$$

To solve above equation put

$$z = \cos \theta$$

$$\therefore \frac{dz}{d\theta} = -\sin \theta$$

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{dz} \times \frac{dz}{d\theta} = -\sin \theta \frac{d\Theta}{dz}$$

$$\begin{aligned} \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) &= \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \times -\sin \theta \frac{d\Theta}{dz} \right) = \frac{1}{\sin \theta} \frac{d}{dz} \left[(\cos^2 \theta - 1) \frac{d\Theta}{dz} \right] \frac{dz}{d\theta} \\ &= \frac{1}{\sin \theta} \frac{d}{dz} \left[(1 - \cos^2 \theta) \frac{d\Theta}{dz} \right] \sin \theta = \frac{d}{dz} \left[(1 - z^2) \frac{d\Theta}{dz} \right] \end{aligned}$$

Substitute in equation (17)

$$\frac{d}{dz} \left[(z^2 - 1) \frac{d\Theta}{dz} \right] + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (18)$$

This equation is called as associated Legendre differential equation and can be solved provided that the constant l is an integer equal to or greater than $|m_l|$. This requirement can be expressed as a condition on m_l in the form $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. The constant l is called orbital quantum number and $l = 0, 1, 2, 3, \dots$

The solution of equation (18) is the associated Legendre polynomial of degree l and is given by

$$\Theta_{lm_l}(\theta) = \sqrt{\left[\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!} \right]} P_{lm_l}(\cos \theta) \quad (19)$$



Solution of radial function $R(r)$

Radial equation for H-atom is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right) R = 0 \quad (20)$$

Let us suppose

$$R(r) = \frac{u(r)}{r} \Rightarrow \frac{dR}{dr} = -\frac{1}{r^2} u(r) + \frac{1}{r} \frac{du}{dr}$$

or
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = \frac{1}{r^2} \frac{d}{dr} \left(-u + r \frac{du}{dr} \right) = \frac{1}{r^2} \left(-\frac{du}{dr} + \frac{du}{dr} + r \frac{d^2u}{dr^2} \right) = \frac{1}{r} \frac{d^2u}{dr^2}$$

$$\therefore \frac{1}{r} \frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right) \frac{u}{r} = 0$$

or
$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right) u = 0$$

Put

$$\sigma = \gamma r \Rightarrow \frac{d^2u}{dr^2} = \gamma^2 \frac{d^2u}{d\sigma^2}$$

$$\therefore \frac{d^2u}{d\sigma^2} + \left[\frac{2mE}{\hbar^2\gamma^2} + \frac{2me^2}{4\pi\epsilon_0\hbar^2\gamma} \cdot \frac{1}{\sigma} - \frac{l(l+1)}{\sigma^2} \right] u(\sigma) = 0$$

We choose γ such that

$$\frac{2mE}{\hbar^2\gamma^2} = -\frac{1}{4} \Rightarrow \gamma^2 = -\frac{8mE}{\hbar^2} \text{ and } \lambda = \frac{2me^2}{4\pi\epsilon_0\hbar^2\gamma}$$

$$\therefore \frac{d^2u}{d\sigma^2} + \left[-\frac{1}{4} + \frac{\lambda}{\sigma} - \frac{l(l+1)}{\sigma^2} \right] u(\sigma) \quad (24)$$



let us seek asymptotic solution for equation (24). For $\sigma \rightarrow \infty$, the above equation reduces to

$$\frac{d^2u}{d\sigma^2} - \frac{u}{4} = 0 \quad (25)$$

The acceptable solution of equation (25) is

$$u = e^{-\sigma/2}$$

For $\sigma \rightarrow 0$, the equation (24) reduces to-

$$\frac{d^2u}{d\sigma^2} - \frac{l(l+1)}{\sigma^2}u = 0 \quad (26)$$

The acceptable solution of equation (26) is

$$u = \sigma^{l+1}$$

The possible solution of equation (24) is the product of asymptotic solution and an arbitrary function $F(\sigma)$. So

$$u(\sigma) = A\sigma^{l+1}e^{-\sigma/2}F(\sigma) = G(\sigma) \times F(\sigma) \quad (27) \quad \text{where } G(\sigma) = A\sigma^{l+1}e^{-\sigma/2}$$

$$u'' = G \times F'' + 2G' \times F' + G'' \times F \quad (28)$$

$$\text{Now } G(\sigma) = A\sigma^{l+1}e^{-\sigma/2}$$

$$G' = \left[\frac{l+1}{\sigma} - \frac{1}{2} \right] G(\sigma) \quad (29)$$



$$\begin{aligned} G'' &= \left[-\frac{l+1}{\sigma^2}\right]G(\sigma) + \left[\frac{l+1}{\sigma} - \frac{1}{2}\right]G'(\sigma) = \left[-\frac{l+1}{\sigma^2}\right]G(\sigma) + \left[\frac{l+1}{\sigma} - \frac{1}{2}\right]^2 G(\sigma) \\ &= \left[\frac{l(l+1)}{\sigma^2} - \frac{l+1}{\sigma} + \frac{1}{4}\right]G(\sigma) \quad (30) \end{aligned}$$

Substitute eq(29) and eq(30) in eq(28), we get

$$u'' = G \times F'' + 2 \left[\frac{l+1}{\sigma} - \frac{1}{2}\right]G \times F' + \left[\frac{l(l+1)}{\sigma^2} - \frac{l+1}{\sigma} + \frac{1}{4}\right]G \times F \quad (31)$$

Substitute equation (31) in equation (24) we get

$$\begin{aligned} G \times F'' + 2 \left[\frac{l+1}{\sigma} - \frac{1}{2}\right]G \times F' + \left[\frac{l(l+1)}{\sigma^2} - \frac{l+1}{\sigma} + \frac{1}{4}\right]G \times F + \left[-\frac{1}{4} + \frac{\lambda}{\sigma} - \frac{l(l+1)}{\sigma^2}\right]G \times F \\ = 0 \end{aligned}$$

$$\text{or } F'' + 2 \left[\frac{l+1}{\sigma} - \frac{1}{2}\right]F' + \left[\frac{\lambda - l - 1}{\sigma}\right]F = 0$$

$$\text{or } \sigma F'' + [2l + 2 - \sigma]F' + [\lambda - l - 1]F = 0$$

The solution of this equation will remain finite for all values of σ , if we get

$$\lambda - l - 1 = N$$

Where N is a positive integer.

$$\frac{2me^2}{4\pi\epsilon_0\hbar^2\gamma} = l + N + 1$$

$$\text{or } \gamma = \frac{2me^2}{4\pi\epsilon_0\hbar^2(l + N + 1)}$$

$$\text{or } \frac{8mE}{\hbar^2} = -\frac{4m^2e^4}{16\pi^2\epsilon_0^2\hbar^4(l + N + 1)^2}$$



$$\text{or } E = - \frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2 (l + N + 1)^2}$$

Let $n = l + N + 1$

$$E = - \frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

Where n is principal quantum number



Unit 111

Space quantization

Classically, the angular momentum of a particle is represented by a vector $\vec{L} = \vec{r} \times \vec{p}$, where \vec{r} is the position vector that locates the particle and \vec{p} is its linear momentum. Quantum theory gives a relation between the length of the angular momentum vector and the angular momentum quantum number l

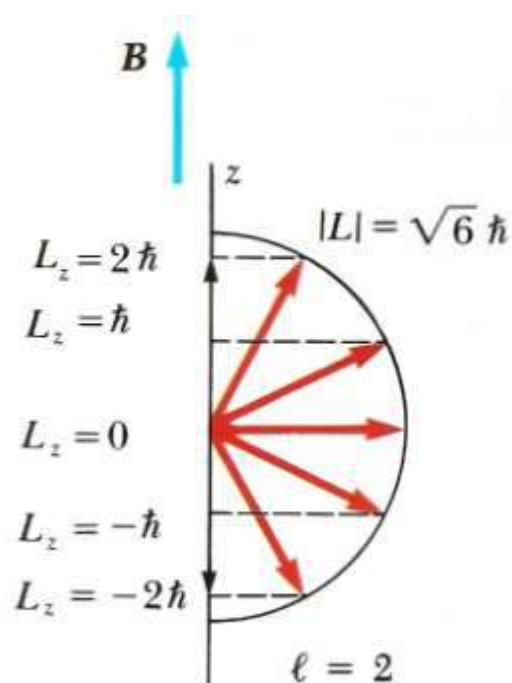
$$L = \sqrt{l(l+1)} \hbar$$

Just as an ordinary classical vector, the vector L has components along any axis in space. The z component of L which we denote by L_z is restricted to the values

$$L_z = m_l \hbar$$

Where m_l is the magnetic quantum number, which takes values $0, \pm 1, \pm 2, \dots, \pm l$

The components of L for $l = 2$ are illustrated in figure. Each orientation in space of the vector L corresponds to a different m_l value. The polar angle θ that the vector L makes with the z axis can be found by referring to the figure. Since $L_z = L \cos \theta$, we have





$$\cos \theta = \frac{L_z}{L} = \frac{m_l}{\sqrt{l(l+1)}}$$

This behavior represents a curious aspect of quantum mechanics called spatial quantization—only certain orientations of angular momentum vectors are allowed.

Electron spin Hypothesis

Goudsmit and Uhlenbeck In 1925 proposed that an electron must be looked upon as a charged sphere spinning about its own axis having a quantized intrinsic angular momentum and an intrinsic magnetic moment. They are called spin angular momentum S spin magnetic moment μ_s respectively.

In 1928, Dirac gave the relativistic quantum theory and confirmed the electron spin. The magnitude of spin angular momentum is given by:

$$S = \sqrt{s(s+1)}\hbar$$

Where $s = 1/2$ is spin quantum number.

$$\therefore S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

Just like the orbital angular momentum \vec{L} , the spin angular momentum \vec{S} is space quantized. The component of \vec{S} along a magnetic field parallel to z direction is

$$S_z = m_s\hbar$$

Where m_s is the spin magnetic quantum number and takes $(2s + 1) = 2$ values which are $+s$ and $-s$, i.e.



$$m_s = +\frac{1}{2} \quad \text{and} \quad m_s = -\frac{1}{2}$$

Thus $S_z = +\frac{1}{2}\hbar \quad \text{and} \quad -\frac{1}{2}\hbar$

Magnetic moment

Electrons in an atom are orbiting around the nucleus. These orbiting electrons are equivalent to current-carrying loop and thus possess orbital magnetic moments.

The electrons have also spin motion. Thus, the magnetic moment associated with spin motion of electrons is called spin magnetic moment.

Orbital magnetic moment:

Let $-e$ is the charge of an electron revolving in a circular orbit of radius r with uniform angular velocity ω , the equivalent current I is given by

$$I = -\frac{e}{T} \quad \text{where } T \text{ is period of revolution} = \frac{2\pi}{\omega}$$

$$\therefore I = -\frac{e}{\frac{2\pi}{\omega}} = -\frac{e\omega}{2\pi} \quad (1)$$

If A be the area enclosed by the current loop, then

$$\vec{A} = \pi r^2 \hat{n} \quad (2)$$

Where \hat{n} is a unit vector perpendicular to loop

Magnetic moment of the atom is given by

$$\mu_l = I \times A = -\frac{e\omega}{2\pi} \times \pi r^2 \hat{n} = \frac{e\omega r^2}{2} \hat{n} \quad (3)$$

Angular momentum of an electron is



$$\vec{L} = mr^2\omega\hat{n}$$

or $r^2\omega\hat{n} = \frac{\vec{L}}{m}$ put in(3)

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L}$$

Here -ve sign shows that the direction of orbital magnetic moment is opposite to the direction of angular momentum.

Generally we can write

$$\mu_l = -g_l \frac{e}{2m}\vec{L}$$

The z component of orbital magnetic moment is

$$\mu_{l,z} = -g_l \frac{e}{2m}L_z = -g_l \frac{e}{2m}m_l\hbar = -g_l m_l \mu_B$$

Where $g_l = 1$ is orbital g factor and m_l is an integer called as magnetic quantum number, which can assume values

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

As the magnitude of orbital angular momentum is

$$L = \sqrt{l(l+1)}\hbar \quad \text{where } l = 0, 1, 2, 3, \dots$$

$$\therefore |\mu_l| = \frac{e}{2m}\sqrt{l(l+1)}\hbar = \mu_B\sqrt{l(l+1)}$$

Here $\frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ Am}^2$ is used as a unit of magnetic moment. It is called Bohr magneton.

Spin magnetic moment



The gyromagnetic ratio for electron spin is $\mu_s/S = e/m$ is twice the corresponding ratio $\mu_L/L = e/2m$ for orbital motion. Thus the spin magnetic moment can be written as

$$\vec{\mu}_s = -\frac{e}{m}\vec{S}$$

The above equation can be written as

$$\vec{\mu}_s = -g_s \frac{e}{2m}\vec{S}$$

Where $g_s = 2$ is called as spin g factor of electron. Here -ve sign shows that the direction of spin magnetic moment is opposite to the direction of spin angular momentum.

The z component of spin magnetic moment is

$$\mu_{s,z} = -g_s \frac{e}{2m} S_z = -g_s \frac{e}{2m} m_s \hbar = -g_s m_s \mu_B$$

As the magnitude of spin angular momentum is given by

$$S = \sqrt{s(s+1)} \hbar = \frac{\sqrt{3}}{2} \hbar \quad \text{where } s = 1/2$$

$$\therefore |\mu_s| = \frac{e}{m} \sqrt{s(s+1)} \hbar = g_s \mu_B \sqrt{s(s+1)} = \sqrt{3} \mu_B$$

Total angular momentum

In general, an electron in an atom has both orbital angular momentum characterized by the quantum number l and spin angular momentum characterized by the quantum numbers. Classically the total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$



For a classical system, the magnitude of the total angular momentum J may have any value between $L + S$ and $|L - S|$

The magnitude of \vec{J} is

$$J = \sqrt{j(j + 1)} \hbar$$

Where the total angular momentum quantum number j can be either

$$j = l + s \text{ Or } j = |l - s|$$

The spin and orbital angular momentum vectors are said to be “parallel” when $j = l + s$ and “anti parallel” when $j = |l - s|$

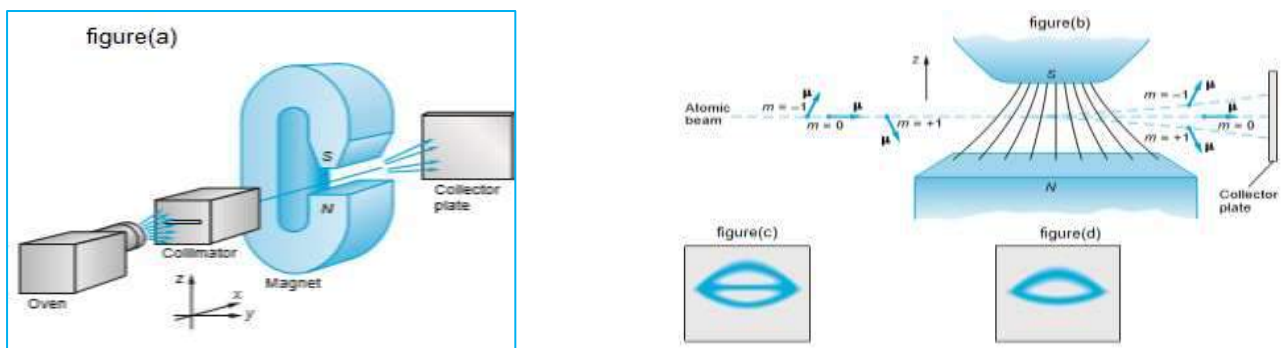
Since both \vec{L} and \vec{S} are space quantized, thus the \vec{J} will also be space quantized. The space quantization of \vec{J} is described by a number m_j called total magnetic quantum number. The z component of \vec{J} is given by

$$J_z = m_j \hbar$$

Here $m_j = -j, -j + 1, \dots, j - 1, +j$

Stern-Gerlach Experiment

Stern and Gerlach in 1921 (before spin) performed an experiment to prove existence of electron spin angular momentum and its possible orientations in space of





the magnetic moments of silver atoms. The experiment was repeated in 1927 (after spin) by Phipps and Taylor using hydrogen atoms.

The experimental setup is shown in Figure (a). Atoms from an oven are collimated and sent through a magnet whose poles are shaped so that the magnetic field B_z increases slightly with z , while B_x and B_y are constant in the x and y directions, respectively. The atoms then strike a collector plate.

Figure (b) illustrates the effect of the $\frac{dB}{dz}$ on several magnetic moments of different orientations. In addition to the torque, which merely causes the magnetic moment to precess about the field direction, there is the force F_z in the positive or negative z direction, depending on whether μ_z is positive or negative, since $\frac{dB}{dz}$ is always positive. This force deflects the magnetic moment up or down by an amount that depends on the magnitudes of both $\frac{dB}{dz}$ and the z component of the magnetic moment μ_z . Classically, one would expect a continuum of possible orientations of the magnetic moments. However, since the magnetic moment is proportional to \mathbf{L} , which is quantized, quantum mechanics predicts that μ_z also can have only the $2l + 1$ values corresponding to the $2l + 1$ possible values of m . We therefore expect $2l + 1$ deflections.

Using neutral silver atoms, Stern and Gerlach expected to see only a single line, the middle line in Figure(c) , because the ground state of silver was known to be a $l = 0$ state; therefore, $m = 0$ and $\mu_z = 0$. The force F_z would then be zero and no deflection of the atomic beam should occur. However, when the experiment was done with either silver or hydrogen atoms, there were two lines as shown in figure (d). Since the ground state of hydrogen also has $l = 0$, we should again expect only one line, were it not for the electron spin. If the electron has spin angular momentum of magnitude $S = \sqrt{s(s + 1)} \hbar$ where $s = 1/2$, the z component can be either $+\hbar/2$



or $-\hbar/2$. Since the orbital angular momentum is zero, the total internal angular momentum of the atom is simply the spin and two lines would be expected. Stern and Gerlach had made the first direct observation of electron spin and space quantization.

Pauli's Exclusion Principle

The Pauli Exclusion Principle for electrons states that

“No more than one electron may occupy a given quantum state specified by a particular set of single-particle quantum numbers n, l, m_l, m_s ”

The effect of the exclusion principle is to exclude certain states in the many electron system. Particles such as α particles, deuterons, photons, and mesons have symmetric wave functions under exchange of particle labels and do not obey the exclusion principle.

Symmetric and Antisymmetric Wave function

The wave functions which do not change sign on exchange of particles are called symmetric wave function.

For symmetric wave function

$$\psi(x_1, x_2) = +\psi(x_2, x_1)$$

$$\text{or } \psi_n(x_1)\psi_m(x_2) = \psi_m(x_1)\psi_n(x_2)$$

The linear combination of these two wave functions gives symmetric wave function.

$$\psi_s = C [\psi_n(x_1)\psi_m(x_2) + \psi_m(x_1)\psi_n(x_2)]$$



The wave functions which do change sign on exchange of particles are called anti symmetric wave function.

For anti symmetric wave function

$$\psi(x_1, x_2) = -\psi(x_2, x_1)$$

$$\text{or } \psi_n(x_1)\psi_m(x_2) = -\psi_m(x_1)\psi_n(x_2)$$

The linear combination of these two wave functions gives anti-symmetric wave function.

$$\psi_A = C [\psi_n(x_1)\psi_m(x_2) - \psi_m(x_1)\psi_n(x_2)]$$

If we interchange x_1 and x_2 , we get a different wave function, implying that the particles can be distinguished.

Coupling schemes

Depending upon nature of interactions among electrons of various atoms, there are two types of coupling schemes to find the resultant angular momenta of an atom containing more than one valance electrons:

L-S Coupling

The LS coupling occurs most frequently and hence it is also called the normal coupling. It is also called Rusell Saunders coupling after the name of two astronomers who first used it in studying atomic spectra of stars. In this coupling

- (i) Due to strong spin-spin interaction the individual spin angular momentum vectors of orbital electrons are strongly coupled with one another to form a resultant spin angular momentum \vec{S} .



i.e. $\vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \dots$

The magnitude of S is $\sqrt{s(s+1)} \hbar$ where s is total spin quantum number. It takes all values between the maximum and minimum value corresponding to s_1, s_2, s_3, \dots with a difference of 1.

- (ii) Due to strong residual electrostatic interaction the individual orbital angular momentum vectors of optical electrons are strongly coupled with one another to form a resultant orbital angular momentum \vec{L}

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_3 + \dots$$

The magnitude of L is $\sqrt{l(l+1)} \hbar$ where l is total orbital quantum number. It takes all values between the maximum and minimum value corresponding to l_1, l_2, \dots with a difference of 1.

- (iii) As a result of spin orbit interaction, the resultant orbital angular momentum vector \vec{L} and resultant spin angular momentum vector \vec{S} combine less strongly to form a total angular momentum vector \vec{J} i.e.

$$\vec{J} = \vec{L} + \vec{S}$$

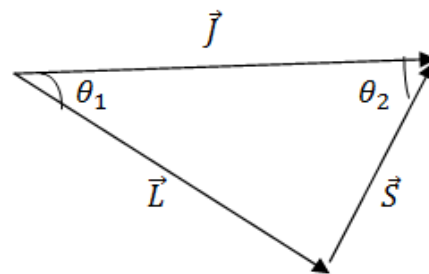
J-J Coupling

In an ideal form, the j-j coupling is an opposite extreme to the ideal LS coupling and is approached by the heavier atoms, for which the spin-orbit (magnetic) interaction term in the Hamiltonian predominates over the residual electrostatic (orbital-orbital) interaction and the spin-spin correlation.

- (i) Due to stronger spin-orbit interaction, the orbital and spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum vector J of magnitude $\sqrt{j(j+1)} \hbar$, where $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$



(ii) Due to residual electrostatic (orbital-orbital) interaction and spin-spin correlation, the resultant angular momentum vector J of the individual electrons are less strongly coupled with one another to form the total angular momentum vector J of the atom, of magnitude $\sqrt{j(j+1)}$ where quantum number j has the values corresponding to different j 's between maximum and minimum with a difference of unity.



The Lande g factor

The total angular momentum of an electron is given by

$$\vec{J} = \vec{L} + \vec{S}$$

In magnitude, $J = \sqrt{j(j+1)}\hbar$

The orbital magnetic moment is given by

$$\vec{\mu}_l = -\frac{g_l \mu_B \vec{L}}{\hbar} = -\frac{\mu_B \vec{L}}{\hbar}$$

or
$$\mu_l = -\frac{\mu_B L}{\hbar}$$

Where $\mu_B =$ Bohr magneton

And $L = \sqrt{l(l+1)}\hbar$

The spin magnetic moment is given by

$$\vec{\mu}_s = -\frac{g_s \mu_B \vec{S}}{\hbar} = -\frac{2\mu_B \vec{S}}{\hbar}$$



or
$$\mu_s = -\frac{2\mu_B S}{\hbar}$$

Where $\mu_B =$ Bohr magneton

And
$$S = \sqrt{s(s+1)}\hbar$$

Now

$$\mu_j = \mu_l \cos \theta_1 + \mu_s \cos \theta_2 = -\frac{\mu_B}{\hbar} (L \cos \theta_1 + 2S \cos \theta_2)$$

Now from figure

$$\cos \theta_1 = \frac{J^2 + L^2 - S^2}{2JL} = \frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{l(l+1)}}$$

Similarly

$$\cos \theta_2 = \frac{J^2 + S^2 - L^2}{2JS} = \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}\sqrt{s(s+1)}}$$

$$\begin{aligned} \therefore \mu_j &= -\frac{\mu_B}{\hbar} \left(L \frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{l(l+1)}} \right. \\ &\quad \left. + 2S \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}\sqrt{s(s+1)}} \right) \\ &= -\mu_B \left(\sqrt{l(l+1)} \frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{l(l+1)}} \right. \\ &\quad \left. + 2\sqrt{s(s+1)} \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}\sqrt{s(s+1)}} \right) \end{aligned}$$



$$= -\mu_B \left(\frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right) \sqrt{j(j+1)} = -\mu_B g \sqrt{j(j+1)}$$

Where

$$g = \frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$
$$= 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \text{ is the Lande } g \text{ factor}$$

Zeeman Effect

It is magneto optical phenomenon discovered by Zeeman in 1896. Zeeman observed that when a source of light producing line spectrum is placed in an external magnetic field, the spectral lines split up into two or more components. The effect is called Zeeman Effect. The Zeeman effect that occurs for spectral lines resulting from a transition between singlet states is traditionally called the normal effect, while that which occurs when the total spin of either the initial or final states, or both, is non zero is called the anomalous effect.

Lorentz Classical theory of normal Zeeman Effect

Lorentz gave simple explanation of normal Zeeman Effect on the basis of classical theory. The assumptions of Lorentz theory are

1. The electron within atom executes simple harmonic motion.
2. An oscillating electron emits a radiation of the same frequency as the frequency of simple harmonic motion.
3. Any linear simple harmonic motion can be regarded as made up of three components: a S.H.M along the field and two circular motions perpendicular to each other as well as to field, one being clockwise and the other anticlockwise.



When magnetic field is applied, the linear motion along the field remains unaffected by the field since the magnetic field does not exert any force on charged particle parallel to the field. Obviously only the circular components of vibration of the electron will be affected by the field.

Expression for Zeeman Effect

Let's consider an electron of mass m and charge e moving in a circular orbit of radius r with uniform angular velocity ω . Then the centripetal force acting on the revolving electron is given by

$$F = mr\omega^2$$

Now, if an external magnetic field of induction B is applied in a direction perpendicular to the plane of the orbit of the electron, an additional force $er\omega B$ starts acting on the electron radially outward or inwards depending whether the motion of electron is clockwise or anticlockwise.

Let $d\omega$ be the change in angular velocity of the electron because of additional force. Then motion in dynamic equilibrium becomes

$$F \pm er\omega B = mr(\omega + d\omega)^2$$

$$mr\omega^2 - mr(\omega + d\omega)^2 = \pm er\omega B$$

$$\text{or} \quad -2m\omega d\omega - m(d\omega)^2 = \pm e\omega B$$

$$\text{or} \quad d\omega = \pm \frac{Be}{2m}$$

$$\text{or} \quad 2\pi dv = \pm \frac{Be}{2m}$$



$$\text{or } dv = \pm \frac{Be}{4\pi m}$$

$$\text{but } dv = -\frac{c}{\lambda^2} d\lambda$$

$$\therefore d\lambda = \pm \frac{Be}{4\pi m} \frac{\lambda^2}{c}$$

The above equation represents the change in wavelength or Zeeman shift of the spectral lines.

In transverse view the three lines of frequency $\nu - dv, \nu$ and $\nu + dv$ are observed, while in longitudinal view the original line of frequency ν is not observed because of unaltered linear component along the field direction due to transverse nature of light waves.

Quantum theory for normal Zeeman Effect

For singlet states, the spin is zero and the total angular momentum J is equal to the orbital angular momentum L . When placed in an external magnetic field, the energy of the atom changes because of the energy of its magnetic moment in the field, which is given by

$$\Delta E = -\vec{\mu}_j \cdot \vec{B} = -\vec{\mu}_l \cdot \vec{B} = -\mu_l B \cos \theta = -\mu_{l,z} B = g_l m_l \mu_B B$$

When magnetic field B is applied, the total energy of electron in atom in its initial higher energy state and final lower state is given by

$$E_i = E_{0i} + \Delta E_i$$

$$E_f = E_{0f} + \Delta E_f$$



Where E_{0i} and E_{0f} is the energy of electron in initial and final energy state, when magnetic field is absent. When an electron jumps from initial higher energy state to final lower energy state, the frequency of emitted spectral line is

$$\nu = \frac{E_i - E_f}{h} = \frac{E_{0i} - E_{0f}}{h} + \frac{\mu_B B}{h} (g_{li} m_{li} - g_{lf} m_{lf})$$

or

$$\nu = \nu_0 + \Delta\nu (g_{li} m_{li} - g_{lf} m_{lf}) \quad \text{where } \Delta\nu = \frac{\mu_B B}{h}$$
$$= \frac{eB}{4\pi m}$$

In normal Zeeman Effect $s = 0 \quad \therefore g_{li} = g_{lf} = 1$

$$\therefore \nu = \nu_0 + \Delta\nu (m_{li} - m_{lf}) = \nu_0 + \Delta\nu \Delta m_l$$

For allowed transition $\Delta m_l = 0$ or ± 1

Thus we get $\nu = \nu_0 + \Delta\nu$ for $\Delta m_l = 1$

$$\nu = \nu_0 - \Delta\nu \quad \text{for } \Delta m_l = -1$$

$$\nu = \nu_0 \quad \text{for } \Delta m_l = 0$$

Thus in normal Zeeman effect, a single spectral line is split into three spectral lines. The middle line occupies the same position as the original line and other two lines displaced equally on both sides of the original line by:

$$\Delta\nu = \frac{eB}{4\pi m}$$

The frequencies of displaced lines are

$$\nu_1 = \nu_0 + \frac{eB}{4\pi m}$$



$$\nu_1 = \nu_0 - \frac{eB}{4\pi m}$$

Change in frequency is given by:

$$d\nu = \pm \frac{eB}{4\pi m}$$

∴ Change in wavelength is given by:

$$d\lambda = \pm \frac{\lambda^2}{c} \frac{eB}{4\pi m}$$

Quantum theory for Anomalous Zeeman Effect

For states other than singlet, the spin is not zero. When placed in an external magnetic field, the energy of the atom changes because of the energy of its magnetic moment in the field, which is given by

$$\Delta E = -\vec{\mu}_j \cdot \vec{B} = -\mu_j B \cos \theta = -\mu_{j,z} B = g_j m_j \mu_B B$$

When magnetic field B is applied, the total energy of electron in atom in its initial higher energy state and final lower state is given by

$$E_i = E_{0i} + \Delta E_i$$

$$E_f = E_{0f} + \Delta E_f$$

Where E_{0i} and E_{0f} is the energy of electron in initial and final energy state, when magnetic field is absent. When an electron jumps from initial higher energy state to final lower energy state, the frequency of emitted spectral line is

$$\nu = \frac{E_i - E_f}{h} = \frac{E_{0i} - E_{0f}}{h} + \frac{\mu_B B}{h} (g_{ji} m_{ji} - g_{jf} m_{jf})$$



or
$$\nu = \nu_0 + \Delta\nu(g_{ji}m_{ji} - g_{jf}m_{jf})$$

where
$$\Delta\nu = \frac{\mu_B B}{h} = \frac{eB}{4\pi m}$$

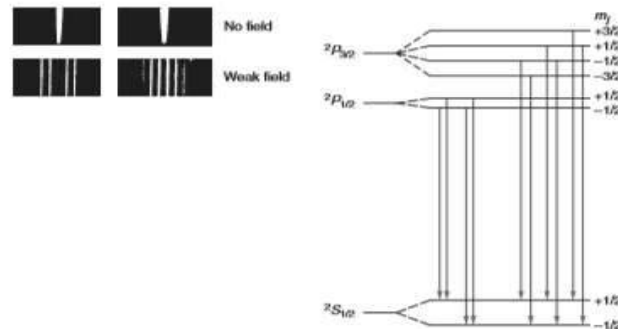
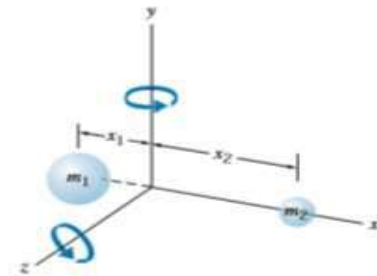


Figure shows the splitting of sodium doublet levels, $2P_{3/2}$, $2P_{1/2}$ and $2S_{1/2}$. The selection rule $\Delta m_j = \pm 1$ or 0 gives four lines for the transition $2P_{1/2} \rightarrow 2S_{1/2}$ (D_1) and six lines for the transition $2P_{3/2} \rightarrow 2S_{1/2}$ (D_2), as indicated.

Rotational energy levels

The lowest energy states which originate due to rotation of the molecule as a whole are rotational energy levels.



Consider the diatomic molecule shown in Figure.

The origin of the coordinate system is at the center of mass of the molecule, so that

$$m_1 x_1 = m_2 x_2 \quad (1)$$

The rotational inertia of the molecule is

$$I = m_1 x_1^2 + m_2 x_2^2 \quad (2)$$

The equilibrium separation



$$R = x_1 + x_2 \quad (3)$$

By using eq. (1) and (3)

$$\therefore x_1 = \frac{m_2 R}{m_1 + m_2}$$

And
$$x_2 = \frac{m_1 R}{m_1 + m_2}$$

Substituting these values in (2), we get

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} R^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} R^2 = \frac{m_1 m_2}{m_1 + m_2} R^2 = \mu R^2$$

where
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$
 is known as reduced mass

Energy of rotating molecule is given by

$$E_{rot} = \frac{1}{2} I \omega^2 = \frac{J^2}{2I} \quad (4)$$

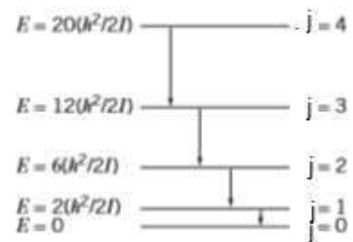
Where J is rotational angular momentum of the molecule about the axis of rotation

According to quantum mechanics

$$J = \sqrt{j(j+1)}\hbar \quad \text{where } j = 0, 1, 2, \dots \text{ is rotational quantum number}$$

$$\therefore E_{rot} = \frac{j(j+1)\hbar^2}{2I} = B j(j+1) \quad (5)$$

Where $B = \frac{\hbar^2}{2I}$ is rotational constant for the molecule.





Rotational spectrum

The emitted or absorbed photons must follow the rotational selection rule $\Delta j = \pm 1$, so the energy of an emitted photon is the energy difference between two adjacent levels:

$$\Delta E_{rot} = E_{j+1} - E_j = B[(j+1)(j+2) - j(j+1)] = 2B(j+1)$$

\therefore Frequency of emitted radiation is

$$\nu_{rot} = \frac{2B}{h}(j+1) \quad j = 0, 1, 2, \dots$$

The emitted photons have energies $2B, 4B, 6B, \dots$

The cause of rotational spectrum is transitions between rotational energy states. Only molecules which have electric dipole moments can absorb or emit electromagnetic radiations in such transitions. The emission of radiation is due to the rotation of electric dipole moment. Rotational spectrum corresponds to the far infrared and microwave region.

Vibrational energy levels

The energy states which originate due to vibration of the molecule are vibrational energy levels. A non rigid diatomic molecule has rotational as well as vibrational motion. The molecular vibrations are due to change in bond length or bond angle in a molecule. The vibrating diatomic molecule can be considered as linear harmonic oscillator. For the classical oscillator, there are no restrictions on the total energy or the oscillator frequency-any value of energy is allowed, and the frequency and energy can be varied independently.



The quantum oscillator behaves very differently. Only certain values of the energy are allowed. The allowed energy values, for one dimensional oscillator are

$$E_v = \left(v + \frac{1}{2} \right) h\nu_0 \quad v = 0, 1, 2, \dots$$

Where v is vibrational quantum number.

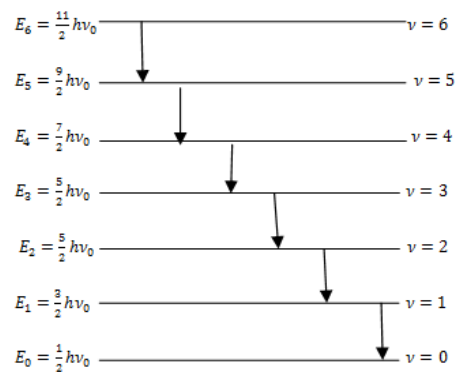
$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}, \text{ is natural vibrational frequency of oscillator.}$$

When $v = 0, E_0 = \frac{1}{2} h\nu_0$ is known as zero point energy.

Vibrational spectra

The oscillator can emit electromagnetic radiation in jumps to lower states, or it can absorb radiation in jumps to higher states. However, the jumps cannot occur in arbitrary steps. The allowed transitions are those that change v by one unit. This restriction is called a selection rule and applies only to transitions that occur through the emission or absorption of electromagnetic radiation.

Vibrational selection rule: $\Delta v = \pm 1$



Thus the energy of vibrational transition from lower level to upper level is given by

$$\Delta E_{vib} = E_{v+1} - E_v = h\nu_0$$



Hence pure vibrational spectra will consist of one line. The homonuclear molecules like H_2, N_2, O_2 do not show a vibrational spectrum, because they do not possess a permanent electric dipole moment.



Unit IV

X-Rays:

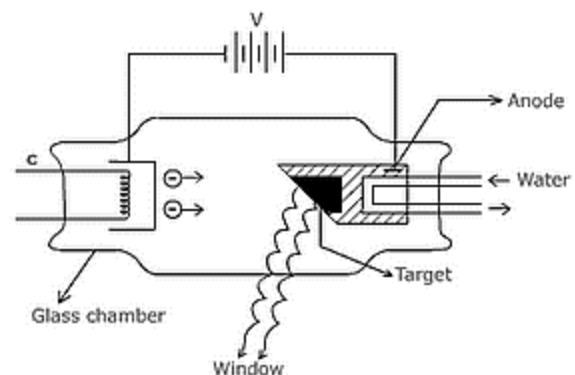
X-rays are a type of radiation called electromagnetic waves of wavelength of the order of 1\AA . X-rays are produced when fast moving beam of electrons is suddenly stopped by a target of high atomic weight.

W.C. Roentgen accidentally discovered X-rays in 1895. He found that photographic film wrapped light tight in black paper become fogged when placed near a cathode ray tube. He naturally concluded that fogging of photographic film was caused by some invisible but penetrating radiation coming out of the discharge tube. He named these radiations as X-rays because nature and properties of the radiations was unknown at that time.

The most familiar use of x-rays is checking for broken bones, but x-rays are also used in other ways. For example, chest x-rays can spot pneumonia. Mammograms use x-rays to look for breast cancer.

Production of X-rays:

A device used to produce X-rays is generally called an X-ray tube. This was originally designed by Dr. William Coolidge in 1913 and hence also known as Coolidge tube. Figure shows schematic diagram of such a device.



A filament and a metallic target are fixed in an evacuated glass chamber C. The filament is heated electrically and emits electrons by thermionic emission. A constant potential



difference of about 50kV is maintained between the filament and target. Target is kept at higher potential than the filament. The electrons emitted by the filament are, therefore, accelerated by the electric field set up between the filament and target and hit the target at high speed. These electrons are stopped by the target of high atomic weight and in the process X-rays are emitted. These X-rays are brought out of the tube through a window made of thin mica or Mylar.

In the process large amount of heat is developed, and thus an arrangement is provided to cool down the tube continuously by running water.

Control of intensity (quantity) of X- Rays:

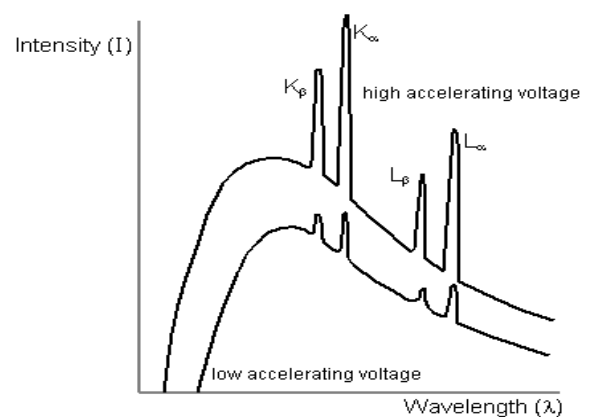
The intensity of X- rays emitted is directly proportional to the number of electrons strikes per second to the target. This, in turn, depends upon the filament temperature, which can be controlled by filament current.

Control of quality of X- Rays:

The quality of X-rays depends upon the energy of the electrons bombarding the target. This energy is determined by the potential difference between the filament (cathode) and the target. Higher is the applied voltage between filament (cathode) and target, higher is the energy of bombarding electrons and hence X-rays with high frequency are emitted.

X-Ray spectra:

When a beam of X-rays emitted by a target of an X-ray tube is examined by Bragg's X-





ray spectrometer, two distinct types of spectra are seen as shown in fig.

1. **A continuous spectrum** is the bremsstrahlung (braking) X-rays. Continuous spectrum consists of radiations of all possible wavelengths within a certain range. It is because generally an electron suffers all sorts of collision, right from the glancing collision to the direct hit; they suffer varying retardation and consequently radiation of all possible wavelengths within a certain range are emitted, thus accounting for the continuous spectrum of X-rays. However minimum wavelength ($\lambda_{min} = \frac{hc}{eV}$) of X-rays correspond to the condition when the bombarding electron loses all its kinetic energy in one impact.
2. **Characteristic or sharp X-ray** consists of definite wavelengths superimposed on the continuous spectrum. The spectrum lines are characteristic of the material used as a target. The lines generally occur in the form of small groups. The group in the short wavelength region is termed K- series, the next group in the direction of increasing wavelength as L-series, then M-series and so on. It is because the bombarding electrons may knock out the electrons from the inner shells of atoms of target, thus emitting characteristic X-rays.

Moseley's law:

The first systematic study of the characteristic X-ray spectrum of different elements was carried out by Moseley in 1913. On the basis of his observations, Moseley stated that: *the frequency of any line in the characteristic X-ray spectrum varies directly as the square of the atomic number of the element emitting it. This is known as Moseley's law.*

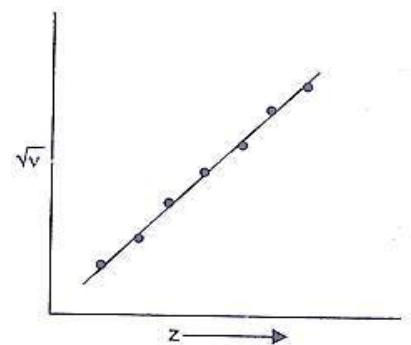


FIGURE Moseley plot

Moseley's observations can be mathematically expressed as



$$\nu \propto (Z - b)^2$$

or $\sqrt{\nu} = a(Z - b)$

Where, Z is the atomic number of the element and a and b are constants for given series. However, the values of a and b are different for different series.

Significance of Moseley's law:

Although Moseley's law was an empirical law, yet it has great significance due to the following reasons:

- (a) **It removed discrepancies in periodic table:** - Moseley established that it is the atomic number and not atomic weight that determines the physical and chemical properties of element. Therefore he suggested that we should place the elements in the periodic table in the order of their atomic numbers. E.g. cobalt ($Z=27$) should come before nickel ($Z=28$) in the periodic table though their atomic weights are 58.94 and 58.69 respectively.
- (b) **It helped in the discovery of new elements:** - when elements were placed in the order of their atomic numbers in the periodic table, several places were found vacant. This led to the discovery of new elements.
- (c) **It gives proof for the validity of Bohr's theory:** - Moseley gave another proof for the validity of Bohr's theory. According to Bohr's theory, when an electron jumps from higher orbit (n_i) to the lower orbit (n_f), the frequency of emitted radiation is

$$\nu = \frac{me^4}{8\epsilon_0^2 h^3} Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \left[\frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right] Z^2$$

$\therefore \nu \propto Z^2$



Bohr did not take into account the screening effect of electrons in various shells. However Moseley, incorporated the screening effect of electrons and therefore above equation is modified as $\nu \propto (Z - b)^2$.

Composition of nucleus:

To explore the composition of nucleus several hypothesis have been put forward. Prominent among them are

1. Electron-proton hypothesis
2. Proton-neutron hypothesis

Proton electron hypothesis:

This was put forward in 1930. According to this hypothesis, a nucleus of an atom of mass number A and atomic number Z is made up of A protons and $(A - Z)$ electrons, thus giving it a net charge $+Ze$. The nucleus was supposed to be surrounded by Z extra-nuclear electrons, thereby making the atom on the whole neutral. However, this hypothesis was rejected later on in view of following drawbacks:

- (a) According to uncertainty principle, electron confined in the nucleus must have kinetic energy of the order of 100 MeV. But electrons emitted during beta decay are found to have energy only of the order of 4 MeV. This shows electrons cannot be present in the nucleus.
- (b) If electrons are to be present in the nucleus, the magnetic moment of nucleus cannot be less than the magnetic moment of electron. But magnetic moments of nuclei are only $(1/1000)$ th of this. This shows electrons cannot be present in the nucleus.



(c) Both protons and electrons have a spin of $\frac{1}{2}$. Thus nuclei with even number of protons and electrons must have zero or integral spin, while those with odd number should have half integral spin. But this fact does not agree with experimental results.

Proton-neutron hypothesis: -

This hypothesis was put forward by Heisenberg after the discovery of neutron by Chadwick.

According to this hypothesis, a nucleus of mass number A and atomic number Z contains Z protons and $(A - Z)$ neutrons. As atom is neutral, therefore number of peripheral electrons must be equal to Z .

This hypothesis explained all the discrepancies of proton-electron hypothesis.

Size and shape of nucleus: -

A nucleus is believed to be nearly spherical. Experimental measurements show that volume of nucleus is proportional to its mass number A .

$$\therefore \frac{4}{3}\pi R^3 = A$$

Where R is radius of the nucleus. Hence

$$R \propto A^{1/3}$$

$$\text{or } R = R_0 A^{1/3}$$

Where $R_0 = 1.2 \text{ fm} = 1.2 \times 10^{-15} \text{ m}$, is an empirical constant.

Isotopes:

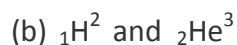
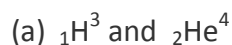


The atoms of element which have same atomic number but different mass number are called isotopes of that element. Because of the same atomic number, the isotopes of an element have same place in the periodic table. Though isotopes have the same chemical properties but their nuclear and physical properties are highly dissimilar. Almost every element has isotopes. Isotopes of some elements are the following:



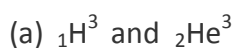
Isotones:

Atoms whose nuclei have same number of neutrons are called Isotones. Examples of isotones are as under:



Isobars:

Isobars are the atoms of different elements having same mass number but different atomic number. The chemical properties of isobars are different. Some of the examples of isobars are:





(c) ${}_8\text{O}^{17}$ and ${}_9\text{F}^{17}$

Nuclear forces:

The strong forces of attraction which firmly hold the nucleons in the nucleus are known as nuclear forces. Nuclear forces are highly complex in nature and are quite different from ordinary forces (e.g. gravitational, electrostatic force etc.) found in nature. Very little is known about the nature of these forces as yet. However, it is undoubtedly established that these forces exist between the nucleons. The stability of the nucleus is accounted for due to the presence of these forces.

Properties of nuclear forces:

On the basis of extensive experiments, the nuclear forces were found to have the following properties:

1. **Nuclear forces are short range** i.e. they act over a short range of distances. These forces vanish for all practical purposes at distances greater than about $4.2 \times 10^{-15}m$.
2. **Nuclear forces are charge independent** i.e. these forces are of same strength between a proton and neutron or between proton and proton or between neutron and neutron.
3. **Nuclear forces are spin dependent.** It has been observed that the nuclear force between nucleons having parallel spin is strong than the nuclear force between the nucleons having anti-parallel spin.
4. **Nuclear forces have saturation property** i.e. each nucleon interacts with limited number of nucleons nearest to it.
5. **Nuclear forces are non-central.** The force between the nucleons has non-central component that does not point along the line joining the two nucleons. The non-central



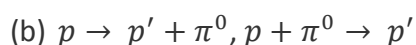
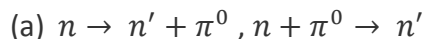
component depends upon how the nuclear spins are oriented relative to the line joining the nucleons.

6. **Nuclear forces are strongest forces known in nature.** The magnitude of nuclear forces is about 100 times stronger than electrostatic repulsive force between the protons and about 10^{38} times stronger than the gravitational force between the nucleons.

Meson (Yukawa's) theory of nuclear forces:

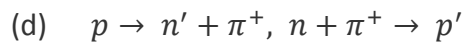
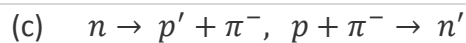
In 1935, a Japanese physicist, H. Yukawa, suggested that nuclear forces arise from the continuous exchange of particles, called mesons, back and forth between neighbouring nucleons. According to meson theory of nuclear forces,

1. All nucleons consist of identical cores surrounded by a pulsating cloud of π mesons.
2. Mesons may be neutral (π^0) or may carry either charge (π^+ or π^-).
3. The sole difference between neutron and proton is supposed to lie in the composition of their respective meson clouds.
4. The forces between a pair of neutrons or a pair of protons are the result of the exchange of neutral meson (π^0). The interactions are represented as follows



In both the cases, a proton or a neutron is converted into a new state after emitting or absorbing the π^0 meson.

5. The forces between neutrons and protons are due to exchange of charged meson between them. The reactions are represented as follow



Mass defect:

A survey of nuclear masses shows that stable nuclei invariably have smaller rest mass than the sum of masses of their constituent nucleons in the Free State. The difference between the actual mass of the nucleus and the sum of the masses of the nucleons is called mass defect.

Consider a nucleus having atomic number Z and mass number A . It consists of Z protons and $(A - Z)$ neutrons. If m_p be the mass of proton, m_n be the mass of neutron and m_N be the mass of nucleus. Then,

$$\text{mass defect}(\Delta m) = Zm_p + (A - Z)m_n - m_N \quad (1)$$

Binding energy:

Inside the nucleus, nucleons are bound together with nuclear forces. A definite amount of work has to be done to decompose a nucleus into its constituent nucleons. This work done is a measure of binding energy. Thus binding energy is the energy required to decompose a nucleus into its constituent nucleons.

Or

Inside the nucleus, nucleons are bound together with nuclear forces. By virtue of mutual interaction among nucleons, they give up their surplus energy lying with them so that a stable nucleus is formed. This energy is called binding energy of the nucleus. Thus binding energy is the energy which nucleons release in order to form a stable nucleus.

Or



Binding energy may also be defined as the energy equivalent of the mass defect of the nucleus.

Expression for binding energy:

Consider a nucleus having atomic number Z and mass number A . It consists of Z protons and $(A - Z)$ neutrons. If m_p be the mass of proton, m_n be the mass of neutron and m_N be the mass of nucleus. Then,

$$\text{mass defect}(\Delta m) = Zm_p + (A - Z)m_n - m_N \quad (1)$$

Using Einstein's mass energy equivalence,

$$\text{Binding energy} = \Delta m \times c^2$$

$$B.E = (Zm_p + (A - Z)m_n - m_N) \times c^2 \quad (2)$$

Where c is velocity of light.

If m is the mass of atom containing Z electrons each of mass m_e , then

$$m = m_N + Zm_e - \frac{B.E \text{ of } Z \text{ electrons}}{c^2} \quad (3)$$

For Hydrogen atom of mass m_H , we can write

$$m_H = m_p + m_e - \frac{B.E \text{ of one electrons}}{c^2} \quad (4)$$

Now, the binding energy of electron is much smaller as compared to the rest mass energy of a nucleon. Therefore eq. (3) and eq. (4), reduces to

$$m = m_N + Zm_e \quad (5)$$



$$m_H = m_p + m_e \tag{6}$$

Rewriting eq. (2), as

$$B.E = [Z (m_p + m_e) + (A - Z)m_n - m_N - Zm_e] \times c^2$$

or $B.E = [Z (m_p + m_e) + (A - Z)m_n - (m_N + Zm_e)] \times c^2$

Using eq. (5) and eq. (6), we get

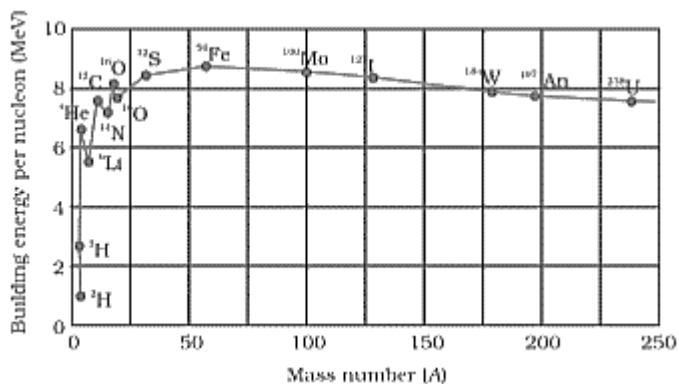
$$B.E = [Z m_H + (A - Z)m_n - m] \times c^2$$

This is required expression for binding energy.

Average binding energy per nucleon:

Average binding energy per nucleon is the average energy required to remove a nucleon from the nucleus. It is given by total binding energy divided by the mass number of the nucleus.

The variation of binding energy per nucleon with mass number A is shown in fig.



The curve reveals the following facts:



1. Average B.E/ nucleon for light nuclei like ${}^1_1\text{H}^1$, ${}^1_1\text{H}^2$, ${}^1_1\text{H}^3$ is small.
2. For mass numbers ranging from 2 to 20, there exists cyclic recurrences of peaks corresponding to ${}^2_2\text{He}^4$, ${}^4_2\text{Be}^8$, ${}^6_6\text{C}^{12}$, ${}^8_8\text{O}^{16}$ etc. The peaks indicate that these nuclei are relatively stable than the other nuclei in their neighbourhood.
3. The binding energy per nucleon has broad maximum in the range $A=30$ to $A=120$ corresponding to average binding energy per nucleon ≈ 8.5 MeV. The curve has a maximum of about 8.75 MeV per nucleon for $A = 56$.
4. As the mass number increases, the binding energy per nucleon decreases gradually and falls to about 7.6 MeV per nucleon for ${}^{92}_{92}\text{U}^{238}$. The decrease may be due to Coulomb repulsion between the protons. The heavy nucleus is therefore, relatively less stable.

Importance of binding energy curve:

We can draw some conclusions from these observations:

A very heavy nucleus, say $A = 240$, has lower binding energy per nucleon compared to that of a nucleus with $A = 120$. Thus if a nucleus $A = 240$ breaks into two $A = 120$ nuclei, nucleons get more tightly bound. This implies energy would be released in the process. It has very important implications for energy production through fission.

Consider two very light nuclei ($A \leq 10$) joining to form a heavier nucleus. The binding energy per nucleon of the fused heavier nuclei is more than the binding energy per nucleon of the lighter nuclei. This means that the final system is more tightly bound than the initial system. Again energy would be released in such a process of fusion. This is the energy source of sun

Radioactivity:



Radioactivity is spontaneous and self-disruptive activity exhibited by number of heavy elements occurring in nature. The elements which show this property (spontaneous and self-disruptive) are called radioactive substances.

A. H. Becquerel discovered radioactivity in 1896 purely by accident. While studying the fluorescence and phosphorescence of compounds irradiated with visible light, Becquerel observed an interesting phenomenon. After illuminating some pieces of uranium-potassium sulphate with visible light, he wrapped them in black paper and separated the package from a photographic plate by a piece of silver. When, after several hours of exposure, the photographic plate was developed, it showed blackening due to something that must have been emitted by the compound and was able to penetrate both black paper and the silver. He was thus led to the conclusion that Uranium and its salt emits some invisible radiation which can pass through paper, wood, glass etc. and effect photographic plate as well. These radiations were called Becquerel rays. Madam Curie was able to discover an element 400 times more active than uranium which was named as Polonium. In 1898, Piere Curie and Madam Curie discovered a new element called Radium which was found to be 10^6 times more active than Uranium. Further experimental study reveals that there are about 40 elements which emit these radiations.

Further studies of this newly discovered phenomenon revealed that the emission of these mysterious radiation was spontaneous and was quite unaffected by any change of physical or chemical condition. These experimental facts led to the conclusion that this phenomenon was deeply rooted in the interior of the atom i.e. nucleus.

Properties of α -rays:

1. **IDENTITY:** α - rays have been identified as beam of helium nucleus.
2. **CHARGE:** α – rays carry two units of positive charge.



3. **MASS:** Mass of each α - particle is 4 times that of a proton or H-atom.
4. **VELOCITY:** Their velocity range is 3×10^7 m/s to 3×10^6 m/s.
5. **IONIZATION:** Because of large mass and velocity, Ionization power of α - rays is very high.
6. **PENETRATION POWER:** Penetration power of α - rays is very small.
7. **FLUORESCENCE:** α - rays produce fluorescence on different substances.
8. **DEFLECTION:** α - rays can be deflected by both electric and magnetic field.
9. **EFFECT ON HUMAN BODY:** α - rays produce burns on human body.

Properties of β -rays:

1. **IDENTITY:** β - rays have been identified as beam of electrons.
2. **CHARGE:** β -rays carry one unit of negative charge.
3. **REST MASS:** Rest mass of each β - particle is 9.1×10^{-31} kg.
4. **VELOCITY:** Their velocity range is from 9×10^7 m/sec to 27×10^7 m/sec.
5. **IONIZATION:** Ionization power of β –rays is small.
6. **PENETRATION POWER:** Penetration power of β –rays is higher than α -rays. They can pass through matter up to depth of 10 mm.
7. **FLUORESCENCE:** β - rays produce fluorescence in different substances.
8. **DEFLECTION:** β - rays can be deflected by both electric and magnetic field.

Properties of: γ -rays:



1. **IDENTITY:** γ - rays have been identified as electromagnetic radiation of short wavelength.
2. **CHARGE:** : γ -rays carry no charge.
3. **REST MASS:** Rest mass of γ - particle is zero.
4. **VELOCITY:** They travel with the velocity of light (i.e. 3×10^8 m/sec.)
5. **IONIZATION:** Ionization power of γ - rays is very small.
6. **PENETRATION POWER:** Penetration power of γ -rays is higher than β -rays. They can pass through several cm of lead.
7. **FLUORESCENCE:** γ - rays can produce less fluorescence than α and β - ray.
8. **DEFLECTION:** γ - rays cannot be deflected by both electric and magnetic field.

Laws of radioactive disintegration:

Soddy and Rutherford from their experimental study put forward following laws regarding radioactive decay:

1. The radioactive decay is spontaneous with the emission of α , β and γ - rays. It is not influenced by external conditions such as temperature, pressure, electric and magnetic fields etc.
2. During decay of an atom, either an α - particle or β -particle is emitted. Both of these particles are never emitted simultaneously. Also at a time, an atom will not emit more than one α - particle or more than one β -particle.
3. The emission of α - particle from an atom will change it, into a new atom whose charge number is reduced by two and mass number reduced by four.



4. The emission of β - particle from an atom will change it, into a new atom whose charge number is raised by one and without any change into mass number.
5. The number of atoms disintegrated per second at any instant is directly proportional to the number of radioactive active atoms actually present in the sample at that instant.

Decay law:

This law states that “the rate of disintegration of radioactive atoms at any instant is directly proportional to the number of radioactive atoms actually present in the sample at that instant.

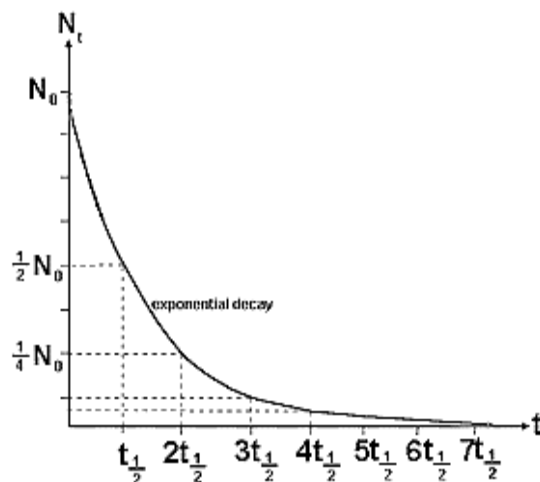
Suppose at the beginning of disintegration (i.e. at $t = 0$) the number of radioactive atoms present is N_0 . Suppose after time t the number of atoms left is N . Let’s now suppose that dN atoms now disintegrate in small time dt . Then according to decay law

$$\frac{dN}{dt} \propto N$$

or
$$\frac{dN}{dt} = -\lambda N \quad (1)$$

or
$$\frac{dN}{N} = -\lambda dt \quad (2)$$

Where λ is constant of proportionality and is called decay constant or disintegration constant. The minus sign indicates that N is decreasing with respect to time.





Integrating eq. (2) from $N = N_0$ to $N = N$ corresponding to $t = 0$ to $t = t$

$$\int_{N_0}^N \frac{dN}{N} = -\lambda \int_0^t dt$$

$$(\log_e N)_{N_0}^N = -\lambda (t)_0^t$$

$$\text{or } \log_e N - \log_e N_0 = -\lambda (t - 0)$$

$$\text{or } \log_e \frac{N}{N_0} = -\lambda t$$

$$\text{or } \frac{N}{N_0} = e^{-\lambda t}$$

$$\therefore N = N_0 e^{-\lambda t} \quad (3)$$

This equation is known as decay equation. Hence number of radioactive atoms of a given radioactive sample decreases exponentially with time.

Half-life period:

Half-life period of radioactive element is defined as the time taken by half the number of atoms of the radioactive element to disintegrate themselves completely.

Let $t_{1/2}$ represent the half-life of a radioactive substance. If N represents the number of atoms left after time $t_{1/2}$. We have $N = \frac{N_0}{2}$,

Substituting in decay equation, we have

$$\frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}}$$



$$\text{or } \frac{1}{2} = e^{-\lambda t_{1/2}}$$

$$\text{or } \lambda t_{1/2} = \log_e 2$$

$$\text{or } t_{1/2} = \frac{\log_e 2}{\lambda}$$

$$\text{or } t_{1/2} = \frac{0.693}{\lambda}$$

This shows that the half-life is inversely proportional to decay constant.

Derive $\frac{N}{N_0} = \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$

According to decay equation

$$\frac{N}{N_0} = e^{-\lambda t}$$

$$\text{or } \frac{N}{N_0} = e^{-\lambda t_{1/2} \times \frac{t}{t_{1/2}}} \quad (1)$$

Now when $t = t_{1/2}$, $N = \frac{N_0}{2}$ $\therefore \frac{1}{2} = e^{-\lambda t_{1/2}}$ substituting in eq. (1), we have

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

Average life or mean life:

Average or mean life of radioactive element is defined as the average time for which an atom of radioactive element exists.



Suppose at the beginning of disintegration (i.e. at $t = 0$) the number of radioactive atoms present is N_0 . Suppose after time t the number of atoms left is N . Let's now suppose that dN atoms further disintegrate between time t to $t + dt$.

Total life of dN atoms = number of atoms \times life of each of dN atoms = $dN \times t$

$$\therefore \text{Total life of all atoms} = \int_0^{N_0} t \, dN$$

$$\therefore \text{Average life } T_{av} = \frac{1}{N_0} \int_0^{N_0} t \, dN \quad (1)$$

According to decay equation

$$N = N_0 e^{-\lambda t}$$

$$\therefore dN = -\lambda N_0 e^{-\lambda t} dt \quad (2)$$

Substitute eq. (2) in eq. (1), we get

$$T_{av} = -\frac{1}{N_0} \int_0^{N_0} t \times \lambda N_0 e^{-\lambda t} dt = \lambda \int_0^{\infty} t e^{-\lambda t} dt$$

$$= \lambda \left[\left[\frac{t e^{-\lambda t}}{-\lambda} \right]_0^{\infty} - \int_0^{\infty} 1 \frac{e^{-\lambda t}}{-\lambda} dt \right]$$

$$= \lambda \left[(0 - 0) - \left[\frac{e^{-\lambda t}}{\lambda^2} \right]_0^{\infty} \right] = \frac{1}{\lambda}$$

$$\therefore T_{av} = \frac{1}{\lambda}$$



This shows that average life of radioactive atom is equal to reciprocal of decay constant.

$$\text{since } t_{1/2} = \frac{0.693}{\lambda} \therefore t_{1/2} = 0.693 T_{av}$$

Units of radioactivity:

Activity of a radioactive substance can be expressed in the following units

1. **Curie:** if a radioactive substance disintegrates at a rate of 3.7×10^7 disintegrations per second, its activity is said to be one Curie. i.e.

$$1Ci = 3.7 \times 10^7 \text{ decay per second}$$

2. **Rutherford:** if a radioactive substance disintegrates at a rate of 10^6 disintegrations per second, its activity is said to be one Rutherford. i.e.

$$1Rd = 10^6 \text{ decay per second}$$

3. **Becquerel:** if a radioactive substance disintegrates at a rate of 1 disintegration per second, its activity is said to be one Becquerel. i.e.

$$1Bq = 1 \text{ decay per second}$$

It is S.I unit of activity.