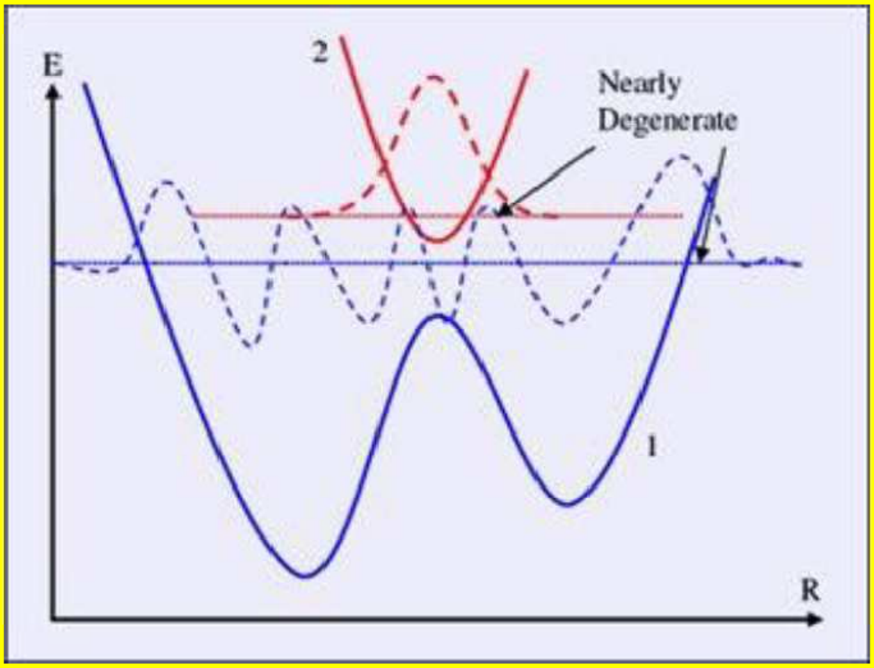
MSCPH503

M. Sc. Ist Semester

QUANTUM MACHANICS



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QUANTUM MECHANICS

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UNIT -1 : ORIGIN OF QUANTUM MECHANICS

Structure

1.1 INTRODUCTION

This unit entitled “Origin of quantum mechanics” includes mainly limitations of classical theories and origin of quantum mechanics.Planck’spostulate and description of experiments that are at the origin of quantum mechanics,namely the study of blackbody radiation, the photoelectric effect andthe Compton effect. Then Classical theories of heat capacity of solids, Einstein theory of heat capacity of solids, Debye theory heat capacity of solids, Bohr’s theory of H atom and Wilson-Sommerfeld quantization rule discussed.

1.2 LEARNING OBJECTIVES

After going through this unit, you will be able to:

- Understand the need and limitations of quantum mechanics.
- Understand black body radiation, Rayleigh Jean’s law andWien’s distribution law
- Understand Planks hypothesis
- Explain the photoelectric effect and the Compton effect
- Differentiate between Einstein theories to Debye theory of heat capacity of solids.
- Understand Bohr’s theory of H atom.
- KnowWilson-Sommerfeld quantisation rule.

1.3 INADEQUACIES OF CLASSICAL MECHANICS

Classical mechanics or Newtonian mechanics is a very elegant and successful theory that describes the dynamics of the all kind of macroscopic systems , such as cluster stars, planets, moon, tennis ball and dust particles as well as microscopic systems such as motion of a bacteria, virus. It describe the motion of a particle in non-relativistic limit. i.e. $v<<c$.The foundation of Newtonian mechanics is based on concept ofabsolute Space,Absolute Time andAbsolute mass.till the end of the nineteenth century, it was assumed that all physical events can be explained under the three branches of physics named classical mechanics, the theory of electromagnetism, and thermodynamics. Classical mechanics was used to study 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 remarkable success of classical physics— classical mechanics, classical theory of electromagnetism, and thermodynamics—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. In the early years of the twentieth century, in 1905 when Einstein proposed theory of relativity and showed that the validity of Newtonian mechanics ceases at very high speeds (i.e., at speeds comparable to that of light) and due the development of advancedexperimental techniques to study 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 that *new*

concepts had to be needed to describe, for instance, the structure ofatoms and molecules and how light interacts with them.

Due to certain limitation of classical mechanics and it's wrong assumption this theory could not explain following physical phenomena.

1. It fails to explain the spectrum of black body radiation.

2. It fails to explain the stability of atoms.

3. It fails explain discrete atomic spectrum:

4. It fails not explain photoelectric effect:

5. It fails to explain the phenomena of pair production .
6. It fails to explain the phenomena of Compton scattering.

7. It fails to explain variation of electric conductivity of solid (super conductivity).

8. Classical mechanics could not explain the phenomena associated with spinning motion of electron. 9. Classical mechanics could not explain Zeeman effect, Stark effect, Raman effect.

10. It could not explain phenomena of radioactivity likeβ-decay and α- decay .

To solve above physically observable problem Scientists purposed, a new field of physics based on uncertainity principle and wave-matter duality of particles. This new field of physics is known as quantum mechanics. The early development of atomic theory consisted of efforts to overcome these difficulties by modifying the laws of Classical Physics. These efforts reached their successful conclusion in the period from 1925 to 1930, when an entirely new theoretical discipline, Quantum Mechanics was developed by Schrödinger, Heisenberg, Dirac and others. Quantum Mechanics can be regarded as the fundamental theory of atomic phenomena. The experimental data on which it is based are derived from physical events that lie almost entirely beyond the range of human perception. It is not surprising, that the theory embodies physical concepts that are foreign to common daily experience.

1.4 BLACKBODY RADIATION

In 1860, Gustav Kirchhoff introduced the concept of a “black body”, an object that absorbs all electromagnetic radiation that falls upon it. Since no light is reflected or transmitted, the object appears black when it is cold. However, above absolute zero, a black body emits thermal radiation with a spectrum that depends on temperature.

The energy of blackbody radiation is not shared evenly by all wavelengths of light. The spectrum of blackbody radiation (below) shows that some wavelengths get more energy than others. Three spectra are shown, for three different temperatures.

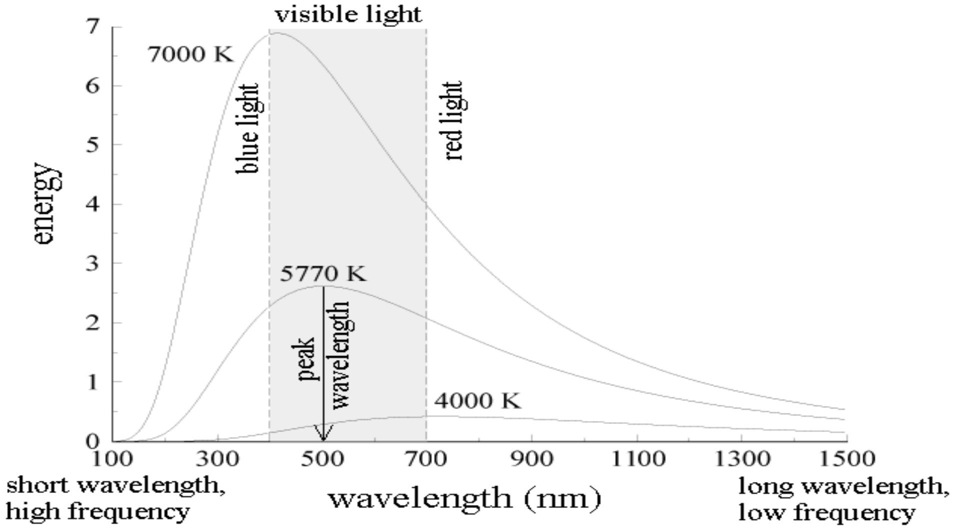


Fig (1.1)

Here are some experimental facts about blackbody radiation:

a. The blackbody spectrum depends only on the temperature of the object, it is not depend on the type of material, ie all materials emit the same blackbody spectrum if their temperatures are the same.

b. As the temperature of an object increases, it emits more blackbody energy at all wavelengths.

c. As the temperature of an object increases, the peak wavelength of the blackbody spectrum shifts toward shorter wavelength. For example, blue stars are hotter than red stars.
d. The blackbody spectrum always becomes small at the left-hand side (the short wavelength, high frequency side).

1.4.1 WIEN’S ENERGY DENSITY DISTRIBUTION

A number of attempts were carried out to explain thecharacteristics of black body radiation. by using classical thermodynamics and Stefan–Boltzmann law Wilhelm Wien in 1896 derived the energy distribution formula (energy per unit volume per unit frequency)

$$u(\nu,T) = A\nu^3 e^{-\beta\nu/T}$$

Called Wien’s radiation law.in this relation A and are empirically defined parameters (they can be adjusted to fit the experimental data) .This radiation law was correct only for short wavelength region but it fails badly at high wavelength region of the black body spectrum.

1.4.2 RAYLEIGH'S ENERGY DENSITY DISTRIBUTION

In 1900 Rayleigh focused on understanding the nature of the electromagnetic radiationinside the cavity. He considered the radiation to be consists of standing waves having atemperature T with nodes at the cavity surface. The energy radiated by the cavity can be estimated by considering the resonant modes. In three-dimensions, the number of modes, per unit frequency per unit volume is given by

$$N(\nu)d\nu = \frac{8\pi\nu^2}{c^3}d\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (1)$$

Gives the number ofmodes of oscillation per unit volume in the frequency range ν to $\nu + d\nu$. So the electromagnetic energy density in the frequency range ν to $\nu + d\nu$ is given by

$$u(\nu,T) = N(\nu)\overline{E} = \frac{8\pi\nu^2}{c^3}\overline{E} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where $\overline{E}$ is the average energy of the oscillators present on the walls of the cavity (or of the electromagnetic radiation in that frequency interval)According to the equipartition theorem of classical thermodynamics,all oscillators in the cavity have the same mean energy, irrespective of their frequencies:

$$\overline{E} = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = kT \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

An insertion of (3) into (2)
Leads to the Rayleigh–Jeans formula:

$$u(\nu,T) = N(\nu)\overline{E} = \frac{8\pi\nu^2}{c^3}kT \quad \ldots\ldots.. (4)$$

this law is in complete disagreement with experimental data, except for low frequencies. uas given by (4) *diverges* for high values of ν, whereas experimentally it must be finite (Fig 1.2). the integration of this equation over all frequencies *diverges*, impliesthat the cavity contains an *infinite* amount of energy. This result is absurd. Divergence of this equation for*high* frequencies (i.e., in the *ultraviolet* range)called the *ultraviolet catastrophe*.The origin of this failure is due to the classical assumption of the average energy (eq.3).

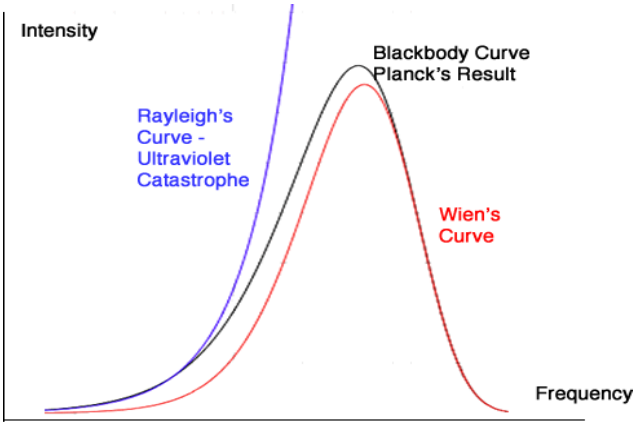


Fig (1.2)

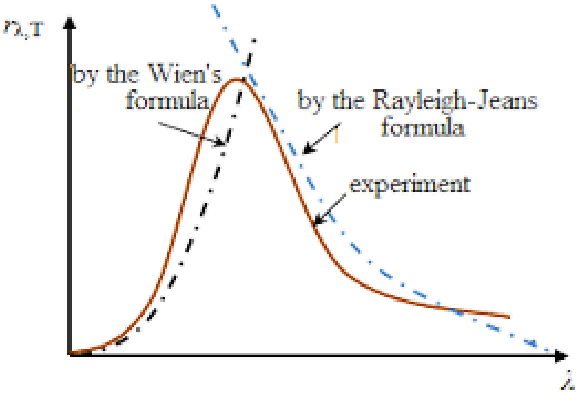


Fig (1.3)

1.5 PLANCK'S HYPOTHISIS

In 1900 Planck succeeded in resolving the ultraviolet catastropheby suggesting the quantum theory of radiation and put forward an accuratedescription of blackbody radiation. He suggested that the correct results could be obtained if the energy of oscillator is taken as discrete rather than continuous. Planck derived a formula, which agrees extremely well with experimental results. He derived the radiation law by using the following assumptions.a. A black body chamber is filled up not only with radiation, but also with simple harmonic oscillators or harmonic oscillators or resonators of molecular dimensions. They can vibrate with all possible frequencies.

b. The frequency of radiation emitted by an oscillator is the same as the frequency of its vibration.

c. An oscillator cannot emit energy in a continuous manner. It can emit energy in the multiples of a small unit called Quantum (Photon).

If an oscillator is vibrating with a frequency υ , it can radiate in quantas of magnitude $h\upsilon$. The oscillator can have only discrete energy E given by

$E = nh\upsilon$

The emission of radiation corresponds to a decrease and absorption to an increase in the energy and amplitude of an oscillator.

1.5.1PLANK'S RADIATION LAW

Since Planck assumed that the energy of an oscillator is quantized, he showed that the relation for the average radiationenergy can be obtained by replacing theintegration of eq.3 of art. 1.4.2bysummation ,which correspondingto the discreteness of the oscillators' energies.
Hence

$$\overline{E} = \frac{\sum_{0}^{\infty} E e^{-E/kT} dE}{\sum_{0}^{\infty} e^{-E/kT} dE} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

By putting $E = n h\upsilon$ and solving , we get

$$\overline{E} = \frac{\sum_{0}^{\infty} nh\nu e^{-nh\nu/kT} dE}{\sum_{0}^{\infty} e^{-nh\nu/kT} dE} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The energy density per unit frequency of the radiation emitted from the hole of a cavity is given by

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

This is known as *Planck's distribution relation.*This relation can be rewritten in terms of wavelength. thePlanck's energy density or the energy density per unit wavelength

$$u(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

In the region of very low frequencies $h\nu << kT$

$$e^{h\nu/kT} \approx 1 + h\nu / kT \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Hence the relation reduces to

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Which is the Rayleigh–Jeans law .
In the region of very high frequencies $h\nu >> kT$

$$e^{h\nu/kT} - 1 \approx e^{h\nu/kT} \quad \ldots\ldots\ldots \quad (7)$$

Hence the relation reduces to

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3} e^{-h\nu/kT} \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

Which is Wien's energy density distribution law.In summary, the spectrum of the blackbody radiation reveals the quantization of radiation, notably the particle behavior of electromagnetic waves

1.6 PHOTOELECTRIC EFFECT

The phenomenon of photoelectric effect was first observed by Heinrich Hertz in 1887, when he was performing an experiment for production of electromagnetic waves by means of spark discharge, Hertz observed that sparks occured more rapidly in the air gap of his transmitter when ulraviolet radiations was directed at one of the metal plates. But he could not explain the reason of his observations. In 1902, Philipp Eduard Anton von Lenard observed that the energy of individual emitted electrons increases with the frequency of the light. This experimental observation did not match with Maxwell's wave theory of light,which predicted that the electron energy would be proportional to the intensity of the radiation.

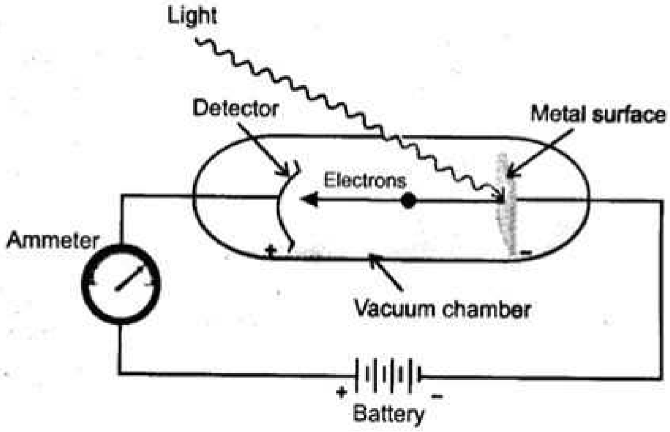
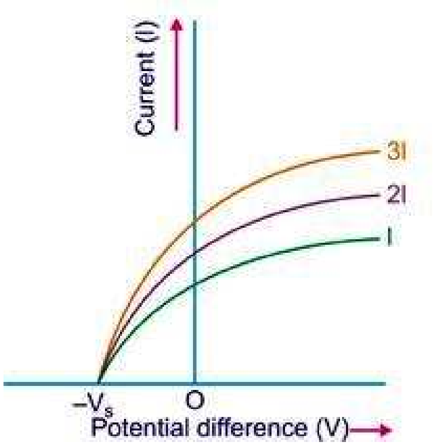


Fig (1.4)

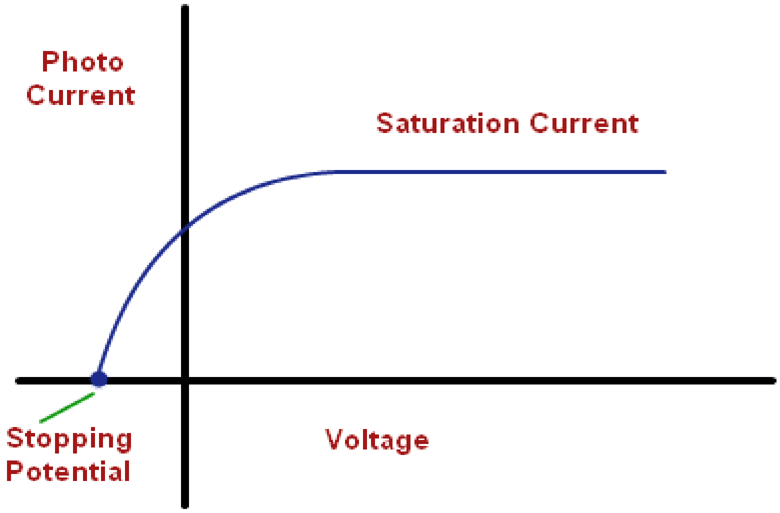
When light shines on the surface of a metallic substance, electrons in the metal absorb the energy of the light and they can escape from the metal's surface. This is called the photoelectric effect. It was found that the magnitude of the electric current thus produced is proportional to the intensity of the striking radiation provided that the frequency of the light is greater than a minimum value characteristic of the metal, while the speed of the electrons does not depend on the light intensity, but on its frequency. These results could not be explained by the theory of classicalelectromagnetism.

1.6.1 CHARACTERISTICS OF PHOTOELECTRIC EFFECT

(i) Effect of Intensity : It was observed that for a given frequency, if intensity of incident light is increased, the photoelectric current increases and with decrease of intensity, the photoelectric current decreases; but the stopping potential remains the same.

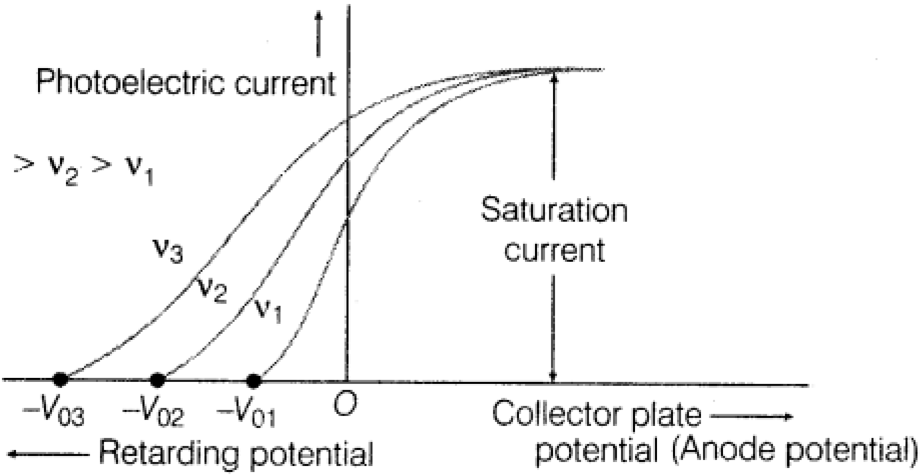


Fig(1.5)



Fig(1.6)

This means that the intensity of incident light affects the photoelectric current but leaves the maximum kinetic energy of photoelectrons unchanged. **(ii) Effect of Frequency :** When the intensity of incident light is kept fixed and frequency is increased, the photoelectric current remains the same; but the stopping potential increases.If the frequency is decreased, the stopping potential decreases and at a particular frequency of incident light, the stopping potential becomes zero. This value of frequency of incident light for which the stopping potential is zero is called threshold frequency ν_0 .If the frequency of incident light (ν) is less than the threshold frequency (ν_0), no photoelectric emission takes place.Thus, the increase of frequency increases the maximum kinetic energy of photoelectrons but leaves the photoelectric current unchanged.



Fig(1.7)

(iii) Effect of metal : When frequency and intensity of incident light are kept fixed and photometal is changed, we observe that stopping potentials (V_s) versus frequency (v) graphs are parallel straight lines, cutting frequency axis at different points (Fig). This shows that threshold frequencies are different for different metals, the slope (V_s/v) for all the metals is same and hence a universal constant.

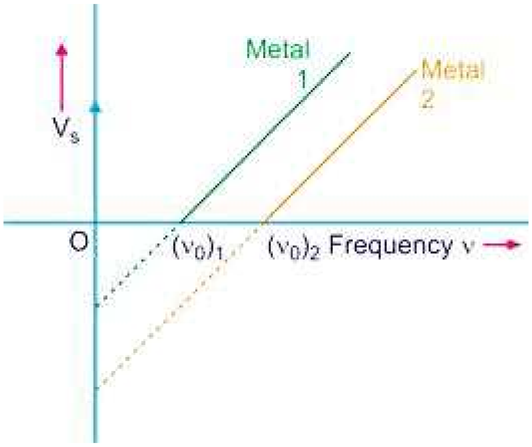


Fig (1.8)

(iv) Effect of Time: There is no time lag between the incidence of light and the emission of photoelectrons.

1.6.2 EINSTEIN`S EXPLANATION OF PHOTOELECTRIC EFFECT

The wave theory of light failed to explain the observed characteristics of photoelectric effect. Einstein in 1905 explained these results by assuming light, in its interactionwith matter, consisted of corpuscles of energy *hv,* called photons. According to this idea, "The energy of electromagnetic radiation is not continuously distributed over the wavefront like the energy of water waves but remains concentrated in packets of energy content *hv*, where *v* is frequency of radiations and *h*is universal Planck's constant (6.625×10^{-34}Js). Each packet of energy is called a *photon or quantum* and travels with the speed of light.When a photon encounters an electron of the metal it is entirely absorbed,and the electon, after receiving the energy *hv,* spends an amount of work*W* equal to its binding energy in the metal, and leaves with a kinetic energy. Accordingly, if *hv* is the energy of incident photon, then the kinetic energy of ejected photo electron is given by

$$E_{max} = \frac{1}{2} m v_{max} = h\nu - W \text{ .... (1)}$$

Whereworkfunction $W = h\nu_0$,in terms of stopping potential V_s

$$eV_s = h\nu - W \text{ .... (2)}$$

$$\text{or } V_s = \frac{h\nu}{e} - \frac{W}{e} \text{ .... (3)}$$

Thus, a plot of V_s versus ν for different frequencies of light will yield a linear plot with a slope (*h*/e) and a V intercept of (- W/e).

Equation(1) is referred as *Einstein's photoelectric equation* and explains all experimental results of photoelectric effect.From Einstein's relation, it follows that :

1. No electron will be emitted from the metalsurface if the frequency of the incident light is less than a certain value called as thresholdfrequency, ν_0 . If $\nu < \nu_0$ then the kinetic energy of the photoelectrons will become negative physically impossible.Thus the frequency of incident radiation should be greater than the thresholdfrequency(ν_0) for the metal for the ejection of electrons.
2. Equation (1) shows that the photoelectrons with greater value of maximum kinetic energy will come out of the metal surface, when the frequency of incident radiation is increased. Since the equation (1) does not involve the term of intensity so the maximum kinetic energy does not depend upon the intensity.
3. The rate of emission of photoelectrons will be large, when intense beam of light is incident on the metal surface. This is because, an intense beam of light contains a large number of photons which transfers their energy to a larger number of electrons and hence more photoelectrons are emitted.
4. The electron is emitted from the metal surface in a time less than one nanosecond so the photoelectric effect is an instantaneous process.The predictions of Classical Physics, using just the electromagnetic wave nature of light, are drastically different. In 1913 and 1914 Robert A Millikancarried out careful experiments and measured precisely what Einstein's new theory

predicted.Thus quantitative theory of photoelectricity has been completely verifiedby experiment and establishing the corpuscular nature of light.

1.7 COMPTON EFFECT

Compton effect is a process in which x-rays collide with electrons and are scattered. In order to establish the particle nature of radiation, it is necessary that photons must carry momentum. In 1923, Arthur Compton studied the scattering of x-rays of known frequency from graphite and looked at the recoil electrons and the scattered x-rays. Unlike the prediction of classical wave theory, the wavelength of the scattered radiation does not depend on the intensity of radiation but depends on the scattering angle and the wavelength of the incident beam.

According to wave theory, when an electromagnetic wave of frequency υ_0 is incident on an atom, it would cause electrons to oscillate. The electrons would absorb energy from the wave and re-radiate electromagnetic wave of a frequency $\upsilon_s<\upsilon_0$. The frequency of scattered radiation would depend on the amount of energy absorbed from the wave, i.e. on the intensity of incident radiation and the duration of the exposure of electrons to the radiation and not on the frequency of the incident radiation.

Compton found that the wavelength of the scattered radiation does not depend on the intensity of incident radiation but it depends on the angle of scattering and the wavelength of the incident beam. The wavelength of the radiation scattered at an angle θ is given by

$$\lambda_s = \lambda_0 + \frac{h}{m_0 c}(1-\cos\theta)$$

Where m_0 is the rest mass of the electron. The constant $\frac{h}{m_0 c}$ is known as the Compton wavelength of the electron and it has a value 0.0024 nm.

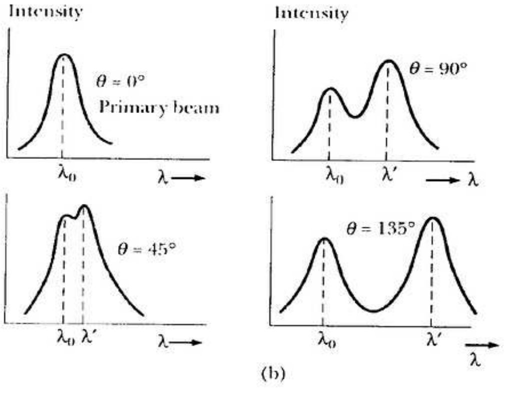


Fig (1.9)

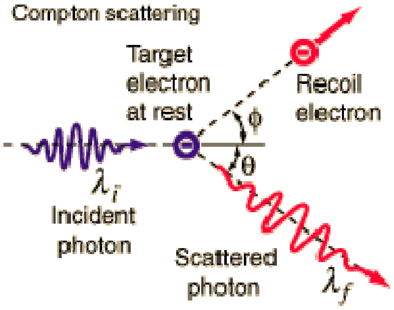
The spectrum of radiation at an angle θ consists of two peaks, one at and λ_0 the other at λ_s . Compton effect can be explained by assuming that the incoming radiation is a beam of particles with Energy $E = h\nu_0$ and momentum $p = \frac{h\nu_0}{c}$

Which comes from the energy - momentum relation of the *special theory of relativity* , according to which, $E^2 = m_0{}^2c^4 + p^2c^2$

Where m_0 is the rest mass of a particle. Since photons are massless ($m_0=0$), we get E=pc. Compton's observation is consistent with what we expect if photons, considered as particles, collide with electrons in an elastic collision.

1.7.1 COMPTON'S FORMULA

Consider a photon of energy $h\nu_0$ and momentum $p_i = \frac{h\nu_0}{c}$ colliding *elastically* with an electron at rest. Let the direction of incoming photon be along the x-axis. After scattering, the photon moves along a direction making an angle θ with the x-axis while the scattered electron moves making an angle ϕ. Let the magnitude of the momentum of the scattered electron be p_e while that of the scattered photon be p_f



Fig(1.10)

Applying the law of conservation of momentum in x-direction :

$p_i = p_f \cos\theta + p_e \cos\phi$ ………………….. (1)

Applying the law of conservation of momentum in y-direction :

$0 = -p_f \sin\theta + p_e \sin\phi$ ……………… (2)

From the relation (1) and (2)

$p_e^2 = (p_i - p_f \cos\theta)^2 + (p_f \sin\theta)^2$

$= p_i^2 + p_f^2 - 2p_i p_f \cos\theta$ ………… (3)

Conservation of Energy : (relativistic effect)

If the rest mass of the electron is taken to be m_0 , the initial energy is m_0c^2 and the final energy is given by the relation

$E^2 = m_0{}^2c^4 + p_e^2c^2$

$h\nu_0 + m_0c^2 = h\nu + \sqrt{m_0{}^2c^4 + p_e^2c^2}$ ………………………… (4)

From Eqn. (4), we get, on squaring, Thus,

$m_0{}^2c^4 + p_e^2c^2 = (h\nu_0 - h\nu + m_0c^2)^2$ ……………. (5)

$p_e^2c^2 = (h\nu_0 - h\nu)^2 + 2m_0c^2(h\nu_0 - h\nu)$ ……………. (6)

On substituting expression (3) for in the above equation, we get

$p_i^2c^2 + p_f^2c^2 - 2p_i p_f c^2 \cos\theta == (h\nu_0 - h\nu)^2 + 2m_0c^2(h\nu_0 - h\nu)$ ….. (7)

Recalling $p_i = \frac{h\nu_0}{c}$ and $p_f = \frac{h\nu}{c}$ and on simplification, we get

$h\nu\nu_0(1-\cos\theta) = m_0c^2(\nu_0-\nu)$ ………………… (8)

Using $\lambda = c/\nu$, we get Compton's formula

$$\lambda_s = \lambda_0 + \frac{h}{m_0c}(1-\cos\theta)$$ ………………….. (9)

Or

$$\Delta\lambda = \lambda_s - \lambda_0 = \frac{h}{m_0c}(1-\cos\theta)$$ …………………. (10)

$\lambda_c = \frac{h}{m_0c}$ is known as the Compton Wavelengthof an electron.

01: EXAMPLE :

A photon of wavelength 6000 nm collides with an electron at rest. After scattering, the wavelength of the scattered photon is found to change by exactly one Compton wavelength. Calculate (i) the angle by which the photon is scattered, (ii) the angle by which the electron is scattered and (iii) the change in the energy of the electron due to scattering.

SOLUTION :

i. Since the change in wavelength is one Compton wavelength

$\Delta\lambda = \lambda_c(1-\cos\theta) = \lambda_c$, i.e. $\theta = 90^0$

Thus the photon is scattered at right angles to the incident direction.

ii. Initial momentum of the photon is

$$\frac{h\nu_0}{c} = \frac{h}{\lambda_0} = \frac{6.63\times10^{-34}}{6\times10^{-12}} = 1.105\times10^{-22}\,Js/m$$ in x direction

The final momentum of the photon is

$$\frac{h\nu}{c} = \frac{h}{\lambda} = \frac{6.63\times10^{-34}}{8.4\times10^{-12}} = 7.9\times10^{-23}\,Js/m$$ iny direction

Thus the final momentum of the electron is

$1.11\times10^{-22}\,\hat{x} - 7.9\times10^{-23}\,\hat{y}$

The Final direction of electron makes with the x-axis is

$\phi = \tan^{-1}(-7.9/11.1) = 35.6^0$

iii. The change in the energy of the electron is negative of the change in the energy of the photon which is

$$\frac{hc}{\lambda_0} - \frac{hc}{\lambda} = 9.47\times10^{-15}J = 59.2keV$$

1.8 HEAT CAPACITY OF A SOLID

In 1819 Pierre Louis Dulong and A. T. Petit conducted someexperimentson three dimensional solid crystals to determine the heat capacities of a variety of these solids.Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49x 10^4 JKilomol^{-1}K^{-1} at room temperatureroom temperature (300K). The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate). Each atom has an energy of ½kT .Thus C_v= 6/2 R= 3R.The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids.The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviation in the heat capacity experiments. The first model was constructed by Einstein and the second was proposed by Debye.

Any theory used to calculate heat capacities of crystalline solids must explain two things:

1. Near room temperature, the heat capacity of most solids is around 3k per atom (the molar heat capacity for a solid consisting of n-atom molecules is ~3nR). This is the well-known Dulong and Petit law.
2. At low temperatures, Cv decreases, becoming zero at T=0. Heat capacities have a temperature dependence of the form $\alpha T^3 + \gamma T$, where the T^3 term arises from lattice vibrations, and the linear term from conduction electrons.

Classical mechanics would predict Cv = 3R at all temperatures, in violation of both experiment and the third law of thermodynamics.

1.8.1 MATHEMATICAL ANALYSIS

Suppose we have a solid crystal having N monoatomic atoms, then 3N-6 vibrational modes will be there. Since N iv vary large number , then 3N-6 ≈ 3N. So, we will have 3N normal modes of frequency of the jth mode be

$$\nu_j = \frac{1}{2\pi}\sqrt{\frac{k_j}{\mu_j}}$$

We shall replace ν_j by a distribution which is called phonon density of state (the normal modes are called phonons).

Now the partition function of the crystals is

$$Q_N\left(V,T\right) = e^{-\beta U_0}\prod_{j=1}^{3N} q_{vib,j}$$

Here $q_{vib,j}$ is the vibrational partition function (PF) of the jth normal mode. Let us now evaluate the vibrational PF. Consider a harmonic oscillator of frequency ν. Energy of a particular level is given by

$$E_j = \left(j + \frac{1}{2} \right) h\nu \ , \qquad \text{j = 0,1,2,3…………..}$$

Partition function is

$$q_{vib} = \sum_{j=0}^{\infty} e^{-\beta E_j} = e^{-\frac{1}{2}\beta h\nu} \sum_{j=0}^{\infty} e^{-j\beta h\nu}$$

$$= \frac{e^{-\frac{1}{2}\beta h\nu}}{1 - e^{-\beta h\nu}}$$

So, the total PF is

$$Q_N\left(V,T\right) = e^{-\beta U_0} \prod_{j=1}^{3N} \left(\frac{e^{-\frac{1}{2}\beta h\nu_j}}{1 - e^{-\beta h\nu_j}} \right)$$

Taking the logarithm of the PF ,we have

$$\ln Q_N\left(V,T\right) = -\frac{U_0}{k_B T} - \sum_{j=1}^{3N} \left[\ln\left(1 - e^{-h\nu_j / k_{BT}}\right) + \frac{h\nu_j}{k_B T} \right]$$

Now, we introduce a phonon density of states g(ν) which should follow the following equation

$$\int_0^{\infty} g\left(\nu\right) d\nu = 3N$$

So the logarithm of the PF can be written as the following integral equation

$$-\ln Q_N\left(V,T\right) = \frac{U_0}{k_B T} + \int_0^{\infty} \left[\ln\left(1 - e^{-h\nu \ / k_{BT}}\right) + \frac{h\nu}{2k_B T} \right] g\left(\nu\right) d\nu$$

Now we will try to get integral equation of different thermodynamics properties of the crystal using this PF.

Let us get the integral equation for energy of the system E. Using the relation of canonical ensemble $E = k_B T^2 \left(\frac{\partial \ln Q_N\left(V,T\right)}{\partial T} \right)_V$, we get

$$E = U_0 + \int_0^{\infty} \left[\frac{h\nu e^{-h\nu / k_B T}}{\left(1 - e^{-h\nu / k_B T}\right)} + \frac{h\nu}{2} \right] g\left(\nu\right) d\nu$$

We can also get an expression for heat capacity C_V using the thermodynamics relation

($C_V = \left(\frac{\partial E}{\partial T}\right)_V$) as

$$C_V = k_B \int_0^\infty \frac{\left(h\nu / k_B T\right)^2 e^{-h\nu/k_B T} g(\nu)\, d\nu}{\left(1 - e^{-h\nu/k_B T}\right)^2}$$

At this point given a suitable expression for phonon density of states g(ν), one can get the thermodynamics properties and their temperature dependence.

To explain the low temperature behavior of specific of solids, Einstein treated the atoms in a crystal as N simple quantum mechanical harmonic oscillators, all having the same frequency ν_E, termed as Einstein frequency. He considered a simple model of a solid, in which the atoms were represented as weakly-coupled quantum harmonic oscillators. The frequency ν_E depends on the strength of the restoring force acting on the atom.Since the equation of motion for each atom decomposes into three independent equations for the x, y and z components of displacement, and N atom solid is equivalent to 3N harmonic oscillators, each vibrating independently at frequency ν. So, according to the proposal the phonon density of states will take the form

$$g(\nu) = 3N\delta(\nu - \nu_E)$$

So the C_V will take the form

$$C_V = 3Nk_B \left(\frac{h\nu_E}{k_B T}\right)^2 \frac{e^{-h\nu_E/k_B T}}{\left(1 - e^{-h\nu_E/k_B T}\right)^2}$$

Now we will define a characteristic temperature called Einstein temperature (Θ_E) for crystal as

$$\Theta_E = \frac{h\nu_E}{k_B}$$

Now the expression of C_V will read as a function Θ_E

$$C_V = 3Nk_B \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{-\Theta/T}}{\left(1 - e^{-\Theta/T}\right)^2}$$

Let us now examine the above equation at two different conditions:

1. **At very high temperature regime**

If temperature is vary high

$$\frac{\Theta_E}{T} \to 0,$$

$$e^{-\Theta_E/T} \to 1 \text{and} \left(1-e^{-\Theta_E/T}\right)^2 \approx \left(1-1+\Theta_E/T+.......\right)^2 \to \left(\frac{\Theta_E}{T}\right)^2$$

So, $$C_V\left(T\to\infty\right)\to 3Nk_B$$

This is the dulong-petit's law of heat capacity, classical limit

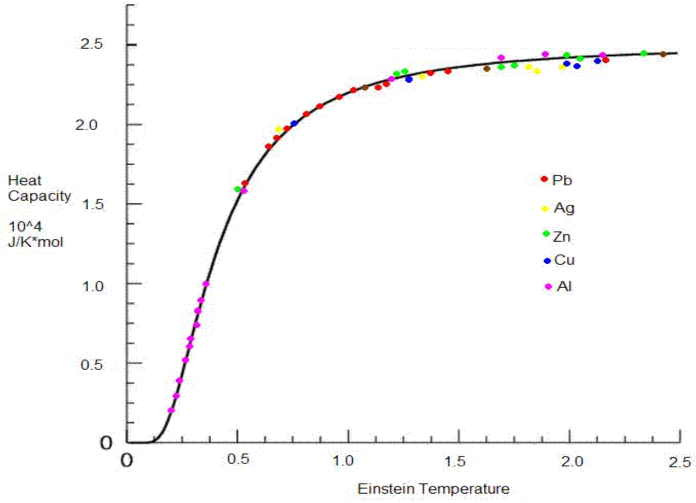
2. **At very low temperature regime**

$$\frac{\Theta_E}{T}\to\infty \text{ and} \left(1-e^{-\Theta_E/T}\right)^2 \to 1$$

So, the expression for heat capacity at low temperature regime will be

$$C_V\left(T\to 0\right)=3Nk_B\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

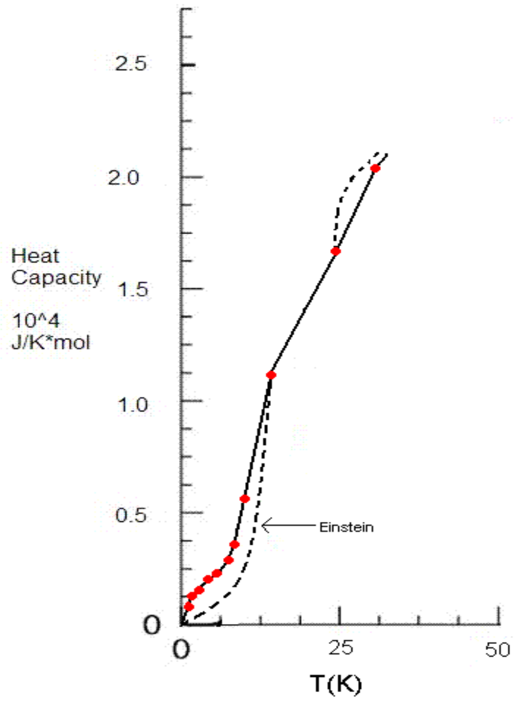
Before going into the limitation of the theory, we would like to point out one important feature of the above equation. The equation predicts that C_V is the same function for all the substances if it is plotted against the reduced temperature T/Θ_E.



Fig(1.11)

1.8.2 LIMITATION OF EINSTEIN THEORY

The temperature dependence of heat capacity derived from Einstein model is capable of giving an impressive qualitative agreement with experiment. However, quantitative agreement is somewhat poor, especially in the low temperature regime. The experimental temperature dependence of the heat capacity follows a T^3 law at lower temperature regime. The low temperature dependence of the heat capacity predicted by the theory falls to zero value more rapidly than T^3 law.



Fig(1.12)

The reason for this breakdown at low T, low frequency or long wavelength modes get more populated and that needs to be treated explicitly. Debye theory which we will discuss next has solved the issue.

1.8.3 DEBYE THEORY OF SOLIDS

The disagreement between Einstein's result and the experimental data is due to the fact that Einstein's assumptions about the atoms in a crystal do not strictly apply to real crystals. The main problem lies in the assumption that a single frequency of vibration characterizes all $3N$ oscillators. Debye improved on Einstein's theory by considering the vibrations of a body as a whole, regarding it as a continuous elastic solid. He associated the internal energy of the solid with stationary elastic sound waves. Each independent mode of vibration (or normal mode) is treated as a degree of freedom.

In Debye's theory a solid is viewed as a *phonon gas.* Vibrational waves are matter waves, each with its own de Broglie wavelength and associated particle. The particle is called a phonon, with characteristics similar to those of a photon. We are interested in determining the number of possible wavelengths or frequencies within a given range. For quantum waves in a one-dimensional box we saw that the wave function is $\psi = A\sin kx$, where

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L}, \qquad n=1,2,3\ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here λ is the de Broglie wavelength, n is the quantum number and L is the dimension of the box. Using the fundamental equation of wave motion, $\nu = \frac{\upsilon}{\lambda}$, where υ is the wave velocity and ν is the frequency, we obtain

$$n = \frac{2L}{\lambda} = \frac{2L}{\upsilon}\nu \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

If we consider an elastic solid as a cube of volume $V = L^3$ we get

$$n = \frac{2V^{1/3}}{\upsilon}\nu \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where, in this case $n^2 = n_x^2 + n_y^2 + n_z^2$.The quantum numbers n_x,n_y and n_z are positive integers. Thus the possible values that they can assume occupy the first octant of a sphere of radius

$$n = \left(n_x^2 + n_y^2 + n_z^2\right)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

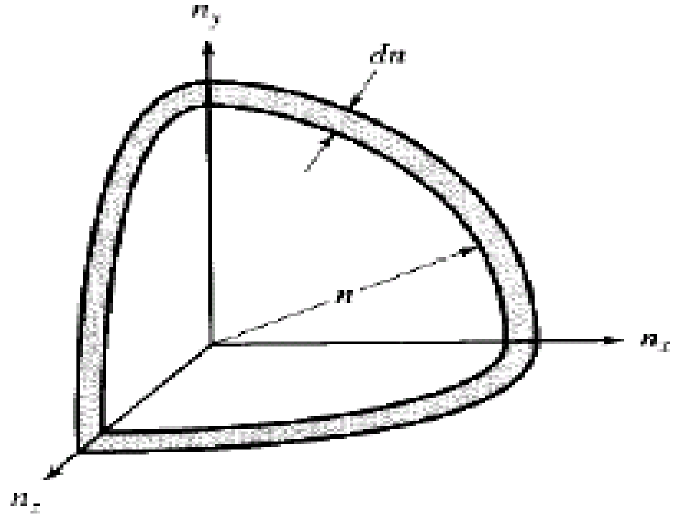


Fig (1.13)

Let g(ν)dν be the number of possible frequencies in the range ν to ν+ dν . Since n is proportional to ν, $g(\nu)d\nu$ is the number of positive sets of integers in the interval n to $n + dn$ that is, within a shell of thickness dn of an octant of a sphere with radius n:

$$g(\nu)d\nu = \frac{1}{8}4\pi n^2 dn = \frac{1}{2}\pi n^2 dn$$

$$= \frac{4\pi V}{\upsilon^3} \nu^2 d\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5)}$$

In a vibrating solid, there are three types of waves: one longitudinal with velocity υ_l and two transverse with velocity υ_t. All are propagated in the same direction. When all three waves are taken into account, the above equation becomes

$$g(\nu)d\nu = 4\pi V\left(\frac{1}{\upsilon_l^3} + \frac{2}{\upsilon_t^3}\right)\nu^2 d\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

Since each oscillator of the assembly vibrates with its own frequency, and we are considering an assembly of 3*N* linear oscillators, there must be an upper limit to the frequency spectrum. The maximum frequency ν_D is determined from the fact that there are only 3*N* phonons:

$$3N = \int_0^{\nu_D} g(\nu)d\nu = 4\pi V\left(\frac{1}{\upsilon_l^3} + \frac{2}{\upsilon_t^3}\right)\nu_D^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

Combining this result with the second last equation, we get

$$g(\nu)d\nu = \frac{9\pi\nu^2 d\nu}{\nu_D^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(8)}$$

Now, we can understand the principle difference between Einstein and Debye model is the assumption about the frequency spectrum of the lattice vibration (shown below Fig (1.14)).

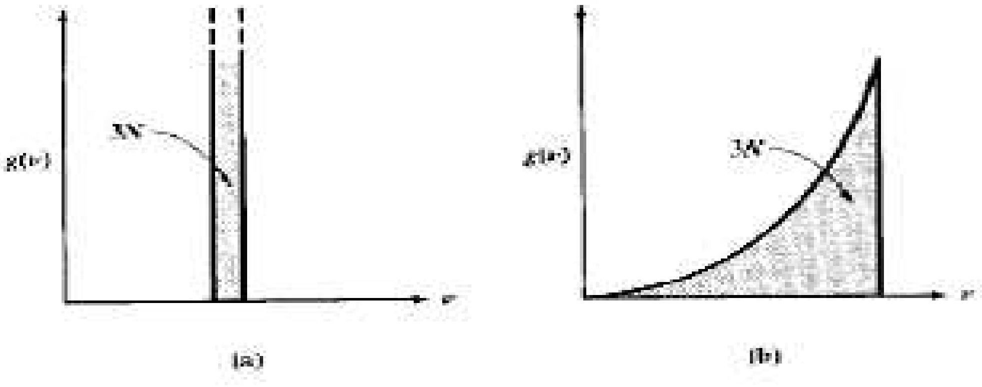


Fig (1.14)

Now put the expression for g(ν) in the integral expression of C_V and we will get

$$C_V = \frac{9Nh}{\nu_D^3}\int_0^{\nu_D} \frac{h\nu}{k_B T^2}\frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT}-1\right)^2}\nu^3 d\nu \qquad \text{………………..} (9)$$

Now, we will define x = hν/k$_B$T and Debye characteristic temperature Θ_D = hν$_D$/k$_B$. The above equation will take a form after certain step of mathematical manipulation

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x-1\right)^2}dx \qquad \text{………………} (10)$$

Let us examine the above equation in two conditions

1. **At very high temperature regime**

$x \to 0$, $\left(e^x-1\right) \to x$, and $e^x \to 1$

So, the heat capacity will be

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} x^2 dx = 3Nk_B\left(\frac{T}{\Theta_D}\right)^3\left(\frac{\Theta_D}{T}\right)^3 \qquad \text{…………} (11)$$

$$C_V = 3Nk_B$$

This is heat capacity predicted by Dulong-petit's law (classical equi-partition theory)

2. **At very low temperature regime**

$\Theta_D / T \to \infty$

So, the integral equation for C_V can be written as

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} \frac{x^4 e^x}{\left(e^x-1\right)^2}dx \qquad \text{……………………} (12)$$

The integral appears on the RHS is a standard and equals to $4\pi^4/15$. So the expression for C_V becomes

$$C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta_D}\right)^3 \qquad \text{…………………….} (13)$$

$$= aT^3$$

Here a is constant for a particular solid. This is the famous T^3-law. This theory predicts the temperature dependence of the heat capacity of monatomic solids in the whole temperature range quiet well both qualitatively and quantitatively.

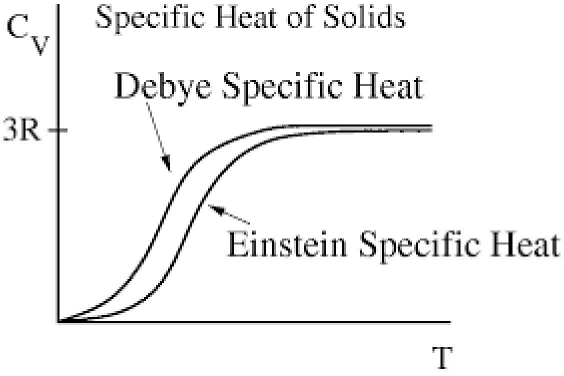


Fig (1.15)

1.9 BOHR'S MODEL H ATOM

Neil Bohr modified Rutherford atomic model by using Plank's Quantum theory of radiation and purposed the model of hydrogen atom which could explain successfully the origin of spectral line in hydrogen atom and also gave a model for all other atoms. For simplicity Bohr considered only circular orbits and introduced several, arbitrary assumption which violate classical physics but which are immensely successful in explaining many properties of hydrogen atom. The force of attraction between the nucleus and the electron

$$=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{r^2}$$

The centripetal force acting on the electron due to its mechanical motion in circular orbit mv^2/r.

For equation of the electron due to the electron in circular orbit Coulomb's force of attraction must be equal to the centripetal force upon the electron *i.e.*

$$\frac{mv^2}{r}=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{r^2}$$

$$r=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{mv^2} \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

From the second postulates we have angular momentum of electron

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

$$v=\frac{nh}{2\pi mr}$$

Substituting value of v from eqn. (3) in eqn. (2)

$$r=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{m(nh/2\pi mr)^2}=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2\times4\pi^2m^2r^2}{mn^2h^2}$$

$$r = \frac{\varepsilon_0 h^2}{\pi m Z e^2} \cdot n^2 \qquad \ldots\ldots\ldots\ldots\ldots \qquad (2)$$

This eqn. gives the radius of nth stationary orbit. We denote it by r_n. Thus

$$r_n = \frac{\varepsilon_0 h^2 n^2}{\pi m Z e^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \qquad (3)$$

The kinetic energy of the electron in nth orbit $= \frac{1}{2} m v_n^2$ where v_n is the velocity of the electron in nth orbit.

For nth orbit eqn. (2) may be written as

$$r_n = \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{m v_n^2} \quad or \quad v_n^2 = \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{m r_n} \ldots\ldots\ldots \quad (4)$$

Substituting value of the vn^2 from this eqn. We get the kinetic energy of the electron in *n*th orbit

Potential energy in *n*th orbit $= \frac{1}{2} m \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{m r_n} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{2r_n}$

P.E in *n*th orbit $= \frac{1}{4\pi\varepsilon_0} \cdot \frac{(Ze)(-e)}{r_n} = -\frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{r_n}$

The total energy of the electron in nth orbits given by

$$E_n = \text{K.E} + \text{P.E} \equiv \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{2r_n} - \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{r_n} = -\frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{2r_n} \ldots\ldots\ldots\ldots \quad (5)$$

Substituting value of r_n from eqn. (3) in eqn. (5)

$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0{}^2h^2} \cdot \frac{1}{n^2} = z^2 \left(\frac{me^4}{8\varepsilon_0^2 c h^3}\right) \frac{hc}{n^2} \ldots\ldots\ldots\ldots\ldots \quad (6)$$

Let us introduce Rydberg constant as

$$R = \frac{me^4}{8\varepsilon_0^2 c h^3} \qquad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

Now eqn. (6) may be written as

$$E_n = \frac{Z^2 Rhc}{n^2} \qquad \ldots\ldots\ldots\ldots.. (8)$$

Let an electron jump from a stationary orbit of higher energy to a stationary orbit of lower energy. Now if n_i and n_f are the Quantum numbers of initial and final state, E_i and E_f are respective energies,

$$E_i = -\frac{Z^2 Rhc}{n_i^2}$$

And

$$E_f = -\frac{Z^2Rhc}{n_f^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

If υ is the frequency of emitted radiation, from Bohr's fourth postulate,

$$\upsilon = \frac{E_i - E_f}{h} = -\frac{Z^2Rc}{n_i^2} — \frac{Z^2Rc}{n_f^2} = Z^2Rc\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The wave number of emitted radiation is given by

$$\bar{\upsilon} = \frac{1}{\lambda} = Z^2R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

This relation explains the origin of spectral lines. For Hydrogen atomic number is unity. (i.e. Z=1)

Therefore for hydrogen, equation (14) becomes

$$\boldsymbol{\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} \quad \ldots\ldots\ldots\ldots \quad \mathbf{(11)}$$

Different observed series in the spectrum of hydrogen can be obtained from this equation.

1. **Lyman series.** This series of spectral lines in the spectrum of hydrogen is found in the ultraviolet region. This series is produced by jumping of electron from higher orbits to orbit for which$n_f = 1$.
   This is for series

$$\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n_i^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Where $n_{i=}$2,3,4,5 ...

2. **Balmer series.** This series is found in the visible spectrum. This is produced when electron jumps from higher orbit to orbit 2.
   Hence for this series

$$\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

Where $n_{i=}$3,4,5,6 ...

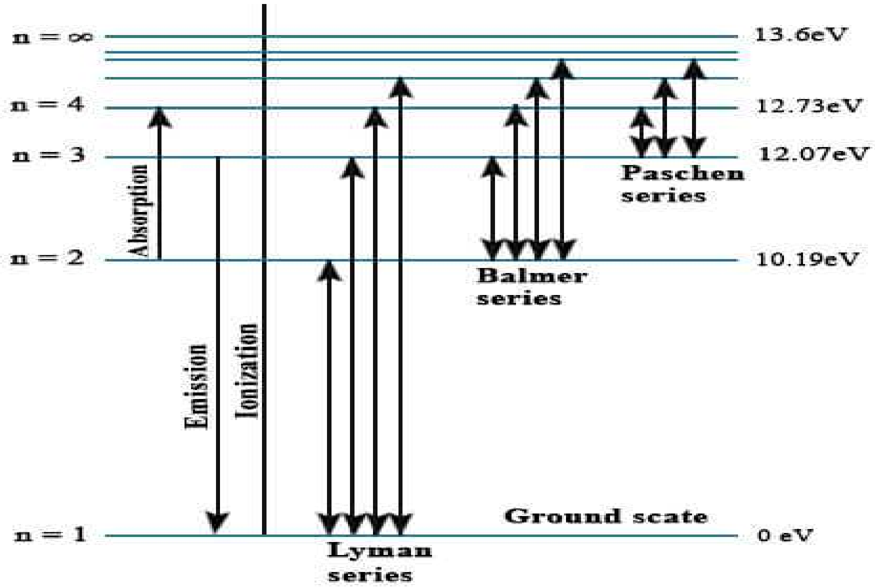


Fig (1.16)

3. **Paschen series.** This series is found in infra-red region and is produced when electron jump from higher orbit to third stationary orbit,

   $\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_i^2}\right)$ ……………… (14)

Where $n_{i=}$4,5,6,7 ...

4. **Brackett series.** This series is found in infra-red region and is produced when electron jump from higher orbit to fourth stationary orbit,

   $\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n_i^2}\right)$ ………………….. (15)

Where $n_{i=}$5,6,7,8 ...

This was discovered by Brackett in 1922 and hence called Brackett series.

5. **Pfund series.** This is obtained by the jump of electron from higher orbits to fifth stationary orbit. This series is found in far infra red region

$\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n_i^2}\right)$ …………… (16)

Where $n_{i=}$6,7,8,9 ...

The variation of Rydberg constant with mass of nucleus led to discovery of Deuterium. The Deuterium is an isotope of hydrogen having a mass exactly double the ordinary hydrogen. Therefore Rydberg constant for deuterium is slightly greater then hydrogen. As a result the wave no. of special lines of deuterium are slightly greater and wavelength slightly shorter than corresponding spectral lines of hydrogen. Urey in 1932 concluded that the faint line was due to some isotope of Hydrogen. This isotope is known as heavy hydrogen or deuterium.

1.10 THE WILSON-SOMMERFELD QUANTIZATION RULE

In 1916 Wilson and Sommerfeld, independently discovered a set of rules for the quantization of any physical system for which the coordinates are periodic functions of time. These rules included both the Planck and the Bohr quantization as special cases. These rules can be stated as follows:

For any physical system in which the coordinates are periodic functions of time, there exists a quantum condition for each coordinate.These quantum conditions are :

$$\oint p_q dq = n_q h$$

Where q is one of the coordinates, pqis the momentum associated with that coordinate, nq is a quantum number which takes on integral values, and means that the integration is taken over one period of the coordinate q.

let us understand these rules by on simple example. consider we have a one dimensional harmonic oscillator of mass m and force constant k oscillating along x axis with frequency ν . At any instant the total energy of the oscillator is sum of the kinetic energy to potential energy.

$$E = P.E + K.E$$

$$E= \frac{1}{2}kx^2 + \frac{p^2_x}{2m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Divided by E both sides, and rearranging gives

$$1 = \frac{x^2}{2E/k} + \frac{p^2_x}{2mE} \text{ or}$$

$$\frac{x^2}{\left(\sqrt{2E/k}\right)^2} + \frac{p^2_x}{\left(\sqrt{2mE}\right)^2} = 1$$

We can compare it with equation of ellipse $\frac{x^2}{(a)^2} + \frac{y^2}{(b)^2} = 1$, so it is an ellipse in x-p_x plane with semi-major axis a = $\sqrt{2E/k}$ and semi minor axis b = $\sqrt{2mE}$, fig. (17).

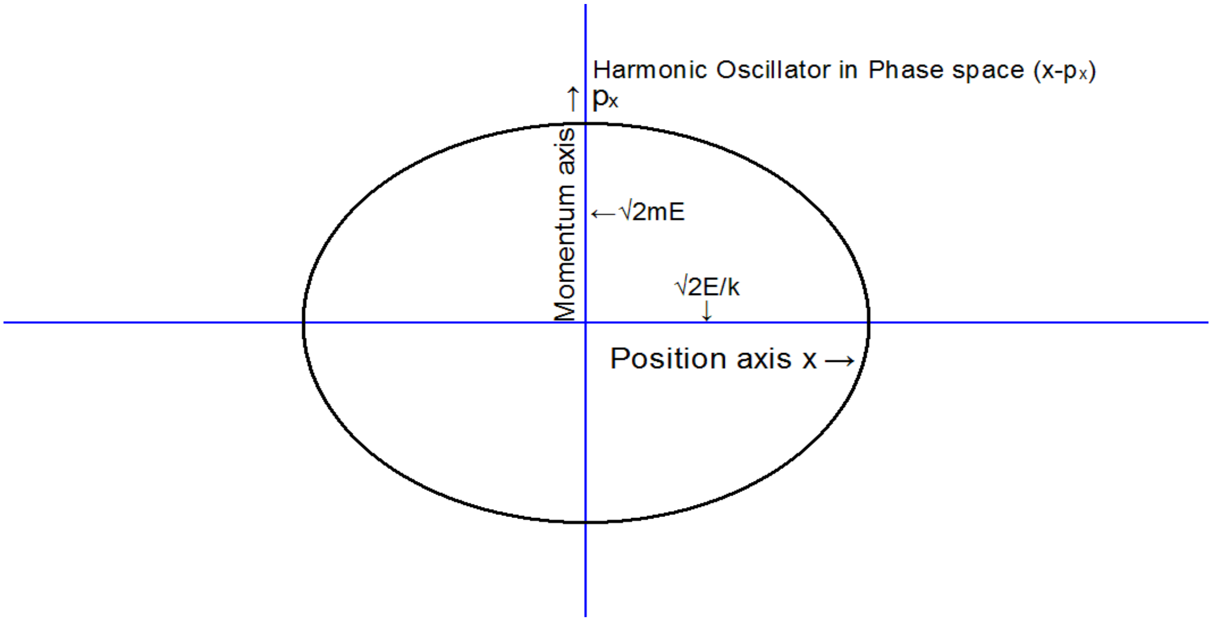


Fig (1.17)

So a one dimensional harmonic oscillator which executes to and fro motion along x axis in static space , will have elliptical trajectory in phase space . The total energy of oscillator along the ellipse will remain constant. The area of this ellipse gives the phase area available from energy range 0 to E.

The total phase area of ellipse or action integral $\oint p_q dq$ = πab

$$=\pi\sqrt{2E/k}\,.\sqrt{2mE} \quad \text{........... (4).}$$

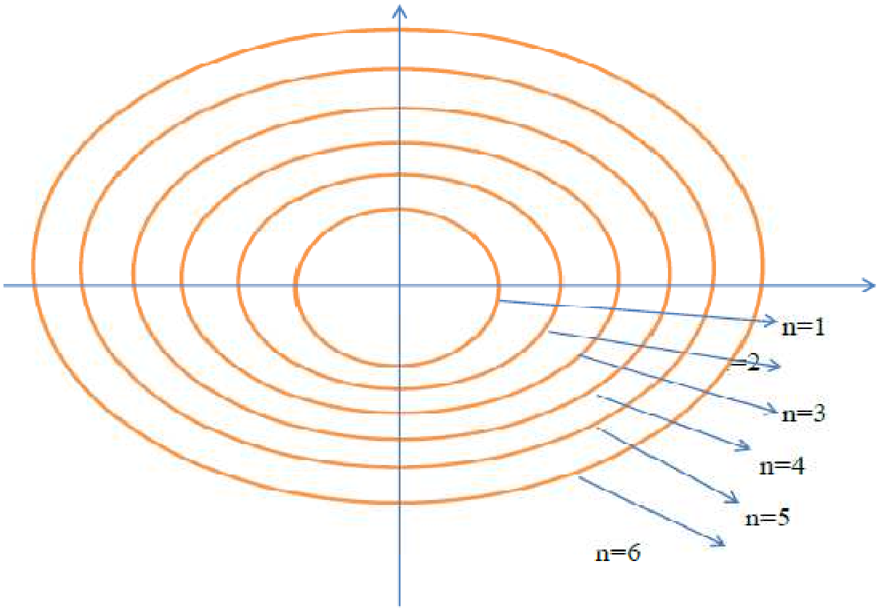
Since frequency $\nu = \frac{1}{2\pi}\sqrt{\frac{m}{k}}$

Hence , by applying Wilson-Sommerfeldquantisation condition

$$\oint p_q dq = \frac{E}{\nu} = nh$$

Then E = n $h\nu$ or the energy of harmonic oscillator will be in multiples of $h\nu$. which is identical with Planck's quantization rule.

Note that the allowed energy states of oscillation are represented by a series of ellipses in phase space, the area enclosed between successive ellipses always being h as in fig.(18):



Fig(1.18)

We find that the classical situation corresponds to h →0, all values of E and hence all ellipses being allowed if that were true.
From the Wilson-Sommerfeld rule, (Eq.1), We can also deduce the Bohr quantization of orbital angular momentum(L = nh/2π) .

An electron moving in a circular orbit of radius r has an angular momentum, mvr = L, which is constant. The angular coordinate is θ, which is a periodic function of the time. That is θ versus t is a function increasing linearly from zero to 2π rad in one period and repeating this pattern in each succeeding period. The quantization rule $\oint p_q dq = n_q h$

In this case

$\oint L d\theta = nh$ integrating from 0 to 2π

We have $L = \dfrac{nh}{2\pi} = n\hbar$

Physical meaning of Bohr’s Second Postulate:

A more physical interpretation of the Bohr quantization rule was given in 1924 by de Broglie. The Bohr quantization of angular momentum can be written as:
L = mvr = pr = nh/2π = nħ n = 1, 2, 3, .. .

Where p is the linear momentum of an electron in an allowed orbit of radius r. If we substitute into this equation the expression for p in terms of the corresponding de-Broglie wavelength($p=h/\lambda$),the Bohr equation becomes: $L=\frac{hr}{\lambda}=\frac{nh}{2\pi}$

Or $2\pi r=n\lambda$ n= 1,2,3…….

Thus the allowed orbits are those in which the circumference of the orbit can contain exactly an integral number of de Broglie wavelengths. If the orbit circumference is not equal to an integer of the wavelength, overlapped will cancel each other and will be accompanying wave in this case is zero. This means that there is no electron orbit and is not available for an electron to exist in it(see fig.1.19).

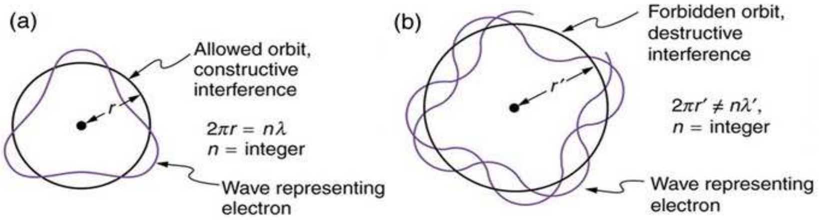


Fig (1.19)

One of the important applications of the Wilson-Sommerfeld quantization rules is to the case of a hydrogen atom in which it was assumed that the electron could move in elliptical orbits. Sommerfeld first evaluated the size and shape of the allowed elliptical orbits, as well as the total energy of an electron moving in such an orbit using the formulas of classical mechanics. Describing the motion in terms of the polar coordinates r and θ by applied the quantization rule to fined :

$$\oint L d\theta = n_\theta h$$

And $\oint P_r dr = n_r h$

1.11 CHECK YOUR PROGRESS

Q1.Apply Planck's radiation law, to derive; Wien's law; and Stefan's law (for black body radiation).

Q2. Explain Debye's model of a solid, and discuss the significance of vibrational modes and theirquantisation (phonons).

Q3. Use Debye's model to derive expressions for the heat capacity of a solid in the limits of low and high temperature.
Q4.Explain what was learned about quantization of radiation or mechanical system from two of the following experiments:
(a) Photoelectric effect.
(b) Black body radiation spectrum.
(c) Davisson-Germer experiment.
(d) Compton scattering.
Describe the experiments selected in detail, indicate which of the measured effects were non-classical and why, and explain how they can be understood as quantum phenomena. Give equations if appropriate.
Q5.(a) Show that the maximum of the Planck energy density (1.9) occurs for a wavelength of the form $\lambda_{\max} = b / T$, where T is the temperature and b is a constant that needs to be estimated.
(b) Use the relation derived in (a) to estimate the surface temperature of a star if the radiation it emits has a maximum intensity at a wavelength of 446 nm. What is the intensity radiated by the star? (6500 K, $1.0\text{x}10^8$ W/m^2)
(c) Estimate the wavelength and the intensity of the radiation emitted by a glowing tungsten filament whose surface temperature is 3300 K. (878.45 nm, $6.7\text{x}10^6$ W/m^2)

Q6. Discuss the Einstein's explanation of photoelectric effect .State the laws of photoelectric emission.

Q7.If the stopping potential of a metal when illuminated with a radiation of wavelength 480 nm is1.2V, find

(a) The work function of the metal,
(b) The cutoff wavelength of the metal, and
(c) The maximum energy of the ejected electrons.

Q8.Find the maximum Compton wave shift corresponding to a collision between a photon and a proton at rest.

Q9. Photons of wavelength 5 nm are scattered from electrons that are at rest. If the photons scatterat 60^0 relative to the incident photons, calculate
(a) The Compton wave shift,
(b) The kinetic energy imparted to the recoiling electrons, and
(c) The angle at which the electrons recoil.

Q10. A photon has the same wavelength as the Compton wavelength of an electron. What is the energy of the photon in eV ?
Q11. Find the smallest energy that a photon can have in order to be able to transfer half of its energy to an electron at rest (rest mass of an electron is 0.5 Mev) (Ans. 0.256 Mev)
Q12. A photon scatters from a proton, initially at rest. After the collision, the proton is found to scatter at an angle of 30 with the original direction of the incident photon with a kinetic

energy of 100 MeV.

Find (i)the initial energy of the photon and
(ii) the angle through it is scattered
(329Mev ,104^0)

Q13.A photon of wavelength 6000 nm collides with an electron at rest. After scattering, the wavelength of the scattered photon is found to change by exactly one Compton wavelength.

Calculate (i) the angle by which the photon is scattered, (ii) the angle by which the electron is scattered and (iii) the change in the energy of the electron due to scattering.

Q14.Using the Bohr model, find the speed, the radius, and the energy of the system in the case of circular orbits. Determine also the angular frequency of the radiation generated by a transition of the system from an energy state n to m.

Q.15.Positronium is the bound state of an electron and a positron; it is a short-lived, hydrogen-like atom where the proton is replaced by a positron.

(a) Calculate the energy and radius expressions, $E_n$and r_n.

(b) Estimate the values of the energies and radii of the three lowest states.

(c) Calculate the frequency and wavelength of the electromagnetic radiation that will just ionize the positronium atom when it is in its first excited state.

Q.16.What are the longest and shortest wavelengths in the Balmer and Paschen series for hydrogen?

Q.17.What is ultra-violet catastrophe ? How Plank's theory resolved it.

Q.18. Discuss Einstein theory of specific heat of solids.What are its shortcomings ?

Q.19. Discuss Debye theory of specific heat of solids.

Q.20. What is Wilson-Sommerfeldquantisation rule discuss in detail .

1.12 REFERENCES AND RELEVANT RESOURCES

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UNIT–2: BASICS OF QUANTUM MECHANICS

2.1 INTRODUCTION

The unit called « **Basics of quantum mechanics** » introduces De-Broglie hypothesis and experimental evidence of matter wave, phase and group velocity, Time dependent and independent Schrodinger wave equation, the concepts of the wave function. The statistical interpretation of the wave function and its properties .Then expectation values, Probability current density, Ehrenfest's theorem, Uncertainty principle and solving the Schrödinger equation for simple cases is also discussed.

2.2 LEARNING OBJECTIVES

After going through this unit, you will be able to:

- Understand the dual nature of matter and wave .
- Know the De-Broglie hypothesis and its experimental varification .
- Understand time dependent and independent Schrodinger wave equation.
- Understand the concept phase and group velocity of wave packet.
- Understand Physical significance wave function and its properties.
- Understand Probability current density.
- Drive and explain Ehrenfest's theorem
- Explain Uncertainty principle.

2.3 DUAL NATURE OF WAVE AND MATTER

There are some phenomenon involving light like photoelectric effect, Compton scattering etc which can be explained only on the particle nature of light. Whereas, some other phenomenon like Interference, diffraction, polarization etc. can be explained on the wave nature of light. This implies that light possess both the particle as well as wave nature.

Thus, phenomenon depicted by light can be classified into three categories

i. The phenomenon like photoelectric effect or Compton scattering which can be explained using particle character

ii. The phenomenon like diffraction or polarization, which can be, explained only using wave character.

iii. Phenomenon like refraction or refraction, which can be, explained either by particle or wave character.

2.3.1 DE BROGLIE HYPOTHISIS

In 1924, Lewis de-Broglie proposed that matter also has dual characteristic just like radiation. It means when the matter is moving it shows the wave properties (like interference, diffraction etc.) are associated with it and when it is in the state of rest then it shows particle properties. Thus the matter has dual nature. The waves associated with moving particles are matter waves or de-Broglie waves.

2.3.2 WAVELENGTH OF DE-BROGLIE WAVES

Consider a photon whose energy is given by $E=h\upsilon=hc/\lambda$ ……………………… (1)

If a photon possesses mass (rest mass is zero), then according to the theory of relatively,its energy is given by

$E=mc^2$ ……………………(2)

From (1) and (2) ,we haveMass of photon $m= h/c\lambda$Therefore Momentum of photon $p=mc=hc/c\lambda=h/\lambda$ ……………… (3)

Or $\lambda = h/p$

If instead of a photon, we consider a material particle of mass m moving with velocity v,then the momentum of the particle, p=mv. Therefore, the wavelength of the wave associated with this moving particle is given by:

Or $\lambda = h/p$ (But here $p = mv$)

$\lambda =h/mv$ ………………… (4)

If E is the kinetic energy of the material particle of mass m moving with velocity v,then

$E=1/2\ mv^2=1/2\ m^2v^2=p^2/2m$

Or $p=\sqrt{2mE}$

Therefore the by putting above equation in equation (4), we get de-Broglie wavelength equation for material particle as:

$\lambda = h/\sqrt{2mE}$ ………… (5)

2.4 EXPERIMENTAL EVIDENCES OF MATTER WAVE:

2.4.1 DAVISSON AND GERMER EXPERIMENT

In 1927 C. J. Davisson and L. H. Germerset an experiment to observe diffraction of electrons from the surface of a solid crystal. by this experiment they demonstrated that de-Broglie wave is associated with the moving electron ie it is a solid experimental confirmation of De Broglie's hypothesis of 'Matter Waves'.

The experimental set-up is consists of an electron gun. It was directed to strike normally on the (1,1,1) face of a nickel crystal. Electrons were scattered in all directions from the nickel crystal which was held fixed throughout the experiment. Scattered electrons were collected in a movable detector mounted on an arc which could be rotated through an angle about an axis passing through the point of incidence of electrons on the crystal. The detector was adjusted at different angles for collecting electrons and the electric current was recorded for each setting of accelerating voltages . The electric current was directly proportional to the number of scattered electrons per second collected in the detector.

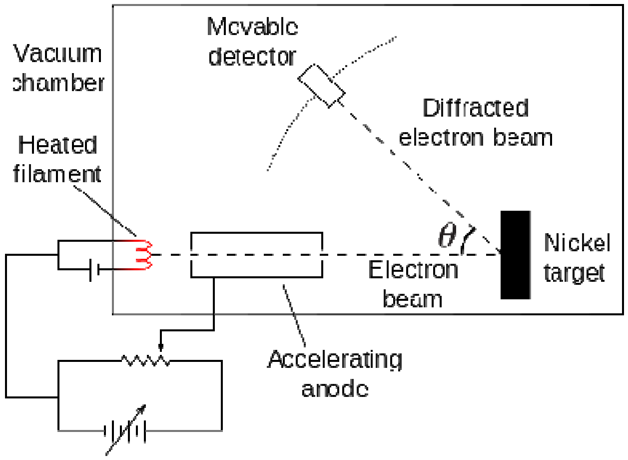


Fig (2.1)

The intensity of scattered electrons was obtained at different scattering angle φ. Different sets of observations were taken corresponding to fixed potential differences (e.g. from 40V to 68V). Polar graphs are plotted between the intensity (I) of scattered electron and the latitude angle Θ for different accelerating voltages. From the graphs it is clear that the intensity of scattered beam is maximum for Θ = 50^0 at 54 volt.

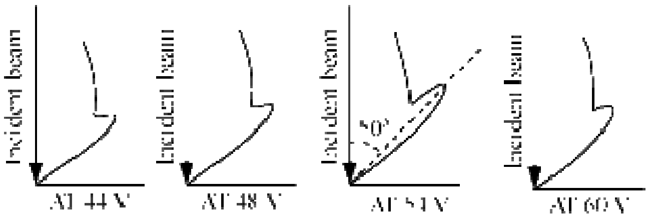


Fig (2.2)

The peak indicates that the waves associated with the moving electrons scattered by the periodic arrangement of atoms in the crystal interfere constructively. It is similar to Bragg reflections of X rays from atoms in the crystal and confirms the wave-like behavior of electrons. for an single electron the pattern of electron scattering is same as that of the electron beam. It indicates that different portions of the wave associated with a single electron are scattered from different parts of the crystal and interfere constructively to produce the peak.

2.4.2 MATHEMATICAL ANALYSIS

According to de Broglie hypthisis , The de Broglie wavelength λ of matter waves of moving electrons having mass m and momentum p=mv is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The velocity **v** of electrons due to the potential difference V can be obtained from kinetic energy (non relativistic kinetic energy) of the electron is :

$$\frac{p^2}{2m} = eV \text{ gives } p = \sqrt{2meV} \quad \ldots\ldots\ldots\ldots\ldots.. (2)$$

Hence

$$\lambda = \frac{h}{\sqrt{2meV}} = \frac{12.27}{\sqrt{V}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

V=54V gives $\lambda = 0.167nm$

The experimental value of λ is calculated as follows

The interplanar spacing d of the crystal measured by X-ray scattering comes to be equal to 0.091 nm.the angle of scattering of electrons $\theta = 50^0$

Corresponding to the scattering angle of 50^0, the angle ϕ in the Bragg's law is given by

$$\phi = 90^0 - \theta / 2 = 65^0 \ldots\ldots\ldots\ldots\ldots.. (4)$$

The wavelength of electrons is calculated using Bragg's Law $2d \sin\phi = n\lambda$

d is the spacing between lattice planes

λ is the Wavelength of matter waves associated with electrons

$2d \sin\phi = n\lambda$

nλ = 2 x 0.091 x sin 65^o

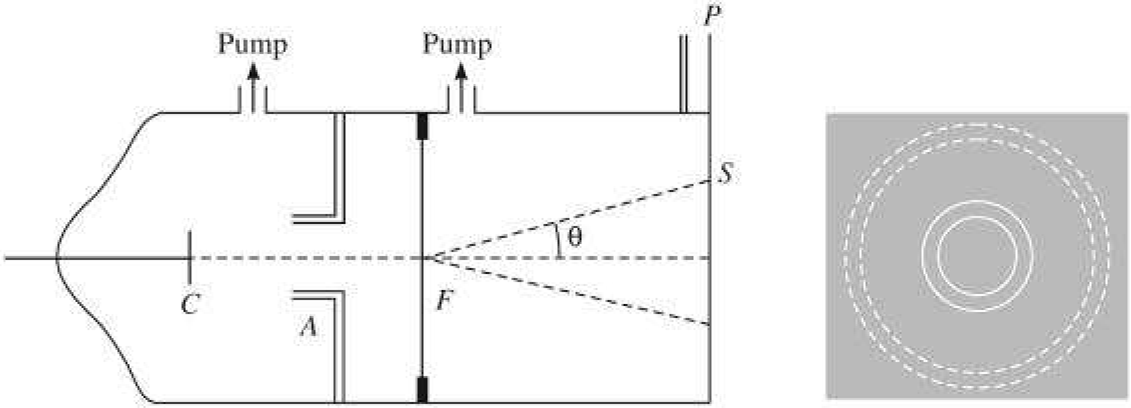
λ = 0.165 nm (for n=1)

The experimental value agrees very well with the theoretical value of the wavelength of electrons. Thus the experiment gives confirmation to the de Broglie's hypothesis.

2.4.3 THOMSON EXPERIMENT

After the experiments on diffraction of electrons by C. J. Davisson and L. H. Germer, G. P. Thomson also replicated the experiment on electron diffraction in 1927.

Electrons from an electron gun were accelerated towards a thin, rolled foil of gold. After passing through the hole in the gold foil, the electron beam was received on a photographic plate placed perpendicular to the direction of the beam. The diffraction pattern was in the form of continuous, concentric, alternate black and white rings as diffraction was due to the crystalline grains which were randomly oriented at all possible angles in the gold foil. Thus transmission of electrons through a thin foil of a polycrystalline material was studied.



Thomson's experiment

a) G. P Thomson's apparatus for electron diffraction

b) Diffraction pattern of a beam of electrons by thin gold foil

Fig (2.3)

The diffraction rings on the photographic plate had narrowly defined radii and always seemed to occur in multiples i.e. circles of radii $2r, 3r\ldots\ldots$ They were similar to the sharply defined principle maxima of the intensity pattern for N-slits. Here the planes of atoms in the crystal act as slits. The radii of the different sets of rings were found to correspond precisely to the spacing of the various planes of atoms. Electrons were scattered at different angles from the atoms of crystallites and produced interference pattern with maxima corresponding to those angles satisfying the Bragg condition. In terms of the probabilistic interpretation of matter waves, the probability of finding an electron scattered at an angle θ is exactly equal to computed intensity pattern of interfering waves associated with electron beam.

The diffraction pattern due to polycrystalline material was similar to the powder diffraction pattern of X-rays having wavelength equal to the de Broglie wavelength of electrons. The wavelength of electrons was varied by changing the incident energy of the electrons, then diameters of the diffraction rings changed proportionately according to the Bragg's equation.

The diffraction pattern due to electrons was similar to the Debye-Scherrer diffraction pattern due to X-rays.

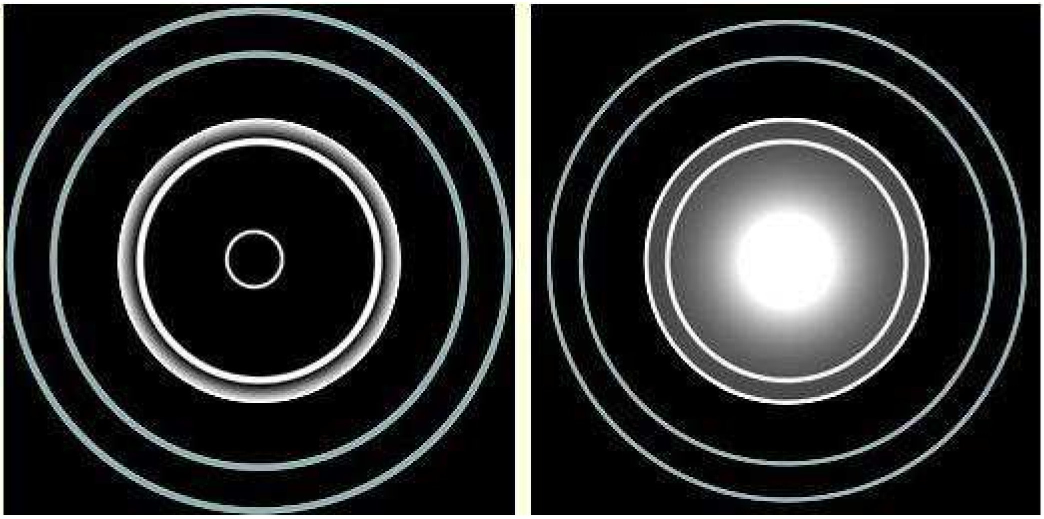


Fig.(2.4)

When crystalline sample of aluminium was used, the diffraction pattern changed to spots lying around a ring-like structure.

For Aluminium, the spacing between atomic planes d=2.34 Å..

According to the N-slit interference formula, the n-th order principle maximum occurs at angle   Bragg's condition is

$2d\sin\theta = n\lambda$ ………………….. (1)

$\mathit{Wavenumberk} = 2\pi / \lambda$

$k = 2\pi / d\sin\theta$ for n=1 (i.e. the first-order principle maximum).

From the experimental observations it is found that k depends on the voltage V as

$k \propto V^{1/2}$…………………… (2)

For electron having mass m, velocity v, the momentum p in potetial V is given by

Kinetic Energy   the relations are

$p = \sqrt{2meV}$.

$p \propto V^{1/2}$ ……………………. (3)

Momentum p is controlled by the voltage V

Thus momentum p and wave number k both are proportional to $V^{1/2}$

Since $k = p / \hbar$

This is the relation between two intrinsic properties k and Momentum p of electrons.

By substituting the values for the constants m,e and using the relation

$\hbar = p / k$,Value of the proportionality constant $\hbar$ comes out to be about 1×10^{-34} J s

This value is quite close to the official value of $\hbar$ which is a universal constant of nature known as reduced Planck's constant and given by

$\hbar = 1.005 \times 10^{-34} J.s$

Thus the de Broglie's relation and his hypothesis of matter waves are verified.

G.P. Thomson and C. J. Davisson shared the Nobel Prize in 1937 for Their experiments proved independently the wave-like behavior of electron (i.e. matter) and confirmed quantitatively the de Broglie hypothesis of matter waves. These experiments proved that de Broglie's waves are not just mathematical tools, but exhibit real physical effects which can be observed in the laboratory.

2.5 THE SCHRÖDINGER EQUATION

Schrödinger developed his equation after his prior attempts to explain with de Broglie's relation the Bohr model at a more fundamental level failed.

The one-dimensional wave equation is

$$\frac{\partial \Psi}{\partial t} = \gamma \frac{\partial^2 \Psi}{\partial x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The wave equation has solutions of the form $\cos(kx \pm \omega \cdot t)$, $\sin(kx \pm \omega \cdot t)$, and $e^{\pm i(kx - \omega \cdot t)}$. These are all traveling harmonic waves, where the *wave number* is $k = \frac{2\pi}{\lambda}$ and the angular frequency is $\omega = 2\pi \cdot f$.

Taking $\Psi = Ae^{\pm i(kx - \omega \cdot t)}$. Then the derivatives are

$$\frac{\partial \Psi}{\partial t} = \pm i\omega \, \Psi \text{ and} \frac{\partial^2 \Psi}{\partial x^2} = \pm k^2 \Psi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Evidently,

$$\frac{\partial \Psi}{\partial t} = \frac{i\omega}{k^2} \frac{\partial^2 \Psi}{\partial x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Whence we can identify $\gamma = \frac{i\omega}{k^2}$.

For a *free particle*, $E = \frac{p^2}{2m}$, just the kinetic energy. We can express this in terms of the frequency and wave number, since $E = \hbar\omega$ and $p = \frac{2\pi\hbar}{\lambda} = \hbar k$: $\hbar\omega = \frac{\hbar^2 k^2}{2m}$.

Solving for the frequency, we obtain what is called a *dispersion relation*.

$$\omega = \frac{\hbar k^2}{2m}$$

If we substitute this for ω in the wave equation, we obtain the following:

$$\frac{\partial\Psi}{\partial t} = \frac{i\hbar k^2}{k^2}\frac{\partial^2\Psi}{\partial x^2} = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} \quad \text{…………….} \ (4)$$

If we multiply and divide the r.h.s. by $i\hbar$, we can see that the r.h.s. is just the momentum operator squared, divided by $2m$.

$$\frac{\partial\Psi}{\partial t} = \frac{i\hbar}{i\hbar}\frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{i\hbar 2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2\Psi$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \quad \text{……………} \ (5)$$

The left hand side (l.h.s.) must be the total energy operator, $\hat{E} = i\hbar\frac{\partial}{\partial t}$, since for a free particle, the total energy is the kinetic energy.

For a conservative force acting on a particle, $F_x = -\frac{\partial V(x,t)}{\partial x}$, where $V(x,t)$ is the potential energy function.

We'll just add it to the kinetic energy operator on the r.h.s. of the wave equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right]\Psi$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x,t)\Psi\right] \quad \text{…………….} \ (6)$$

This equation is known as the *Time Dependent Schrödinger Equation*. This equation tells us how the initial information about the system changes with time according to a particular physical circumstance that a system finds itself in. The solution of this equation gives us the wave function as the time passes in a particular physical situation.

2.5.1 SOLUTION OF THE TIME DEPENDENT SCHRÖDINGER EQUATION

Let us say that V is independent of time. The potential energy function is constant.

Assume that $\Psi(x,t)=\psi(x)f(t)$. Substitute into the Schrödinger equation. The partial derivatives become $\frac{\partial\Psi}{\partial t}=\psi\frac{df}{dt}$ and $\frac{\partial^2\Psi}{\partial x^2}=f\frac{d^2\psi}{dx^2}$.

$$i\hbar\psi\frac{df}{dt}=-\frac{\hbar^2}{2m}f\frac{d^2\psi}{dx^2}+V(x)\cdot\psi\cdot f \quad \text{.................. (1)}$$

Divide both sides by $\psi\cdot f$.

$$\frac{i\hbar}{f}\frac{df}{dt}=-\frac{\hbar^2}{2m\psi}\frac{d^2\psi}{dx^2}+V(x) \quad \text{............... (2)}$$

The two sides must equal the same constant, namely the total energy, *E*.

$$i\hbar\frac{df}{dt}=Ef \quad \text{................. (3)}$$

And

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi \quad \text{.................... (4)}$$

It is called timeIndependent, steady-state or stationary Schrödinger equation in one dimensions

if we have an arbitrary potential energy function V(x) there are no explicit analytical solutions to this equation.

From

$$i\hbar\frac{df}{dt}=Ef$$

$$f(t)=e^{-\frac{iEt}{\hbar}} \quad \text{………………..} \ (5)$$

This is an oscillatory solution, as we always get with a wave equation.in this equation E is the total energy, which we can normalize to be the kinetic energy plus the potential energy. Hence solution of the time-dependent Schrodinger equation is written as

$$\Psi(x,t)=\psi(x)f(t)=\psi(x)e^{-\frac{iEt}{\hbar}} \quad \text{………………….} \ (6)$$

This wave function gives complete information about the position, momentum and energy of a particle at any time. Since superposition principle assert that any linear combination of various solutions will also be a valid solution. applying superposition principle on a particle that can be in any one of the infinitely many discrete positions, the most general solution to the time-dependent Schrodinger equation can be written as

$$\Psi(x,t)=\sum_{n=1}^{\infty}a_n\psi_n(x)e^{-\frac{iE_nt}{\hbar}} \quad \text{…………………….} \ (7)$$

It is clear that the probability density. $|\Psi(x,t)|^2=\Psi^*\Psi=\psi^*e^{+\frac{Et}{\hbar}}\cdot\psi e^{-\frac{Et}{\hbar}}=|\psi(x)|^2$. This is constant in time, therefore it is called a *stationary state*. A stationary state has a definite total energy; the uncertainty $\Delta E=0$.

2.6 WAVE FUNCTION

We propose to describe the motion or state of a particle by a *wave function*—a solution to a *wave equation*.

2.6.1 STATISTICAL INTERPRETATION OF THE WAVE FUNCTION

The wave function is a complex function of position (x) and of time (t), denoted $\Psi(x,t)$. it contains a complete description of the behavior of a particle, such as an electron. In quantum Mechanics the state of particle is describes by a wave function $\psi(\vec{r},t)$.

So, $\psi(\vec{r},t)$ describes the wave properties of particle. 1927 Born interpreted $|\psi|^2$ as the probability density and $|\psi(\vec{r},t)|d^3r$ as probability, $dp(\vec{r},t)$of finding a particle at the time t in the volume element located between $\vec{r}$ and$\vec{r}\ +d\vec{r}$.

$$|\psi(\vec{r},t)|^2\, d^3r \;=\; dp(\vec{r},t)$$

Where $|\psi|^2$has dimension of$[\text{Length}]^{-3}$? Thus, the total probability of finding the particle somewhere in space must be equal to one.

$$\int |\psi(\vec{r},t)|^2\, d^3r \;=\; 1$$

2.6.2 PHYSICAL INTERPRETATION OF THE WAVE FUNCTION

In the beginning it was considered that the wave function ψ is just an auxiliary mathematical quantity to facilitate computation relative to experimental results. It is true to certain extent in certain cases:

In calculating the intensity of waves scattered by a crystal in direction of the detector; but it does not seem reasonable to introduce an isolated mathematical function without inquiring into its physical significance. Schrodinger himself attempted the physical interpretation of ψ in terms of charge density. If ψ is the amplitude of matter wave at any point in space then, the particle density must be proportional to ψ^2. Thus $|\psi|^2$is measure of charge density. Usually $\psi^*\psi$ is written instead of $|\psi|^2$, where is the complex conjugate of ψ.

This interpretation was finding to lead very satisfactory result, when wave mechanics applied to the distribution of photon (electron), intensity distribution in Compton scattering, the stable state of Bohr atom or emission of spectral line. But difficulty arises when we talk about flight of electron. To remove this difficulty another physical interpretation of the wave function generally accepted at present, was suggested by Max-Born in 1926 and then developed by Bohr Dirac, Heisenberg and others. According to this view $\psi\psi^* = |\psi|^2$ represent probability density of particle in the state ψ .the p [probability of finding the particle in volume element $d\tau = dxdydz$ about point r at time t expressed as:

$$P(r)\, d\tau = |\psi(r, t)|^2\, d\tau$$

Ψ sometimes called probability amplitude for the position of particle; the postulates suggested by born show that the Quantum mechanical laws and result of their measurement can be interpretened on the basis of probability consideration.

conditions for physical acceptability of a wave function are :
(1) A well behaved wave function always obeys the Schrodinger equation.
(2) It must be finite, single-valued and continuous everywhere.
(3) The partial derivatives of the wave function must also be finite, single-valued and continuous everywhere.

2.6.3 NORMALIZATION

The probability of finding the particle someplace must be 1, therefore,

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 dx = 1.0$$

if the wave function is to represent a physically realistic particle. That is, a wave function must be *normalizable*. This boils down to the requirement that $\Psi(x,t) \to 0$ as $|x| \to \infty$. Some wave functions satisfy the wave equation but are not normalizable.

2.6.4 EXPECTATION VALUES

To relate a quantum mechanical calculation to something you can observe in the laboratory, the "expectation value" of the measurable parameter is calculated.Imagine a large number of identical but independent regions in space. In each region is a particle described by the wave function, $\Psi(x,t)$. The particles and wave functions are identical. In each of these identical systems we measure the position of the particle, x. The average of all the independent measurements of x is

$$< x >= \int_{-\infty}^{+\infty} \Psi^* x \Psi dx = \int_{-\infty}^{+\infty} x |\Psi|^2 dx .$$

This is called the *expectation value* of x. Note that this is not the most probable value of x. That occurs where $|\Psi|^2$ is a maximum. The variance of the measurements of x is

$$\sigma^2 =< x^2 > - < x >^2 .$$

EXAMPLE :let us calculate expectation value <x> and <p> for the ground state wave function in the infinite square well

Since the normalized wave function for the 1-D infinite square well is given by

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L}, \underline{\qquad\qquad} \qquad n = 1,2,3,...$$

As there is no i, the conjugate complex function has the same form and the ψ^2 are simply

$$\psi_n^2 = \frac{2}{L}\sin^2\frac{n\pi x}{L}, \underline{\qquad\qquad} \quad n = 1,2,3,...$$

So the integral becomes

$$< x >= \int_{-\infty}^{\infty} x\,\psi(x)^*\,\psi(x)\,dx = \frac{2}{L}\int_0^L x\,(\sin\frac{n\pi x}{L})(\sin\frac{n\pi x}{L})\,dx$$

$$< x >= \frac{2}{L}\int_0^L x\cdot\sin^2\frac{n\pi x}{L}\,dx = \frac{2}{L}[\frac{x^2}{4} - \frac{x\,\sin(\frac{2n\pi x}{L})}{\frac{4n\pi}{L}} - \frac{\cos(\frac{2n\pi x}{L})}{8(\frac{n\pi}{L})^2}]_0^L$$

Since sin (nπ) = 0, cos (2nπ) = 1 and cos 0 = 1, for all values of n the expectation value of x is

$$< x >= \frac{2}{L}(\frac{L^2}{4}) = \frac{L}{2}$$

In all quantum states, the arithmetic mean position of the particle is in the middle of the box.

For n = 2,4,6 the "average" position is also $^L/_2$ and this has nothing to do with $\psi^2 = 0$ the probability density of finding the particle there

$$< p >= \int_0^L \sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L})(\frac{\hbar}{i}\frac{\partial}{\partial x})\sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L})\,dx$$

Simplifies to

$$< p >= \frac{\hbar}{i}\frac{2}{L}\frac{\pi}{L}\int_0^L \sin(\frac{\pi x}{L})\cos(\frac{\pi x}{L})\,dx = 0$$

This is of course because sin x = 0 at the nodes.so the expectation value <p> is zero, what does it mean, simply the particle is just as likely moving to the right as it is moving to the left, the arithmetic mean must, thus, give zero.

2.7 PROBABILITY CURRENT DENSITY

The state of a system is described by the wavefunction $\Psi(\vec{r},t)$. this wavefunction is a solution of the time dependent Schrodinger wave equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=H\,\Psi(\vec{r},t), \qquad (1)$$

Where *H* is a differential operator called the Hamiltonian. For a single particle of mass *m* moving in a scalar potential energy field $V(\vec{r},t)$, the Hamiltonian is

$$H=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\vec{r},t)=-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r},t)\ \ldots. \qquad (2)$$

And the normalization condition (probability of finding the particle is one) is

$$\int_V \Psi(\vec{r},t)^*\,\Psi(\vec{r},t)\,dV=1.\ \ldots\ldots\ldots\ldots\ldots(3)$$

The probability density ρ associated with the single particle is

$$\rho(\vec{r},t)=\Psi(\vec{r},t)^*\,\Psi(\vec{r},t)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

The probability that the particle is in the finite volume τ

$$P=\int\rho(\vec{r},t)=\int\Psi(\vec{r},t)^*\,\Psi(\vec{r},t)d\tau\ \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ (5)$$

The time rate of change of this probability is

$$\frac{\partial P}{\partial t}=\int\left(\frac{\partial\Psi^*}{\partial t}\Psi+\Psi^*\frac{\partial\Psi}{\partial t}\right)d\tau\ \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (6)$$

The time dependent Schrodinger wave equation is

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t)=-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t)+V\Psi(r,t)\ \ \mathbf{\ldots\ldots..\ (7)}$$

Gives

$$\frac{\partial}{\partial t}\Psi(r,t)=\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t)+V\Psi(r,t)\right)\text{ …….. (8)}$$

Taking complex conjugate of eq (7)

$$-i\hbar\frac{\partial}{\partial t}\Psi^*(r,t)=-\frac{\hbar^2}{2m}\nabla^2\Psi^*(r,t)+V\Psi^*(r,t)\text{ ……… (9)}$$

Hence

$$\frac{\partial}{\partial t}\Psi^*(r,t)=-\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi^*(r,t)+V\Psi^*(r,t)\right)\text{ ….. (10)}$$

Substituting eq 8 and 10 in following expression

$$\frac{\partial\Psi^*}{\partial t}\Psi+\Psi^*\frac{\partial\Psi}{\partial t}=\frac{i\hbar}{2m}\left(\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right)\text{ …… (11)}$$

$$=\frac{i\hbar}{2m}\nabla\square\left(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*\right)\text{ ……… (12)}$$

Considering $j=\frac{i\hbar}{2m}\left(\Psi\nabla\Psi^*-\Psi^*\nabla\Psi\right)$ as current probability density

$$\int\left(\frac{\partial\Psi^*}{\partial t}\Psi+\Psi^*\frac{\partial\Psi}{\partial t}\right)d\tau=-\int\nabla.j\,d\tau\text{ ……………….. (13)}$$

From above

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial t}\int\rho\,d\tau=-\int\nabla.j\,d\tau\text{ …………….. (14)}$$

Gives $$\frac{\partial\rho}{\partial t}+\nabla j=0$$

This equation expresses the conservation of probability density.In quantum mechanics, a particle does not have a definite location. Instead, it is considered to be located over all space as defined by the probability densityρ=ψ∗ψ . J is the probability current density. This gives the rate at which the probability density of the particle is moving at any point in space.

2.8 EHRENFEST THEOREM :

Suppose that ψ(x,t) is a state function representing a one dimensional wave packet . So the time rate of change of the expectation value of position x is

$$\frac{d}{dt}< x >=\frac{d}{dt}\int \Psi^{*} x\Psi d\tau \text{ ……………… (1)}$$

$$=\int \Psi^{*} x\frac{\partial \Psi}{\partial t}d\tau+\int \frac{\partial \Psi^{*}}{\partial t}x\Psi d\tau \text{ ……. (2)}$$

Using the time dependent Schrodinger wave equation

$$i\hbar\frac{\partial}{\partial t}\Psi=-\frac{\hbar^{2}}{2m}\nabla^{2}\Psi+V\Psi \text{ ……………… (3)}$$

We get

$$\frac{\partial}{\partial t}\Psi=\frac{1}{i\hbar}\left(-\frac{\hbar^{2}}{2m}\nabla^{2}\Psi+V\Psi\right) \text{ …………… (4)}$$

Similarly the complex conjugate of the time dependent Schrodinger wave equation gives

$$\frac{\partial}{\partial t}\Psi^{*}=-\frac{1}{i\hbar}\left(-\frac{\hbar^{2}}{2m}\nabla^{2}\Psi^{*}+V\Psi^{*}\right) \text{ ……………….. (5)}$$

Substituting eq (4) and(5) in eq (2), we have

$$\frac{d}{dt}< x >=\int \Psi^{*} x\left\{\frac{1}{i\hbar}\left(-\frac{\hbar^{2}}{2m}\nabla^{2}\Psi+V\Psi\right)\right\}d\tau+\int\left\{-\frac{1}{i\hbar}\left(-\frac{\hbar^{2}}{2m}\nabla^{2}\Psi^{*}+V\Psi^{*}\right)\right\}x\Psi d\tau \text{ …….. (6)}$$

Solving and arranging it we get

$$\frac{d}{dt}< x >=-\frac{\hbar}{2im}\int \Psi^{*} x\left\{\nabla^{2}\Psi\right\}d\tau+\frac{\hbar}{2im}\int\left\{\nabla^{2}\Psi^{*}\right\}x\Psi d\tau \text{ ………… (7)}$$

Integrating the second integral by parts

$$\int\left\{\nabla^{2}\Psi^{*}\right\}x\Psi d\tau=\int \Psi^{*}\nabla^{2}\left\{x\Psi\right\}d\tau \text{ …………………………. (8)}$$

Putting it in equation (7)

$$\frac{d}{dt}< x >=-\frac{\hbar}{2im}\int \Psi^{*}\left\{x\nabla^{2}\Psi-\nabla^{2}(x\Psi)\right\}d\tau \text{ ………………… (9)}$$

Since

$$x\nabla^2\Psi - \nabla^2(x\Psi) = -2\frac{\partial\Psi}{\partial x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (10)$$

Hence eq (9) reduced to

$$\frac{d}{dt} < x > = \frac{1}{m}\int \Psi^* \left\{ -i\hbar\frac{\partial\Psi}{\partial x} \right\} d\tau = \frac{1}{m} < p_x > \quad \ldots\ldots\ (11)$$

Generalisation of which gives $\frac{d}{dt} < r > = \frac{1}{m} < p >$ …………………… (12)

Now the time rate of change of expectation of p_x

$$\frac{d}{dt} < p_x > = \frac{d}{dt}\int \Psi^* \left\{ -i\hbar\frac{\partial\Psi}{\partial x} \right\} d\tau \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (13)$$

$$= -i\hbar\left(\int \Psi^* \frac{\partial}{\partial x}\left\{ \frac{\partial\Psi}{\partial t} \right\} d\tau + \int \frac{\partial\Psi^*}{\partial t}\frac{\partial\Psi}{\partial x} d\tau \right) \quad \ldots\ldots\ldots\ldots\ (14)$$

Substituting eq (4) and(5) in eq (14), we have

$$\frac{d}{dt} < p_x > = \int \Psi^* \left\{ \frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \right) \right\} d\tau + \int (-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^*)\frac{\partial\Psi}{\partial x} d\tau \quad \ldots\ldots.(15)$$

Solving it we have

$$\frac{d}{dt} < p_x > = \int \Psi^* \left(\frac{\partial V}{\partial x} \right) \Psi d\tau \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (16)$$

Or in general

$$\frac{d}{dt} < p > = < -\nabla V > \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (17)$$

We recognize it as **Newton's second law**. This is an example of the **correspondence principle**, the result manifests as Newton's second law in the case of having so many particles that the net motion is given exactly by the expectation value of a single particle.

2.9HEISENBERG UNCERTAINITY PRINCIPLE

This principle is direct result of Dual nature of particle .According to classical mechanics a moving particle has a definite momentum occupies a definite position, it is also possible to determine both its velocity and position (momentum). Therefore if the initial coordinates position $\vec{r}$(t) and velocity$\vec{v}$(t) and all force acting on the particle are known then the position $\vec{r}$(t) and velocity$\vec{v}$(t) are uniquely determine by the means of Newton's second law. In recent it is clear that the classical view is based on the approximation which is valid for the object of noticeable size. It does not describe the behavior of atomic dimensions.

In quantum mechanics it is described by wave packets which represent all about particle and move with group velocity. According to Born's probability "the position of the particle is uncertain with the limits of wave packets". It is impossible to know where within the wave packet the particle is and what is the exact velocity or momentum.

For large wave packets with many crests the velocity spread is very small. So the particle velocity can be easily determined but the position of particle is very uncertain.

For small wave packets the position can be more or less fixed, but the velocity spread is very large. Thus the velocity of particle remains uncertain.

For infinitely large wave packet the velocity becomes certain but the position becomes completely uncertain.

For infinitely small wave packet the position becomes certain but the velocity becomes quite uncertain.

Hence it is impossible to determine simultaneously both the position and the momentum of the particle with accuracy.

2.9.1 STATEMENT OF UNCERTAINTY PRINCIPLE

The product of uncertainty in position and momentum of particle is approximately equal to a no. of other ħ.

$\Delta p.\Delta q \approx \hbar$ ……………….1

Where, $\hbar = h/2\pi$

Δp = Uncertaininty in determining position

Δq = Uncertainity in determining velocity

According to above relation smaller is the value of Δq more exactly we can determine the position. Larger the value of Δ p, less exactly we can determine the momentum and velocity. That is, it is impossible to determine simultaneously both the position and momentum of particle accurately.

This relation holds for all canonical conjugates physical quantities. Such as position and momentum, energy and time, angular momentum and angle etc.
Thus similarly,

$\Delta E.\Delta t \approx \hbar$ …………………2

$\Delta J.\Delta\theta \approx \hbar$ ……..……………3

The product of uncertainties in determining the position and momentum of a particle can never be smaller than the no. of order ½ ħ.

Equation 1 becomes

$$\Delta p.\Delta q \geq \frac{1}{2}\hbar$$

$$\Delta E.\Delta t \geq \frac{1}{2}\hbar$$

$$\Delta J.\Delta\theta \geq \frac{1}{2}\hbar$$

Examples of position momentum uncertainity

1) Heisenberg gamma ray microscope
2) Diffraction of a beam of electrons by a slit

Application of uncertainty principle

1) The existence of the electron in the nucleus.
2) The radius of Bohr's first orbit.
3) Light quanta
4) Bohr's atomic energy levels and uncertainty principle.
5) Minimum energy of harmonic oscillator.
6) Energy of particle in one-dimensional box.

2.10HARMONIC OSCILLATOR PROBLEM

Harmonic oscillator is a particle which is bound to an equilibrium position by a force which is proportional to the displacement from that position **.** *The potential for the harmonic ocillator is the natural solution for every potential with small oscillations at the equilibrium . Harmonic motion is one of the most important examples of motion in all of physics because almost all potentials in nature have small oscillations at the equilibrium , including many systems studied in quantum mechanics. so the study of harmonic motion plays a fundamental role as a stepping stone towards more rigorous applications.*
The classical potential for a harmonic oscillator is derivable from Hooke's law. It is conventionally written:

$$V(x)=\frac{1}{2}kx^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Hamiltonian

$$E=T+V=\frac{1}{2}mv^2+\frac{1}{2}kx^2 \qquad \ldots\ldots\ldots\ldots.. \quad (2)$$

Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi=E\psi$$

The total energy operator is called the *Hamiltonian*: $\hat{H}\psi = E\psi$.

2.10.1 SOLUTION: THE ANALYTICAL METHOD

Asymptotic behavior of ψ

$$\left(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}m\omega^2x^2\psi=E\psi\right)\cdot\left(-\frac{2m}{\hbar^2}\right)$$

$$\frac{d^2\psi}{dx^2}-\frac{m^2\omega^2x^2}{\hbar^2}\psi=-\frac{2mE}{\hbar^2}\psi$$

$$\frac{d^2\psi}{dx^2}=\left(\frac{m^2\omega^2}{\hbar^2}x^2-\frac{2mE}{\hbar^2}\right)\psi \qquad \ldots\ldots\ldots\ldots\ldots\ldots. (3)$$

If $x\rightarrow\infty$, then $\frac{d^2\psi}{dx^2}\approx\frac{m^2\omega^2}{\hbar^2}x^2\psi$, which has solutions of the form

$$\psi(x) = Ae^{-\frac{m^2\omega^2}{2\hbar^2}x^2} + Be^{\frac{m^2\omega^2}{2\hbar^2}x^2} \text{ ……………….. (4)}$$

$B = 0$ because that term diverges as $x \to \infty$. So, let us propose that

$$\psi(x) = h(x)e^{-\frac{m^2\omega^2}{2\hbar^2}x^2} \text{ …………… (5)}$$

By substituting the assumed ψ into the Schrödinger equation, and making a change of variable, we'll produce a differential equation for that unspecified function, $h(x)$.

Let $y = \sqrt{\frac{m\omega}{\hbar}}\, x$.

Then $\psi(y) = h(y)e^{-\frac{m\omega}{2\hbar}y^2}$.

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

$$\frac{m\omega}{\hbar}\frac{d^2\psi}{dy^2} = \left(\frac{m\omega}{\hbar}y^2 - \frac{2mE}{\hbar^2}\right)\psi \text{ ………………… (6)}$$

The first and second derivatives of ψ with respect to y are

$$\frac{d\psi}{dy} = \frac{d}{dy}\left(he^{-\frac{y^2}{2}}\right) = e^{-\frac{y^2}{2}}\frac{dh}{dy} - hye^{-\frac{y^2}{2}} = \left(\frac{dh}{dy} - hy\right)e^{-\frac{y^2}{2}}$$

$$\frac{d^2\psi}{dy^2} = e^{-\frac{y^2}{2}}\left(\frac{d^2h}{dy^2} - y\frac{dh}{dy} - h\right) - \left(\frac{dh}{dy} - yh\right)ye^{-\frac{y^2}{2}}$$

$$= \left(\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (y^2 - 1)h\right)e^{-\frac{y^2}{2}} \text{ ………… (7)}$$

The $e^{-\frac{y^2}{2}}$ divides out, so we have an equation for the $h(y)$.

$$\frac{m\omega}{\hbar}\left(\frac{d^2h}{dy^2}-2y\frac{dh}{dy}+(y^2-1)h\right)=\left(\frac{m\omega}{\hbar}y^2-\frac{2mE}{\hbar^2}\right)h$$

$$\frac{d^2h}{dy^2}-2y\frac{dh}{dy}+(y^2-1)h=y^2h-\frac{2E}{\hbar\omega}h$$

$$\frac{d^2h}{dy^2}-2y\frac{dh}{dy}+(\kappa-1)h=0 \qquad \ldots\ldots\ldots (8)$$

Where we have set $\kappa=\frac{2E}{\hbar\omega}$.

Solution of the Sturm-Liouville equation

The standard tack is to assume a series solution:

$$h(y)=a_o+a_1y+a_2y^2+a_3y^3+\cdots . \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Put this into the S-L equation, and we obtain a recursion relation for the coefficients. We'd like to have all the sums start at the same place, as well.

$$\frac{dh}{dy}=\sum_{j=1}^{\infty}ja_jy^{j-1}=\sum_{j=0}^{\infty}(j+1)a_{j+1}y^j$$

$$\frac{d^2h}{dy^2}=\sum_{j=2}^{\infty}j(j-1)a_jy^{j-2}=\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}y^j$$

$$y\sum_{j=1}^{\infty}ja_jy^{j-1}=\sum_{j=1}^{\infty}ja_jy^j=\sum_{j=0}^{\infty}(j+1)a_{j+1}y^{j+1} \qquad \ldots\ldots\ldots\ldots (10)$$

$$\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}y^j-2\sum_{j=0}^{\infty}(j+1)a_{j+1}y^{j+1}+(\kappa-1)\sum_{j=0}^{\infty}a_jy^j=0 \qquad \ldots\ldots (11)$$

Collect the coefficients of y^j and set equal to zero.

$$(j+2)(j+1)a_{j+2}-2ja_j+(\kappa-1)a_j=0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Solve for

$$a_{j+2}=\frac{2j+1-\kappa}{(j+2)(j+1)}a_j . \quad \ldots\ldots\ldots\ldots\ldots (13)$$

This result is a recursion relation for two sequences of coefficients. Namely

$\{a_0,a_2,a_4,\ldots\}$and $\{a_1,a_3,a_5,\ldots\}$.

However, an infinite series is not normalizable. So the series must terminate at some finite number of terms; say at $j_{\max} = n$. That is $a_{n+2} = 0$ and all succeeding $a_j = 0$ also. The $h(y)$ is a finite polynomial of degree n. Of course, n is going to be the principle quantum number.

Through the κ, the n is related to the total energy, E.

Set $2j + 1 - \kappa = 0$, solve for E when $j = n$.

$$\kappa_n = 2n + 1$$

$$E_n = (n + \frac{1}{2})\hbar\omega \quad \text{………….. (14)}$$

These are the energy levels for the harmonic oscillator. We have to solve finally for the $h(y)$.

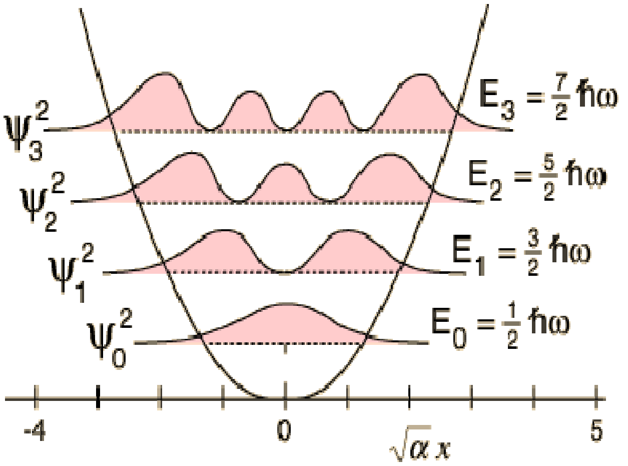


Fig (2.5)

2.10.2 HERMITE POLYNOMIALS

We have found an infinite number of energies for each energy level, n. The formula for the wave function is incomplete, however, because the power series solution is incomplete. The solution of differential equation (8) (itresembles with Hermite differential equation) is $h(y) = N_n H_n(y)$,where $H_n(y)$ is Hermite polynomials. The first several Hermite polynomials are tabulated below in table(2.1).

So the wave functions of the harmonic oscillator are

$$\psi_n(x) = N_n H_n\left(\sqrt{\alpha}\ x\right) e^{-\frac{\alpha x^2}{2}} \quad \text{………………… (15)}$$

Where N_n is the normalization constant, after normalization the complete solution is

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}\, x\right) e^{-\frac{m\omega}{2\hbar}x^2} \qquad \ldots\ldots\ldots\ldots\ldots (16)$$

n = 0	$H_0(y)=1$	$\psi_0(y) = N_0 e^{-\frac{y^2}{2}}$	$E_0 = \frac{\hbar\omega}{2}$
n = 1	$H_1(y)=2y$	$\psi_1(y) = N_1(2y)e^{-\frac{y^2}{2}}$	$E_1 = \frac{3\hbar\omega}{2}$
n = 2	$H_2(y)=4y^2-2$	$\psi_2(y) = N_2(4y^2-2)e^{-\frac{y^2}{2}}$	$E_2 = \frac{5\hbar\omega}{2}$
n = 3	$H_3(y)=8y^3-12y$	$\psi_3(y) = N_3(8y^3+12y)e^{-\frac{y^2}{2}}$	$E_3 = \frac{7\hbar\omega}{2}$

Table (2.1)

2.11PHASE AND GROUP VELOCITY

Phase and group velocity are twovary important and related concepts in wave mechanics. They arise in quantum mechanics in the time development of the state function for the continuous case.

2.11.1 HARMONIC WAVES AND PHASE VELOCITY

A harmonic wave of constant frequency (monochromatic wave) propagating in one-dimension (along x-axis)is described by a wave equation : (Figure 1)

$$u(x,t) = A\sin(\omega t - kx + \phi)$$

Where *k* is the wave number; and ϕ is an initial, constant phase.

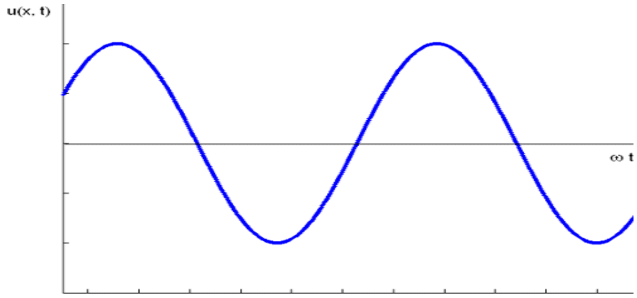


Fig.(2.6)

In general, these waves propagate in space without distortion and remains same throughout time and space. That is, the phase $\theta(x,t)$ remains constant with time :

$$\frac{d\theta}{dt} = \omega - k\frac{dx}{dt} = 0$$

Gives phase velocity

$$v_{phase} = \frac{dx}{dt} = \frac{\omega}{k}$$

Obviously particle can not be represented by a single , since matter wave must be *localized* around the region of space within which the particle is confined.

However if we study the superposition of two harmonic waves with very close frequencies and of the same amplitude. The equations for the motion are,

$$u(x,t) = A\cos(\omega_1 t - k_1 x) + A\cos(\omega_2 t - k_2 x)$$

$$= 2A\cos\left(\frac{(\omega_2 - \omega_1)t}{2} - \frac{(k_2 - k_1)x}{2}\right) \times \cos\left(\frac{(\omega_2 + \omega_1)t}{2} - \frac{(k_2 + k_1)x}{2}\right)$$

$$= u_1 \times u_2$$

The superposition of many such waves of varying frequencies can results an "envelope" calledwave packet . This wave packet can be considered to be a superposition of a number of harmonic waves. A wave packet therefore consists of agroup of waves of slightly different frequencies or wavelengths, with phases and amplitudes so chosen that they interfere constructively .The plot of such a wave is shown in Figure 2.

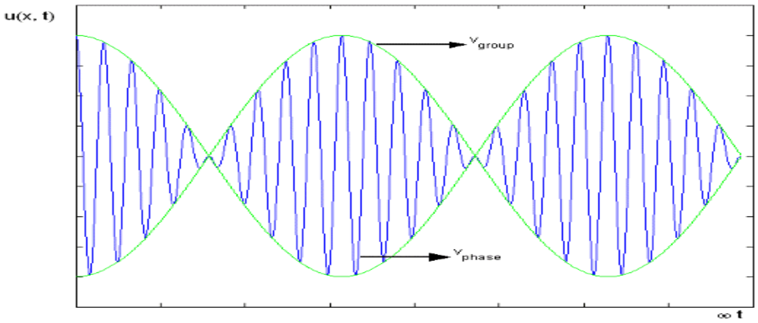


Fig.(2.7)

The envelope is given by u_1 and travels at the group velocity. The carrier wave travels at the phase velocity and is given by u_2. The wave packet moves at the group velocity. Group velocity and phase velocity are not necessarily the same. Group velocity is given by,

$$v_{group} = \frac{\omega_2 - \omega_1}{k_2 - k_1} = \frac{\Delta\omega}{\Delta k}$$

Phase and group velocity are related through Rayleigh's formula,

$$v_g = v_{ph} + k\frac{dv_{ph}}{dk}$$

If the derivative term is zero, group velocity equals phase velocity. In that case, there is no dispersion. Dispersion is when the distinct phase velocities of the components of the envelope cause the wave packet to "spread out" over time. The components of the wave packet (or envelope) move apart to the degree where they no longer combine to complete the envelope.

2.11.2 WAVE PACKETS

A microscopic particle can be not represented by a single de Broglie wave of well-defined frequency and wavelength, but by a wave packet that is obtained by adding a large number of

waves of different frequencies . This wave packet must then be *localized* means the wave function which vanishes everywhere except in the neighborhood of the particle. A localized wavefunction or a wavepacket can be constructed by the superposition of harmonic waves of slightly different wavelengths, but with phases and amplitudes chosen to make the superposition constructive in the desired region. consider a one-dimensional wave packet; describes a classical particle confined to a one-dimensional region, for instance, a particle moving along the *x*-axis. the mathematical repersentation the packet $\Psi(x,t)$ propagating along the *x*-axis is

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\varphi(k)e^{i(kx-\omega t)}dk$$

………….. (1)

At t=0 , the wavepacket represented by

$$\Psi(x,0)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\varphi(k)e^{ikx}dk$$

……………..(2)

$\varphi(k)$ is the amplitude of the wave packet.It is the Fourier transform of $\Psi(x,0)$ and is given by

$$\varphi(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\Psi(x)e^{-ikx}dx$$

……………….. (3)

The wave packet travels with a speed called the *group velocity*, v_g. The individual ripples within the packet travel with a speed called the *phase velocity*, v_p. The phase velocity is the familiar wave speed.

$$v_p=\frac{\omega}{k}=\frac{E}{p}\quad\text{…………}\quad(4)$$

The angular frequency of a harmonic wave is $\omega=\frac{\hbar k^2}{2m}$. This is called a *dispersion relation*, because it implies that waves of different frequency travel with different wave speeds.

Let's say that the wave packet is composed of harmonic waves with a narrow range of *k*-values, centered on k_o. We might expand $\omega(k)$ in a Taylor's Series about k_o, and keep just the first two terms.

$$\omega(k)=\omega_o+\left.\frac{d\omega}{dk}\right|_{k_o}\cdot(k-k_o)=\omega_o+\omega_o{}'\cdot(k-k_o)$$

……….. (5)

Put this in the Ψ for ω.

$$\Psi(x,t)\cong\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\phi(k)e^{i\left(kx-\left(\omega_o+\omega_o{}'\cdot(k-k_o)\right)t\right)}dk$$

……………….. (6)

$$\Psi(x,t)\cong\frac{1}{\sqrt{2\pi}}e^{i\left(-\omega_o\cdot t+\omega_o{}'\cdot k_o\cdot t\right)}\int_{-\infty}^{+\infty}\phi(k)e^{i\left(k\left(x-\omega_o{}'\cdot t\right)\right)}dk$$

………….. (7)

$$\Psi(x,t)\cong\frac{1}{\sqrt{2\pi}}e^{i\left(-\omega_o\cdot t+\omega_o{}'\cdot k_o\cdot t\right)}\Psi\left(x-\omega_o{}'\,t,0\right)$$

………………. (8)

Evidently, the wave packet slides along the *x*-axis at the speed $v_g = \left.\frac{d\omega}{dk}\right|_{k_o}$.

$$v_g = \left.\frac{d\omega}{dk}\right|_{k_o} = \left.\frac{d}{dk}\left(\frac{\hbar k^2}{2m}\right)\right|_{k_o} = \frac{\hbar k_o}{m} = \frac{dE}{dp} \qquad \ldots\ldots\ldots\ldots.. \quad (9)$$

Note that the classical speed of a particle with momentum *p*is $\frac{p}{m} = \frac{\hbar k}{m}$, where $k = \frac{2\pi}{\lambda}$ and λ is the deBroglie wavelength.

EXAMPLE .

Calculate the group and phase velocities for the wave packet corresponding to a relativisticparticle.

SOLUTION

Since ,as we know that the energy and momentum of a relativistic particle are given by

$$E = mc^2$$

$$= \frac{m_0 c^2}{\sqrt{1 - v^2 / c^2}}$$

And $$p = mv = \frac{m_0 v}{\sqrt{1 - v^2 / c^2}}$$

wherem_0 is the rest mass of the particle and *c* is the speed of light in a vacuum. Squaring and adding the expressions of *E* and *p*, we obtain

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

or

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

group velocity $v_g = \frac{dE}{dp}$

$$= \frac{d}{dp}\sqrt{m_0{}^2 c^4 + p^2 c^2}$$

$$= \frac{pc}{\sqrt{m_0{}^2c^2 + p^2}} = v$$

and phase velocity $v_p = \frac{E}{p} = \frac{c^2}{v}$

This shows that the phase velocity of the wave corresponding to a relativistic particle having non zero mass, is larger than the speed of light, $v_p > c$. it seems unphysical because it violates the law of special theory of relativity, according to which the speed of material particles cannot exceed *c*. In fact, this principle is not violated because $v_p$does not represent the velocity of the particle; the velocity of the particle is represented by the group velocity . As a result, the phase speed of a relativistic particle has no meaningful physical significance.

2.12 CONCLUSIONS

This unit describes the experimental findings that lead to a new concept and a new scientific approach towards understanding the physical phenomena at the microscopic level. In addition, it describes the formal terminology based on assumptions derived from these experimental observations, such as Schrödinger's wave mechanics and the fundamental principles of quantum mechanics. Examples of applications can aid in supporting the results of abstract ideas which bring about the various formal theories of quantum mechanics.

2.13 Terminal Questions

Q1. Write down two expressions of the uncertainty principle.

Q2.Discuss the wave nature of matter and obtain an expression of de Broglie wavelength for

matter waves

Q3.What is the relation between energy and momentum for a particle without mass?

Q4. What is the relation between energy and momentum for a particle with mass?

Q5.In Davission and germer experiment, state the observations which led to (i) show the weave

nature of electrons and (ii) confirm de Broiglie relation.

Q6..Describe the experiment of G.P. Thomoson .Explain the results obtained.

Q7. Deduce de Broglie wavelength of electrons accelerated by a potential of v volt. Draw a schematic diagram of a localized wave describing the wave nature of moving electron.

Q8.An electron isconfined in the ground state in a one-dimensional box of width 1O^{-10} m. Its energy is 38 eV. Calculate:

(a) The energy of the electron in its first excited state. (152 eV.)

(b) The average force on the walls of the box when the electron is in the ground state.

(7.6 x 10^{9}eV/cm)

Q9.Show that the minimum energy of a simple harmonic oscillator is $\frac{\hbar\omega}{2}$ if $\Delta x\Delta p = \frac{\hbar}{2}$, where $\left(\Delta p\right)^2 = <\left(p-<p>\right)^2>$.

Q10. A proton is confined in an in_nite square well of width 10 fm. (The nuclear potential that

binds protons and neutrons in the nucleus of an atom is often approximated by an infnite

square well potential.)

i. Calculate the energy and wavelength of the photon emitted when the proton undergoes a

transition from the first excited state (n = 2) to the ground state (n = 1).

ii. In what region of the electromagnetic spectrum does this wavelength belong?

(E = 6:15MeV and λ= 202 fm)

Q11. An electron is described by the wave function $\psi(x) = 0$ for x<0 ; $\psi(x) = Ce^{-x}(1-e^{-x})$ for x>0 where x is in nm and C is a constant.
i. Determine the value of C that normalizes $\psi(x)$.
ii. Where is the electron most likely to be found? That is, for what value of x is the probability of finding the electron the largest?
iii. Calculate the average position <x> for the electron. Compare this result with the most likely position, and comment on the difference. (C= $2\sqrt{3}nm^{-1/2}$, xm = 0.693 nm, <x> =1.083 nm)

Q12. Use the uncertainty principle to estimate:

(a) the ground state radius of the hydrogen atom and

(b) the ground state energy of the hydrogen atom.

Q13. A simple one-dimensional harmonic oscillator is a particle acted upon by a linear restoring force $F(x) = m\omega^2 x$. Classically, the minimum energy of the oscillator is zero, because we can place it precisely at $x = 0$, its equilibrium position, while giving it zero initial velocity. Quantum mechanically, the uncertainty principle does not allow us to localize the particle precisely and simultaneously have it at rest. Using the uncertainty principle, estimate the minimum energy of the quantum mechanical oscillator.

Q14.Show that for those waves whose angular frequency ω and wave number k obey the relation $k^2c^2 = \omega^2$, the product of the phase and group velocities is equal to c^2, $v_g.v_p=c^2$, where c is the speed of light.

Q15. The angular frequency for a wave propagating inside a waveguide is given in terms of the wave number k and the width b of the guide by $\omega = kc\left[1-\pi^2/(bk)^2\right]^{-1/2}$. Find the phase and group velocities of the wave.

Q.16. Obtain the wave equation for a linear harmonic oscillator and solve it.

Q.17. State and prove Heisenberg's uncertainty principle.

Q.18.State and prove Ehrenfest's theorem

Q.19.Show equation $\frac{\partial\rho}{\partial t} + \nabla j = 0$ expresses the conservation of probability density.

Q.20.Distinguish between phase velocity and group velocity

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UNIT 3: APPLICATION OF SCHRODINGER'S EQUATION

3.1 INTRODUCTION

3.2 LEARNING OBJECTIVES

3.3 SCHRÖDINGER EQUATION IN SPHERICAL COORDINATES

3.3.1 SEPARATION OF VARIABLES

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3.1 INTRODUCTION

In this unit we learn how to solve the Schrödinger equation using spherical polar coordinatesfor spinless particles moving in three-dimensional potentials. We describe the motion of a particle in spherically symmetric potentials. After presenting a general treatment, we consider several applicationsranging from the free particle and the isotropic harmonic oscillator to the hydrogen atom.

3.2 LEARNING OBJECTIVES

After going through this unit, you will be able to:

- Understand the of separation of the variables method.
- Understand the Schrödinger equation in a spherically symmetric potential.
- Solve the various three dimensonal problems in spherical coordinates
- Understand and solve the Hydrogen atomproblem.

3.3 SCHRÖDINGER EQUATION IN SPHERICAL COORDINATES

Three dimensional time dependent Schrödinger equation is given as-

$$H\psi = E\psi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [1]$$

Where Ĥ is Hamiltonian operator representing a certain way of expressing the total energy of the system and $E = i\hbar\partial/\partial t$ is thenumerical value of total energy.

As H is the total energy value of the system. Hence its value can be obtained classically by H = K.E. + P.E. Hence

$$\mathrm{H} = \frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

Also we know that(see operators in next chepter)

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x},\ p_y = \frac{\hbar}{i}\frac{\partial}{\partial y}\ \ and\ \ p_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \quad \ldots\ldots\ldots\ldots\ldots \ [2]$$

So we can write in general- $p = \frac{\hbar}{i}\nabla$

so

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [3]$$

Here $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ isaLaplacian operator in Cartesian coordinates.

As the potential energy V and the wave function ψ are now functions of r = (x, y, z) and t. The probability of finding the particle in infinitesimal volume $d^3 r = dx dy dz$ will be $|\psi(r,t)|^2 d^3 r$ for which normalization condition can be given as-

$$\int |\psi|^2 d^3 r = 1 \text{ …………….. } \quad [4]$$

Here the integral is taken all over the space.

Let we assume that the potential be independent of time, then there will be a complete set of stationary states which will follow-

$$\psi_n(r,t) = \psi_n(r) e^{-iE_x t/\hbar} \text{ ………….. } \quad [5]$$

This is simply the evolution of the wave with time. Thus the general solution for time dependent Schrödinger equation will be given as-

$$\psi(r,t) = \sum c_n \psi_n(r) e^{-iE_x t/\hbar} \quad \text{ ………………… } [6]$$

Here the constant c_n can be found by initial wave function $\psi(r,0)$ and the wave function ψ_n satisfies the time-independent Schrodinger equation given by-

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_{n=}E_n\psi_n \quad \text{ …………………… } [7]$$

3.3.1 SEPARATION OF VARIABLES

In the case where potential is a function only of distance from the origin than we should adopt spherical coordinates (r, θ, ϕ) as the Hamiltonian in that case will be spherically symmetric. Spherical coordinates can be shown as-

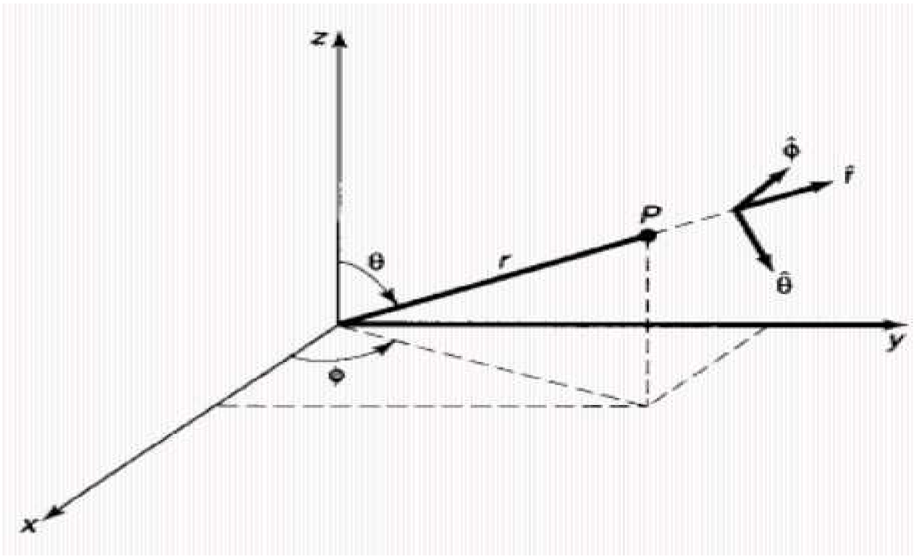

Fig. (3.1)
Where r is the radius, θ be the polar angle and Φ being the azimuthal angle.
In spherical coordinates the Laplacian is given as-

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \quad \ldots.\ [1]$$

So by putting value of laplacian, the time-independent Schrödinger equation can be given as-

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right]+V\psi = E\psi \quad \ldots\ldots\ [2]$$

We start by looking for the solutions that are separable into product-

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ [3]$$

Putting this value of ψ in equation [2]-

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]+VRY = ERY$$

Dividingit by Y R and multiplying by $-\frac{2mr^2}{\hbar^2}$

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\}+\frac{1}{Y}\left\{\frac{1}{\operatorname{Sin}\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)\right\} = 0$$

We observe that the term in first bracket depends only upon r, whereas the second bracketed term depends on both θ and ϕ .

Let us designate this equation as-

$$\left\{ \frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E \right] \right\} = l(l+1) \quad \text{...............} \; [4]$$

And

$$\frac{1}{Y}\left\{ \frac{1}{\mathrm{Sin}\,\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} \right) \right\} = -l(l+1) \quad \text{.............} \; [5]$$

Where $l(l+1)$ is called as separation constant.

Thus we can transform the equation as separated variable equation.

Let we designate the Laplacian ∇^2 into one radial part ∇_r^2 and one angular part then by considering derivatives as partial and using the separation eqn. [4]

$$\nabla^2 = \nabla_r^2 - \frac{1}{\hbar^2 r^2}\nabla_\Omega^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{1}{r^2\hbar^2}\hat{L}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2\hbar^2}\hat{L}^2 \quad \text{.....} [6]$$

Where $\hat{L}^2$ is given by separation eqn. [5] as-

$$\vec{L}^2 = -\hbar^2 \left\{ \frac{1}{\mathrm{Sin}\,\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right\} \quad \text{...........} \; [7]$$

These equations are the equation for separating laplacian into one radial & one angular part.

Now we study the structure of Schrödinger equation for a particle of mass M moving in a *sphericallysymmetricpotential*

$$V(\vec{r}) = V(r) \quad \text{.........................} \; [8]$$

This potential is also known as the *centralpotential*.

The time independent Schrödinger equation for this particle of momentum $-i\hbar\vec{\nabla}$ and position vector $\vec{r}$ is-

$$\left[-\frac{\hbar^2}{2M}\nabla^2 + V(r) \right]\psi(\vec{r}) = E\psi(\vec{r}) \quad \text{................} \; [9]$$

No as we know that the Hamiltonian is spherically symmetric so we have to use spherical coordinates (r,θ,ϕ) which are related to their counterpart Cartesian coordinates as-

$x = r\sin\theta\cos\phi$, $\quad$ $y = r\sin\theta\sin\phi$, $\quad$ $z = r\cos\theta$

Thus putting the value of ∇^2 into eqn. [9] using the separation eqn. [6] which is

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2\hbar^2}\hat{L}^2$$

the Schrödinger equation in spherical coordinates can be given as-

$$\left[-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{\partial^2}{\partial r^2}r + \frac{1}{2Mr^2}\hat{\vec{L}}^2 + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}) \quad \text{………} [10]$$

Here the first term can be viewed as radial kinetic energy.

$$-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{\partial^2}{\partial r^2}r = \frac{\hat{P}_r^2}{2M} \quad \text{…………..} \quad [11]$$

Since the radial momentum operator is given by the Hermitian form-

$$\hat{P}_r = \frac{1}{2}\left[\left(\frac{\vec{r}}{r}\right).\hat{\vec{p}} + \hat{\vec{p}}.\left(\frac{\vec{r}}{r}\right)\right] = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \equiv -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r \quad \text{………} [12]$$

The second term $\frac{1}{2Mr^2}\hat{\vec{L}}^2$ of eqn. [10] can be identified with the rotational kinetic energy because this term can be considered as generated from a *pure rotation of particle* about the origin.

From eqn. [7] is it clears that $\hat{\vec{L}}^2$ doesn't depend on r. Hence it commutes with both V(r) and radial kinetic energy {from eqn. [11]} as both the potential and radial kinetic energy is pure functions of r only. Hence it also commutes with Hamiltonian Ĥ which can be seen by eqn. [10]. From angular momentum theory we know that $\hat{\vec{L}}^2$ commutes with $\hat{L}_Z$, hence we observe that these three operators mutually commute-

$$\left[\hat{\vec{L}}^2, \hat{H}\right] = \left[\hat{H}, \hat{L}_z\right] = 0 \quad \text{………..} \quad [13]$$

Hence Ĥ, $\hat{\vec{L}}^2$ and $\hat{L}_z$ have common eigenfunctions as they commute mutually and also we know that simultaneous eigenfunctions of $\hat{\vec{L}}^2$ and $\hat{L}_z$ are given by the special harmonics $Y_{lm}(\theta,\varphi)$:

$$\hat{\vec{L}}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi) \quad \text{…………………} \quad [14]$$

And

$$\hat{L}_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi) \quad \text{………………} [15]$$

As Hamiltonian in eqn. [10] is a sum of a radial and an angular part so we start by looking for the solution which are the product of one radial and one angular part, where the angular part is simply the spherical harmonics $Y_{lm}(\theta,\varphi)$ .and also the orbital angular momentum of a system moving in a central potential is conserved, hence it also commutes with the Hamiltonian.

Let we begin by the solution-

$$\psi(\vec{r}) = \langle \vec{r} | nlm \rangle = \psi_{nlm}(r,\theta,\varphi) = R_{nl}(r) Y_{lm}(\theta,\varphi) \quad \text{.................}[16]$$

We have also to find the radial function $R_{nl}(r)$. Let the quantum number n is introduced to identify the eigenvalues of Ĥ such that:

$$\hat{H} \, |nlm\rangle = E_n |nlm\rangle \quad \text{.....................} [17]$$

Putting value of $\psi(\vec{r})$ in eqn. [10] and then multiplying whole eqn. by 2Mr² and dividing throughout by $R_{nl}(r)Y_{lm}(\theta,\varphi)$, and using the values from eigenvalues and eigenfunctions eqn. of $\vec{L}^2$ we obtain an eqn. where radial and angular degrees of freedom are separated-

$$\left[-\hbar^2 \frac{r}{R_{nl}} \frac{\partial^2}{\partial r^2}(rR_{nl}) + 2Mr^2 (V(r) - E) \right] + \left[\frac{\hat{L}^2 Y_{lm}(\theta,\varphi)}{Y_{lm}(\theta,\varphi)} \right] = 0 \quad \text{.......} [18]$$

The terms inside the first square bracket are independent of θ and φ hence it is free from angular degrees and similarly the second term second term is independent of r so it can be considered free from radial degrees. These terms must be

separately equal to constants and their sum equals to zero. The second term has the value $l(l+1)\hbar^2$ from eqn. [14] so the first bracketed term must have the value $-l(l+1)\hbar^2$ for the sum to be zero.

Which yields the same result of separation as obtained in last article of separation of variables.

Thus we obtain an eqn. known as the radial eqn. for central potential-

$$-\frac{\hbar^2}{2M} \frac{d^2}{dr^2}\{rR_{nl}(r)\} + \left[V(r) + \frac{l(l+1)\hbar^2}{2Mr^2} \right] \{rR_{nl}(r)\} = E_n \{rR_{nl}(r)\} \quad \dots [19]$$

This eqn. shows that the energy levels of the system, does not depend on the azimuthal quantum number m. for a given l, there are (2l+1) different eigenfunctions ψ_{nlm} corresponding to same eigenenergy ,E_n . Thus the energy E_n is (2l+1)-fold degenerate.

This degeneracy is peculiar to central potential problem.

This eqn. [19] has the structure of a-one dimensional eqn. in r.

$$-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2}+\left[V(r)+\frac{l(l+1)\hbar^2}{2Mr^2}\right]U_{nl}(r)=E_nU_{nl}(r) \quad \text{.......} \ [20]$$

Or $$-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2}+V_{eff}U_{nl}(r)=E_nU_{nl}(r) \quad \text{................} \ [21]$$

Here we defined the wave function as $U_{nl}(r)=rR_{nl}(r)$ …….. [22]

And the potential by $\left[V(r)+\frac{l(l+1)\hbar^2}{2Mr^2}\right]=V_{eff}(r)$ ………… [23]

Solutions of this eqn.gives the energy levels of the system.

The potential given by eqn. [23] known as the effective or centrifugal potential, inwhile the V(r) is central potential and $\frac{l(l+1)\hbar^2}{2Mr^2}$ is called as repulsive potential associated with the orbital angular momentum, which tends to repel the particle away from the centre. In case of atoms V(r) is the Coulomb potential resulting from the attractive forces between the electron and the nucleus.

We require the wave function $\psi_{nlm}(r,\theta,\phi)$ to be finite for all values of r between zero to infinity, notably for r=0. For the eigenvalue eqn. [21] to describe bound states, the potential V(r) must be attractive (i.e. negative potential) because $\frac{l(l+1)\hbar^2}{2Mr^2}$ is repulsive potential.

Thus we want to emphasize the fact that, for spherically symmetric potentials, the Schrödinger equation [10] reduces to a trivial angular equation [14] for $\hat{\vec{L}}^2$ and a one-dimensional radial equation .

3.3.2 THE FREE PARTCLE

Now we want to apply the general formalism of central potential to study the motion of a free particle of mass M and energy $E_{k} = \frac{\hbar^2 k^2}{2M}$ and k is the wave number ($k = |\vec{k}|$). The Hamiltonian $\hat{H} = \frac{-\hbar^2 k^2}{2M}$ of the free particle commutes with $\hat{\vec{L}}^2$ and $\hat{L}_z$. Since V(r) =0 the Hamiltonian of a free particle is rotationally invariant.Thus the free particle can be viewed as a special case of central potential.

Separation of wave function in radial and angular part can be given as-

$$\langle r\theta\varphi|klm\rangle = \psi_{klm}(r,\theta,\varphi) = R_{kl}(r)Y_{lm}(\theta,\varphi) \quad \cdots\cdots\cdots\cdots\cdots [1]$$

Radial eqn. for free particle is obtained by setting V(r) =0in eq. [19] of last article -

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}\{rR_{kl}(r)\} + \left[\frac{l(l+1)\hbar^2}{2Mr^2}\right]R_{kl}(r) = E_k R_{kl}(r) \quad \cdots\cdots\cdots [2]$$

This can be rewritten as-

$$-\frac{1}{r}\frac{d^2}{dr^2}\{rR_{kl}(r)\} + \left[\frac{l(l+1)}{r^2}\right]R_{kl}(r) = k^2 R_{kl}(r) \quad \cdots\cdots\cdots [3]$$

Here $k^2 = 2ME_k\frac{1}{\hbar^2}$. Using the change of variable ρ=kr, eqn. [3] can be reduced to-

$$\frac{d^2 R_{l(p)}}{d\rho^2} + \frac{2}{\rho}\frac{dR_1(\rho)}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]R_l(\rho) = 0 \quad \cdots\cdots\cdots [4]$$

Here $R_l(\rho) = R_l(kr) = R_{kl}(r)$. This differential equation is known as the spherical Bessel equation. The general solutions to this equation are given by an independent linear combination of Spherical Bessel functions $j_l(\rho)$ and the Spherical Neumann functions $n_l(\rho)$.

$$R_l(\rho) = A_l j_l(\rho) + B_l n_{l(\rho)} \quad \cdots\cdots\cdots\cdots\cdots\cdots [5]$$

These function $j_l(\rho)$ and $n_l(\rho)$ are given by-

$$j_l(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\sin\rho}{\rho}$$

And

$$n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho} \frac{d}{d\rho} \right)^l \frac{\cos\rho}{\rho} \quad \text{.... [6]}$$

Expanding sinρ/ρ and cosρ/ρ in a power series of ρ, we see that the functions $j_l(\rho)$ and $n_l(\rho)$ reduce for small values of ρ near the origin to-

$$n_l(\rho) \approx -\frac{(2l)!}{2^l l!} \rho^{-l-1}$$

And

$$j_l(\rho) \approx \frac{2^l l!}{(2l+1)!} \rho^l \quad \rho << 1 \quad \text{.... [7]}$$

And for large values of ρ to-

$$n_l(\rho) \approx -\frac{1}{\rho} \cos\left(\rho - \frac{l\pi}{2} \right)$$

And

$$j_l(\rho) \approx \frac{1}{\rho} \sin\left(\rho - \frac{l\pi}{2} \right) \quad \rho >> 1 \quad \text{..... [8]}$$

As Neumann functions diverge at origin and also the wave function is required to be finite everywhere in space hence the Neumann function become unacceptable solutions of the problem. Hence in such cases only spherical Bessel functions $j_l(kr)$ contribute to the eigenfunctions of the free particle.

$$\psi_{klm}(r, \theta, \psi) = j_l(kr) Y_{lm}(\theta, \varphi) \qquad k = \sqrt{\frac{2ME_k}{\hbar}} \quad \text{.....[9]}$$

Some first few spherical Bessel and Neumann function are given by-

l	BESSEL FUNCTIONS $j_l(r)$	NEUMANN FUNCTION $n_l(r)$
l=0	$j_0(r) = \frac{\sin r}{r}$	$n_o(r) = -\frac{\cos r}{r}$
l=1	$j_1(r) = \frac{\sin r}{r^2} - \frac{\cos r}{r}$	$n_1(r) = -\frac{\cos r}{r^2} - \frac{\sin r}{r}$
l=2	$j_2(r) = \left(\frac{3}{r^3} - \frac{1}{r} \right) \sin r - \frac{3\cos r}{r^2}$	$n_2(r) = -\left(\frac{3}{r^3} - \frac{1}{r} \right) \cos r - \frac{3\sin r}{r^2}$

Table(3.1)

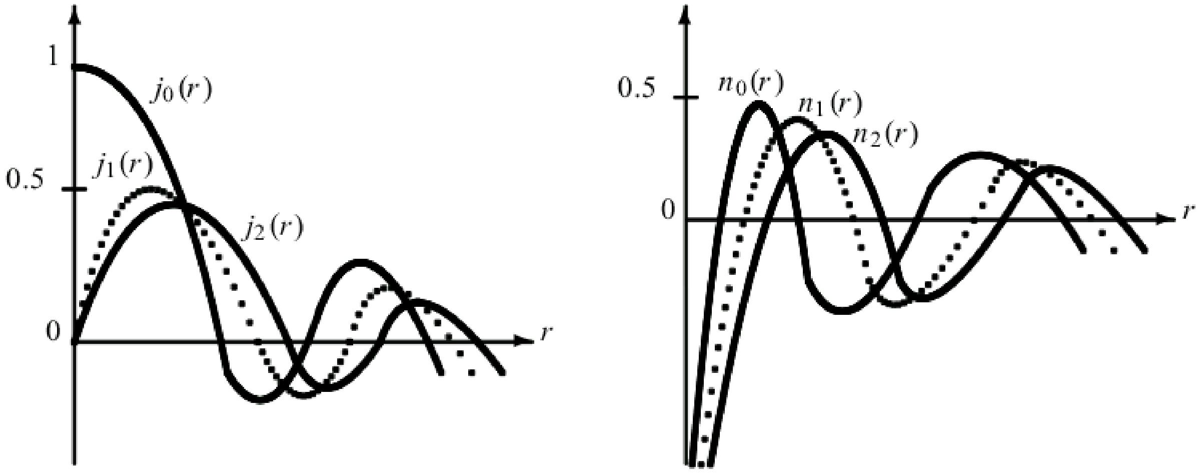

Fig.(3.3)

The Spherical Bessel function and Neumann function can be plotted as above figure (3).

We observe that only the Bessel functions are finite at origin. Also the amplitude of wave function becomes smaller and smaller as r increases. At larger distances, the wave functions are represented by spherical waves.

Also the index k in energy $E_k = \frac{\hbar^2 k^2}{2M}$ as $k = \sqrt{\frac{2ME_k}{\hbar}}$ varies continuously, so the energy spectrum of a free particle is infinitely degenerate. This is because all orientation this vector k in space correspond to the same energy.

Problem- Finding the l=0 energy and wave function of a particle of mass m that is subjected to following central potential- $V(r) = \begin{cases} 0 & a<r<b \\ \infty & \text{elsewhere} \end{cases}$

Solution- the l=0 radial equation between a<r<b can be given by radial equation

$$\frac{d^2U_{n0}(r)}{dr^2} + k^2U_{n0}(r) = 0 \qquad \text{..............} \; (a)$$

Where $U_{n0}(r) = rR_{n0}(r)$ and $k^2 = \frac{2mE}{\hbar^2}$

Since the solution has to satisfy $U_{n0}(a) = 0$ so-

$$U_{n0}(r) = A\sin[k(r-a)] \qquad \text{......................} \; (b)$$

The radial function is zero elsewhere. So $U_{n0}(r) = 0$ for 0<r<a and r>b

Also the radial function must vanish at r=b, $U_{n0}(b) = 0$

So Asin[k(b-a)]=0 so k(b-a)=nπ where n=1,2,3..... .... (c)

And we know

$$E_k = \frac{\hbar^2k^2}{2M} \quad \text{as} \quad k = \sqrt{\frac{2ME_k}{\hbar}} \quad \text{energy } E_n = \frac{\pi^2\hbar^2}{2m(a-b)^2} \qquad \text{.........} \; (d)$$

We we normalise the radial function we find the constant

$$A = \frac{b-a}{2}A^2 \qquad \text{............}(e)$$

Here we have to integrate the radial function between limits a to b.

And $K_n = \frac{n\pi}{b-a}$ so the normalised radial function is given by-

$$R_{n0}(r) = \frac{1}{r}U_{n0}(r) = \begin{Bmatrix} \sqrt{\frac{2}{b-a}}\frac{1}{r}\sin\frac{n\pi(r-a)}{b-a} & a<r<b \\ 0 & \text{elsewhere} \end{Bmatrix}$$

It is the required solution.

3.4 3D PROBLEMS IN SPHERICAL COORDINATES :

Now we will try to solve some problems for a particle by applying the Schrödinger time independent equation in spherical coordinates using the theory we have studied.

3.4.1 THE SPHERICAL SQUARE WELL POTENTIAL

Consider the problem of a particle of mass M in an attractive spherical well potential

$$v(r) = \begin{cases} -v_{0,} & r < a \\ 0, & r > a \end{cases}$$

<u>Case1</u>: where 0 < r < a

Inside the well, 0< r< a, the time-independent Schrödinger equation for this particle-

$-\frac{h^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}\left(r, R_l(r)\right) + \frac{l(l+1)h^2}{2Mr^2}R_l(r) = (E + v_0)Rl(\text{r})$ ...(1)

Using the change of variable ρ =k1r, where k1 is now given by k1=$\sqrt{2M(E+v_0)}\big/_{h}$, we

reduces to the spherical Bessel differential equation. As in the case of
a free particle, the radial wave function must be finite everywhere, and is given as follows in terms of the spherical Bessel functions $J_1(k_1 r)$:

$R_1(r) = A_{jl}(k_1 r) = A_{jl}\left(\frac{\sqrt{2M(E+v_0}}{h}r\right), \quad for\ r < a,$...(2)

Where A is a normalization constant

<u>Case2</u>: where r > a

Outside the well, r > a, the particle moves freely; its Schrödinger equation is-

$-\frac{h^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}\left(r, R_{kl}(r)\right) + \frac{l(l+1)h^2}{2Mr^2}R_{kl}(r) = (E_k R_{kl}(r) \quad (r > a)$...(3)

Two possibilities arise here, depending on whether the energy is negative or positive.

The negative energy case corresponds to bound states (i.e., to a discrete energy spectrum). The general solutions of (3).are similar to those of (2), but k is now an imaginary number; that is, we must replace k by ik2 and, hence, the solutions are given by linear combination of jl (ik2r) and nl (ik2r):

$R_l(ik_2 r) = B[jl(ik_2 r) \pm nl(ik_2 r)]$...(4)

Where B is a normalization constant, with k2 =$\sqrt{-2ME}/h$.
Linear combinations of jl (ρ) and nl(ρ)an be expressed in terms of the spherical Hankel functions of the first kind, $h_l^{(1)}(\rho)$, and the second kind, $h_l^{(2)}(\rho)$ as follows:

$h_1^{(1)}(\rho) = jl(\rho) + inl(\rho)$,....(5)
$h_l^{(2)}(\rho) = jl(\rho) - inl(\rho) = (h_l^{(1)}(\rho))$.....(6)

The first few spherical Hankel functions of the first kind are :

$h_0^{(1)}(\rho) = -i\frac{e^{i\rho}}{\rho}, \quad h_h^{(1)}(\rho) = -\left(\frac{1}{\rho}+\frac{1}{\rho^2}\right)e^{i\rho}, \quad h_2^{(1)}(\rho) = \left(\frac{1}{\rho}-\frac{3}{\rho^2}-\frac{3I}{\rho^3}\right)e^{ip}$...(7)

The asymptotic behavior of the Hankel functions when $\rho \to \infty$

$$h_l^{(1)}(\rho) \to -\frac{i}{\rho} e^{i(\rho - l\pi/2)}, h_l^{(2)}(\rho) \to \frac{i}{\rho} e^{-i(\rho - l\pi/2)} ...(8)$$

The solutions that need to be retained in (4) must be finite everywhere. As can be inferred from Eq (8), only the Hankel functions of the first kind $h_l^{(1)}(ik_2r)$ are finite at large values of r (the functions $h_l^{(2)}(ik_2r)$ diverge for large values of r). Thus, the wave functions outside the well that are physically meaningful are those expressed in terms of the Hankel functions of the first kind (see (4)):

$$R_l(ik_2r) = Bh_l^{(1)}\left(i\frac{\sqrt{-2ME}}{h}r\right) = Bjl\left(i\frac{\sqrt{-2ME}}{h}r\right) + iBjl\left(i\frac{\sqrt{-2ME}}{h}r\right)....(9)$$

The continuity of the radial function and its derivative at r =a yields

$$\frac{1}{h_l^{(1)}(ik_2r)}\frac{dh_l^{(1)}(ik_2r)}{dr}|r = a = \frac{1}{jl(k_1r)}\frac{djl(k_1r)}{dr}|r = a...(10)$$

For the l = 0 states, this equation reduces to

$$-k_2 = k_1 \cot(k_1 a) \qquad .....(11)$$

This continuity condition is analogous to the transcendental equation.
The positive energy case corresponds to the continuous spectrum (unbound or scattering states), where the solution is asymptotically oscillatory. The solution consists of a linear combination of jl(k\`r) and nl(k\`r), where k\`=$\sqrt{2ME}/h$. Since the solution must be finite everywhere, the continuity condition at r = a determines the coefficients of the linear combination. The particle can move freely to infinity with a finite kinetic energy E=$h^2k^{`2}/(2M)$.

3.4.2 THE ISOTROPIC HARMONIC OSCILLATOR

The radial Schrödinger equation for a particle of mass M in an isotropic harmonic oscillator Potential

$$v(r) = \frac{1}{2}M\omega^2r^2.....(1)$$

Is

$$-\frac{h^2}{2M}\frac{d^2U_{nl}(r)}{dr^2} + \left[\frac{1}{2}M\omega^2r^2 + \frac{l(l+1)h^2}{2Mr^2}\right]U_{nl}(r) = EU_{nl(r)}....(2)$$

We are going to solve this equation by examining the behavior of the solutions at the asymptotic limits (at very small and very large values of r). On the one hand, when r → 0, the E and M$\omega^2 r^2/2$ terms become too small compared to the l(l+1)$h^2/2Mr^2$ term. Hence, when r →0, Eq. (2) reduces to

$$-\frac{h^2}{2M}\frac{d^2U(r)}{dr^2}+\frac{l(l+1)h^2}{2Mr^2}U(r)=0 \quad ....(3)$$

The solutions of this equation are of the form U(r)~r^{l+1}. On the other hand, when r → ∞, the E and l(l+1)$h^2/2Mr^2$ terms become too small compared to the M$\omega^2 r^2/2$ term; hence, the asymptotic form of (2) when r → ∞ is

$$-\frac{h^2}{2M}\frac{d^2U(r)}{dr^2}+\frac{1}{2}M\omega^2r^2U(r)=0...(4)$$

Which admits solutions of type U(r) ~ $e^{-M\omega^2r^2/2h}$. Combining (3) and (4), we can write the solutions of (2) as-

$$U(r)=f(r)r^{l+1}e^{-M\omega r^2/2h}....(5)$$

Where f (r) is a function of r. Substituting this expression into (4), we obtain an equation for f(r) :

$$\frac{d^2f(r)}{dr^2}+2\left(\frac{l+1}{r}-\frac{M\omega}{h}r\right)\frac{df(r)}{dr}+\left[\frac{2ME}{h^2}-(2l+3)\frac{M\omega}{h}\right]f(r)=0.....(6)$$

Let us try a power series solution

$$f(r)=\sum_{n=0}^{\infty}a_nr^n=a_0+a_1r+a_2nr^2+\ ...+a_nr^n+\ ....(7)$$

Substituting this function into (6), we obtain

$$\sum_{n=0}^{\infty}\left\{n(n-1)a_nr^{n-2}+\ 2\left(\frac{l+1}{r}-\frac{M\omega}{h}r\right)na_nr^{n-1}+\left[\frac{2ME}{h^2}-(2l+3)\frac{M\omega}{h}\right]a_nr^n\right\}=0..(8)$$

Which in turn reduces to

$$\sum_{n=o}^{\infty}\left\{n(n+2l+1)a_nr^{n-2}+\left[-\frac{2M\omega}{h}n+\frac{2ME}{h^2}-(2l+3\frac{M\omega}{h}\right]a_nr^n\right\}=0....(9)$$

For this equation to hold, the coefficients of the various powers of r must vanish separately. For instance, when n = 0 the coefficient of r^{-2} is indeed zero:
0 . (2l +1)a_0=0 ....(10)

Note that a_0 need not be zero for this equation to hold. The coefficient of r^{-1} corresponds to n = 1 in (9); for this coefficient to vanish, we must have

$$1.(2l+2)a_1=0...(11)$$

Since (2l +2) cannot be zero, because the quantum number l is a positive integer, a1 must vanish.

The coefficient of r^n results from the relation

$\sum_{n=0}^{\infty}\left\{(n+2)(n+2l+3)a_{n+2}+\left[\frac{2ME}{h^2}-\frac{M\omega}{h}(2n+2l+3\right]a_n\right\}r^n=0$....(12)

Which leads to the recurrence formula

$(n+2)(n+2l+3)a_{n+2}=\left[\frac{-2ME}{h^2}+\frac{M\omega}{h}(2n+2l+3\right]a_n$....(13)

This recurrence formula shows that all coefficients a_n corresponding to odd values of n are zero, since a1 = 0 (see (11)). The function f (r) must therefore contain only even powers of r:

$f(r)=\sum_{n=0}^{\infty}a2nr^{2n}=\sum_{n`_{0,2,4,....}}^{\infty}a_{n`}r^{n`}$,...(14)

Where all coefficients a2n, with n ≥ 1, are proportional to a_0.
Now note that when n → $+\infty$ the function f (r) diverges, for it behaves asymptotically like e^{r^2}. To obtain a finite solution, we must require the series (14) to stop at a maximum power $r^{n`}$ ; hence it must be polynomial. For this, we require an`+2 to be zero. Thus, setting $a_{n+2}=0$ into the recurrence formula (13) and since $a_{n`}$ ≠0, we obtain at once the quantization condition

$2\frac{M}{h^2}E_{n`l}-\frac{M\omega}{h}(2n`+2l+3)=0$,....(15)

$E_{n`l}=\left(n`+l+\frac{3}{2}\right)h\omega$,...(16)

Where n` is even (see (14)). Denoting n` by 2N, where N = 0,1,2,3,..., , we rewrite this energy expression as

$\boxed{E_n=\left(n+\frac{3}{2}\right)h\omega \qquad (n=0,1,2,3,\dots)}$....(17)

Where n =n`+l=2N+l
The ground state, whose energy is E_0 =${}^{3}/_{2}\,h\omega$, is not degenerate; the first excited state, E_1 = ${}^{5}/_{2}\,h\omega$, is threefold degenerate; and the second excited state, E_2 =${}^{7}/_{2}\,h\omega$, is sixfold degenerate A table . As shown in the following example, the degeneracy relation for the nth level is given by

$\boxed{g_n=\frac{1}{2}(n+1)(n+2).}$....(18)

This expression is in agreement with an eq. obtained for an isotropic harmonic oscillator in Cartesian coordinates.
Finally, since the radial wave function is given by

$R_{nl}(r)=U_{nl}(r)/r$,

whereUnl(r) is listed in (16) with f(r) being a polynomial in r^{2l} of degree $(n,-l)/2$, the total wave function for the isotropic harmonic oscillator is

$$\varphi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) = \frac{Unl(r)}{r}Y_{lm}(\theta,\varphi) = r^l f(r)Y_{lm}(\theta,\varphi)e^{-M\omega r^2/2h} \text{...(19)}$$

Table For The Representation Of Energy Levels E_n and g_n For An Isotropic Harmonic Oscillator -

nE_n		**Nl**	**m**	**g_n**
0	**3/2hω**	**0 0**	**0**	**1**
1	**5/2hω**	**0 1**	**$\pm 1, 0$**	**3**
2	**7/2hω**	**1 0**	**0**	**6**
0 2	**$\pm 2, \pm 1, 0$**			
3	**9/2hω**	**1 1**	**$\pm 1, 0$**	**10**
0 3	**$\pm 3, \pm 2, \pm 1, 0$**			

Table (3.2)

Where l takes only odd or only even values. For instance, the ground state corresponds to (n,l,m)=(0,0,0) its wave function is –

$$\varphi_{000}(r,\theta,\varphi) = R_{00}(r)Y_{00}(\theta,\varphi) = \frac{2}{\sqrt{\sqrt{\pi}}}\left(\frac{M\omega}{h}\right)^{3/4} e^{-\frac{M\omega r^2}{2h}} Y_{00}(\theta,\varphi) \text{..........(20)}$$

The (n,l,m) configurations of the first, second, and third excited states can be determined as follows. The first excited state has three degenerate state : (1,1,m)with m= -1,0,1. The second excited states has 6 degenerate states: (2,0,0) and (2,2,m) with m =-2,-1,0,1,2.The third excited state has 10 degenerate states: (3,1,m) with m =-1,0,1 where m -3,-2,-1,0,1,2,3 . Some of these wave functions are given by-

$$\varphi_{11m}(r,\theta,\varphi) = R_{11}(r)Y_{1m}(\theta,\varphi) = \sqrt{\frac{8}{3\sqrt{\pi}}}\left(\frac{M\omega}{h}\right)^{5/4} r e^{-\frac{M\omega r^2}{2h}} Y_{1m}(\theta,\varphi) \text{ .. ..(21)}$$

$$\varphi_{200}(r,\theta,\varphi) = R_{20}(r)Y_{00}(\theta,\varphi) = \sqrt{\frac{8}{3\sqrt{\pi}}}\left(\frac{M\omega}{h}\right)^{3/4}\left(\frac{3}{2} - \frac{M\omega}{h}r^2\right) e^{-\frac{M\omega r^2}{2h}} Y_{00}(\theta,\varphi) \text{...(22)}$$

$$\varphi_{31m}(r,\theta,\varphi) = R_{31}(r)Y_{1m}(\theta,\varphi) = \frac{1}{\sqrt{15\sqrt{\pi}}}\left(\frac{M\omega}{h}\right)^{7/4} r e^{-\frac{M\omega r^2}{2h}} Y_{1m}(\theta,\varphi) \text{..............(23)}$$

3.5 HYDROGEN ATOM

The hydrogen atom is one of the precious few realistic systems which can actually be solved analytically.The form of the Schrödinger equationfor the hydrogen atom in spherical coordinates

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \text{ .... (1)}$$

Where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right) \quad \ldots\ldots(2)$$

And **r** is the position of the electron ($r = |\mathbf{r}|$ is the magnitude of the position), theSpherically Symmetric Potential Energy Function(s) $V(\vec{r}) = V(r)$, with no dependence on θ or φ is due to the coloumb interaction and $m = \frac{m_e m_p}{m_e + m_p}$, is the 2-body reduced mass of the hydrogen nucleus(a proton) of mass m_p and the electron of mass m_e. The reduced mass in place of the electron mass is used since the electron and proton together orbit each other about a common centre of mass, and constitute a two-body problem to solve. The motion of the electron is the prime interest, so the equivalent one-body problem is the motion of the electron using the reduced mass.Assume that $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$ and substitute that into the Schrödinger equation.

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] + VRY = ERY \quad \ldots\ldots\ldots (3)$$

Divide both sides by RY and multiply both sides by $-\frac{2mr^2}{\hbar^2}$, and collect terms.

$$\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]\right\} + \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\} = 0 \quad \ldots\ldots\ldots (4)$$

The quantities in thebrackets must separately be equal to a constant, $\pm C$, else the equation won't be valid for all r,θ,φ. Therefore, we have two equations,

Angular equation:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -CY \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Radial equation:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)R = CR \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

These have to be solved separately.

3.5.1 THE ANGULAR SOLUTIONS

From the relation

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}=-CY \qquad \ldots\ldots\ldots\ldots (7)$$

We need to solve for *Y* and evaluate the *C*.

Assume that $Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$. Substitute into the differential equation and divide both sides by *Y*.

$$\left\{\frac{1}{\Theta}[\sin\theta\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta})]+C\sin^2\theta\right\}+\left\{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}\right\}=0 \qquad \ldots\ldots\ldots (8)$$

As usual, the two terms must separately be equal to a constant, $\pm D$.

$$\frac{d^2\Phi}{d\varphi^2}=-D\Phi$$

$$\sin\theta\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta})+(C\sin^2\theta-D)\Theta=0 \qquad \ldots\ldots\ldots (9)$$

It can be shown that in fact $C=\ell(\ell+1)$ and $D=m^2$. We have $\Phi=e^{im\varphi}$. What remains is to solve for the $\Theta(\theta)$.

$$\sin\theta\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta})+[\ell(\ell+1)\sin^2\theta-m^2]\Theta=0 \qquad \ldots\ldots\ldots\ldots (10)$$

This is a well known differential equation, whose solutions are the *Associated Legendre Functions*, $P_\ell^m(\cos\theta)$. These are defined in turn in terms of the *Legendre Polynomials*, $P_\ell(x)$, with $x=\cos\theta$.

$$P_\ell(x)=\frac{1}{2^\ell\,\ell!}\left(\frac{d}{dx}\right)^\ell(x^2-1)^\ell$$

$$P_\ell^m(x)=(1-x^2)^{\frac{|m|}{2}}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

So, we do not have to solve for Θ all over from scratch .Now we have to normalize the angular solution. $Y_\ell^m(\theta,\varphi)=e^{im\varphi}P_\ell^m(\cos\theta)$

$$\int_0^{2\pi}\int_0^{\pi}\left|Y_\ell^m\right|^2\sin\theta\,d\theta\,d\varphi=1 \qquad \ldots\ldots\ldots\ldots\ldots (12)$$

This has been done already, so we just look up the result:

$$Y_\ell^m(\theta,\varphi) = \varepsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\varphi}P_\ell^m(\cos\theta)$$

$$\text{where } \varepsilon = \begin{cases} (-1)^m \text{ if } m \geq 0 \\ 1 \text{ if } \; m \leq 0 \end{cases} \qquad \ldots\ldots\ldots \quad (13)$$

The Y_ℓ^m are called *Spherical Harmonics*, and comprise a complete set of orthogonal functions. That means that any function of θ and φ can be expanded as a sum of Y_ℓ^m.

3.5.2 RADIAL EQUATION AND SOLUTION

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m_e r^2}{\hbar^2}\big(V(r)-E\big)R = \ell(\ell+1)R \qquad \ldots\ldots\ldots.. \;(14)$$

Since we have *m* for the azimuthal, or magnetic, quantum number, we'll start using $m_e$for the mass of the electron. In addition, we'll find it convenient to make a change of variable, letting $u(r) = rR(r)$.

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left(V(r) + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right)u = Eu \qquad \ldots\ldots\ldots\ldots \;(15)$$

Classically, we do the same thing when solving Newton's "Law" for orbits in a gravitational field.

For the Hydrogen atom, the force acting on the electron is the electrostatic Coulomb force: The potential energy function is $V(r) = -\dfrac{e^2}{4\pi\varepsilon_o r}$. The radial equation therefore becomes

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left(\frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_o r}\right)u = Eu \qquad \ldots\ldots\ldots\ldots \;(16)$$

To simplify it, we'll change the variable again. Firstly, let $\kappa = \dfrac{\sqrt{-2m_eE}}{\hbar}$. Secondly, let $\rho = \kappa\, r$ and $\rho_o = \dfrac{m_e e^2}{2\pi\varepsilon_o\hbar^2\kappa}$. Now, the radial equation at least has a cleaner appearance:

$$\frac{d^2u}{d\rho^2} = \left(1 - \frac{\rho_o}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u \qquad \ldots\ldots\ldots \quad (17)$$

The solution is divided into two parts. The first part is called the *asymptotic behavior*, related to the solution at very large distance from the proton or very close to the proton.

a. Asymptotic behavior

i) as $\rho \to \infty, \frac{d^2u}{d\rho^2} \approx u$, which has the solution $u(\rho) = Ae^{-\rho}$.

ii) as $\rho \to 0, \frac{d^2u}{d\rho^2} \approx \frac{\ell(\ell+1)}{\rho^2}u$, which has the solution $u(\rho) = C\rho^{\ell+1}$.

Therefore, we propose that the radial solution has the form $u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho)$. We'll plug this into the radial equation and assume that $v(\rho)$ is a power series in ρ.

b. Series solution

We'll need

$$\frac{du}{d\rho} = \rho^{\ell}e^{-\rho}[(\ell+1-\rho)v + \rho\frac{dv}{d\rho}] \quad \text{.....................} (18)$$

And

$$\frac{d^2u}{d\rho^2} = \rho^{\ell}e^{-\rho}\left\{[-2\ell - 2 + \rho + \frac{\ell(\ell+1)}{\rho}]v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\} \text{.........} (19)$$

In the radial equation, the common factors of $\rho^{\ell}e^{-\rho}$ will divide out.

$$[-2\ell - 2 + \rho + \frac{\ell(\ell+1)}{\rho}]v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2} = [1 - \frac{\rho_o}{\rho} + \frac{\ell(\ell+1)}{\rho^2}]v \quad \text{........} (20)$$

Collect the like terms.

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_o - 2(\ell+1)]v = 0 \quad \text{..........} (21)$$

At this point, we assume that $v(\rho) = \sum_{j=0}^{\infty} a_j\rho^j$ and substitute it into the differential equation.

$$\frac{dv}{d\rho} = \sum_{j=1}^{\infty} ja_j\rho^{j-1} = \sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j \quad \text{..................} (22)$$

$$\frac{d^2v}{d\rho^2} = \frac{d}{d\rho}\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j = \sum_{j=0}^{\infty} j(j+1)a_{j+1}\rho^{j-1} \quad \text{............} (23)$$

$$\rho\sum_{j=0}^{\infty} j(j+1)a_{j+1}\rho^{j-1} + 2(\ell+1-\rho)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^{j} + [\rho_o - 2(\ell+1)]\sum_{j=0}^{\infty} a_j\rho^j = 0 \quad \ldots\ldots\ldots (24)$$

The coefficient of <u>each</u> power of ρ must vanish separately.

$$j(j+1)a_{j+1} + 2(\ell+1)(j+1)a_{j+1} - 2ja_j + [\rho_o - 2(\ell+1)]a_j = 0 \quad \ldots\ldots\ldots\ldots (25)$$

Solve for a_{j+1}.

$$\begin{aligned} a_{j+1} &= a_j\,\frac{-\rho_o + 2(\ell+1) + 2j}{j(j+1) + 2(\ell+1)(j+1)} \\ &= a_j\,\frac{2(j+\ell+1) - \rho_o}{(j+1)(j+2\ell+2)} \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots \quad (26)$$

The first coefficient is determined by the normalization condition, $a_0 = A$ for the moment, and the rest follow from the formula (called a *recursion relation*) above. However, the series must terminate, else $v(\rho)$ will diverge at large ρ. That is, the series cannot be infinitely long, for physical reasons. There must be some maximum value of j such that $a_{j_{\max}+1} = 0$. In the recursion relation

$$\begin{aligned} &2(j_{\max} + \ell + 1) - \rho_o = 0 \\ &j_{\max} + \ell + 1 = \frac{\rho_o}{2} \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27)$$

We define $n = j_{\max} + \ell + 1$ to be the *principle quantum number*, because it labels the discrete energy levels (through the ρ_o).

3.5.3 RADIAL WAVEFUNCTIONS

Now, we work backward from $v(\rho)$ to $R(r)$. We had set $\rho = \kappa r$ and $R = ru$ and $u = \rho^{\ell+1}e^{-\rho}v(\rho)$.

$$R_{n\ell}(r) = \frac{1}{r}u = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v_n(\rho) \quad \ldots\ldots\ldots\ldots\ldots \quad (28)$$

a. Ground state wave function

The ground state wave function is

$$R_{10} = \frac{1}{r}\rho \cdot e^{-\rho} a_o \cdot 1 = \frac{1}{r}\kappa r e^{-\kappa r} a_o = a_o \kappa e^{-\kappa r}$$

$$= a_o \frac{m_e e^2}{4\pi\varepsilon_o \hbar^2} e^{-\frac{m_e e^2}{4\pi\varepsilon_o \hbar^2} r}$$

$$= \frac{a_o}{a} e^{-\frac{r}{a}} \qquad \text{………………. (29)}$$

Here, the $a = \frac{4\pi\varepsilon_o \hbar^2}{m_e e^2}$ is the *Bohr Radius*. To evaluate the a_o we normalize the R_{10}.

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|a_o|^2}{a^2} \int_0^\infty e^{-\frac{2r}{a}} r^2 dr = \frac{|a_o|^2}{a^2} \frac{a^3}{4} = 1 \qquad \text{……… (30)}$$

$$a_o = \frac{2}{\sqrt{a}}$$

$$R_{10}(r) = \frac{2}{a^{3/2}} e^{-\frac{r}{a}} \qquad \text{…………………. (31)}$$

b. Excited state wave functions

For $n > 1$, $\ell = 0, 1, 2, 3, \ldots, n-1$ and $m = -\ell, \ldots, 0, \ldots, \ell$. The $v_{n\ell}(\rho)$ is a polynomial of degree $n - \ell - 1$ (that is, $j_{\max}$) whose coefficients are given by the recursion relation

$$a_{j+1} = \frac{2(j + \ell + 1 - n)}{(j+1)(j + 2\ell + 2)} a_j \qquad \text{…….. (32)}$$

and a_o is determined by normalizing the function.

As they have been defined, the $v_{n\ell}(\rho)$ are also “well known” as the *Laguerre* and *Associated Laguerre Polynomials*:

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

$$L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \qquad \text{……………….. (33)}$$

For us, $x = \dfrac{2r}{na}$.

After all the normalization, we get the wave functions for the energy states of the electron in the Hydrogen atoms:

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\; e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^{\ell} L_{n-\ell+1}^{2\ell+1}\left(\frac{2r}{na}\right) Y_{\ell}^{m}(\theta,\varphi) \qquad \text{........ (34)}$$

c. Energy levels

The ρ_o is in the total energy, E: $E = -\dfrac{\hbar^2\kappa^2}{2m_e} = -\dfrac{m_e e^4}{8\pi^2\varepsilon_o^2\hbar^2\rho_o^2}$.

$$E_n = -\frac{m_e e^4}{8\pi^2\varepsilon_o^2\hbar^2 4n^2} = -\frac{m_e e^2}{32\pi^2\varepsilon_o^2\hbar^2 n^2} = -\frac{1}{n^2}\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right], n = 1,2,3,\ldots \qquad \text{.......... (35)}$$

These are exactly the same energy levels obtained for the classical Bohr model of the Hydrogen atom. However, Bohr's model does not have ℓ and m.

The ground state wave function is

$$\begin{aligned}\psi_{100}(r,\theta,\varphi) &= R_{10}(r)Y_0^0(\theta,\varphi)\\ &= \frac{2}{a^{3/2}} e^{-\frac{r}{a}} \frac{1}{\sqrt{4\pi}}\\ &= \frac{1}{\sqrt{\pi\,\mathrm{a}^3}} e^{-\frac{r}{a}}\end{aligned} \qquad \text{.................. (36)}$$

The corresponding ground state energy is E_1 = -13.6 eV. The excited states have the energies $E_n = \dfrac{E_1}{n^2}$.

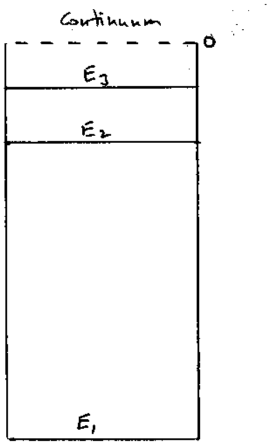

Fig.(3.4)

d. Degeneracy

As we know that for any n, $\ell = 0,1,2,3,\ldots,n-1$ and $m = -\ell,\ldots,0,\ldots,\ell$. Consequently, there may be several states whose energy is the same. This condition is called *degeneracy*. The energy levels are said to be *degenerate*. For instance, let $n = 3$. Then there are three possible values of ℓ. For each value of ℓ, there are $2\ell+1$ possible values of m. Therefore, the degeneracy of the $n = 3$ level is 1 + 3 + 5 = 9. There are nine wave functions that have the same energy, E_3.

e. Unbound states

If $E < 0$, then $\kappa > 0$ and is real. But if $E > 0$, then κ is imaginary and we obtain free-particle oscillating solutions, with continuous energy values rather than discrete. We speak of the *continuum* of energy states lying above the discrete bound states.

3.6 CHECK YOUR PROGRESS

Q1. For the hydrogen atom prove the degeneracy relation $g_n = \sum_{l=0}^{n-1}(2l+1) = n^2$.

Q2. An electron is trapped inside an infinite spherical well $V(r)= 0$ *for* $r<a$ *and* $V(r)=\infty$ for r>a,

(a) Using the radial Schrödinger equation, determine the bound eigenenergies and the correspondingnormalized radial wave functions for the case where the orbital angular momentumof the electron is zero (l=0)
(b) Show that the lowest energy state for $l = 7$ lies above the second lowest energy state for $l = 0$.

(c) Calculate the probability of finding the electron in a sphere of radius $a/2$, and then in a spherical shell of thickness $a/2$ situated between $r = a$ and $r = 3a/2$.

Q3. Consider a hydrogen atom which is in its ground state; the ground state wave function is givenby

$$\psi(r,\theta,\phi)=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

where a_0 is the Bohr radius.
(a) Find the most probable distance between the electron and the proton when the hydrogen atom is in its ground state.
(b) Find the average distance between the electron and the proton.

Q4. A hydrogen atom has the wave function $\psi_{nml}(r)$, where $n = 4$, $l = 3$ and $m = 3$.
(a) What is the magnitude of the orbital angular momentum of the electron around the proton?(c) Sketch the shapes of the radial function and of the probability of finding the electron a distance r from the proton.

Q5. (a) For the following cases, calculate the value of r at which the radial probability density of the hydrogen atom reaches its maximum: (i) $n = 1$, $l = 0$, $m = 0$; (ii) $n = 2$, $l = 1$, $m = 0$;
(iii) $l = n - 1$, $m = 0$.
(b) Compare the values obtained with the Bohr radius for circular orbits.

Q6.Calculate the mean value of r for an electron in the ground state of hydrogen atom

Q7.Calculate the mean value of 1/r for 1s electron in the hydrogen atom.

Q8.Solve the radial part of the Schrodinger's equation for the hydrogen atom.Obtain the energy eigen values and radial wave function.

Q9.Using Schrodinger'sequation discuss and solve the problem of particle in a 3D box.

Q10.Obtain the Schrodinger's equation for a particle moving under a central potential and separate the variables.

Q11.Disscuss the motion of a particle in central potential using spherical coordinate system.

Q12.Discuss the 3D isotropic oscillator using spherical coordinate system.

Q13.Solvethe problem of a particle of mass m in an attractive 3D spherical well potential

Q14.Obtain ground state wavefunction for hydrogen atom and calculate the most probable distance of the electron from the nucleus.

Q.15.Explain how one can solve the problem of the hydrogen atom quantum mechanically.

Q.16.Write polar part of Schrodinger's equation and solve it.

Q.17.Discuss the degeneracy of energy levels of hydrogen atom, explain the conditions under which degeneracy removed.

Q.18.Write angular part of Schrodinger's equation and separate it.

Q.19.Consider an electron in the coulomb field of a stationary proton.Determine energy eigen values and the radial part of the eigen functions of electron.

Q.20.Discuss the motion of free particle in central potential using spherical coordinate system.

Q.21. Show that the wave function

$$\chi(r) = C\ r\ \left(1 - \frac{Zr}{2a_0}\right)\exp(-{Zr}/{2a_0})$$

satisfies the TISE for the radial part of the electron's wave function in a Hydrogen-like atom , where the quantum numbers are *n=2* and *l=0.*

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UNIT – 4: OPERATORS AND EIGENFUNCTIONS

4.1 INTRODUCTION

In the previous chapter we have developed Schrodinger wave equation and applied it to simple problems. We also learnt how to find the expectation values of various physical quantities. Now in this unit we will study the operator formalism of some common physical quantities like position, linear momentum, kinetic energy etc. The various kinds of operators and their properties will be studied in details.

4.2 OBJECTIVES

After going through this unit you will be able to understand what are -

- Operators in quantum mechanics
- Eigen values and Eigen functions
- Orthogonality of Eigen functions
- Various kinds of operators and their properties
- To solve the problems related to the above topics

4.3 DYNAMICAL VARIABLES AS OPERATORS

An operator is a rule by means of which a given function is changed into another function. The dynamical variables like energy, momentum, position etc. are called observables. Each observable has a definite operator associated with it.
An operator may also be defined as a mathematical term which is used in operation on a function such that it is transferred into another function.
Thus if Â is an operator applied to a function u(x), then it is changed into a function v(x); accordingly

$$V(x) = \hat{A}\, u(x)$$

The example of operators are addition, subtraction, multiplication, division, differentiation, integration, operations of grad, div, curl etc.

For example, let $u(x) = \sin\alpha x$

And the operator $\hat{A} = \frac{}{x}$

Then, $v(x) = \hat{A}\, u(x)$

$= \frac{}{x}(\sin \alpha x)$

$= \alpha \cos\alpha x$

Thus the operation of $\frac{}{x}$ on a function sinx transforms it into another function αcosαx.

4.3.1 Linear Operators:-

In quantum mechanics, we deal with linear operators and even if the term operator is used, it means linear operator only. An operator Â is said to be linear if it satisfies the following two condition for arbitrary functions f(x), g(x) and arbitrary constant C.

(a) $A\,[f(x)+g(x)] = A\,[f(x)] + A\,[g(x)]$ …..(1)

(b) $A\,[cf(x)] = C\,[Af(x)]$ …..(2)

According to the first condition, we add two functions f(x), g(x) and then operate A on the resulting function, or, we operate A on f(x) and g(x) separately and then add, we should end up with the same function. The second condition states that if we multiply a function by a constant C and then operate A on the resulting function, or we operate A on the function and then multiply by C, we should end up with the same function.

- Example –

Check whether the following operators are linear or not : (a) Multiplication by x, (b) Squaring.

Solution – (a) Let *f(x)* and *g(x)* be two functions of x. Let *A* denote the operator "multiplication by x"

$A\,[f(x) + g(x)] = x\,[f(x) + g(x)] = xf(x) + xg(x) = A\,[f(x)] + A\,[g(x)]$

$A\,[cf(x)] = x\,[cf(x)] = cxf(x) = c\,[Af(x)].$

Both the required conditions are satisfied. Hence, A is a linear operator.

(b)Let A denote the operator "squaring".

$A\,[f(x) + g(x)] = [f(x) + g(x)]^2$

$A\,[f(x)] = [f(x)]^2,\ A\,[g(x)] = [g(x)]^2.$

We see that $A\,[f(x) + g(x)] \neq A\,[f(x)] + A\,[g(x)].$

So, *A* is not a linear operator.

We can check that the second condition is also not fulfilled.

Properties of linear operators

4.3.1(a) Identity Operator Î :

The identity operator (Î) is an operator, which operating on a function ,leaves the function unchanged,i.e.

$$\hat{I}f(x) = f(x) \qquad \text{.....(3)}$$

(b)Null or zero Operator: An operator which annihilates a function when operates on it is called a null operator. Thus if

$$\hat{O}f(x) = 0 \qquad \text{.....(4)}$$

Then Ô is a null operator.

4.3.2 OperatorAlgebra:

The algebra of linear operators is constructed by their addition, multiplication, power etc. If there are two operators Â and$\hat{B}$ then their sum is

$$\hat{C} = \hat{A} + \hat{B} \qquad \text{.....(1)}$$

If for every function Ψ

$$\hat{C}\Psi = \hat{A}\Psi + \hat{B}\Psi \qquad \text{.....(2)}$$

Similarly, if their product is

$\hat{C} = \hat{A}\hat{B}$, then

$$\hat{A}\hat{B}\Psi = \hat{A}(\hat{B}\Psi) = \hat{C}\Psi \qquad \text{.....(3)}$$

But it is to be noted that product of operators may not be commutative. The operators $\hat{A}\hat{B}$ and $\hat{B}\,\hat{A}$ are in general not the same but addition of operators is commutative.

For example: Let $A = x$ and $B = \frac{d}{dx}$.

Then $\hat{A}\hat{B}\Psi = x\frac{d\Psi}{dx}$

$\hat{B}\hat{A}\Psi = \frac{d}{dx}(x\Psi)$

$= x\frac{d\Psi}{dx} + \Psi$

Hence $\hat{A}\hat{B}\Psi \neq \hat{B}\hat{A}\Psi$

Or $\hat{A}\hat{B} \neq \hat{B}\hat{A}$

The operators Â and$\hat{B}$ will commute only if

$$\hat{A}\hat{B} = \hat{B}\hat{A}$$

The power of an operator is defined as

$$\hat{A}^2 = \hat{A}\hat{A}$$

$$\hat{A}^3 = \hat{A}\hat{A}\hat{A}$$

.

.

.

$$\hat{A}^n = \hat{A}\hat{A}\ldots\ldots\hat{A} \text{ (n times)}$$

4.3.3 Operators associated with dynamical variables

The measurable quantities like energy, momentum position etc. are called observables. Each observable has definite operator associated with it.

Energy operator

The Schrodinger equation

$$H\Psi = E\Psi$$

informs that the operator associated with the energy E is Hamiltonian H, i.e. E_{op} or E = H

The time independent form of E_{op} is

$$E_{op} = H = -\frac{\hbar^2}{2m}+\nabla^2 V$$

The time dependent Schrodinger equation is

$$H\Psi = i\hbar\frac{\Psi}{t} \quad \text{i.e.} \quad (H)\Psi = \left[i\hbar \frac{}{t}\right]\Psi$$

i.e. time dependent value of Hamiltonian is

$$H = i\hbar \frac{}{t}$$

Thus, we have

$$E_{op} = H = -\frac{\hbar^2}{2m}\nabla^2 + V = i\hbar \frac{}{t}$$

Momentum operator

As Hamiltonian

$$H = K.E. + P.E. = \frac{p^2}{2m} + V$$

Also, $$H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$\therefore \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$$

i.e. $$p^2 = -\hbar^2\nabla^2$$

Thus, operator associated with momentum P_{op} is

$$P_{op}^2 = -\hbar^2\nabla^2 = \frac{\hbar^2}{i^2}\nabla^2$$

or, $$P_{op} = \frac{\hbar}{i}\nabla$$

If P_x, P_y and P_z are components of momentum P,

then $(\hat{i}P_x + \hat{j}P_y + \hat{k}P_z) = \frac{\hbar}{i}\left(\hat{\imath}\frac{}{x} + \hat{\jmath}\frac{}{y} + \hat{k}\frac{}{z}\right)$

Accordingly, the following table represents the operators associated with different observables.

Quantity	Operator	Symbol
Position	Multiplication by x	X
Linear momentum (x-component)	$-i\hbar\frac{}{x}$	P_x
Kinetic Energy	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	K
Potential Energy	Multiplication by V(x)	V

Total Mechanical Energy	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)$	H

4.4 EIGEN VALUES AND EIGEN FUNCTIONS

If Ψ is a well behaved function, then an operator A may operate on Ψ in two different ways depending on the nature of function Ψ:

(i) The operator Â operating on the function Ψ may change the function into another function ϕ, i.e.,

$\hat{A}\Psi = \phi$ ….. (1)

Then the new function ϕ will in general be linearly independent of initial function Ψ.

(ii) The operator Â operating on some function Ψ, may leave the function unchanged but with a complex or real multiple, i.e.,

$\hat{A}\Psi = \lambda\Psi$ …..(2)

where λ may be real or complex number. In this case the function Ψ is a member of the class of physically meaningful function, called the eigen function of the operator Â. The number λ is called the eigen value of the operator Â associated with eigen function Ψ. Equation (2)is called Eigen value equation.

NOTE: The eigen functions are selected from a special class of functions. In a bound state problem, for example, all wave functions are required to be continuous, to have continuous derivatives and to vanish at infinity in such a way as to have an integrable square. In the continuum states, the functions are not allowed to become infinite at large distances.

Ex: let operator $\hat{A} = \frac{d}{dx}$

And wave function = e^{-4x}

Then according to the standard eigen value equation $\hat{A}\Psi = \lambda\Psi$.

$$\frac{d}{dx}\,(e^{-4x}) = -4\,e^{-4x}$$

We see that λ = -4 is the eigen value of operator $(\frac{d}{dx})$ associated with the eigen functione^{-4x}.

Example 1: Find the value of the constant B that makes e^{-ax^2}an eigenfunction of the operator $[\frac{d^2}{dx^2}$- Bx^2]. What is the corresponding eigen value?

Solution: The eigen value function of operator Â is

$$\hat{A}\Psi = \lambda\Psi \qquad .....(1)$$

Where λ is eigen value of state Ψ.

Here $\hat{A} = [\frac{d^2}{dx^2} - Bx^2]$ .....(2)

and $\Psi = e^{-ax^2}$

so, $\hat{A}\Psi = [\frac{d^2}{dx^2} - Bx^2]\, e^{-ax^2}$

$=\frac{d^2}{dx^2}(e^{-ax^2})- Bx^2e^{-ax^2}$

$= -2ae^{-ax^2}[1-2ax^2] - Bx^2e^{-ax^2}$

$= [4a^2x^2- 2a-Bx^2]e^{-ax^2}$

$$\hat{A}\Psi = [(4a^2-B)x^2- 2a]e^{-ax^2} \qquad .....(3)$$

If the constant B makes $\Psi = e^{-ax^2}$ on R.H.S., then

$4a^2 - B = 0$ or $B = 4a^2$

So above equation takes the form

$\hat{A}\Psi = -2ae^{-ax^2}$

$$\hat{A}\Psi = -2a\Psi \qquad .....(4)$$

Comparing eqn.(4) with (1)

$\lambda = -2a$

i.e., eigen value of operator Â is (-2a).

4.5 EIGEN VECTOR OF AN OPERATOR

We have studied in section 4.3 that the result of operating on a vector with an operator Â, is in general, a different vector.

$$\hat{A}\Psi = \phi \qquad .....(1)$$

But there may be some vector Ψ with the property

$\hat{A}\Psi = \lambda\Psi$ …..(2)

Where λ is a scalar and Ψ is then called the eigen vector or eigen function of Â belonging to the eigen value λ. A linear operator has in general, several eigen values and eigen vectors, which are distinguished by the subscript:

$\hat{A}\Psi_{k} = \lambda_k\Psi$ …..(3)

The set $[\lambda_k]$ of all the eigen values taken together constitute the spectrum of the operator. The eigen values may be discrete, continuous or partly discrete and partly continuous. An eigen vector belongs to only one eigen value. But several linearly independent eigen vectors may belong to the same eigen value.

We find the eigen vector in the following way:-

Let us consider a matrix A, for which the characteristic matrix is

$A - \lambda I$ …..(4)

where A is the given matrix, λ is the scalar quantity and I is the Identity matrix. Here A and I should have same order and they should be square matrix. Their characteristic equation will be obtained by equating the determinant of equation **(4)**equal to zero.

$|A - \lambda I| = 0$ …..(5)

The roots of the above equation are called the eigen values. For every eigen value there is an eigen vector. For finding the eigen vector, we consider a non-zero characteristic vector 'X' which satisfies the equation

$[A - \lambda I]X = 0$ …..(6)

4.6 ORTHOGONALITY OF EIGEN FUNCTIONS

Two wave functions Ψ_1(x) and Ψ_2(x) are said to be orthogonal or ina definite interval $a \leq x \leq b$ if they follow the condition

$\int_a^b \Psi_2^*(x)\, \Psi_1(x)\, dx = 0$ …..(1)

where $\Psi_2^*(x)$ is the complex conjugate of $\Psi_2(x)$.

If we consider a set of functions $\Psi_1, \Psi_2, \Psi_3 \ldots..\Psi_m, \Psi_n \ldots$, then the two functions Ψ_m and Ψ_n ($m \neq n$) are said to be orthogonal in the interval (a,b) if and only if

$\int_a^b \Psi_m^* \Psi_n dx = 0$ …..(2)

In general if m = n, then

$\int \Psi_m^* \Psi_n dx = 1$

i.e.,$\int \Psi_m^* \Psi_m dx = \int \Psi_n^* \Psi_n dx = 1$ …..(3)

Here Ψ_m and Ψ_n are normalised wave functions. If any wave function Ψ is not normalised, then it can be normalised by multiplying it with a normalisation constant N, i.e.,

$\int N^* \Psi^* N\Psi dx = 1$

$N^* N \int \Psi^* \Psi dx = 1$

$N^* N = |N|^2 = \frac{1}{\int \Psi^* \Psi dx}$[$N^* = N$, it is not imaginary]

In general orthogonal functions satisfy the condition

$\int \Psi_m^*(x) \Psi_n(x) dx = {}_{mn}$

where ${}_{mn} = \begin{cases} 1 \text{ for m } = \text{ n, gives the condition of normalised function} \\ 0 \text{ for m } \neq \text{ n, gives the condition of orthogonal function} \end{cases}$

4.7 HERMITIAN OPERATOR

The expectation average of a dynamical variable, by definition, is the arithmetic mean of the possible results of a precise measurement of this variable, each possible result being weighted by its probability. The possible result of measurements of actual physical variables or observable is real numbers and consequently the average value of any physical variable for any state at any time must be real number. Now if P is the Schrodinger operator associated with an observable quantity then the value of observable quantity is the normalised state Ψ is given by

$avP_\Psi = \langle P \rangle = \int \Psi^* P \Psi dx$ ..…(1)

An operator P associated with dynamical variable is said to be hermitian if its average value in any state Ψ is real. If the average of P for the state Ψ is to be real, the expression $\int \Psi^* P\Psi dx$ must be real or in other words, imaginary factor must be zero, i.e.,

$I_m \int \Psi^* P \Psi dx = 0$ …..(2)

for any normalised wave function Ψ.

All Schrodinger operators associated with real variable must satisfy above relation.

The complex conjugate of the function $\int \Psi^* P\Psi dx$ may be written either as

$\int (\Psi^* P \Psi)^* dx = \int \Psi (P\Psi)^* dx = \int P^* \Psi^* \Psi dx$ …..(3)

Where $(P\Psi)^*=P^*\Psi^*$ denotes the complex conjugate of the function $(P\Psi)$ and $P^*\Psi^*\Psi$ denotes $(P\Psi)^*.\Psi$.

Condition (1) is only satisfied if the complex conjugate of the function $\Psi^*P\Psi$ is equal to the function $\int\Psi^*P\Psi dx$ itself, i.e. *the condition of an operator P to be hermitian is*

$\int\Psi^*P\Psi dx = \int(P\Psi)^*\Psi dx$ …..(4)

To obtain a general condition for a hermitian operator let *u* and *v* be any two acceptable normalisable wave equations *x* and let *P* satisfy (1) so that (4) holds also. Then setting $\Psi=u+v$, equation (4) gives

$\int(u+v)^*\hat{P}\Psi dx = \int [\hat{P}(u+v)]^*.(u+v)dx$ …..(5)

$= \int \hat{P}^*(u+v)^*.(u+v)dx$

That is

$\int u^*\hat{P}\, udx + \int u^*\hat{P}\, vdx + \int v^*P\, udx + \int v^*\hat{P}\, vdx$

$= \int \hat{P}^*u^*u.dx + \int \hat{P}^*u^*v.dx + \int \hat{P}^*v^*u.dx + \int \hat{P}^*v^*v.dx$…..(6)

As P is hermitian operator in the state u and v, therefore relation (4) provides

$\int u^*\hat{P}u\, dx = \int \hat{P}^*u^*u\, dx$

And

$\int v^*\hat{P}v\, dx = \int \hat{P}^*v^*v\, dx$

In view of above, equation (6) gives

$\int u^*\hat{P}v\, dx + \int v^*\hat{P}u\, dx = \int \hat{P}^*u^*v\, dx + \int \hat{P}^*v^*u.dx$ …..(7)

If we use the function iv instead of v in (5), we get instead of (8).

$\int u^*\hat{P}\, iv\, dx + \int (iv)^*\hat{P}u\, dx = \int \hat{P}^*u^*(.iv)dx + \int \hat{P}^*(iv)^*u\, dx$

$i \int u^*\hat{P}v\, dx + i \int v^*\hat{P}u\, dx = i \int\hat{P}^*u^*v\, dx + i \int\hat{P}^*v^*u\, dx$ …..(8)

Cancellation of the factor i in the above equation yields

$\int u^*\hat{P}v\, dx - \int v^*\hat{P}u\, dx = \int\hat{P}^*u^*v\, dx - \int\hat{P}^*v^*u\, dx$ …..(9)

Adding (7) and (9) we get

$2\int_{-\infty}^{+\infty} u^*\hat{P}vdx = 2\int_{-\infty}^{+\infty} \hat{P}^*u^*vdx$

or

$\int_{-\infty}^{+\infty} u^*\hat{P}vdx = \int_{-\infty}^{+\infty} \hat{P}^*u^*vdx$ .....(10)

If an operator satisfies equation (10) whenever u and v are normalisable, we call it Hermitian, self-adjoint or real.

Thus, if u and v are two acceptable normalised wave functions, defined over a certain range of configuration range τ, then operator P associated with a dynamical variable is **Hermitian** if

$\int u^*\hat{P}\, v\, d\tau = \int \hat{P}^* u^*\, v\, d\tau$ …..(11)

This equation may be expressed as

$(u,\hat{P}v) = (\hat{P}u,v)$

i.e. the operator can be applied on the either factor in the scalar product.

We have shown above that equation (10) is deduced from equation (4) and since equation (4) must hold for Schrodinger operators associated with real dynamical variables we conclude that every Schrodinger operator associated with a real dynamical variable is Hermitian.

4.7.1 Properties of Hermitian Operators

Theorem: Hermitian operators have real eigen values.

Proof: Let Ψ be an eigen value of Hermitianoperatorin the state described by normalised wave function Ψ.

Then, eigen value equation is

$\hat{P}\Psi = \lambda\Psi$ …..(1)

Taking its complex conjugate

$\hat{P}^*\Psi^* = \lambda^*\Psi^*$ …..(2)

According to the condition of Hermitian operator

$\int\Psi^*\hat{P}\Psi d\tau = \int \hat{P}^*\Psi^*\Psi\, d\tau$ …..(3)

Using (1) and (2) equation (3) gives

$\int\Psi^*\lambda\Psi d\tau = \int \lambda^*\Psi^*\Psi\, d\tau$

$\lambda \int\Psi^*\Psi\, d\tau = \lambda^*\int\Psi^*\Psi\, d\tau$

$(\lambda - \lambda^*) \int\Psi^*\Psi\, d\tau = 0$

$\int\Psi^*\Psi\, d\tau = 1$ (condition of normalisation)

∴ $\lambda - \lambda^* = 0$ and hence $\lambda^* = \lambda$.

This is only possible if λ is a real number.

This proves that the eigen value of each Hermitian operator is real.

Theorem: Two eigen functions of Hermitian operators, belonging to different eigen values, are orthogonal.

Proof: Let $\hat{P}$ be any Hermitian operator and Ψ_1 and Ψ_2 be two eigen functions of operator $\hat{P}$.

If λ_1 and λ_2 are distinct eigen values of operator $\hat{P}$ corresponding to eigen functions Ψ_1 and Ψ_2 respectively, then eigen value equations are

$$\hat{P}\Psi_1 = \lambda_1\Psi_1$$

$$\hat{P}\Psi_2 = \lambda_2\Psi_2 \qquad \text{.....(1)}$$

Complex conjugates of these equations are

$$\hat{P}^*\Psi_1^* = \lambda_1^*\Psi_1^* \text{ or } \hat{P}^*\Psi_1^* = \lambda_1\Psi_1^*$$

$$\hat{P}^*\Psi_2^* = \lambda_2^*\Psi_2^* \text{or } \hat{P}^*\Psi_2^* = \lambda_2\Psi_2^* \qquad \text{.....(2)}$$

Since λ_1 and λ_2, being eigen value of Hermitian operator, are real.

According to the general condition of Hermitian operator P, we have

$$\int\Psi_2^*\hat{P}\Psi_1 d\tau = \int (\hat{P})^*\Psi_2^*\Psi_1 d\tau$$

Using (1) and (2), we get

$$\int\Psi_2^*\lambda_1 \Psi_1 d\tau = \int\lambda_2 \Psi_2^*\Psi_1 d\tau$$

or $\quad \lambda\int\Psi_2^*\Psi_1 d\tau = \lambda_2\int\Psi_2^*\Psi_1 d\tau$

or $\quad (\lambda_1 - \lambda_2)\int\Psi_2^*\Psi_1 d\tau = 0$

As $\lambda_1 \neq \lambda_2$, we have $\int\Psi_2^*\Psi_1 d\tau = 0$.

Thereby indicating that Ψ_1 and Ψ_2 are orthogonal functions.

This theorem guarantees that the orthogonality relations $\int\Psi_i^*\Psi_j d\tau = \delta_{ij}$ are satisfied for a set of normalised eigen functions belonging to different eigen values λ_i.

Theorem: If two Hermitian operators commute, then their product is also a Hermitian operator.

Proof: Let Ψ_1 and Ψ_2 be two functions and $\hat{A}$and $\hat{B}$ be two Hermitian operators.

Now consider the integral

$\int \Psi_1 \hat{A}\hat{B}\Psi_2 d\tau$

If $\hat{A}$ is Hermitian operator, then

$\int \Psi_1{}^{*}\hat{A}\hat{B}\Psi_2 d\tau = \int \Psi_1{}^{*}\, \hat{A}\, (\hat{B}\Psi_2)\, d\tau($

$= \int \hat{A}^{*}\Psi_1{}^{*}\, (\hat{B}\Psi_2) d\tau$ …..(1)

Again $\hat{B}$ is Hermitian operator, we have

$\int (\hat{A}^{*}\Psi_1{}^{*})\hat{B}\Psi_2 d\tau = \int \hat{B}^{*}\hat{A}^{*}\Psi_1{}^{*}\Psi_2 d\tau$ …..(2)

From (1) and (2), we have (for two operators $\hat{A}$ and $\hat{B}$ to be Hermitian)

$\int \Psi_1{}^{*}\hat{A}\hat{B}\, \Psi_2 d\tau = \int \hat{B}^{*}\hat{A}^{*}\Psi_1{}^{*}\Psi_2 d\tau$ …..(3)

If operators $\hat{A}$ and $\hat{B}$ commute, we have

$\hat{A}\hat{B} = \hat{B}\hat{A}$ or $\hat{A}^{*}\hat{B}^{*} = (\hat{B})^{*}(\hat{A})^{*}$ …..(4)

In view of this equation (3) becomes

$\int \Psi_1{}^{*}\hat{A}\hat{B}\Psi_2 d\tau = \int \hat{A}^{*}\hat{B}^{*}\Psi_1{}^{*}\Psi_2 d\tau$ …..(5)

This is the condition for the product operator ($\hat{A}\hat{B}$) to be Hermitian operator.

Hence, if $\hat{A}$ and $\hat{B}$ are commuting Hermitian operators, then their product $\hat{A}\hat{B}$ is also Hermitian.

Example 3: Show that momentum operator $\frac{\hbar}{i}\frac{}{x}$ is Hermitian.

Sol: Momentum operator $\hat{p} = \frac{\hbar}{i}\frac{}{x}$

Complex conjugate of $\hat{p}$ is $\hat{p}^{*} = -\frac{\hbar}{i}\frac{}{x}$

If p is a hermitian operator its expectation value <p> in any state Ψ must be real i.e.

$<\hat{p}> = \int_{-\infty}^{+\infty} \Psi * \frac{\hbar}{i}\frac{\Psi}{x} dx$ …..(1)

must be real.

Integrating (1) by parts, we get

$<\hat{p}> = \int_{-\infty}^{+\infty} \Psi \left(\frac{\hbar}{i}\frac{\delta\Psi}{\delta x}\right) dx = <\hat{p}>^{*}$ …..(2)

It is obvious from (1) and (2) that <p> is equal to its complex conjugate. In other words <p> is real.

Hence, we may say that the momentum operator $\hat{p} = \frac{\hbar}{i}\frac{}{x}$ is Hermitian.

4.8UNITARY OPERATOR

A linear operator $\hat{U}$ is unitary if it preserves the Hermitian character of an operator under similarity transformation. Now, a similarity transformation of an operator $\hat{A}$[1] by a non singular[2] operator $\hat{S}$, is defined as,

$$\hat{A} \rightarrow A' = \hat{S}\,\hat{A}\,\hat{S}^{-1} \qquad \text{…..(1)}$$

Thus the condition for $\hat{U}$ to be unitary is that

$$(\hat{U}\hat{A}U^{-1})^{\dagger} = \hat{U}\,\hat{A}\,\hat{U}^{-1} \qquad \text{…..(2)}$$

where $\hat{A}^{+}$[3] $= \hat{A}$

But $\quad (\hat{U}\hat{A}\hat{U}^{-1})^{\dagger} = (\hat{U}^{-1})^{\dagger}\,\hat{A}\,\hat{U}^{\dagger}$, so that

$$(\hat{U}^{-1})^{\dagger}\,\hat{A}\hat{U}^{\dagger} = \hat{U}\,\hat{A}\,\hat{U}^{-1}$$

Multiplying from the left by $\hat{U}^{\dagger}$ and from the right by $\hat{U}$, we get

$$\hat{U}^{\dagger}(\hat{U}^{-1})^{\dagger}\,\hat{A}\hat{U}^{\dagger}\hat{U} = \hat{U}^{\dagger}\,\hat{U}\,\hat{A}$$

i.e. $\quad \hat{A}\,(\hat{U}^{\dagger}\,\hat{U}) = (\hat{U}^{\dagger}\hat{U})\,\hat{A} \qquad$ …..(3)

since $\hat{U}^{\dagger}\,(\hat{U}^{-1})^{\dagger} = (\hat{U}^{-1}\hat{U})^{\dagger} = \hat{I}$

Now, only identity operator has the property that

$\hat{A}\hat{I} = \hat{I}\hat{A}$

for arbitrary operator $\hat{A}$, Hence,

$$\hat{U}^{\dagger}\,\hat{U} = \hat{I} \qquad \text{…..(4)}$$

In the case of infinite dimensional space, equation (4) by itself does not imply the condition that $\hat{U}$ should have an inverse. This condition can be incorporated by multiplying both sides of the equation by $\hat{U}^{-1}$. Then, the condition for the unitary of $\hat{U}$ becomes,

$$\hat{U}^{\dagger} = \hat{U}^{-1} \qquad \text{….(5)}$$

or $\quad \hat{U}\hat{U}^{\dagger} = \hat{U}^{\dagger}\hat{U} = \hat{I} \qquad$ ….(6)

Under the operation of $\hat{U}$, a vector X is transformed into a vector $X' = \hat{U}X$. Thus if two vectors X and Y are transformed by the same unitary operator $\hat{U}$, then,

$(X', Y') = (\hat{U}X, \hat{U}Y) = (X, \hat{U}^{\dagger}UY) = (X,Y)$

Thus the transformation by a unitary operator preserves the scalar product of vectors.

The properties of unitary vectors are

(1) The eigen values are unimodular, that is

$\hat{U}X = \alpha X$, then $|\alpha| = 1$.

(2) Eigen vectors belonging to different eigen values are orthogonal.

(3) Product of two or more unitary operators is unitary.

4.9 PROJECTION OPERATORS

Let us consider A and B as complementary subspaces. Any eigen vector possesses 'a' projection in A and 'b' projection in B. Let these component vectors be denoted by Ψ_a and Ψ_b respectively. These vectors are uniquely defined and we may write

$\Psi = \Psi_a + \Psi_b$

To each Ψ there corresponds one and only one Ψ_a. This correspondence is linear and the operator $\hat{P}_a$ which brings out the projection of Ψ in sub space A is denoted by $\hat{P}_a$ and is called the projection operator on sub-space A, i.e.

$\hat{P}_a\Psi = \Psi_a$ …..(1)

Also $(\hat{P}_a)^2\Psi = \hat{P}_a(\hat{P}_a \Psi) = \hat{P}_a\Psi_a = \Psi_a$ …..(2)

Comparing (1) and (2), we get

$(\hat{P}_a)^2 = \hat{P}_a$…..(3)

i.e. the projection vector is idempotent.

Now let us consider a set of basis vectors Ψ_1 , Ψ_2 , Ψ_3……

For projection on ith direction

$\hat{P}_i \Psi = a_i\Psi_i$(eigen value equation)

$\hat{P}_i\hat{P}_j \Psi = \hat{P}_i (a_j\Psi_j) = a_j\hat{P}_i\Psi_j = a_j\times 0 = 0$

Thus, the projection operators on the basis vector have the property

$\hat{P}_i\hat{P}_j = \hat{P}_j\hat{P}_i = 0$ if $i \neq j$ …..(4)

For every Ψ

$\sum_{\lambda=1}^{n} \hat{P}_\lambda \Psi = \sum_{\lambda=1}^{n} a_\lambda \Psi_\lambda = \Psi$ (By expansion theorem)

Hence

$\sum_{\lambda=1}^{n} \hat{P}_\lambda = 1$ …..(5)

4.10 COMMUTATING OPERATORS

4.10.1 Commutator

If A and B are two operators, then AB-BA is called the commutator of A and B and is denoted by [A, B] i.e.

$[A, B] = AB-BA$ …..(1)

(i) $[A, B] = AB-BA$
$= -(BA-AB)$
$[A, B] = -[B,A]$ …..(2)

(ii) $[A, B+C] = A(B+C) - (B+C)A$
$= AB + AC - BA - CA$
$= (AB-BA) + (AC-CA)$
$= [A, B] + [A, C]$ …..(3)

(iii) $[A+B, C] = (A+B)C - C(A+B)$
$= AC + BC - CA - CB$
$= (AC - CA) + (BC - CB)$
$= [A, C] + [B, C]$ …..(4)

(iv) $[A,BC] = ABC - BCA$
Adding and subtracting BAC, we get
$[A, BC] = ABC - BAC + BAC - BCA$
$= (AB-BA)C + B(AC-CA)$
$= [A, B]C + B[A, C]$…..(5)

(v) [AB, C] = ABC – CAB

Adding and subtracting ACB, we get

[AB, C] = ABC – ACB + ACB – CAB

= A(BC - CB) + (AC - CA)B

= A[B, C] + [A, C]B …..(6)

(vi) [A,[B,C]] = [A, (BC - CB)]

= A(BC-CB) – (BC-CB)A

= ABC – ACB – BCA +CBA …..(i)

[B,[C,A]] = [B, (CA-AC)]

= B(CA-AC) – (CA-AC)B …..(ii)

= BCA – BAC – CAB + ACB

Similarly [C,[A,B]] = CAB-CBA-ABC+BAC …..(iii)

Adding (i), (ii) and (iii) we get

[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0

4.10.2 Commutation relation between position and momentum

(i) Let us propose to find the commutation of x and p_x,

where, $x \rightarrow x_{op}$ and $p_x \rightarrow p_{op} = \frac{ħ}{i}\frac{\delta}{\delta x}$

Consider the operation of $[x,p_x]$ on a function $\Psi(x)$.

i.e. $[x, p_x]\Psi(x) = (xp_x - p_xx)\,\Psi(x)$ …..(1)

We have $xp_x\Psi = x\ \frac{ħ}{i}\frac{\delta\Psi}{\delta x}$

And $p_xx\ \Psi = \frac{ħ}{i}\frac{\delta}{\delta x}(x\Psi) = \frac{ħ}{i}\left(\Psi + x\frac{\delta\Psi}{\delta x}\right)$

∴Equation (1) gives

$$[x, p_x]\Psi = x\ \frac{ħ}{i}\frac{\delta\Psi}{\delta x} - \frac{ħ}{i}\left(\Psi + x\frac{\delta\Psi}{\delta x}\right)$$

$$= \frac{ħ}{i}\left(x\frac{\delta\Psi}{\delta x} - \Psi - x\frac{\delta\Psi}{\delta x}\right) = -\frac{ħ}{i}\ \Psi$$

$= i\hbar\Psi$

i.e. $[x, p_x] = i\hbar$ ....(2)

(ii) Also, $[x^2, p_x] = [xx, p_x]$

$= [x, p_x]x + x[x,p_x]$

(since $[ab,c]=[a,c]b + a[b,c]$)

$=i\hbar x + xi\hbar$

$= 2i\hbar x$ ....(3)

Similarly $[x^3, p_x] = [xx^2, p_x] + [x, p_x]x^2$

$= x\, 2i\, \hbar x + i\hbar x^2$

$= 3i\hbar x^2$ ....(4)

Therefore, by induction, we have

$$[x^n, p_x] = ni\hbar x^{n-1}$$

4.10.3 Commutation relation between Momentum and Hamiltonian

The Hamiltonian for a particle is given by

$$H = \frac{p_x^2}{2m} + V(x)$$

Where p_x is momentum operator and $V(x)$ is potential energy. The commutator of H and $p_x$is

$$[H, p_x] = [\frac{p_x^2}{2m} + V(x), p_x]$$

$$= [\frac{p_x^2}{2m}, p_x] + [V(x), p_x]$$

$$= \frac{1}{2m} [p_x^2] + [V(x), p_x]$$

$= 0 + [V(x), p_x]$ {since $[p_x, p_x] = 0$}

Now consider the operation of $[H, p_x]$ on $\Psi(x)$, we have

$[H, p_x]\Psi(x) = \{V(x)p_x - p_xV(x)\}\ \Psi(x)$

$= \left\{V(x)\frac{ħ}{i}\frac{\delta}{\delta x} - \frac{ħ}{i}\frac{\delta}{\delta x}\ V(x)\right\}\Psi(x)$

$= V(x)\frac{ħ}{i}\frac{\delta\Psi(x)}{\delta x}$ - $\frac{ħ}{i}\frac{\delta}{\delta x}V(x)\ \Psi(x)$

$= V(x)\frac{ħ}{i}\frac{\delta\Psi(x)}{\delta x}$ - $\frac{ħ}{i}V(x)\frac{\delta\Psi(x)}{\delta x}$ - $\frac{ħ}{i}\Psi(x)\frac{\delta V(x)}{\delta x}$

$= - \frac{ħ}{i}\frac{\delta V(x)}{\delta x}\Psi(x)$

$\therefore [H, p_x] = iħ\frac{\delta V(x)}{\delta x}$

4.10.4 Angular Momentum Operator and their Commutation Rules

The ortital angular momentum of a particle having momentum p and position vector **r** relative to an arbitrary origin is defined as

$$\mathbf{L=r\times p}$$

The components of angular momentum in cartesian co-ordinates may be obtained as follows:

$$\begin{aligned}(\hat{\imath}L_x + \hat{\jmath}L_y + \hat{k}L_z) &= (\hat{\imath}x + \hat{\jmath}y + \hat{k}z) \times (\hat{\imath}p_x + \hat{\jmath}p_y + \hat{k}p_z)\\ &= (yp_z - zp_y)\hat{\imath} + (zp_x - xp_z)\hat{\jmath} + (xp_y - yp_x)\hat{k}\end{aligned}$$

Comparing coefficient of $\hat{\imath}$, j and $\hat{k}$, we get

$$\begin{aligned}L_x &= yp_z - zp_y = y\left(\frac{i}{ħ}\frac{\partial}{\partial z}\right) - z\left(\frac{i}{ħ}\frac{\partial}{\partial y}\right)\\ L_y &= zp_x - xp_z = z\left(\frac{i}{ħ}\frac{\partial}{\partial x}\right) - x\left(\frac{i}{ħ}\frac{\partial}{\partial z}\right)\\ L_z &= xp_y - yp_x = x\left(\frac{i}{ħ}\frac{\partial}{\partial y}\right) - y\left(\frac{i}{ħ}\frac{\partial}{\partial x}\right)\end{aligned}$$

Since $p_x = \frac{i}{ħ}\frac{\partial}{\partial x}$, $p_y = \frac{i}{ħ}\frac{\partial}{\partial y}$ and $p_z = \frac{i}{ħ}\frac{\partial}{\partial z}$

Commutation Rules: Let us write the commutation relation (L_x, L_y) as

$$[L_x, L_y] = L_xL_y - L_yL_x$$

Substitution operator values

$$L_xL_y = \left(\frac{\hbar}{i}\right)^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$= -\hbar^2\left\{y\frac{\partial}{\partial z}\left(z\frac{\partial}{\partial x}\right) - y\frac{\partial}{\partial z}\left(x\frac{\partial}{\partial z}\right) - z\frac{\partial}{\partial y}\left(z\frac{\partial}{\partial x}\right) + z\frac{\partial}{\partial y}\left(x\frac{\partial}{\partial z}\right)\right\}$$
$$= -\hbar^2\left\{y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right\}$$

Similarly

$$L_yL_x = \left(\frac{\hbar}{i}\right)^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$= -\hbar^2\left\{z\frac{\partial}{\partial x}\left(y\frac{\partial}{\partial z}\right) - z\frac{\partial}{\partial x}\left(z\frac{\partial}{\partial y}\right) - x\frac{\partial}{\partial z}\left(y\frac{\partial}{\partial z}\right) + x\frac{\partial}{\partial z}\left(z\frac{\partial}{\partial y}\right)\right\}$$
$$= -\hbar^2\left\{zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - yx\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right\}$$

On subtracting above two relations, we have

$$[L_x, L_y] = -\hbar^2\left\{y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right\}$$

Provided x, y and z are perfect differentials

i.e. $\frac{\partial^2}{\partial x\partial z} = \frac{\partial^2}{\partial z\partial x}$ and $\frac{\partial^2}{\partial y\partial z} = \frac{\partial^2}{\partial z\partial y}$ and so on.

$$[L_x, L_y] = i\hbar\left\{-i\hbar\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\right\}$$

$$= i\hbar\left\{\frac{\hbar}{i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\right\}$$

$$= i\hbar L_z \qquad \text{.....(1a)}$$

Similarly, we get

$$[L_y, L_z] = i\hbar L_x \qquad \text{.....(1b)}$$

and

$$[L_z, L_x] = i\hbar L_y \qquad \text{.....(1c)}$$

The commutation relations represented by equations (1) can be combined symbolically as follows:

L×L=iħL

Commutation relation of L^2 with components L_x, L_y and L_z,

The totalangular momentum is defined by the relation

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Let us take

$$[L^2, L_x] = \left[L_x^2 + L_y^2 + L_z^2, L_x\right] = [L_x^2, L_x] + \left[L_y^2, L_x\right] + [L_z^2, L_x]$$

But $[L_x^2, L_x] = [L_x L_x, L_x]$

$$= L_x[L_x, L_x] + [L_x, L_x]L_x = 0$$

Since [ab,c]=a[b,c]+[a,c]b

$$[L^2, L_x] = \left[L_y^2, L_x\right] + [L_z^2, L_x]$$

$$= \left[L_y L_y, L_x\right] + [L_z L_z, L_x]$$

$$= L_y[L_y, L_x] + \left[L_y, L_x\right]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$$

But $[L_x, L_y] = i\hbar L_z$ and $[L_y, L_x] = -i\hbar L_{xz}$

Also $[L_z, L_x] = i\hbar L_y$and $[L_x, L_z] = -i\hbar L_y$

Therefore

$$[L^2, L_x] = L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z\left(i\hbar L_y\right) + \left(i\hbar L_y\right)L_z = 0$$

$$[L^2, L_x] = 0 \qquad \text{…..(2a)}$$

Similarly $[L^2, L_y] = 0$ …..(2b)

$$[L^2, L_z] = 0 \qquad \text{…..(2c)}$$

Hence L^2 *commutes with any of the three components of the angular momentum operator.*

From eqn. (2c) it is obvious that L^2 and L_z commute, so they have simultaneous eigen functions and hence are simultaneously measurable.

4.10.5 Ladder Operators L_+ and L_-

Let us define the operators

$L_+ = L_x + iL_y$and$L_- = L_x - iL_y$

Commutation relation of L_z with $L_+$and L_-:

$$[L_z, L_+] = \left[L_z, L_x + iL_y\right] = [L_z, L_x] + i\left[L_z, L_y\right]$$

$$= i\hbar L_y + i(-i\hbar L_x)$$

$$= i\hbar L_y + \hbar L_x$$

$$= \hbar(L_x + iL_y) = \hbar L_+ \qquad \text{…..(1)}$$

$[L_z, L_-] = \left[L_z, L_x - iL_y\right] = [L_z, L_x] - i\left[L_z, L_y\right]$

$= i\hbar L_y - i(-i\hbar L_x)$

$= i\hbar L_y - \hbar L_x$

$= -\hbar(L_x - iL_y) = -\hbar L_-$ …..(2)

Equation (1) and (2) may be expressed form as

$$[L_z, L_\pm] = \pm\hbar L_z$$

Commutation relation of L_+ and L_- mutually:

$[L_z, L_\pm] =[(L_x+iL_y), (L_x-iL_y)]$

$= [L_x, L_x]-i[L_{x,}L_y] + i[L_y, L_x] + [L_y, L_y)]$

$= 0 - i(i\hbar L_z) + i(-i\hbar L_z) + 0$

$[L_z, L_\pm] = \hbar L_z + \hbar L_z = 2\hbar L_z$

$[L_z, L_\pm] = 2\hbar L_z$ …..(3)

4.11 SUMMARY

In this unit, we have studied

- With each physically measurable quantity, there is associated an operator.
- The operators for different measurable quantities are given.
- Linear operators are those which obey the equation
  a) A[f(x) + g(x)] = A [f(x)] + A [g(x)]
  b) A[C f(x)] = C [A f(x)]
- The eigen values and eigen functions of the operator corresponding to a variable have intimate relations with the measurement of that variable.

  ÂΨ = aΨ is called an eigen value equation. In this equation Â is the operator, a is the eigen value and Ψ is the eigen function.

- Two wave functions $\Psi_1(x)$ and $\Psi_2(x)$ are said to be orthogonal if they follow the condition

$$\int_a^b \Psi^*(x)\Psi_1(x)dx = 0$$

Where $\Psi_2^*(x)$ is the complex conjugate of $\Psi_2(x)$.

- The condition of an operator P to be Hermitian is

$$\int \Psi^* P\Psi \, dx = \int (P\Psi)^* \Psi \, dx$$

- Hermitian operators have real eigen values and eigen functions corresponding to different eigen values are orthogonal.
- A linear operator is unitary if it preserves the Hermitian character of an operator under a similarity transformation.
- If two operators commute, then any eigen function of one operator corresponding to a non-degenerate eigen value is also an eigen function of the other.
- For any given function Ψ, one can construct the projection operator $\hat{P}_a$. This operator has eigen values 0 and 1.

4.12 GLOSSARY

Dynamical - pertaining to forces not in equilibrium

Operator - a function over a space of physical state to another physical state

Commuting - to exchange

Bound State - confined or restrained state

Continuum - uninterrupted succession

Discrete - distinct, non-continuous

Orthogonal - no overlap between vectors or states

Normalised Subspace - scaling of wave function, so that all probabilities add to 1.

4.13 TERMINAL QUESTIONS

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1) What is the significance of operators in quantum mechanics? State with specific examples of space and momentum operators.
2) Define (a) linear operator, (b) projection operator and (c) unitary operator.
3) What is Hermitian operator? Show that Hermitianoperatots have real eigen values.
4) Show that -
    (a) Momentum operator is Hermitian.
    (b) If Hermitian operators commute, then their product is also Hermitian operator.
    (c) If a pair of operators A and B possess a complete set of simultaneous eigen functions, then the operators A and B commute.
5) Prove that two commutating operators have simultaneous eigen functions.
6) Describe the basic features of operator formalism in quantum mechanics.
7) Prove that no two of the three components of angular momentum L commute with each other but all of them.
8) Show that eigenfunctions of Hermitian Operator belonging to different eigen values are orthogonal.

NUMERICAL PROBLEMS:

1) Show that :
    i) The operator $\frac{(xp+px)}{2}$ is Hermitian.
    ii) x and $\frac{d}{dx}$ are linear operators.
    iii) The function cos 4x is an eigen function of the operator $\frac{d^2}{dx^2}$.

2) Two operators A and B are given as

    A = x^3 , B = x$\frac{d}{dx}$

    Find the commutator [A,B].[Ans – $3x^2$]

3) If A and B are two operators which both commute with their commutator [A,B], then show that

    i) $[A,B^n] = nB^{n-1}[A,B]$
    ii) $[A^n,B] = nA^{n-1}[A,B]$

4) Find the value of commutators $[x^3,P_x]$, $[x^2,P_x]$ and $[x ,P_x]$.

[Ans – $3i\hbar x^2$, $2i\hbar x$, $i\hbar$]

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UNIT 5: MATRIX FORMULATION OF QUANTUM MECHANICS

5.1 INTRODUCTION

In the previous chapter the quantum theory has been developed in terms of wave function Ψ occurring in Schrodinger equation and in terms of operators which operate on this function Ψ and is in general combination of x and$\hat{P}_x = \frac{\hbar}{i}\frac{}{x}$. Now in this chapter we are going to study Heisenberg's approach to employ operators as matrices. In this approach, the wave function Ψ is regarded as a representative of a vector, and the operators transform one vector into another. The vector represents different states of a physical system and can be combined linearly to represent other states. The transformations representing linear relations among vectors can be expressed by matrices. Thus in this new approach the Schrodinger's operators appear as matrices and the wave function as representative of vectors.

5.2 OBJECTIVES

After going through this unit you will be able to understand:

- Vector Space
- What is matrix algebra?
- Characteristic equation of matrix
- Hermitian matrix
- Unitary matrix
- Hilbert space
- State vectors and operators in Hilbert Space
- Matrix form of Operator
- Schrodinger, Heisenberg and Interaction matrix representation
- Dirac's Bra and Ket Vectors
- Solved numerical problems

5.3 VECTOR SPACE

A vector space is a collection of objects that can be added and multiplied by scalars. The operations called addition and multiplication are not necessarily our familiar algebraic operations, but they must obey certain rules. We know how the vectors are added or multiplied. But the intention here is not to give a complete discussion but to highlight a number of properties of such vectors that are analogues in the case of quantum states. Let us take two vectors $\hat{v}_1$and$\hat{v}_2$, then their linear combination will be

$$V = a\hat{v}_1 + b\hat{v}_2 \qquad .....(1)$$

where a and b are scalar numbers. The right hand side is called linear combination of vectors $\hat{v}_1$and $\hat{v}_2$. Just like combination of vectors produce another vector, we in quantum mechanics study that combining states produces other states.

In quantum physics, let us take a set L = {u, v, w, ….} in which elements can be multiplied by complex number α or added to one another to give the members of the same set, is said to form a linear vector space L. The elements of vector space are vectors.

If u and v are in L, then

αu and u+v

are also in L.

The operations of multiplication and addition must satisfy conditions

- u + v = v + u (Commutative Law of addition)
- (u + v) + w = u + (v + w) (Associative Law of addition)
- (α + β) u = αu + βu (Distributive Law of multiplication)
- α(u + v) = αu + αv (Distributive Law of multiplication)
- αβ(u) = α(βu) (Associative Law of multiplication)
- Iu = u, where I is unit or identity operator.

The space L will contain a zero(null) vector 0 such that

u + 0 = u for all u.

The elements of linear vector space L can be multiplied by complex numbers. The linear vector space is also called vector space.
If the multipliers like a and b in equation (1)are real multipliers, we obtain a real space. The three dimensional space of position vector is an example of real vector space. This can be shown as below
If u and v are also any two vectors of this space, then u + v = v + u is also a vector of this space.
The identity element is null vector 0. The inverse of u is (-u) because u + (-u) = 0. The vector addition is associative. Thus the position vectors satisfy all the above properties and hence is an example of real vector space.

5.3.1 Linear independence of vectors and Dimensions

A linear combination of vectors $u_1, u_2, ... u_n$ is suppose u of the form

$$u = \alpha_1 u_1 + \alpha_2 u_2 + \ldots . \alpha_n u_n = \sum_{i=1}^{n} \alpha_i u_i \qquad .....(2)$$

whereα_i(i = 1, 2, ….n) are complex numbers. The vectors $u_1, u_2, ... u_n$ are said to be linearly dependent if

$$\alpha_1 u_1 + \alpha_2 u_2 + \ldots . \alpha_n u_n = 0$$

i.e.$\sum_i \alpha_i u_i = 0$ (with $\alpha_i \neq 0$, for $i = 1, 2, \ldots n$) …..(3)

On the other hand if no relation of the form(3) exists unless $\alpha_i = 0$, for all values of i (=1, 2, ….n) then vectors $u_1, u_2, \ldots u_n$ are said to be linearly independent.

5.3.2 Inner Product and unitary spaces

A vector of magnitude 1 is called a unit vector. To represent an arbitrary vector, we introduce unit vector u_1, $u_2$and u_3 along the positive direction of right handed system OXYZ of three mutually perpendicular axes. Then any vector α can be expressed as

$$\alpha = \alpha_1 u_1 + \alpha_2 u_2 + \alpha_3 u_3 \qquad \ldots(1)$$

where α_1, α_2 and α_3 are scalars. Given a vector 'α' the scalorsα_1, α_2 and α_3 in equation **(1)** are uniquely determined. The unit vectors u_1, $u_2$and u_3 are said to form a basis for the set of all vectors in three dimensions. Further, since u_1, $u_2$and u_3 are unit vectors along perpendicular direction, we call them orthonormal basis. The scalars α_1, α_2 and α_3 are the components of α in the basis (u_1, u_2, u_3) we represent α as a column

$$\alpha = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix}$$

The components of $\alpha_1$are 1,0,0; those of α_2 are 0,1,0 and those of α_3 are 0,0,1. Hence on expressing them as column vectors, we have

$$u_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad u_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad u_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

The totality of vectors in three dimensions, is called the dimensional space.

Given two vectors

$$u = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} \text{and } v = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$$

in this space, the scalar or inner product of u and v, denoted by u.v or (u,v) is defined as

$$(u,v) = \sum_{i=1}^{3} u_i v_i \qquad \ldots(2)$$

In n-dimensional real space, the inner product is defined as

$$(u,v) = \sum_{i=1}^{n} u_i v_i \qquad \ldots(3)$$

If the vectors are complex, that is, if the components of the vectors are complex numbers, the inner product is defined as

$$(u.v) = \sum_{i=1}^{n} u_i^* v_i \qquad \text{…..(4)}$$

where u_i^* is complex conjugate of u_i. Thus we observe that for any vector u,

$$(u,u) = \sum_{i=1}^{n} u_i^* u_i = \sum_{i=1}^{n} |u_i|^2 \qquad \text{…..(5)}$$

is real. We now define the norm(N) of a vector u by

$$N = (u,u)^{1/2} \qquad \text{…..(6)}$$

A vector whose norm is unity is said to be normalised. Thus for a normalised vector u, we have

$$(u,u) = \sum_{i=1}^{n} u_i^* u_i = \sum_{i=1}^{n} |u_i|^2 = 1 \qquad \text{…..(7)}$$

Two vectors u and v are said to be orthogonal if

$$(u,v) = 0 \qquad \text{…..(8)}$$

Using the concept of inner product we say that the vectors u_1, u_2….form an orthogonal set if and only if

$$(u_i, u_j) = {}_{ij}, \quad i,j = 1,2,3,\ldots \qquad \text{…..(9)}$$

Where ${}_{ij}$ is the kronecker delta, defined by

$${}_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & if\ i \neq j \end{cases} \qquad \text{…..(10)}$$

5.4 MATRIX ALGEBRA

A matrix may be defined as a square or rectangular array of numbers or functions that obeys certain laws. The individual numbers (or functions) of the array are called the elements of the matrix and are represented by capital or small letters A_{kl} or a_{kl} such that *k* gives the number of row and *l* gives the number of columns in the matrix.

Two matrices can be added when they have the same rank, i.e., the same number of rows and the same number of columns. Addition is Commutative. If A and B denote two matrices, then

$$A + B = B + A \qquad \text{…..(1)}$$

If the sum matrix is called C, then

$$C_{kl} = A_{kl} + B_{kl} \qquad \text{…..(2)}$$

A matrix A can be multiplied from the left into a matrix B if the number of columns of A is equal to the number of rows of B; then the product matrix C has the number of rows of A and the number of columns of B.

$$C = A\,B \qquad \text{.....(3)}$$

Or $$C_{kl} = \textstyle\sum_{m} C_{km} B_{ml} \qquad \text{.....(4)}$$

where the summation is over the subscript m, which denotes the columns of A and the rows of B. it follows from equations (2) and (4), that the distributive law of multiplication is valid.

$$A\,(B + C) = AB + AC \qquad \text{.....(5)}$$

Also, associative law of multiplication is seen to be valid :

$$A\,(BC) = (AB)\,C \qquad \text{.....(6)}$$

where the left side means that A is multiplied from the left into the product of B and C, and the right side means that the product of A and B is multiplied from the left into C. The product (equation 6) can be written simply as ABC, hence

$$D = ABC \qquad \text{.....(7)}$$

or, $$D_{kl} = \textstyle\sum_{m,n} A_{km} B_{mn}\, C_{nl} \qquad \text{.....(8)}$$

Thus it is clear from equation (4) that AB is not, in general, equal to BA; thus the commutative law of multiplicationof matrices is not generally valid.

Example – Given $A = \begin{bmatrix} 1 & -1 & 1 \\ -3 & 2 & -1 \\ -2 & 1 & 0 \end{bmatrix}$ and $B = \begin{bmatrix} 1 & 2 & 3 \\ 2 & 4 & 6 \\ 1 & 2 & 3 \end{bmatrix}$. Compute AB and BA and hence show that $AB \neq BA$.

Solution – As A is a 3×3 matrix and B is also 3×3 matrix, therefore the product AB and BA are 3×3 matrices.

$$AB = \begin{bmatrix} 1 & -1 & 1 \\ -3 & 2 & -1 \\ -2 & 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 2 & 4 & 6 \\ 1 & 2 & 3 \end{bmatrix}$$

$$= \begin{bmatrix} 1\times1+(-1)\times2+1\times1 & 1\times2+(-1)\times4+1\times2 & 1\times3+(-1)\times6+1\times3 \\ (-3)\times1+2\times2+(-1)\times1 & (-3)\times2+2\times4+(-1)\times2 & (-3)\times3+2\times6+(-1)\times3 \\ (-2)\times1+1\times2+0\times1 & (-2)\times2+1\times4+0\times2 & (-2)\times3+1\times6+0\times3 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$BA = \begin{bmatrix} 1 & 2 & 3 \\ 2 & 4 & 6 \\ 1 & 2 & 3 \end{bmatrix}\begin{bmatrix} 1 & -1 & 1 \\ -3 & 2 & -1 \\ -2 & 1 & 0 \end{bmatrix}$$

$$=\begin{bmatrix} 1\times1+2\times(-3)+3\times(-2) & 1\times(-1)+2\times2+3\times1 & 1\times1+2\times(-1)+3\times0 \\ 2\times1+4\times(-3)+6\times(-2) & 2\times(-1)+4\times2+6\times1 & 2\times1+4\times(-1)+6\times0 \\ 1\times1+2\times(-3)+3\times(-2) & 1\times(-1)+2\times2+3\times1 & 1\times1+2\times(-1)+3\times0 \end{bmatrix}$$

$$=\begin{bmatrix} -11 & 6 & -1 \\ -22 & 12 & -2 \\ -11 & 6 & -1 \end{bmatrix}$$

Hence AB ≠ BA.

The basic concepts of Matrix algebra is already studied in the previous classes. Here we study some special kind of matrices.

5.4.1 Transpose of a matrix

A matrix of the order n × m obtained by interchanging the rows and columns of (m × n) matrix A is called the transpose of A and is denoted by the symbol A' or Ā or A^T (A transpose) i.e.

$$\text{if}A = \begin{bmatrix} a_{11} & a_{12} & a_{1n} \\ a_{21} & a_{22} & a_{2n} \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ a_{m1} & a_{m2} & a_{mn} \end{bmatrix}, \text{ then } A^T = \begin{bmatrix} a_{11} & a_{21} & a_{m1} \\ a_{12} & a_{22} & a_{m2} \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ a_{1n} & a_{2n} & a_{mn} \end{bmatrix}$$

For example, if $A = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{bmatrix}$, then

$$A^T = \begin{bmatrix} 1 & 4 \\ 2 & 5 \\ 3 & 6 \end{bmatrix}$$

Let A^T and B^Tbe the transpose of matrices A and B respectively, then some properties of transpose of a matrix are:-

1. $(A^T)^T = A$
2. $(\lambda A)^T = \lambda A^T$, λ being any scalar (real or complex)
3. $(A + B)^T = A^T + B^T$, A and B being conformable for addition
4. $(AB)^T = B^T A^T$, A and B being conformable for multiplication.

5.4.2 Conjugate of a matrix

If A is any matrix having complex numbers, then the matrix obtained from A by replacing its each element by its conjugate complex number, is called the conjugate of matrix A and is denoted by A^*. Thus, if $A = [a_{ij}]$, then $A^* = [a_{ij}^*]$

wherea_{ij}^* is the complex conjugate of a_{ij}.

Example –if A = $\begin{bmatrix} 1+2i & 2 & i \\ 3 & 5i & 2-3i \end{bmatrix}$

thenA^* = $\begin{bmatrix} 1-2i & 2 & -i \\ 3 & -5i & 2+3i \end{bmatrix}$

If A^* and B^* are the conjugates of matrices A and B respectively, then some properties of conjugate of matrix are

1. $(A^*)^* = A$
2. $(A + B)^* = A^* + B^*$, A and B being conformable for addition
3. $(\lambda A)^* = \lambda^* A^*$, λ being any complex number
4. $(AB)^* = A^* B^*$, A and B being conformable for multiplication.

5.4.3 The transposed conjugate of a matrix

The conjugate of the transpose of a matrix A is called the conjugate transpose of A and is denoted by $A^\dagger = (A^T)^*$.

It is obvious that the conjugate of that transpose of a matrix is the same as the transpose of the conjugate of that matrix i.e. $A^\dagger = (A^T)^* = (A^*)^T$.

Thus if $A = [a_{ij}]_{m \times n}$, then $A^\dagger = \left|a_{ji}^*\right|_{n \times m}$

For example, if $A = \begin{bmatrix} 1+2i & 5i & 2+9i \\ 5-i & 0 & 5i \\ 1 & 3 & 5-3i \end{bmatrix}$

then $A^\dagger = \begin{bmatrix} 1-2i & 5+i & 1 \\ -5i & 0 & 3 \\ 2-9i & -5i & 5+3i \end{bmatrix}$

If $A^\dagger$ and $B^\dagger$are the transposed conjugates of matrices A and B respectively, then some properties of transposed conjugate of a matrix are –

1. $(A^\dagger)^\dagger = A$
2. $(A+B)^\dagger = A^\dagger + B^\dagger$, A and B being conformable for addition
3. $(\lambda A)^\dagger = \lambda^* A^\dagger$, λ being any complex number
4. $(AB)^\dagger = B^\dagger A^\dagger$, A and B being conformable for multiplication.

5.4.4 Symmetric and antisymmetric matrices

A square matrix A = $[a_{ij}]$ is said to be symmetric, provided

$a_{ij} = a_{ji}$ for all values of i and j …..(1)

If A^T is the transpose of a square matrix A = $[a_{ij}]_{n \times n}$, then

$A^T = [a_{ji}]_{n \times n}$

Therefore (1) implies that

$A^T = A$ …..(2)

Thus a symmetric matrix is one whose transpose coincides with the matrix itself.

For example the matrices $\begin{bmatrix} a & b & c \\ b & c & d \\ c & d & e \end{bmatrix}$, $\begin{bmatrix} 1 & 2 & 3 \\ 2 & 4 & 5 \\ 3 & 5 & 6 \end{bmatrix}$ are symmetric matrices.

A square matrix A = $[a_{ij}]$ is said to be antisymmetric or skew symmetric provided

$a_{ij} = -a_{ji}$ for all values of i and j. …..(3)

If A^T is the transpose of the square matrix A = $[a_{ij}]_{n \times n}$, then

$A^T = [a_{ji}]_{n \times n}$

Therefore equation (3) implies that

$A^T = -A$ …..(4)

Thus a skew-symmetric matrix A is one for which $A^T = -A$.

The examples of skew symmetric matrices are –

$$\begin{bmatrix} 0 & 2 & 3 \\ -2 & 0 & 5 \\ -3 & -5 & 0 \end{bmatrix}, \begin{bmatrix} 0 & a & b \\ -a & 0 & c \\ -b & -c & 0 \end{bmatrix}$$

5.4.5 Hermitian and Skew – Hermitian Matrices

A square matrix A = $[a_{ij}]_{n \times n}$ is said to be Hermitian matrix if

$a_{ij} = a_{ji}^*$ for all values of i and j …..(1)

If $A^\dagger$ is the transposed conjugate of A = $[a_{ij}]_{n \times n}$,then

$A^\dagger = [a^*_{ji}]_{n \times n}$

Now equation (1) implies

$$A^\dagger = [a_{ij}]_{n \times n} = A \qquad \text{…..(2)}$$

Thus a Hermitian matrix is one whose transposed conjugate or Hermitianadjoint coincides with the matrix itself. Equation (2) represents the necessary and sufficient condition for a matrix A to be Hermitian.

For i = j, equation (1) gives

$a_{ii} = a^*_{ii}$ for all values of i …..(3)

i.e. every diagonal elements of a Hermitian matrix is equal to its complex conjugate and it is only possible if all the diagonal elements of a Hermitian matrix are real numbers.

The examples of the Hermitian matrices are

$$\begin{bmatrix} 1 & i & 0 \\ -i & 0 & -2i \\ 0 & 2i & 0 \end{bmatrix} \begin{bmatrix} 0 & -i & -3i \\ i & 5 & 0 \\ 3i & 0 & 2 \end{bmatrix}$$

If A is any Hermitian matrix, then kA is Hermitian if k is any real number.

Any square matrix A = $[a_{ij}]$ is said to be skew – Hermitian (or anti – Hermitian) matrix if

$a_{ij} = -a^*_{ji}$ for all values of i and j …..(4)

If $A^\dagger$ is the transposed conjugate of $A = [a_{ij}]_{n \times n}$,then

$A^\dagger = [a^*_{ji}]_{n \times n}$

Now equation (1) implies$A^\dagger = -[a_{ij}]_{n \times n} = -A$ …..(5)

Thus a skew - Hermitian matrix is one whose transposed conjugate coincides with negative of the matrix. Equation (5) represents the necessary and sufficient condition for a matrix A to be skew - Hermitian.

For i = j, equation (4) gives

$a_{ii} = -a^*_{ii}$ i.e.$a_{ii} + a^*_{ii} = 0$ …..(6)

Now writing $a_{ii} = x + iy$, where x and y are real numbers

Then$a^*_{ii} = x - iy$

Therefore $a_{ii} + a^*_{ii} = 2x$ …..(7)

Comparing (6) and (7), we get x = 0

Therefore $a_{ii} = iy$

This proves that every diagonal element of a skew – Hermitian matrix either zero or a pure imaginary number.

The examples of the skew – Hermitian matrices are:

$$\begin{bmatrix} i & -1 & 2 \\ -1 & i & 3 \\ -2 & -3 & i \end{bmatrix}, \begin{bmatrix} 0 & 1+i \\ -1+i & 0 \end{bmatrix}$$

5.4.6 UnitaryMatrix

A matrix is known as a unitary matrix if its Hermitianadjoint is equal to its inverse. Thus U is a unitary matrix if

$$U^{\dagger} = U^{-1}$$

or $UU^{\dagger} = 1$ and $U^{\dagger}U = 1$

5.4.7 OrthogonalMatrices

A square finite matrix A is said to be orthogonal if

$$A^{T}A = I$$

This implies that $AA^{T} = I$

where A^{T} is transpose of A and I is unit matrix.

We know that

$|A^{T}| = |A|$ and $|A^{T}A| = |A^{T}||A|$

Hence if $A^{T}A = 1$; we have $|A|^{2} = 1$ i.e. $|A| = 1$.

This shows that the determinant of an orthogonal matrix can only have values +1 or -1.

5.4.8 Diagonal Matrix

The diagonal matrix has zero element everywhere except for elements in principal diagonal. Thus

$$D = \begin{bmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{bmatrix} = D_{kl} \quad {}_{kl}$$

The unit matrix $_{kl}$ can be regarded as a special kind of diagonal matrix in which diagonal elements are unit.

The elements in the diagonal of the diagonal matrix are known as eigen values of the matrix and have special significance in quantum mechanical representation.

5.5 LINEAR TRANSFORMATIONS

Let $X = \{x_1, x_2, \ldots x_n\}$ and $Y = \{y_1, y_2, \ldots y_n\}$ be two column vectors of vector space $V_n(F)$, their co-ordinates being related to the same basis of space. Let the coordinates of X and Y be related by the following n – linear equations

$$\left.\begin{matrix} a_{11}x_1 + & a_{12}x_2 + & \ldots + & a_{1n}x_n = & y_1 \\ a_{21}x_1 + & a_{22}x_2 + & \ldots + & a_{2n}x_n = & y_2 \\ \cdots & \cdots + & \ldots & \cdots & \cdots \\ \cdots & \cdots + & \ldots & \cdots & \cdots \\ a_{n1}x_1 + & a_{n2}x_2 + & \ldots + & a_{nn}x_n = & y_n \end{matrix}\right\} \qquad \ldots..(1)$$

In matrix notation this set of equations is written as

$$AX = Y \qquad \ldots..(2)$$

where $A = [a_{ij}]_{n \times n}$ is over F.

Then relation (1)represents a transformation which carries any vector X of $V_n(F)$ into another vector Y of the same space. Matrix A is called the matrix of transformation.

If the transformation (1) transforms X_1 into Y_1 and X_2 into Y_2, then

(a) It transforms $k\,X_1$ into $k\,Y_1$ for every scalar k, and
(b) It transforms $k_1X_1 + k_2X_2$ into $k_1Y_1 + k_2Y_2$ for every pair of scalars k_1 and k_2

Due to this reason the transformation is called linear transformation.

If $|A| \neq 0$, then the transformation is called non – singular.

If $|A| = 0$, then the transformation is called singular.

The rank of transformation matrix A is said to be the rank of transformation.

The transformation (2) assigns to each n – vector X another n – vector Y.

If$|A| \neq 0$, then from(2) we have

$$A^{-1}\,Y = X \qquad \ldots..(3)$$

This transformation assigns to each n – vector Y another n – vector X.

Thus, if$|A| \neq 0$, then the correspondence between vectors X and Y is one – one.

Now consider the transformations

$$AX = Y \qquad \text{.....(4)}$$

and $$BY = Z \qquad \text{.....(5)}$$

Then $$Z = BY = B\,(AX) = (BA)\,X \qquad \text{.....(6)}$$

This transformation assigns to each vector X another vector Z and is called the product or resultant of the transformations (4) and (5). Obviously the matrix of product transformation is the product (BA).

5.6 ORTHOGONAL AND UNITARY TRANSFORMATIONS

Consider a linear transformation

$$Y = AX \qquad \text{.....(1)}$$

Such that X and Y are column vectors of order $n \times 1$ and A is a square transformation matrix of order $n \times n$. If the matrix A of transformation is unitary, the linear transformation is said to be a unitary transformation. From definition of unitary matrix

$$A^\dagger A = AA^\dagger = I \qquad \text{.....(2)}$$

Hence we have $$Y^\dagger Y = (AX)^\dagger (AX) = X^\dagger A^\dagger AX = X^\dagger X \qquad \text{.....(3)}$$

Or$$\sum_{i=1}^{n} y_i^* y_i = \sum_{i=1}^{n} x_i^* x_i \qquad \text{.....(4)}$$

This shows that the norm of the vector remains invariant under a unitary transformation.

As in inverse case let us consider a linear transformation matrix A which leaves the norm of every vector of a vector space unchanged that is

$$|Y| = |X| \quad \text{or} \quad |AX| = |X|$$

or $$X^\dagger X = (AX)^\dagger AX = X^\dagger A^\dagger AX \qquad \text{.....(5)}$$

Obviously $A^\dagger A = I$, showing that A is unitary.

Thus a linear transformation acting on a vector space is unitary if and only if it leaves the norm of every vector in the vector space unchanged.

If the matrix of linear transformation is further restricted to be real, it is called a real orthogonal transformation. In this case equation (3) reduce to

$Y^{\dagger} Y = X^T A^T AX = X^T X$ …..(6)

(since $A^T A = I$)

Here A^T represents transpose of matrix A.

i.e.$\sum_{i=1}^{n} y_i^2 = \sum_{i=1}^{n} x_i^2$ …..(7)

Obviously the condition of transformation Y = AX to be orthogonal is that the transformation matrix A satisfies the condition

$A^T A = AA^T = I$

and the transformed vectors satisfy condition (6).

5.7 CHARACTERISTIC EQUATION OF A MATRIX

Let A be a matrix operating upon a set of eigen vectors Ψ and λ is the eigen value of this operation. Then the eigen value equation can be written as:

$A\,\Psi = \lambda\,\Psi = \lambda\, I\,\Psi$ where I is the unit matrix.

$[A - \lambda I]\Psi = 0$

But Ψ's are generally not zero.

Therefore, $[A - \lambda I] = 0$ …..(1)

The det of $|A - \lambda I| = 0$ and is known as the characteristic equation of matrix A. Here A and I should have same order and they should be square matrix. Its roots are the eigen values of matrix A. For every eigen value there is an eigen vector. For finding the eigen vector we consider a non – zero characteristic vector "X" which satisfies the equation

$[A - \lambda I]\, X = 0$ …..(2)

This is demonstrated by considering the example of a 3 × 3 matrix:

Example – let $A = \begin{bmatrix} 8 & -6 & 2 \\ -6 & 7 & -4 \\ 2 & -4 & 3 \end{bmatrix}$

Then, $[A - \lambda I] = \begin{bmatrix} 8 & -6 & 2 \\ -6 & 7 & -4 \\ 2 & -4 & 3 \end{bmatrix} - \lambda \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$= \begin{bmatrix} 8-\lambda & -6 & 2 \\ -6 & 7-\lambda & -4 \\ 2 & -4 & 3-\lambda \end{bmatrix}$$

Since $[A - \lambda I] = 0$.

Therefore, $\begin{vmatrix} 8-\lambda & -6 & 2 \\ -6 & 7-\lambda & -4 \\ 2 & -4 & 3-\lambda \end{vmatrix} = 0$

$(8 - \lambda)\ [\ (7 - \lambda)(3 - \lambda) - (-4 \times -4)] + 6\ [-6\ [3 - \lambda] - 2\ [-4]] + 2\ [-6 \times -4 - (2 \times (7 - \lambda)] = 0$

On solving, gives

$\lambda^3 - 18\lambda^2 + 45\lambda = 0$

$\lambda\ (\lambda^2 - 18\lambda + 45) = 0$

this gives $\lambda = 0$ and $(\lambda^2 - 18\lambda + 45) = 0$

Solving the quadrating equation we get

$\lambda = 15$ and $\lambda = 3$

Thus the three eigen values are $\lambda = 0$, 15 , 3.

For every eigen value we can find the eigen vector

$[A - \lambda I][X] = [0]$

$$\begin{bmatrix} 8-\lambda & -6 & 2 \\ -6 & 7-\lambda & -4 \\ 2 & -4 & 3-\lambda \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

Where, x , y , z are non – zero quantities.

Now, putting $\lambda = 0$ in the above equation,

$$\begin{bmatrix} 8 & -6 & 2 \\ -6 & 7 & -4 \\ 2 & -4 & 3 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

On solving gives,

$8x - 6y + 2z = 0$ …..(3)

$-6x + 7y - 4z = 0$ …..(4)

$2x - 4y + 3z = 0$ …..(5)

Using determinant method in equation (3) and (4)

$$\frac{x}{24-14} = \frac{-y}{-32-(-12)} = \frac{z}{56-36}$$

Or $\frac{x}{10} = \frac{y}{20} = \frac{z}{20}$

Or $\frac{x}{1} = \frac{y}{2} = \frac{z}{2}$

Thus $\begin{bmatrix}1\\2\\2\end{bmatrix}$ is the eigen vector corresponding to the eigen value λ = 0.

Similarly, we can find the eigen vector for λ = 15 and λ = 3.

5.7.1 Diagonalization of Matrices

The roots or eigen values of matrix A can also be obtained by using the method of diagonalization.

A matrix which is similar to a diagonal matrix is said to be diagonable.

Let λ_1 , λ_2 , ... λ_n be distinct eigen values of a diagonable matrix A and X_1 , X_2 , ...$X_n$bethecorrespondingeigen vectors. Let the column vector X_i be given by

$$X_i = \begin{bmatrix}X_{1i}\\X_{2i}\\\cdots\\\cdots\\X_{ni}\end{bmatrix} \qquad \text{…..(1)}$$

Consider a matrix P whose column vectors are *n*eigen vectors such that

$$P = \begin{bmatrix}X_{11}X_{12}\cdots X_{1n}\\X_{21}X_{22}\cdots X_{2n}\\\cdots\ \cdots\ \cdots\ \cdots\\\cdots\ \cdots\ \cdots\ \cdots\\X_{n1}X_{n2}\cdots X_{nn}\end{bmatrix} = [X_{ij}] \qquad \text{…..(2)}$$

Let D be the diagonal matrix such that

$$D = \begin{bmatrix} \lambda_1\, 0\ \ 0 \cdots 0 \\ 0\ \lambda_2\, 0 \cdots 0 \\ 0\ \ 0\ \lambda_3 \cdots 0 \\ \dots \dots \dots \cdots \dots \\ \dots \dots \dots \cdots \dots \\ 0\ \ 0\ \ 0 \cdots \lambda_n \end{bmatrix} = \text{diag}\,[\,\lambda_1, \lambda_2, \dots \lambda_n\,] \qquad \text{.....(3)}$$

$$\text{Then } PD = \begin{bmatrix} \lambda_1 X_{11} \lambda_2 X_{12} \cdots \lambda_n X_{1n} \\ \lambda_1 X_{21} \lambda_2 X_{22} \cdots \lambda_n X_{2n} \\ \dots \quad \dots \cdots \dots \\ \dots \quad \dots \cdots \dots \\ \lambda_1 X_{n1} \lambda_2 X_{n2} \cdots \lambda_n X_{nm} \end{bmatrix} = [\lambda_j X_{ij}] \qquad \text{.....(4)}$$

$= (A\,X_1, A\,X_2, \dots A\,X_n)$

$= A\,[X_1, X_2, \dots X_n] = AP$ .....(5)

If P is a non – singular matrix, then multiplying (5) by P^{-1}, we get

$D = P^{-1} A\, P$ .....(6)

Thus, premultiplying A by P^{-1} and postmultiplying by P , we get the diagonal matrix whose elements in diagonal are the eigen – values. This process is said to be diagonalization of matrix A.

Example – Diagonalise the following matrix

$$\begin{bmatrix} 4/3 & \sqrt{2}/3 \\ \sqrt{2}/3 & 5/3 \end{bmatrix}$$

Solution – Let $A = \begin{bmatrix} 4/3 & \sqrt{2}/3 \\ \sqrt{2}/3 & 5/3 \end{bmatrix}$

The characteristic equation is

$$|A - \lambda\, I| = \begin{vmatrix} (4/3) - \lambda & \sqrt{2}/3 \\ \sqrt{2}/3 & (5/3) - \lambda \end{vmatrix} = 0$$

i.e. $(\frac{4}{3} - \lambda)\ (\frac{5}{3} - \lambda) - \frac{2}{9} = 0$ or or $\lambda^2 - 3\,\lambda + 2 = 0$

or $(\lambda - 1)\,(\lambda - 2) = 0$

Therefore the characteristic roots λ's are 1,2.

Thus the diagonal matrix is $D = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}$.

5.8 HILBERT SPACE

The transformation of a vector a into another vector a' in three dimensional space is represented by a linear transformation

$a' \equiv Ta$

where transformation is represented by T which is a 3×3 matrix. We have seen earlier that the wave function Ψ can be represented as a column matrix or as a vector in a suitable vector space. As Ψ may have components which are complex and sometimes infinite, hence this vector space must be of infinite dimensions and complex. This type of space is known as Hilbert space. In other words, the vector space is said to be Hilbert space if it is complex and of countable infinite dimensions such that all infinite series occurring in it are convergent.

Some properties of Hilbert space alongwith some operations are discussed below :

The scalar product of two functions , i.e., $f(q_1, q_2, \ldots q_i)$ and $g(q_1, q_2, \ldots q_i)$ is written as

$$[\, f(q_1, q_2, \ldots q_i),\, g(q_1, q_2, \ldots q_i)\,]$$

$$= \int f^* (q_1, q_2, \ldots q_i)\, g(q_1, q_2, \ldots q_i)\, dq_1, dq_2, \ldots dq_i \qquad \ldots..(1)$$

If one puts up a restriction that the scalar product

$$|u^2| = (u, u) = \sum_{i=1}^{\infty} u_i^2 \qquad \ldots..(2)$$

exists where $u = (u_1, u_2, \ldots)$ is a sequence of real or complex scalars and is called a vector.

Using equation (1) the equation (2) becomes

$$\int |f^2|\, dq_1\, dq_2 \ldots dq_i = C \text{ exists} \qquad \ldots..(3)$$

which is true for wave functions.

The wave functions are orthogonal when

$$\int f^* (q_1, q_2, \ldots q_i)\, g(q_1, q_2, \ldots q_i)\, dq_1, dq_2, \ldots dq_i = 0 \qquad \ldots..(4)$$

The state function Ψ gives all the information about a physical system at a given instant of time and is represented by a vector along a direction in the Hilbert space. Thus the arbitrary representative vector of the ray is generally normalised to one.

The states specified by different functions $\Psi_i$and represented by vectors along mutually perpendicular axes in such a way that complete set of states forms a complete orthogonal system of coordinate axes in the Hilbert space. By completeness of the system means that any wave function associated with vector Ω in the Hilbert space can be represented as a vector sum of its component along these axes. Thus

$\Omega = \sum_i b_i \Psi_i$ …..(5)

For every Ψ_i there being an axis and each b_i corresponds to the component of an arbitrary vector along i – axis.

We have already seen that the multiplication of two finite matrices are given by

$[AB]_{mn} = \sum_i A_{mi} B_{in}$ …..(6)

This law can be extended to the matrices having infinite number of rows and columns in the Hilbert space. Thus any operator A can be associated with matrix A whose matrix elements are expressed as

$A\ \Psi_m = \sum_n A_{nm} \Psi_n = \sum_n \Psi_n A_{nm}$ …..(7)

where$A_{nm} = \int \Psi_n^* A\ \Psi_m dq = (\ \Psi_n,\ A\ \Psi_m\ )$

with respect to basic set of eigen functions Ψ_n . Since every integral has a certain numerical value, hence

$A_{nm} = \int \Psi_n^* A\ \Psi_m dq = (\ \Psi_n A \Psi_m\ )$

gives a doubly infinite array of numbers which is also called matrix.

5.9 Operators as Matrices

The wave function can be considered as a vector in some imaginary space in quantum mechanics. If any operator Â operates on the function Ψ(x), we can write

$\hat{A}\ \Psi(x) = \phi(x)$ …..(1)

For passing from x representation to F representation, we have to expand the function Ψ(x) and ϕ(x) in terms of the eigen functions

$\Psi_m(x)$ of the operator $\hat{F}$as given below:

$\Psi(x) = \sum_m C_m \Psi_m\ (x)$ …..(2)

$\phi(x) = \sum_n B_n \Psi_n\ (x)$ …..(3)

Substituting equations (2) and (3) in (1) we get

$\sum_n B_n \Psi_n(x) = \sum_m C_m \hat{A}\ \Psi_m(x)$ …..(4)

On multiplying equation (4) by $\Psi_i^*(x)$ and integrating over the entire region of variation of the independent variables, we get

$B_t = \sum_m A_{lm} C_m$ …..(5)

Where$A_{lm} = \int \Psi_l^*(x)\, \hat{A}\, \Psi_m(x)\, dV$ …..(6)

The equation (5) gives the transformation of the function Ψ into the function ϕ in the F representation when the operator is $\hat{A}$. Thus, the operator $\hat{A}$in this representation is given by equation (6), in the form of a matrix.

It can be concluded that the definition of matrix A is equivalent to the definition of the operator $\hat{A}$itself.

The matrix element A_{ik} is also known as the matrix element corresponding to the transition from the kth state, i.e.

$\Psi(x) = \Psi_k(x)$

By the action of the operator $\hat{A}$the transformation (1) takes place. Now using the equations (2) and (5) and considering that in the given case

$C_m = \quad _{mk}$ and $B_n = A_{nk}$, we get

$\phi(x) = A\ \Psi_k = \sum_n B_n \Psi_n = \sum_n A_{nk} \Psi_n(x)$ …..(7)

The square of the matrix element A_{lk} gives the probability of finding the system in the i^{th} state.

Now, knowing the matrix corresponding to the quantity A we can get the mean value of this quantity in certain state Ψ, i.e.

$\bar{A} = \int \Psi^* \hat{A} \Psi\, dV$

On substituting the expression (2) instead of Ψ, we get

$\bar{A} = \sum_m \sum_n C_m^* C_n \int \Psi_m^* A \Psi_n dV$

$= \sum_m \sum_n C_m^* A_{mn} C_n$ …..(8)

Thus if we determine the matrix elements (6) by using the wave functions Ψ_m which are the eigen functions of the operator $\hat{A}$, then we also determine the matrix A of the operation in its own representation

$A_{ml} = \int \Psi_m^* \hat{A}\ \Psi_l dV = A_l \int \Psi_m^* \Psi_l dV$

$= A_l\, \delta_{ml}$ …..(9)

Hence we see that the matrix element with $m = l$ are different from zero. Such types of matrices are known as diagonal matrices, i.e.,

$$A = \begin{bmatrix} A_{11} & 0 & 0 & \cdots\cdots \\ 0 & A_{22} & 0 & \cdots\cdots \\ 0 & 0 & A_{33} & \cdots\cdots \\ \ldots & \ldots & \ldots & \cdots\cdots \\ \ldots & \ldots & \ldots & \cdots\cdots \end{bmatrix}$$

Thus we see that each operator has a representation as a diagonal matrix if the wave function is expanded in terms of eigen functions.

In other words we can say that the definition of operator A is equivalent to the matrix $[A]$. The matrix representation of the operator helps us to determine the eigen values and the eigen functions of the corresponding operator. Hence on knowing the operator A, the matrix elements can be found.

5.10 Matrix Representation of wave function

The wave functions can be represented by matrices in the following three ways:

- (i) Schrodinger representation
- (ii) Heisenberg representation
- (iii) Interaction representation

5.10.1 Schrodinger Representation

In Schrodinger picture the state vectors are time dependent while the operators are time independent.

Any wave function can be expressed as a linear combination of a set of basic functions which are orthogonal and time independent. The expression can be written as:

$$\Psi (r , t) = \sum_n \Psi_n(t)\, \phi_n(r) \qquad \text{.....(1)}$$

where $\Psi_n(t)$ are the expansion coefficients and $\phi_n(r)$ are the orthonormal set of basic functions. The Schrodinger equation in the Hamiltonian form can be written in terms of time independent functions as:

$$H\, \Psi (r , t) = i\,\hbar \frac{\partial \Psi(r ,t)}{\partial t} \qquad \text{.....(2)}$$

By substituting the values of $\Psi (r , t)$ from the equation (1) in the above equation (2) we get

$$H\, \sum_n \Psi_n(t)\, \phi_n(r) = \; i\,\hbar \frac{\partial}{\partial t} \sum_n \Psi_n(t)\, \phi_n(r)$$

Or $\sum_n \Psi_n(t)\, H\, \phi_n(r) = \; i\,\hbar \frac{\partial}{\partial t} \sum \Psi_n(t) \phi_n(r)$

On multiplying above equation by $\phi_m^*(r)$ and integrating over all r, we get

$$\int \sum_n \Psi_n(t)\, \phi_m^*(r) H \phi_n(r)\, dr = i\,\hbar \frac{\partial}{\partial t} \sum_n \Psi_n(t) \; \int \phi_m^*(r)\, \phi_n(r)\, dr$$

Or $\int \sum_n \Psi_n(t)\, H_{mn} = i\,\hbar \frac{\partial}{\partial t} \sum_n \Psi_n(t)\, \delta_{mn}$

$= i\hbar \frac{\partial \Psi_m}{\partial t}$ …..(3)

Where $H_{mn} = \int \phi_m^*(r)\, H\phi_n(r)\, dr$

Therefore equation (3) can be expressed as

$i\hbar\, \Psi_m = \sum_m H_{mn} \Psi_n(t)$ …..(4)

The equation (4) completely defines how the expansion coefficients Ψ_n's change with time if Ψ_n are known at any instant. It means that the time dependence of the value of Ψ_n is entirely due to time dependence of the state.

The matrix representation for equation (4)is as follows:

$H\Psi = i\hbar\frac{d\Psi}{dt}$ …..(5)

Where $\frac{d\Psi}{dt}$ is a matrix whose each element is the time derivative of the corresponding elements of the matrix Ψ.

The representation given by equation (5) in which the basic functions are independent of time is called the Schrodinger representation.

5.10.2 Heisenberg Representation

In Heisenberg picture the state vectors are time independent and the time dependence is carried by the operators.

In this representation the basic functions are chosen to be position as well as time dependent. In other words, the wave function $\Psi(r, t)$ has the form

$\Psi(r, t) = \sum \Psi_n \phi_n(r, t)$ …..(1)

If the basic functions ϕ_n satisfy Schrodinger equation, then ϕ_n can be shown to satisfy the orthonormality condition at all time, i.e.,

$\int \phi_m^* \phi_n dr = \delta_{mn}$ …..(2)

Each term of equation (1) in the sum satisfies Schrodinger's equation; hence the sum with constant coefficients Ψ_n will also satisfy this equation. As a result the wave functions $\Psi(r, t)$ will satisfy the Schrodinger's equation in the time dependent form. The operators n this representation will be time dependent which will be clear from the discussion given below:

Let us consider the *ij*the matrix element of the operator which is written as

$$Q_{ij} = \int \phi_i \, Q \, \phi_j dr = (\phi_i \, Q \, \phi_j) \qquad \ldots..(3)$$

The time derivative of the matrix can be written as follows:

$$Q_{ij} = \left(\frac{\partial \phi_i}{\partial t}, Q\phi_j\right) + \left(\phi_i, Q\frac{\partial \phi_i}{\partial t}\right) + \left(\phi_i, \frac{\partial Q}{dt}\phi_j\right) \qquad \ldots..(4)$$

Now we know that ϕ's satisfy Schrodinger's equation

$$H\phi = i\hbar\frac{\partial \phi}{dt}, \text{ so that } H^*\phi^* = -i\hbar\frac{\partial \phi^*}{dt}$$

Hence equation (4)may be written as follows:

$$Q_{ij} = \frac{1}{\hbar i}\{ (-H\phi_i, Q\phi_j) + (\phi_i, QH\phi_j) \} + \left(\phi_i, \frac{\partial Q}{\partial t}\phi_j\right)$$

$$= \frac{1}{\hbar i}\left(\phi_i, [QH - HQ]\phi_j\right) + \left(\phi_i, \frac{\partial Q}{\partial t}\phi_j\right) \qquad \ldots..(5)$$

The equation (5)in matrix form becomes

$$Q = \frac{1}{\hbar i}[Q, H] + \frac{\partial Q}{\partial t} \qquad \ldots..(6)$$

The above relation is similar to the classical relation of Poisson bracket with the Hamiltonian function which is expressed as:

$$Q = [Q, H] + \frac{\partial Q}{\partial t} \qquad \ldots..(7)$$

Similarity between the two relations suggests that Ψ has the representation given by the classical equation of motion. This type of representation (1)is called Heisenberg representation. It establishes a close connection between classical and quantum formulations.

5.10.3 Interaction Representation

In interaction picture the state vectors and operators are both time dependent.

There is yet another representation known as the interaction representation of wave functions. This representation is useful in perturbation representation where the Hamiltonian H can be divided in two parts H_0 and H_1. Here H_0 is unperturbed term and H_1 is the interaction term. In case ϕ_j represents an orthonormal set of functions which are eigen functions of Hamiltonian H_0 , the Schrodinger equation can be expressed as :

$$H_0\phi_j = i\,\hbar\,\frac{\partial \phi_j}{\partial t} \qquad \ldots..(1)$$

The total function Ψcan be represented as a linear combination ofϕ_j as given below:

$$\Psi = \sum_j \Psi_j \phi_j \qquad \ldots..(2)$$

Hence the Schrodinger equation of the complete system becomes

$$H\Psi = i\hbar \frac{\partial\Psi}{dt} \qquad \ldots..(3)$$

or $(H_0 + H_I)\sum_j \Psi_j \phi_j = i\hbar \frac{\partial}{\partial t}\sum_j \Psi_j \phi_j$

or $H_0 \sum \Psi_j \phi_j + H_I \sum_j \Psi_j \phi_j = i\hbar \left\{\sum_j \Psi_{,} \frac{\partial\phi_i}{dt} + \sum_j \frac{\partial\Psi_j}{\partial t}\phi_j\right\} \qquad \ldots..(4)$

Substituting equation (1) in equation (4)we may write

$$\sum_j \Psi_j\, i\hbar \frac{\partial\phi_j}{\partial t} + H_i \sum_j \Psi_j \phi_j = i\hbar \left\{\sum_j \Psi_j \frac{\partial\phi_j}{\partial t} + \sum_j \frac{\partial\Psi_j}{\partial t}\phi_j\right\}$$

Or $H_I \sum_j \Psi_j\, \phi_i = i\hbar \sum_j \frac{\partial\Psi_i}{\partial t}\phi_i \qquad \ldots..(5)$

On multiplying the above equation from the left by ϕ_i^* and integrating for all r, we obtain :

$$\int \phi_i^* H_i \sum_j \Psi_i \phi_j dr = i\hbar \int \Psi_i^* \sum \frac{\partial\Psi_j}{\partial t}\phi_j dr$$

or $(H_i\, \Psi)_{ij} = \left(i\hbar \frac{\partial\Psi}{\partial t}\right)_{ij} \qquad \ldots..(6)$

or $H_i\, \Psi = i\hbar \frac{\partial\Psi}{\partial t} \qquad \ldots..(7)$

This representation is known as interaction representation as it is used for the interaction Hamiltonian. The equations of motion for a time independent matrix operator Q, i.e., $\frac{\partial Q}{\partial t} = 0$ are given below :

$$Q = \frac{1}{i\hbar}[Q, H_0] \qquad \ldots..(8)$$

Or $i\hbar \frac{\partial Q}{\partial t} = [Q, H_0] \qquad \ldots..(9)$

If $H_I = 0$, then interaction representation takes the form of Heisenberg representation.

Such commutation rules in fact are more general and are also used in field theoretical formulations also.

From the above discussion we can conclude that the Schrodinger, Heisenberg and interaction representations use different forms of eigen functions. The Schrodinger representation uses time independent representation of wave functions. In Heisenberg representation the base functions chosen are time dependent and are used for time independent wave function representation. The interaction representation is used where the small interaction term exists in the Hamiltonian. When this interaction term H_I becomes zero, the interaction representation takes the form of Heisenberg's representation.

5.11 Dirac's Bra and Ket Vector

The quantum matrix theory can be put into compact form by making use of notations invented by Dirac. According to him, the state of a system can be represented by a vector called state vector in the vector space. He introduced the symbol$|\ \rangle$ called the Ket vector or simply Ket to denote a state vector which will take different forms in different representations. It is represented by inserting a particular letter in the middle. For example $|\ a\ \rangle$denotes the Ket vector corresponding to state a of the system (which was written as Ψ_a in old notation).

Corresponding to every vector,$|\ a\ \rangle$is defined a conjugate vector $|\ a\ \rangle^*$ for which Dirac used the notation $\langle\ a\ |$ which is called a bra vector or simply bra. The conjugate of a Ket vector is a bra vector and vice versa. A scalar in the ket space becomes its complex conjugate in the bra space. The bra – ket notation is a distorted form of the bracket notation. Thus the bracket symbol (|) is distorted to $\langle\ |$ and $|\ \rangle$in Dirac notation. The scalar product of a bra vector $\langle\ a\ |$ and a ket vector $|\ b\ \rangle$ is represented as $\langle a|b\rangle$. The two vertical lines in the middle are contracted to one.

In terms of bra and ket vectors, the definition of inner product of the state vectors Ψ_a and Ψ_b takes the form

$$(\ \Psi_a\ ,\ \Psi_b\ ) = \int \Psi_a^* \Psi_b d\tau = \langle a|b\rangle \qquad \ldots..(1)$$

Thus a and b in (a, b) are written respectively as $\langle\ a\ |$and $|\ b\ \rangle$, and the scalar product is

$$(a\ ,\ b) = \langle a|b\rangle = \langle b|a\rangle^* \qquad \ldots..(2)$$

The prefactor space is, thus a bra space and the post factor space a ket – space. Since the conjugate of a product of complex function is the product of the conjugates, equation **(2)** implies that

$$|\ a\ \rangle^* = \langle\ a\ | \qquad \ldots..(3)$$

This shows that the two spaces are not independent of each other, they are said to be dual to each other. Not only is there a vector in one space corresponding to every vector in the other space, but also each relationship among vectors in one space has its 'image' in the other space. If the ket space has a finite number of dimensions, the dual space (bra space) has the same number of dimensions. There exists one to one correspondence between the vectors of bra and ket space. For example,

$$|\ v\ \rangle = C_1|\ a\ \rangle + C_2|\ b\ \rangle \qquad \ldots..(4)$$

is a vector of ket space. If $|\ a\ \rangle$ and $|\ b\ \rangle$ are two kets and C_1 and C_2 are two arbitrary complex numbers.

Operation by an operator A on a ket vector produces another ket vector.

$$A\ |\ a\ \rangle\ =\ |\ a'\ \rangle \qquad \ldots..(5)$$

Operation on a bra vector from the right by A gives another bra vector

$\langle b | A = \langle b' |$ …..(6)

The bra conjugate to ket

$| v \rangle = C_1| a \rangle + C_2| b \rangle$

is$\langle v | = C_1^*\langle a | + C_2^*\langle b |$ …..(7)

The norm of a ket$| a \rangle$, denoted by $\langle a|a\rangle$ is a real non – negative number. That is

$\langle a|a\rangle \geq 0$ …..(8)

The equality sign holds only if $| a \rangle = 0$.

The ket$| a \rangle$ is said to be normalised if

$\langle a|a\rangle = 1$ …..(9)

A bra and a ket vector are said to be orthogonal if their scalar product is zero, i.e.,

$\langle a|b\rangle = 0$ …..(10)

The orthogonality relation is expressed as

$\langle a_i|a_j\rangle = {}_{ij}$ …..(11)

In this notation, the condition for an operator to be Hermitian is

$\langle a|A|b\rangle = \langle b|A|a\rangle^*$

Example: If $| a \rangle$ and $| b \rangle$ are arbitrary kets, prove that

$\overline{| a \rangle\langle b |} = | b \rangle\langle a |$

Solution: Let us consider an arbitrary ket$| c \rangle$, so that its operation from left on $| a \rangle\langle b |$ gives $| c \rangle| a \rangle\langle b |$

Taking conjugate imaginary ket

$\overline{| c \rangle| a \rangle\langle b |} = \overline{| a \rangle\langle b |}\langle c |$

Also $\overline{| c \rangle\langle a |\langle b} = \langle a | c \rangle| b \rangle = | b \rangle\langle a | c \rangle$

Hence $\overline{| a \rangle\langle b |} = | b \rangle\langle a |$

5.12 SUMMARY

In this unit we have studied that

- When a set of n linearly independent vectors v_1 , v_2 ….v_n span an n – dimensional space and if any vector lies in this space then it can be expressed in the form

$\phi = \sum_{i=1}^{n} u_i v_i$

The generalization of these concepts to an infinite – dimensional space is called vector space.

- The inner product of u and v is given by

$(u , v) = \sum_{i=1}^{n} u_i v_i$

- What is matrix algebra and kinds of matrices like Transpose of a matrix, Conjugate of a matrix, Hermitian, Symmetric, Unitary matrix etc. and also numerical problems based on them?

- In matrix notation, we can write an equation

$AX = Y$

which represents a transformation which carries a vector X into another vector Y of the same space. Matrix A is called the matrix of transformation.

- The characteristic equation of a matrix is

$(A - \lambda I)X = 0$

where I is the unit matrix. It is also explained how to get the eigen values and eigen vectors of the matrix.

- The vector space is said to be a Hilbert space if it is complete and of countable infinite dimensions such that all infinite series occuring in it are convergent.

- The operator can be represented in matrix form which enables us to determine the eigen value and eigen function of the corresponding operator.
- In Schrodinger representation the state vectors are time dependent while the operators are time independent.

- In Heisenberg picture, the state vectors are time independent and the time dependence is carried by the operators.

- In Interaction picture, both state vectors and operators are time dependent.

- Dirac’s notation to put quantum matrix theory into a compact form. Here each dynamical state is represented by a vector called ket vector ($|\rangle$). Its mirror image is a bra vector ($\langle|$). The correspondence between the kets and bras is analogus to the correspondence between the wave functions of wave mechanics and their complex conjugates.

5.13 GLOSSARY

Independent – not depending on others

Orthogonal – rectangular

Conjugate – combined in pairs

Array – orderly collection of objects

Conformable – corresponding

Symmetric – proportionate parts or relations

Singular – number denoting one person or thing

Transformation– change or transform the character

Invariant – not varying

Characteristic – indicating the character

Generalised – infer as a general principal

Degeneracy – the state of being degenerate

Convergent – tending to one point

Unperturbed – undisturbed

Interaction – to interact between

Dual – composed of two numbers

5.14 TERMINAL QUESTIONS

1) What do you mean by linear vector space and linear operators?

2) What do you mean by inner product?
3) Define with examples the following –
    (a) Unitary matrix
    (b) Hermitian matrix
    (c) Transpose of a matrix
    (d) Conjugate of a matrix
    (e) Symmetric matrix
4) What do you mean by Hilbert space? How a basic set of wave functions is changed into another by unitary transformation in Hilbert space?
5) Explain the principle of matrix mechanics.
6) Show that the eigen values of a diagonal matrix are its diagonal elements.
7) Discuss the Schrodinger, the Heisenberg and the Interaction representations for describing the dynamical behaviour of a system.
8) How do you diagonalise a matrix?
9) Show that the eigen values of a matrix are not changed by a unitary transformation.

NUMERICAL PROBLEMS:

1) Reduce to diagonal form the matrix

$\begin{bmatrix} 1 & 0 \\ 3 & 2 \end{bmatrix}$[Ans - $\begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}$]

2) Find the eigen values and eigen vectors of the matrix

$\begin{bmatrix} 8 & -8 & 2 \\ 4 & -2 & -2 \\ 3 & -4 & 1 \end{bmatrix}$ [Ans - $\lambda = 1,2,3$]

3) Which one of the following matrices areHermitian?

$\begin{bmatrix} 1 & i & 0 \\ -i & 0 & -2i \\ 0 & 2i & 2 \end{bmatrix}$ (ii)$\begin{bmatrix} 0 & -i & -i \\ i & 5 & 0 \\ 3i & 0 & 2 \end{bmatrix}$ [Ans – (i)]

4) If $|\,n\,\rangle$ and $|\,m\,\rangle$ are two arbitrary ket vectors and vector $|\,i\,\rangle$ forms a complete set, then show that

$\langle n|m\rangle = \sum_i \langle n|i\rangle \langle i|m\rangle$

5) Which of the following is a singular matrix

$$\begin{bmatrix} 2 & 1 & 5 \\ 3 & 5 & 7 \\ 2 & 1 & 5 \end{bmatrix} \qquad \text{(ii)} \qquad \begin{bmatrix} 3 & -1 & 1 \\ -15 & 6 & -5 \\ 5 & -2 & 2 \end{bmatrix}$$ [Ans – (i)]

6) Find the elements C_{23}, C_{32}, C_{22}, C_{33} in the product C = AB where

$$A = \begin{bmatrix} 2 & 3 & 4 \\ 1 & 2 & 3 \\ -1 & 1 & 2 \end{bmatrix} \qquad B = \begin{bmatrix} 1 & 3 & 0 \\ -1 & 2 & 1 \\ 0 & 0 & 2 \end{bmatrix}$$ [Ans – 8,-1,7,5]

5.15 REFERENCES

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UNIT-6: IDENTICAL PARTICLES AND SPIN ANGULAR MOMENTUM

Structure

6.1 INTRODUCTION

The study of many particles system is of great importance in both classical and quantum mechanics. Modern physical theories are based on the fact that matter is composed of few types of elementary (fundamental) particles (electrons, positrons, protons, neutrons, mesons, neutrinos, several strange particles etc.). Each type of particle is characterized by some properties like mass, charge, spin and several other quantum numbers. These properties are exactly same for all the particles of the same type. Consequently, the substitution of one particle by another of the same type in the theoretical description of a system cannot effect any prediction about its motion. Such two particles with their physical properties exactly same are known as identical particles. This nature precludes the possibility of an observation which could distinguish these particles. In classical mechanics this property of indistinguishability of identical particles plays a secondary role while in quantum mechanics it raises a serious problem. In classical mechanics, the identical particles do not lose their individuality despite the identity of their physical properties since you can imagine the particles at some instant to be numbered and follow the subsequent motion of each of them in its path and hence at any instant each particle can be identified.On the other hand, by virtue of uncertainty principle in quantum mechanics, the concept of path of an elementary particle ceases to have any meaning and hence theindistinguishability of identical particles leads to several complications in their quantum mechanical description. Even if the position of an electron (for example) is exactly known at a given instant in quantum mechanics (with its most uncertain momentum), its coordinates will have no definite values at the next instant. Furthermore, if the wave functions of the individual identical particles overlap then it is impossible to keep track of individual locations of the particles without seriously affecting their motion. Thus in quantum mechanics there is no way to distinguish the identical particles and consequently the identical particles entirely lose their individuality in quantum mechanics.

It has become clear by many experimental and theoretical arguments that many elementary particles including electrons, protons and neutrons are not adequately described by the model of a massive point whose position in space exhausts its dynamical properties. Experimental developments, during1920’s,

provided data leading to the idea that these particles not only possess wave properties (orbital angular momentum) but also have intrinsic angular momentum (spin) and associated magnetic moment. The existence of intrinsic magnetic moment leads to spin dependent term in the Hamiltonian of an electron in an electromagnetic field. The spins of elementary particles also play an important role in their classifications as bosons and fermions in terms of the different statistics followed by them (spin-statistics relationship for the Identical Particles.

6.2 LEARNING OBJECTIVES

After learning this unit we will ABLE TO understand:

- Identical Particles
- Symmetry of Wave functions of Identical Particles
- Statistics of Identical Particles
- Pauli's Exclusion Principle
- Spin, Angular Momentum
- Stern and Gerlach Experiment
- 8 Pauli Spin Matrices, Spin Quantum Numbers

6.3 INDISTINGUISHABILITY OF IDENTICAL PARTICLES.

The Principle of Indistinguishability plays a fundamental role in the quantum theory of systems composed of identical particles. To say that two particles are identical means that there do not exist the interactions that can distinguish them. In the Hamiltonian formulation of the dynamics, the principle of indistinguishability implies that the Hamiltonian for any system is not affected by an interchange of the symbols which assign the dynamical quantities to the members of any pair of identical particles. For instance, you write in the following manner the Hamiltonian for a system of two identical particles with the corresponding symbols 1 and 2.

$$H(1,2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(|\vec{r}_1 - \vec{r}_2| \qquad (6.1)$$

where the potential $V(r)$ depends on the distance between two identical particles and m is the mass of each of them. This Hamiltonian is un-affected by the exchange of symbols 1 and 2 assigned to the two identical particles in the system. Thus this Hamiltonian is invariant under the interchange of these identical particles;

$$H(1,2) = H(2,1) \qquad (6.2)$$

This invariance represents the symmetry of the Hamiltonian with respect to the exchange (permutation) of the labels attached to the identical particles. In classical mechanics this exchange symmetry does not lead to any particular unusual consequence because the classical path of any particle can be followed from instant to instant.In quantum mechanics, the classical equations of motion are replaced by Schrodinger equation the solution of which gives the probability distribution for the position of the particles at each instant of time. The Schrodinger equation for the system of two identical particles with the Hamiltonian given by equation (6.1) may be written as

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad (6.3)$$

where$\hbar = \frac{h}{2\pi} = 1.1054 \times 10^{-27} ergs - sec$
with $h = 6.63 \times 10^{-27} ergs - sec$ (Planck's constant). Here $\widehat{H}$ is the linear Hermitian operator associated with the Hamiltonian given by eqn.(6.1).The wave functions $\Psi(1,2)$and $\Psi\ (2,1)$, which correspond to two classical motions of the system of two identical particles, are both solutions of this equation. You may write this equation for the first wave function as

$$\widehat{H}(1,2)\Psi(1,2) = \mathrm{i}\hbar \frac{\partial\Psi(1,2)}{\partial t} \qquad (6.4)$$

Interchanging the labels 1 and 2 of the two particles this equation becomes

$$\widehat{H}(2,1)\Psi(2,1) = \mathrm{i}\hbar \frac{\partial\Psi(2,1)}{\partial t} \qquad (6.5)$$

$$\text{or} \widehat{H}(1,2)\Psi(2,1) = \mathrm{i}\hbar \frac{\partial\Psi(2,1)}{\partial t} \qquad (6.5a)$$

whereeqn. (6.2) has been used. Since every linear combination of the functions $\Psi(1,2)$and $\Psi(2,1)$is also a solution of eqn. (6.3), it is possible to separate the states of the system into two distinct categories : symmetric state Ψ_S and antisymmetric state Ψ_A given as

$$\Psi_S = \frac{1}{2}[\Psi(1,2) + \Psi(2,1)] \qquad (6.6)$$

and $$\Psi_A = \frac{1}{2}[\Psi(1,2) - \Psi(2,1)] \qquad (6.7)$$

such that $\Psi(1,2) = \frac{1}{2}\{[\Psi(1,2) + \Psi(2,1)] + [\Psi(1,2) - \Psi(2,1)]\}$

$$= \Psi_S + \Psi_A \qquad (6.8)$$

which may be generalized to

$$\Psi(1,2) = \alpha\Psi_S + \beta\Psi_A \qquad (6.9)$$

and similarly you may write

$$\Psi(2,1) = \alpha\,\Psi_S - \beta\,\Psi_A\ , \qquad (6.9a)$$

whereΨ_S and Ψ_A are the solutions of the Schrodinger equation (6.3) corresponding respectively to the following initial conditions:

$$\Psi_{S0} = \frac{1}{2}\ [\Psi_0(1,2) + \Psi_0(2,1)];$$

$$\Psi_{A0} = \frac{1}{2}\ [\Psi_0(1,2) - \Psi_0(2,1)]$$

If the system is initially in the state

$\Psi_0 = \alpha\Psi_{S0} + \beta\Psi_{A0}$ with $|\alpha|^2 + |\beta|^2 = 1$ at the later time t it will be in the state given by eqn. (6.9).

The probability density P(1,2) of finding one particle at position $\vec{r}_1$ and the other identical particle at the position $\vec{r}_2$ is given by

$$P(1,2) = |\Psi(1,2)|^2 + |\Psi(2,1)|^2$$

$$= 2[\alpha^2|\Psi_S(1,2)|^2 + \beta^2|\Psi_A(1,2)|^2]$$

For this expression to be independent of α and β you must have

$$|\Psi_A(1,2)| = |\Psi_S(1,2)| \qquad (6.10)$$

so far as two particles have not entered into interaction. The separation of a wave function into symmetric and antisymmetric parts according to eqn. (6.9) is permanent in time. This means that an initially symmetric state can never change, either wholly or partially, into antisymmetric state and vice-versa. The relative amplitudes of the symmetric and antisymmetric components of a general wave function, given by eqn. (6.9), are determined by their values at the initial instant and do not change with time.

Equations (6.6) and (6.7) show that under the exchange of labels 1 and 2 the state Ψ_S is not changed while the sign of state Ψ_A is changed. Denote this exchange by the operator $\hat{P}$ then you will have

$$\hat{P}\Psi_S = \Psi_S \text{ and } \hat{P}\Psi_A = -\Psi_A \qquad (6.11)$$

where $\hat{P}^2 = 1$,

showing that the exchange operator $\hat{P}$ is an evolution operator with its eigen values 1 and -1 and the corresponding functions Ψ_S and Ψ_A respectively. You also have

$\hat{P}\hat{H}(1,2)\Psi(1,2) = \hat{H}(2,1)\Psi(2,1) = \hat{H}(1,2)\Psi(2,1) = \hat{H}(1,2)\hat{P}\Psi(1,2)$ which shows that $\hat{P}$ commutes with the Hamiltonian of the system:

$$\hat{P}\hat{H} - \hat{H}\hat{P} = [\hat{P}, \hat{H}] = 0 \qquad (6.12)$$

Thus Ψ_S and Ψ_A are the eigen functions of $\hat{H}$ also, since the commuting operators have simultaneous eigen vectors. The operator $\hat{P}$ is unitary and hence these eigen functions, belonging to two different eigen values, 1 and -1, are mutually orthogonal. Eigen functions $\Psi(1,2) = \Psi_E(1,2)$ of the Hamiltonian operator $\hat{H}$ which satisfy the relation

$\hat{H}\Psi_E(1,2) = E\,\Psi_E(1,2)$ are the stationary states of the system. The symmetric and antisymmetric parts of $\Psi_E(1,2)$, as given by eqn. (6.9), are linearly independent functions belonging to the same eigen value E (energy). This degeneracy is the exchange degeneracy which is the consequence of symmetry of the Hamiltonian operator $\widehat{H}$ under the permutation of labels 1 and 2.

You can generalize this exchange symmetry for the wave function of the system of N identical particles. In this system there are N! different possible permutations of the particles. Let$P_{\upsilon}\Psi(1,2,\dots\dots.N)$ denote the function which can be obtained from $\Psi(1,2,\dots\dots.N)$ by υ consecutive permutations of particle pairs. Then you may get the symmetric and antisymmetric wave functions through the following rules:

$$\Psi_S = A\ \sum_{\upsilon} P_{\upsilon}\,\Psi(1,2,\dots\dots.N) \qquad (6.13)$$

$$\Psi_A = B\ \sum_{\upsilon} (-1)^{\upsilon} P_{\upsilon}\,\Psi(1,2,\dots\dots.N) \qquad (6.14)$$

where summation has been taken over all N!functions corresponding to different possible permutations of N particles in the system. In eqn. (6.14) the terms involving the odd number of permutations from the original product are subtracted to generate an antisymmetric eigen function under the permutations.

The exchange degeneracy, as the result of separation of eigen functionsinto symmetric and antisymmetric parts, does not permit you to decide which of the linear combinations of these states represents the state of the system. This difficulty is resolved by introducing the following symmetry postulate which fixes once for all the coefficients α and β of the linear combination given by eqn. (6.9):

The dynamical states of a system of two identical p[articles are necessarily either all symmetrical $(\alpha = 1, \beta = 0)$ *or all antisymmetrical (* $\alpha = 0, \beta = 1$ *) in the permutation of two identical particles.*

This postulate can be easily generalized to the system of any number of particles as shown in the following section.

6.4 EXCHANGE SYMMETRY THROUGH PERMUTATION OPERATORS

You consider a system of N identical particles, where the observables associated with i^{th} particle are collectively denoted by ξ_i, the space of its dynamical states is F_i and the space $\mathcal{F}$ of the dynamical states of the whole system is the direct product

$$\mathcal{F} = F_1 \otimes F_2 \otimes \dots . \otimes F_N \qquad (6.15)$$

N!permutations of N identical particles are well defined operations to each of which there corresponds a certain operator of this space $\mathcal{F}$. If q is the complete set of commuting observables of $\mathcal{F}$ and $|q_{\upsilon}>$ is the eigen vector of a basis for q with corresponding differenteigenvaluesq_{υ}, then

$$< q_{\upsilon}|q_{\mu} > = \delta_{\upsilon\mu} \qquad (6.16)$$

The i^{th}particle of the N particles has its own set of commuting observables $q^{(i)}$ such that

$Q = [\, q^{(1)}, q^{(2)}, \ldots \ldots . q^{(N)}]$is a complete set of commuting observables for the space $\mathcal{F}$ and the vectors

$$\left|q_\alpha^{(1)}, q_\beta^{(2)}, \ldots \ldots .. q_\upsilon^{(N)} > = \right| q_\alpha >^{(1)} |q_\beta >^{(2)} \ldots . |q_\upsilon >^{(N)}>, \qquad (6.17)$$

formed by taking the direct product of the basis vectors of the spaces $F_{1,}F_{2,} \ldots \ldots F_N$,constitute the basis for a certain representation of the vectors of space $\mathcal{F}$. It is a symmetrical representation where particle- 1 is in the sub-state $|q_\alpha >$, particle-2 is in the sub-state $|q_\beta >$ and so on, and the particle-N is in the sub-state $|q_\upsilon >$. Any permutation of N identical particles modifies their distribution among the states $|q_\alpha >$, $|q_\beta >$,……., $|q_\upsilon >$ but the state (6.17) will remain unchanged under any permutation. To each permutation of N particles a permutation operator $\hat{P}$can be associated such that

$$\hat{P}\hat{P}^\dagger = \hat{P}^\dagger \hat{P} = \hat{I}(\text{unit operator}) \qquad (6.18)$$

showing that the permutation operator satisfies unitarity condition. The transposition (I, j), associated with the permutation operator transforms the state (6.17) into which i^{th} particle of μ^{th} sub-state goes to σ^{th} sub-state ofj^{th} particle and vice versa:

$$\hat{P}_{ij}\left|q_\alpha^{(1)}, q_\beta^{(2)}, \ldots \ldots q_\mu^{(i)} \ldots .. q_\sigma^{(j)} \ldots q_\upsilon^{(N)} > = \right| q_\alpha^{(1)}, q_\beta^{(2)}, \ldots \ldots q_\sigma^{(i)} \ldots .. q_\mu^{(j)} \ldots . q_\upsilon^{(N)} > (6.19)$$

For simplicity, you consider the case where N=3 (the results obtain here will hold for any N). You may associate the operator $\hat{P}_{123}$ with the permutation (1,2,3) in which 1 takes the place of 3, 2 takes the place of 1 and 3 takes the place of 2. Then you have

$$\hat{P}_{123}\left|q_\alpha^{(1)}, q_\beta^{(2)}, q_\gamma^{(3)} > = \right| q_\gamma^{(1)}, q_\alpha^{(2)}, q_\beta^{(3)} > \qquad (6.20)$$

You may also have the product of two successive permutations $\hat{P}_1$ and $\hat{P}_2$as the operator $\hat{P}$ corresponding to the resulting permutation;

$\hat{P} = \hat{P}_2\hat{P}_1$which shows that the permutation operators obey the same algebraic relations as the permutations which they correspond. Any permutation operator $\hat{P}$ can be expressed as the product of transpositions. All such products contain either the even or the odd number of transpositions. The parity of the permutation is + or – according to this number being even or odd and it is represented as $(-1)^P$. The permutations, shown by eqn. (6.19), are equal to their own inverse and the associated operator is an observable with the eigen values ± 1 since you have

$$\hat{P}_{ij}^2 = \hat{I} \qquad (6.21)$$

Thus all the $\frac{1}{2}\,N(N-1)$ transpositions for the system of N particles are evolutions (which satisfy the condition 6.18). The eigen functions of $\hat{P}_{ij}$belonging to the eigen values +1 are symmetric. The projector on the space of all symmetrical eigen vectors (in the interchange of $i^{th}$and j^{th}particles) is the symmetrizing operator

$$\hat{S}_{ij} = \frac{1}{2}\,[\hat{I}+\hat{P}_{ij}] \qquad (6.22)$$

On the other hand, the eigen vectors corresponding to the eigen value -1 of the transposition $\hat{P}_{ij}$ are antisymmetric with their projector on the space of antisymmetric vectors defined as anti-symmetrizing operator

$$\hat{A}_{ij} = \frac{1}{2}\,[\hat{I}-\hat{P}_{ij}] \qquad (6.23)$$

From these equations (6.22) and (6.23) you may readily get the following results

$$\hat{S}_{ij} + \hat{A}_{ij} = \hat{I};\hat{S}_{ij} - \hat{A}_{ij} = \hat{P}_{ij}; \hat{P}_{ij}\hat{S}_{ij} = \hat{S}_{ij}\hat{P}_{ij} = \hat{S}_{ij};\hat{P}_{ij}\hat{A}_{ij} = \hat{A}_{ij}\hat{P}_{ij} = -\hat{A}_{ij}$$
(6.24)

It can also be shown that operators $\hat{P}_{ij}$ do not commute with each other. For example, you consider the wave function $\Psi(q_\alpha\, q_\beta\, q_\gamma\,)$ of the state $|\Psi>$ of three particles in {Q} representation:

$$\Psi\big(q_\alpha\, q_\beta\, q_\gamma\big) = \sum_{\alpha\beta\gamma} |q_\alpha\, q_\beta\, q_\gamma >< q_\alpha q_\beta q_\gamma|\Psi > \qquad (6.25)$$

Then you will have

$$\hat{P}_{13}\hat{P}_{12}\Psi\big(q_\alpha\, q_\beta\, q_\gamma\big) = \hat{P}_{13}\Psi\big(q_\beta\, q_\alpha\, q_\gamma\big) = \Psi\big(q_\gamma\, q_\alpha\, q_\beta\big) = \hat{P}_{23}\Psi\big(q_\gamma\, q_\beta\, q_\alpha\big)$$

$$= \hat{P}_{23}\hat{P}_{13}\Psi\big(q_\alpha\, q_\beta\, q_\gamma\big)$$

which shows that $\hat{P}_{13}\hat{P}_{12} = \hat{P}_{23}\hat{P}_{13}$ (6.26)
and hence $\hat{P}_{13}\hat{P}_{12} \neq \hat{P}_{12}\hat{P}_{13},$ (6.27)

showing non-commutation of operators $\hat{P}_{ij}$.

Following the derivation of eqn. (6.12) you may readily prove that the operators $\hat{P}_{ij}$commute with the Hamiltonian operator of the system. It follows from this commutation and the non-commutation (6.27) that except for N=2, it is not possible to find a complete set of the N degenerate eigen functions of $\hat{H}$which are all simultaneous eigen functions of all the transposition operators.Only two eigen functions satisfy this property of being simultaneous eigen functions of all transposition operators$\hat{P}_{ij}$. The first one is completely symmetric function Ψ_S which belongs to the eign value +1 for every $\hat{P}_{ij}$;

$\hat{P}_{ij}\Psi_S = \Psi_S$ (6.28)The corresponding projection operator $\hat{S}_{ij}$ is given by eqn. (6.22). The other such eigen function is the totally antisymmetric eigen function Ψ_A which belongs to eigen value -1 for every $\hat{P}_{ij}$;

$$\hat{P}_{ij}\Psi_A = \Psi_A \tag{6.29}$$

The corresponding projection operator$\hat{A}_{ij}$ is given by (6.23). For instance, you assume $\Psi(q_\alpha\, q_\beta\, q_\gamma)$as the simultaneous eigen function of operators $\hat{P}_{12}$, $\hat{P}_{13}$ and $\hat{P}_{23}$ with the corresponding eigen values λ_1, λ_2 and λ_3 respectively:

$\hat{P}_{12}\Psi(q_\alpha\, q_\beta\, q_\gamma) = \lambda_1\Psi(q_\alpha\, q_\beta\, q_\gamma)$;

$\hat{P}_{13}\Psi(q_\alpha\, q_\beta\, q_\gamma) = \lambda_2\Psi(q_\alpha\, q_\beta\, q_\gamma)$; (6.30)

$\hat{P}_{23}\Psi(q_\alpha\, q_\beta\, q_\gamma) = \lambda_3\Psi(q_\alpha\, q_\beta\, q_\gamma)$where each of eigen values $\lambda_i$is either 1 or -1. You may use eqn. (6.26) to get

$\lambda_2\lambda_1 = \lambda_3\lambda_2or\lambda_1 = \lambda_3$. Similarly the relation

$\hat{P}_{13}\hat{P}_{12} = \hat{P}_{12}\hat{P}_{23}$implies$\lambda_2 = \lambda_3$. Thus an eigen function, satisfying each of eqns. (6.30), either remains unchanged under every transposition (totally symmetric) or changes its sign under every transposition (it is totally antisymmetric). For the most general case of N particles, you may prove this property of the eigen function using the following generalization of relation (6.26):

$$\hat{P}_{ij}\hat{P}_{ik} = \hat{P}_{jk}\hat{P}_{ij} \tag{6.31}$$

The principle of indistinguishability of identical particles tells that the states represented by Ψ and $\hat{P}\Psi$ are the same state. Thus for every permutation$\hat{P}$, Ψ and $\hat{P}\Psi$ give the same probability amplitude and hence differ only by the phase factor at the most:

$$|\hat{P}\Psi(q_\alpha\, q_\beta \ldots\ldots q_v)| = |\Psi(q_\alpha\, q_\beta \ldots\ldots q_v)| \tag{6.32}$$

which shows that the probability

$$|\Psi(q_\alpha\, q_\beta \ldots\ldots q_v)|^2\, d\vec{r}_1 d\vec{r}_2 \ldots\ldots d\vec{r}_N$$

that one of the particle of the system is in the element $d\vec{r}_1 d\vec{r}_2 \ldots\ldots d\vec{r}_N$ remains unchanged under the permutation of the identical particles. Thus every eigen function $\Psi(q_\alpha\, q_\beta \ldots\ldots q_v)$representing the physical state of the system of identical particles must be a simultaneous eigen function of all the transposition operators. Hence the physical states of a system of any number of identical particles are necessarily either all symmetrical or anti-symmetrical with respect to the permutations of the particles. Consequently, the number of states accessible to a physical system of identical particles is much smaller than that to an equivalent system of non-identical particles.It is entirely different from the classical situation where every solution of equation of motion for non-identical particles leads to a possible solution for identical particles.

The symmetric character of a solution of Schrodinger equation for the system of two or more identical particles is permanent in time and every such physical state is pure one (either totally symmetric of totally antisymmetric). The linear combinations (like those given by eqns. (6.9) and (6.9a) of symmetric and antisymmetric states are impossible in general (for non-zero $\alpha$and βboth) for a system of identical particles and the symmetry properties of their wave functions cannot be changed by an external perturbation. Thus the symmetric character of the wave function for the system of identical particles of given type is permanent in time. Which of these prescriptions (symmetric or antisymmetric) is to be applied on a given system depends on the nature of identical particles constituting the system. The particles with symmetric states are called *bosons* and the particles with antisymmetric states are called *fermions.* This is an empirical law without any exception. All elementary particles occurring in nature are either bosons or fermions.For instance, electrons, positrons, protons,neutrons and neutrinos etc are fermions while photons, all scaler particles, some mesons and all gauge particles are bosons. Though in quantum mechanics (and also in quantum field theory) these two classes (fermions and bosons) of elementary particles are treated as altogether separate and different classes following two different symmetries of their eigen states under the permutation of particles, recently, there has been put forward the idea of another type of symmetry, known as super-symmetry which relates fermions and bosons.

EXAMPLES:

Ex. 6.1: Show that for a system of two identical particles, each of which can be in one of the n quantum states, there are $\frac{1}{2}\, n(n+1)$ symmetric states.

Solution: When there are $n$single-particle states, there are $n$symmetric states in which both particles are in the same state. The number of symmetric states in which both particles are in different states is equal to the number of ways in which we can select two objects from n i.e. $n_{C_1} = \frac{1}{2}\, n(n-1)$.

Thus the total number of symmetric states is

$$n + \frac{1}{2}\, n(n-1) = \frac{1}{2}\, n(n+1)$$

Ex. 6.2: Show that the probability density of finding a system of two identical particles at zero separation is maximum when the particles are bosons and zero when the particles are fermions.

Solution: You consider two free non-interacting identical particles in one dimension (along X-axis). The single particle states may be written in the form e^{ikx}.Then the total symmetrized state of the system may be written as

$$\Psi = \Psi_{kk\prime}(x_1, x_2) = e^{ikx_1}e^{ik\prime x_2} \pm e^{ikx_2}e^{ik\prime x_1} \qquad (6.33)$$

(except for the normalization), where upper sign + sign is for symmetric wave-function (for two bosons) and the lower –sign gives the antisymmetric wave function for two fermions.

Introduce the variables $x = x_1 - x_2$ and $X = \frac{1}{2}(x_1 + x_2)$ and then you may write eqn. (6.33) as

$$\Psi_{kk\prime}(x, X) = e^{i(k+k')X}[e^{\frac{i(k-k')x}{2}} \pm e^{\frac{-i(k-k')x}{2}}] \qquad (6.34)$$

where variables x and X are the relative separation and the center of mass of two particles. This equation leads to the following expression for the probability density of finding the system with an inter-particle separation x;

$P'_{kk}(x) \propto \frac{cos^2(k-k')x}{2}$for symmetric wave function (for bosons) (6.35)

$\propto sin^2 \frac{(k-k')x}{2}$for anti-symmetric wave function (for fermions)(6.35a)

It shows that the probability at zero separation is maximum for bosons and zero for fermions (a simplified version of Pauli's exclusion principle which will be discussed in a following section).

Ex. 6.3: Obtain the symmetric and antisymmetric wave functions by applying the repeated permutations on a solution of Schrodinger equation for a system of three particles.

Solution: For a system of three particles the time independent Schrodinger equation is

$$\widehat{H}(1.2,3)\Psi\,(1,2,3) = \mathrm{E}\,\Psi\,(1,2,3) \qquad (6.36)$$

from any solution of which the following six solutions may be obtained by repeated permutations: $\Psi\,(1,2,3)$; $\Psi\,(2,3,1)$; $\Psi\,(3,1,2)$; $\Psi\,(1,3,2)$; $\Psi\,(2,1,3)\Psi\,(3,2,1)$ first three of which have been obtained by applying even number of permutations on the solution $\Psi\,(1,2,3)$ of the Schrodinger equation (6.36) and the remaining three have been obtained on applying the odd number of permutations on this solution. Now using rules given by eqns.(6.13) and (6.14), you may readily get the following symmetrical and antisymmetric wave functions for the given system :

$$\Psi_S = A[\Psi\,(1,2,3) + \Psi\,(2,3,1) + \Psi\,(3,1,2) + \Psi\,(1,3,2) + \Psi\,(2,1,3) + \Psi\,(3,2,1)]$$

and

$$\Psi_S = A[\Psi\,(1,2,3) + \Psi\,(2,3,1) + \Psi\,(3,1,2) - \Psi\,(1,3,2) - \Psi\,(2,1,3) - \Psi\,(3,2,1)]$$

SELF ASSESSMENTQUESTIONS (SAQ):

Q1. Show that forasystem of two identical fermions, each of which can be in one of the n quantum states, there are $\frac{1}{2}$ n(n − 1)states of the system.

Q2. A configuration for a three particle system has one particle in each of the following orbital states:$\Psi_1 = N_1 \exp(-m_1^2 r_1^2)$; $\Psi_2 = N_2 \sin m_2 r_2$; $\Psi_3 = N_3 \exp(-m_3 x_3)$
where m_i refer to mass of each particle and N_i is the normalization constant. (a) Construct the total state function of the system if the particles are indistinguishable (m_1, m_2 and $m_3$are all different) (b) Construct the state functions of even and odd symmetries if the particles are indistinguishable ($m_1 = m_2 = m_3$).

Q3. Show that any interchange of two particles of the system of identical particles of any type (bosons or fermions) leaves the average or the observed properties of system unchanged.

6.5 STATISTICS OF IDENTICAL PARTICLES

There is a definite connection between the symmetry of the eigen states of identical particles and the Statistics followed by them. You have seen that the quantum mechanical states assessable to a system of identical particles are all symmetric or all antisymmetric under the permutation of the particles. Now youconsider two non-interacting particles for each of which there are available two quantum states $\Phi_1$and Φ_2. Now you have following three different situations:

(i) When two particles are distinguishable then you have following four linearly independent combined states for the system;

$\Phi_1(1)\Phi_1(2)$; $\Phi_1(1)\Phi_2(2)$; $\Phi_1(2)\Phi_2(1)$; $\Phi_2(1)\Phi_2(2)$

(ii) For the identical particles with symmetric wave functions, the following three states can be formed by superposition of the state wave functions:

$\Phi_1(1)\Phi_1(2)$; $[\Phi_1(1)\Phi_2(2)+\Phi_1(2)\Phi_2(1)]$; $\Phi_2(1)\Phi_2(2)$

(iii) For two identical particles with antisymmetric wave function, there exists only one state given by

$[\Phi_1(1)\Phi_2(2)-\Phi_1(2)\Phi_2(1)]$

These three types of systems obey quite differenttypes of statistical laws. In case (i) of distinguishable particles, every permutation of particles corresponds to a different state just as in classical theory following classical statistical behavior known as Maxwell- Boltzmann Statistics. Second system with symmetrical wave functions, specified in class (ii), obeys Bose-Einstein Statistics and the third type of system with antisymmetric wave functions as prescribed in case (iii), obey Fermi-Dirac statistics. As discussed earlier, the particles that are described by antisymmetric wave functions are called fermions as they obey Fermi-Dirac statistics while the particles described by symmetric wave functions obey Bose Einstein statistics and are known as bosons.

Symmetric eigen states form a subspace $\mathcal{F}_S$ of the total space $\mathcal{F}$ described by eqn.(6.15) for N particles. The antisymmetric eigen vectors form the subspace $\mathcal{F}_A$of the space $\mathcal{F}$. These subspaces are mutually orthogonal and the corresponding projectors are given by

$\hat{S} = \frac{1}{N!}\sum_P Pand\hat{A} = \frac{1}{N!}\sum_P (-1)^P P$ (6.37) respectively, where summation has been taken over N! possible permutations. The subset of vectors of eqn. (6.16) may be formed as $|q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} >$by partitioning the total number of particles ($n_1$in q_1 state, n_2 in q_2 state and so on) with the symmetrical wave functions constituting an orthonormal basis in $\mathcal{F}_S$ subspace while the similar set of vectors constructed for particles with antisymmetric states constituting an orthonormal basis in the subspace $\mathcal{F}_A$. The distinction among the three types of statistics, discussed herewith, lies in these state vector subspaces as shown in the following table:

Statistics	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Character of Particles	Distinguishable	Identical	Identical
State Vector- Space	$\mathcal{F}$	$\mathcal{F}_S$	$\mathcal{F}_A$

Even in the idealized quantum systems identical bosons(particles obeying Bose-Einstein statistics) attract each other while the identical fermions (particles obeying Fermi-Dirac statistics) repel each other as shown above in the Examples Ex. 6.2.

6.6 PAULI EXCLUSION PRINCIPLE

It has been shown by eqn. (6.35a) that for two identical fermions the probability density for zero one- dimensional separation is zero which means that the fermions move in such a manner as to exclude other fermions. It may also be noted in eqn. (6.35a) that the probability function vanishes identically when two fermions are in the same momentum states (i.e. for k=k') . In other words, two identical fermions cannot occupy the same Momentum quantum state. It verifies Pauli's exclusion principle for momentum states. To verify this statement in a general case you may note that an antisymmetric eigen vector can exist in the sub-space $\mathcal{F}_A$, introduced in the previous section, only if

$$\hat{A}|q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} > \neq 0 \qquad (6.38)$$

where operator $\hat{A}$ is given by eqn. (6.37). You may start with the assumption that at least one of the integers $n_1, n_2, n_3, \dots \dots . . n_v$ is greater than one. Then in the state of condition (6.38) at least two particles, say i^{th} and j^{th},would occupy the same individual quantum state so that the eigen state of this condition is symmetrical under the exchange of these two particles:

$$|q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} > = \hat{S}_{ij} |q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} >$$

$$= \frac{1}{2}(\hat{I} + \hat{P}_{ij}) |q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} > \qquad (6.39)$$

where use of relation (6.22) has been made. Operating this equation by the operator $\hat{A} = \hat{A}_{ij}$, you may get

$\hat{A}|q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} > = 0$showing that the state $|q_1^{(n_1)}, q_2^{(n_2)}, \dots q_v^{(n_v)} >$ with two identical fermions in the same sub-state cannot exist.In other words none of the integers $n_1, n_2, n_3, \dots \dots . . n_v$ in this state can be greater than one. It verifies Pauli's exclusion principle in a general case.

An alternative proof of this principle may be given in terms of vanishing value of Slater determinant for an antisymmetric state with more than one fermion in the same quantum sub-state. To meet this end you may write eqn. (6.14) in the following normalized form:

$$\Psi_A \, (1,2, \dots \dots \dots , N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \, P[\, \Psi_1(1) \;\; \Psi_2(2) \dots \Psi_N(N)] \qquad (6.40)$$

where$\Psi_1, \Psi_2 \dots . . \Psi_N$are single particle states. You may also write this state as following Slater determinant:

$$\Psi_A \, (1,2, \dots \dots \dots , N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) & \Psi_1(2) & \dots & \Psi_1(N) \\ \Psi_2(1) & \Psi_2(2) & \dots & \Psi_2(N) \\ \vdots & \vdots & \vdots & \vdots \\ \Psi_N(1) & \Psi_N(2) & \dots & \Psi_N(N) \end{vmatrix} \qquad (6.41)$$

The determinant on the right hand side of this equation vanishes when two of the identical fermions are in the same state because in such a case its two rows will be identical. In other words, in any configuration two (or more) identical fermions cannot occupy the same quantum state. Consequently, no two or more

fermions can be assigned the same set of quantum numbers. This is Pauli exclusion principle which is a fundamental law for understanding atomic structureand the properties of the elements as represented in periodic table.

EXAMPLES

Ex. 6.4: Show that the factor $\frac{1}{\sqrt{N!}}$In equation (6.40) is necessary to normalize Ψ_A to unity.

Solution: You have $< \Psi_A \,|\Psi_A\ > =$ $\frac{1}{N!}\{\sum_{P,P}\int d\,\vec{r}_1\, d\vec{r}_2 \ldots\ldots d\vec{r}_N\, (-1)^P(-1)^{P'} P'[\Psi_1^*(1)\Psi_2^*(2)\ldots.\Psi_N^*(N)]P[\Psi_1(1)\ \ \Psi_2(2)\ldots\Psi_N(N)]\}$

Since various $\Psi's$in this expression are mutually orthogonal, the terms corresponding to $P \neq P'$will vanish. Thus you are left with only the sum of N! permutations of unity in the bracket {} in this expression. As such you have

$$< \Psi_A \,|\Psi_A\ > = \hat{I}$$

which confirms the required normalization.

Ex. 6.5: Factorizing the wave function of N identical particles into a product of single particle wave function and anti-symmetrizing it according to Pauli's exclusion principle, reduce the expectation value of an operator describing the action of an external force field into single particle integral.

Solution: Equation (6.40) gives the anti-symmetrized wave function in terms of single particle wave functions $\Psi_1(1), \Psi_2(2) \ldots\ldots \Psi_N(N)$. An operator $\widehat{\Omega}$ describing an external force will act on the particles in the similar way:

$$\widehat{\Omega} = \sum_{v=1}^{N}\widehat{\Omega}_v \qquad (6.42)$$

Its expectation value, with respect to the anti-symmetric wave function of eqn. (6.40), is given by

$$|\hat{\Omega}| = \frac{1}{N!}\sum_{P,P}(-1)^{P+P'} < P'[\Psi_1(1)\Psi_2(2)..]|\sum_{v=1}^{N}\widehat{\Omega}_v\, |P[\ \ \Psi_1(1)\Psi_2(2)..] > \qquad (6.42a)$$

Now you single out from eqn. (6.42a) one term $\widehat{\Omega}_v$of eqn. (6.42) acting only upon the functions of v^{th} particle by using the following orthogonality of single particle functions:

$$< \Psi_j|\, \Psi_k > = \ \delta_{jk}$$

which means the identity of permutations P and P'. Then the term $\widehat{\Omega}_v$ will contribute only one particle integral

$$< P'|\widehat{\Omega}_v|P > = \ \delta_{PP'}\sum_{i=1}^{N} < \Psi_i\,(n)|\hat{\Omega}_v|\Psi_i(v) > \qquad (6.43)$$

In the wave functionΨ the factor $\Psi_i(v)$ with fixed $i\ and\ v$ is combined with a determinant of rank N-1. Then there remains, amongst the total N! permutations, (N-1)! permutations of the remaining (N-1) functions (except $\Psi_i(v)$ functions). Thus you are left with

$$< \Psi|\widehat{\Omega}_v|\Psi > = \frac{(N-1)!}{N!}\sum_{i=1}^{N} < \Psi_i\,(v)|\hat{\Omega}_v|\Psi_i(v) > \qquad (6.44)$$

This result holds for whatever term $\widehat{\Omega}_\upsilon$ you pick out of the sum given by eqn. (6.42). Thus in $< \Psi|\Omega|\Psi >$ you have a total N similar expressions of the form (6.44). Consequently, you have

$$< \Psi|\Omega|\Psi > = \sum_{i=1}^{N} < \Psi_i\,(\upsilon)\big|\hat{\Omega}_\upsilon\big|\Psi_i(\upsilon) >$$

which is the required result.

SELF ASSESSMENTQUESTIONS (SAQ):

Q.4 Find the value of A in eqn. (6.13) for the symmetric normalized state.Q.5 Show that there is some sort of repulsive force between electrons in addition to the Coulomb repulsion. Q.6 Two identical non-interacting particles are in an isotropic harmonic oscillator potential. Show that the degeneracies of three lowest energy levels are: (a) 1,12,39 if particles have antisymmetric eigen states. (b) 6,27,99, if the eigen states of the particles are all symmetric.

6.7 SPIN ANGULAR MONENTUM

The wave mechanical description of quantum mechanics, as proposed by Schrodinger, is complete with reference to only simple model of a point particle in a given external field. It is incapable of accounting for many of finer details. It became clear by many experimental and theoretical arguments that many elementary particles including electrons, protons and neutrons are not described adequately by the model of a massive point whose position in space exhausts its dynamical properties. Experimental developmentsduring 1920's provided data leading to the idea that these particles possesses not only wave properties (orbital angular momentum) but also have intrinsic angular momentum (spin) and associated magnetic moment. In 1922 an experiment by Stern and Gerlach revealed this spin almost dramatically. Before discussing Stern and Gerlach experiment and the consequences of its results in terms of spin of electrons and other elementary particles, you must understand the meaning of angular momentum operator.

6.7.1 Angular Momentum operator.

A vector operator $\hat{J}$is an angular momentum operator if its components are observables (Hermitian) and obey the following commutation relations

$[\hat{J}_x, \hat{J}_y] = i\,\hbar\hat{J}_z$(and other cyclic orders)

or in general $\quad [\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k, \quad (i, j, k = 1,2,3) \qquad (6.45)$

where ε_{ijk}has its value +1 for jkl as even permutation of 1,2,3 and -1 for jkl as odd permutation of 1,2.3 and zero if any two of the indices of jkl are equal. This definition enables you to treat those entities also which have no classical analogue like intrinsic spin of elementary particles. Defining the square of angular momentum operator as

$J^2 = J_x^2 + J_y^2 + J_z^2,$
you may readily show that

$$[\hat{J}, \hat{J}^2] = 0 \qquad (6.46)$$

Equation (6.45) shows that the components of angular momentum operator $\hat{J}$ do not commute among themselves and hence you cannot have a common eigen basis for all these components. On the other hand eqn. (6.46) enables you to form a complete set of common eigen functions of J^2 and one of the components say $\hat{J}_z$. It will be demonstrated in next unit (chapter) that corresponding to such common eigen functions $|j, m_j >$ the eigen values of J^2 and $\hat{J}_z$are $j(j+1)\hbar^2$ and $m_j\hbar$ respectively, where $j = 0, \frac{1}{2} 1, \frac{3}{2}, \ldots\ldots \infty$ and $m_j = -j, -j+1, \ldots\ldots, +j$ showing that for a given value of $j$there are $(2\,j+1)$ values of m_j and the length of angular momentum vector is uniquely fixed as $\sqrt{j(j+1)}\hbar$. These $(2\,j+1)$ allowed values of m_j for the same value of j and the same value of energy eigen values reveals the concept of orientation quantization of angular momentum and leads to $(2\,j+1)$-fold orientation degeneracy for the given eigen value $\sqrt{j(j+1)}\,\hbar$ of the angular momentum operator. For a given value of , there are $(2\,j+1)$ linearly independent eigen vectors $|j, m_j >$ corresponding to $(2\,j+1)$ distinct values of m_j. Thus for the given value of j the angular momentum operator $\hat{J}^2$ may be represented by $(2\,j+1)$-dimensional squarematix with diagonal elements $j(j+1)\hbar^2$.In other words you may write

$$\hat{J}^2 = j(j+1)\hbar^2 \hat{I},$$
$$\text{and} \quad \hat{J}_z = m_j\hbar\,\hat{I}, \qquad (6.47)$$

where $\hat{I}$ is $(2\,j+1)$ – dimensional unit matrix.

Examples:

For $j = \frac{1}{2}$you may readily have

$$\hat{J}^2 = \frac{3}{4}\hbar^2\hat{I} \qquad (6.48)$$

and $\hat{J}_z = \frac{1}{2}\hbar\sigma_z$

where $\hat{I}$ *is* 2×2 *unit* matrix and$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ (6.49)

For,$j = 1$ you may readily write

$$\hat{J}^2 = 2\hbar^2\hat{I} \text{and} \hat{J}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\hbar \qquad (6.50)$$

where $\hat{I}$ is 3×3 unit matrix. It will also be shown in the next unit that the components of angular momentum operator $\hat{L}$ corresponding to orbital angular momentum vector **L** = **r** X **p** satisfy the commutation rule (6.45) and (6.46) and that the eigen values of operators $\hat{L}^2$ and $\hat{L}_z$ are given by $l(l+1)\hbar^2$ and $m_l\,\hbar$ respectively, where $m_l = -l, -l+1, \ldots, l$ showing $(2l+1)$-fold orientation degeneracy. The quantum number m_l, having$(2l+1)$ *possible values* for a given value of orbital quantum number$l$, is known as magnetic quantum number due to its role in describing the effect of a uniform magnetic field on a charged particle as shown in the following subsection.

6.7.2 Charged Particle in Uniform Magnetic Field

It may be shown that reduction in symmetry produced by the uniform magnetic field **B**results in removal of the orientation degeneracy with respect to m_l. A magnetic field may be written as

$\mathbf{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$,

where $\boldsymbol{A}$is a vector potential. For uniform magnetic field this relation gives

$\boldsymbol{A} = \frac{1}{2}\,\boldsymbol{B} \times \boldsymbol{r}$, since$\boldsymbol{\nabla} \times (\boldsymbol{a} \times \boldsymbol{b}) = \boldsymbol{a}(\boldsymbol{\nabla}.\boldsymbol{b}) - \boldsymbol{b}.(\boldsymbol{\nabla}.\boldsymbol{a}) + (\boldsymbol{b}\boldsymbol{\nabla})\mathbf{a} - (\mathbf{a}\boldsymbol{\nabla})\mathbf{b}$. This equation also gives $\nabla.\boldsymbol{A} = 0$, since $\boldsymbol{\nabla}.(\boldsymbol{a} \times \boldsymbol{b}) = \boldsymbol{b}.(\boldsymbol{\nabla} \times \boldsymbol{a}) - \boldsymbol{a}.(\boldsymbol{\nabla} \times \boldsymbol{b})$.

Classically the Hamiltonian of the particle of mass m and charge e is modified by magnetic field in to the following form

$H = \frac{(\boldsymbol{p}-e\boldsymbol{A})^2}{2m} + \mathrm{V}(\mathrm{r}) = \frac{p^2}{2m} + \mathrm{V}(\mathrm{r}) - \frac{e}{2m}\boldsymbol{p}.(\boldsymbol{B} \times \boldsymbol{r}) + \frac{e^2}{2m}\{\frac{1}{2}\,[\boldsymbol{B} \times \boldsymbol{r}]\}^2$which reduces to the following form on assuming that the magnetic field is sufficiently weak to ignore the last term in it:

$$H = \frac{p^2}{2m} - \boldsymbol{\mu}_l.\boldsymbol{B} + V(r) \qquad (6.51)$$

where$\boldsymbol{\mu}_l =$

$$\frac{e}{2m}(\boldsymbol{r} \times \boldsymbol{p}) = \frac{e\boldsymbol{L}}{2m} \qquad (6.52)$$

is the orbital magnetic dipole moment of the charge. When an electron of charge –e and mass m_e describes an orbit under the Coulomb law of attraction, its magnetic moment can be written classically as

$$\boldsymbol{\mu}_e = -\frac{e\boldsymbol{L}}{2m_e} \qquad (6.53)$$

Orienting the coordinate system such that the field $\boldsymbol{B}$is alongZ-direction, you may write the quantum mechanical Hamiltonian for electron corresponding to eqn.(6.51) as

$$\hat{H} = \hat{H}_{cf} + \frac{e}{2m_e}B\hat{L}_z \qquad (6.54)$$

where$\hat{H}_{cf} = \frac{\hat{p}^2}{2m_e} + V(r)$ which obviously satisfies the following commutation relations:

$$\left(\hat{L}^2, \hat{H}_{cf}\right) = 0 \text{and} \quad (\hat{L}_z, \hat{H}_{cf}) = 0 \qquad (6.55)$$

and hence $(\hat{H}, \hat{H}_{cf}) = 0$ showing that $\hat{H}$ and $\hat{H}_{cf}$ have simultaneous eigen functions with the corresponding energy eigen values of $\hat{H}$ given by

$$E_{nlm_l} = E_{nl} + \left(\frac{e}{2m_e}\right) m_l \hbar B = E_{nl} - \mu_l B \tag{6.56}$$

where E_{nl} are eigen values of $\hat{H}_{cf}$. This expression gives normal Zeeman shift. This naïve theory of Zeeman effect must be refined to take into account of the hyperfine experimental details. It needs a refinement in this theory by incorporating the fact that in addition to an orbital magnetic moment

$$\mu_l = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l, \tag{6.57}$$

incorporated in eqn.(6.56), the electron must carry a magnetic dipole generated by its intrinsic spin. In eqn. (6.57) μ_B is Bohr Magnetron given by

$$\mu_B = \frac{e\hbar}{2m_e} = 9.2032 \times 10^{-20} \frac{Joul}{Tesla} = 0.927 \times 10^{-20} ergs/gauss \tag{6.58}$$

The need of postulating the spin quantum number (and hence the spin angular momentum) became a compulsion in view of the results of Stern Gerlach experiment discussed in the following section.

6.7.3 Stern Gerlach Experiment

In this experiment a well collimated beam of silver atoms was passed through a slightly inhomogeneous magnetic field as shown with simple line diagram in fig. (6.1) where by measuring the deflection, through inspection of the trace left by the beam on the screen one can determine its motion.

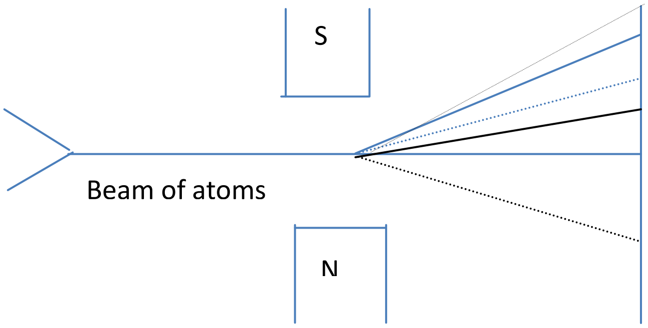

Fig. 6.1: Sketch of Stern Gerlach Experiment

The inhomogeneous magnetic field in the experiment produces the net force on the magnetic dipole associated with the atoms of the beam and provides a direction of spatial quantization (orientation quantization) (say z-direction). The atoms are deflected by this force which is classically given as

$\boldsymbol{F} = \boldsymbol{\nabla}(\boldsymbol{\mu}.\boldsymbol{B})$ or $F_z = \mu_z \frac{\partial B_z}{\partial z}$ where μ_z is the component of the atom's dipole moment along Z-axis. A magnetic moment arises due to orbital motion of electron about the nucleus of the atom. Let this moment be due to the single outer electron of each silver atom. Then from eqn.(6.57) we get

$$\mu_z = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l \quad (6.57a)$$

whereyou have $(2l + 1)$ allowed values for a given l which is always an integer and hence the number of

sub-states, $(2l + 1)$, is always odd. Thus one must expect the atomic beam in Stern-Gerlach experiment to give an odd number of traces on the screen as shown due to dotted lines in fig. 6.1. In the actual experiment only two traces were found as shown due to continuous lines in the figure. Thus the dipole moments of the silver atoms could have not been produced only by the orbital angular momentum. The exciting implications of this experiment could not be understood immediately and several efforts were made to interpret the results of this experiment in terms of equations (6.52) and (6.57).

The correct interpretation of Stern-Gerlach observations and several fine structure spectroscopic measurements of emission spectra of atoms was given by the hypothesis of Uhlenbeck and Goudsmit in 1925 that in addition to an orbital angular momentum, the electron possessed an intrinsic spin (an intrinsic angular momentum) characterized by quantum numbers $s \; and \; m_s$ which are analogue of $l \; and \; m_l$ associated with orbital angular momentum operator. To explain two projections in Stern-Gerlach experiment, Uhlenbeck and Goudsmit restricted these quantum numbers to $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. Accordingly, each electron has an intrinsic angular momentum of magnitude $\frac{1}{2}\hbar$(i.e. spin $\frac{1}{2}$) with which is associated the following magnetic moment analogues to that given by eqn.(6.53) for orbital angular momentum):

$$\boldsymbol{\mu_s} = -g_s \frac{e}{2m_e} \boldsymbol{S} \quad (6.58)$$

where g_s is adjustable constant. The theory based on hypothesis of Uhlenbec and Goudsmit is in excellent agreement with experiment if you take $g_s = 2$ and then write

$$\boldsymbol{\mu_s} = -\frac{e}{m_e} \boldsymbol{S} \quad (6.58a)$$

Experiments show that the nucleons (proton and neutron) also have spin- $\frac{1}{2}$. It should be reemphasized that spin is a quantum number and it has no classical analogue. It is absurd to visualize the electron as a sphere rotating about its axis.

6.8SPIN ANGULAR MOMENTUM OPERATOR

Orbital angular momentum operator arising due to orbital motion in classical mechanics has only integral values of its quantum number . Thus eqns. (6.48) for quantum number $j = \frac{1}{2}$ give the angular momentum operators corresponding to intrinsic angular momentum or spin-$\frac{1}{2}$. In general case the components of spin angular momentum operator $\hat{S}$ also satisfy the similar commutations rules as given by eqn. (6.45) i.e.

$$[\hat{S}_j, \hat{S}_k] = i\hbar\varepsilon_{jkl}\hat{S}_l \tag{6.59}$$

or$\hat{S} \times \hat{S} = i\hbar\hat{S}$ (6.59a)

Defining the squareof spin angular momentum operator as

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \tag{6.60}$$

you may readily prove that

$$[\hat{S}^2, \hat{S}] = 0 \tag{6.61}$$

which implies that $[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y]$=$[\hat{S}^2, \hat{S}_z] = 0$ (6.61a)

In view of eqns. (6.47) the eigen values of operators$\hat{S}^2$ *and* $\hat{S}_z$ may be written as

$$\hat{S}^2 = s(s+1)\,\hbar^2\hat{I}\text{and}\hat{S}_z = m_s\hbar\hat{I} \tag{6.62}$$

where s is integer (including zero) or half integer giving the spin of the corresponding particle:

s= 0, ½, 1, 3/2,……… and $-s \leq m_s \leq s$ i.e. $m_s = -s, -s+1, \dots\dots\dots s-1, s$ (6.63)

Thus m_s have distinct (2s+1) values for a given value of spin s. The particles with integral spins are bosons and those with half odd integral spins are fermions. Thus the eigen states of the particles with integral spins are always symmetrical under permutations of these identical particles and consequently these particles obey Bose-Einstein statistics. On the other hand the eigen states of the particles with half odd integral spins are always antisymmetric under permutation of such identical particles and hence these particles follow Fermi -Dirac statistics. For spin-$\frac{1}{2}$ case you can rewrite eqns. (6.48) as follows:

$$\hat{S}^2 = \frac{3}{4}\hbar^2\hat{I}\text{and}\hat{S}_z = \frac{1}{2}\hbar\sigma_z \tag{6.63}$$

where $\hat{I}$ *is* 2×2 *unit* matrix and $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. (6.63a)

Matrices $\hat{S}^2$ and $\hat{S}_z$ are obviously matrices of order 2X2 each. Eigen value of matrix $\hat{S}^2$ is $\frac{3}{4}\hbar^2$ (repeated twice) and the eigen values of matix$\hat{S}_z$are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ which corresponds to two spin- states. The eigen values of matrix σ_z are obviously +1 and -1. You may directly prove that the square of matrix σ_z is unit matrix i.e.

$\sigma_z{}^2 = \hat{I}$ (6.64)

Using relations (6.63), (6.63a) and (6.64) you may readily prove that the eigen values of operators $\hat{S}_x$ and $\hat{S}_y$ are also $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.You may also represent these operators by 2X2 matrices in the similar manner as operator $\hat{S}_z$ has been written in eqn. (6.63a) i.e.

$$\hat{S}_x = \frac{1}{2}\hbar\sigma_x$$

and$\hat{S}_y = \frac{1}{2}\hbar\sigma_y$ (6.65) with eigen values of each of matrices σ_x and $\sigma_y$as +1 and -1 and square of each of them as unit matrix

$\sigma_x{}^2 = \hat{I}$and$\sigma_y{}^2 = \hat{I}$ (6.64a)

For the case of spin-1, the matrices representing intrinsic angular momentum operator may be written as follows from eqns (6.50):

$$\hat{S}^2 = 2\hbar^2\hat{I} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}\hbar^2 \text{and} \hat{S}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\hbar$$

Using these results in the following equation

$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,$

you may readily obtain following matrices for the operators $\hat{S}_y$ and $\hat{S}_z$

$$\hat{S}_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\hbar$$

and

$$\hat{S}_y = \frac{i}{\sqrt{2}}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}\hbar$$

Using these properties of spin angular momentum operators in the following section, you will study the theory of spin of electrons but it may be generalized to higher intrinsic spin values.

6.9 PAULI THEORY OF ELECTRON SPIN (PAULI SPIN MATRICES)

Using Uhlenbec and Goudsmit hypothesis, Pauli developed the theory to give mathematical formulation to spin -1/2 of electrons. In a simple version of his formulation you may combine eqns. (6.63) and (6.65) to write the spin operator for electron in the following matrix representation

$$\hat{S}= \frac{1}{2}\hbar\boldsymbol{\sigma} \tag{6.65a}$$

where the components of the vector operator $\boldsymbol{\sigma}$ are operators $\sigma_x, \sigma_y$and $\sigma_z$satisfying eqns. (6.64) and (6.64a) where the matrix representation of $\sigma_z$is given in eqn.(6.63a). The matrices representing σ_y and $\sigma_z$will also be of order 2X2 each with eigen values +1 and -1 as shown previous section. Using relations (6.59) and (6.65a), you may readily prove the following commutation relation for these matrices:

$$[\sigma_j, \sigma_k] = 2i\varepsilon_{jkl}\sigma_l, j, k, l = 1,2,3 \tag{6.66}$$

which may be elaborated in the following form

$$\sigma_x\sigma_y - \sigma_y\sigma_x = 2i\ \sigma_z; \sigma_y\sigma_z - \sigma_z\sigma_y = 2i\ \sigma_x;\ \sigma_z\sigma_x - \sigma_x\sigma_z = 2i\ \sigma_y \tag{6.66a}$$

Now you may write

$$2i(\sigma_x\sigma_y + \sigma_y\sigma_x) = (2i\sigma_x)\ \sigma_y + \sigma_y(2i\sigma_x) = 0,$$

whereyou have used second of eqns. (6.66a). Similar relations you may get by using other relations of eqns.(6.66a).Thus you have following anti-commutation relations for matrices σ_x, σ_y and σ_z:

$$\sigma_x\sigma_y + \sigma_y\sigma_x = 0\ \ ;\ \ \sigma_y\sigma_z + \sigma_z\sigma_y = 0;\ \sigma_z\sigma_x + \sigma_x\sigma_z = 0 \tag{6.67}$$

Combining these relations with relations (6.62) and (6.64), you may readily write the following general anti-commutation rules for these matrices

$$\{\sigma_j, \sigma_k\} = \sigma_j\sigma_k + \sigma_k\sigma_j = 2\ \delta_{jk} \tag{6.67a}$$

Combining this anti-commutation relation with the commutation relation (6.66), you may readily get

$$\sigma_j\sigma_k = \delta_{jk} + i\varepsilon_{jkl}\sigma_l \tag{6.68}$$

which give $\sigma_x\sigma_y = i\sigma_z; \sigma_y\sigma_z = i\sigma_x; \sigma_z\sigma_x = i\sigma_y$ (6.69)

Using these relations and relations (6.62) and (6.64), you may readily get

$$\sigma_x\sigma_y\sigma_z = \sigma_y\sigma_z\sigma_x = \sigma_z\sigma_x\sigma_y = i\hat{I} \tag{6.70}$$

Using these relations (6.66)- (6.70) and the matrix of eqn. (6.63a) for σ_z, the following matrices may readily be obtained forσ_x *and* σ_y :

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \text{ along with } \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (6.71)$$

These matrices are called Pauli matrices. They satisfy all the properties given by eqns. (6.66)-(6.70) and square of all of these individual matricesis unityas shown in eqns.(6.64) and (6.64a). Moreover, trace of each of these matrices is zero and determinant of each of them is -1 i.e

$$tr\,\sigma_j = 0, \quad (j = x, y, z\,) \qquad (6.72)$$

$$\det \sigma_j = -1\,, (j = x, y, z\,) \qquad (6.73).$$

You may also have the matrix representing operator $\boldsymbol{\sigma}$of eqn. (6.65a) satisfying the following property

$$\boldsymbol{\sigma}^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3\hat{I} \qquad (6.74)$$

From this relation you get

$$[\boldsymbol{\sigma}^2, \sigma_x] = [\sigma_x^2, \sigma_x] + \left[\sigma_y^2, \sigma_x\right] + [\sigma_z^2, \sigma_x] \qquad (6.75)$$

where$[\sigma_x^2, \sigma_x] = \sigma_x^3 - \sigma_x^3 = 0$;

$\left[\sigma_y^2, \sigma_x\right] = \sigma_y[\sigma_y, \sigma_x] + [\sigma_y, \sigma_x]\,\sigma_y = \sigma_y(-2i\sigma_z) + (-2i\sigma_z)\sigma_y = 0$where second of relations (6.66a) has been used. Similarly, you may get

$[\sigma_z^2, \sigma_x] = 0$.

Using these relations in eqn.(6.75) you may readily get

$$[\boldsymbol{\sigma}^2, \sigma_x] = 0$$

and similarly, $\left[\boldsymbol{\sigma}^2, \sigma_y\right] = [\boldsymbol{\sigma}^2, \sigma_z] = 0$

This commutation of $\boldsymbol{\sigma}^2$ with its component matrices readily follows from eqns.(6.61), (6.61a) and (6.63) also. These Pauli matrices given by eqns. (6.71) are widely used to describe the spin of electron, hypothesized by Uhlenbec and Goudsmit, without exploring the origin of spin-1/2 (intrinsic angular momenta) in electrons. This spin-1/2 of electron was automatically incorporated later in the solution of Dirac's relativistic quantum equation.

6.10 EIGEN STATES (SPINORS) OF SPIN OPERATORS

On using eqns. (6.63) and (6.63a), you may readily write the spin operators in the following matrix form

$\hat{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}and\hat{S}_z = \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ (6.76)

It can be readily shown that these matrices commute with each other. This commutation also follows from eqns. (6.61a). Consequently these spin operatorshave simultaneous eigen vectors. Both these operators have been represented by 2X2 diagonal Hermitian matrices in eqns. (6.76) and hence elements along the principal diagonals in these matrices give the eigen values of these operators respectively. Both the eigen values of operator $\hat{S}^2$are identical, each equal to $\frac{3}{4}\hbar^2$ and the eigen values of operator $\hat{S}_z$are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ respectively. The simultaneous eigen states of these matrices are two component eigen vectors which constitute an eigen basis which spans the space (spin space) in which these operators are represented by matrices given in eqns. (6.76). These two- component columneigen vectors in spin space are called spinors (i.e. spin vectors). You may write any such column vector as

$$\chi = \begin{pmatrix}u\\ v\end{pmatrix}$$

Then you have $\hat{S}_z\chi = \pm\frac{1}{2}\hbar\chi$where upper sign gives $v = 0$ and the lower sign gives $u = 0$.Thus the normalized eigen vectors corresponding to these eigen values of the spin operator$\hat{S}_z$ may be written as follows

$\chi_+ = \begin{pmatrix}1\\ 0\end{pmatrix}and\chi_- = \begin{pmatrix}0\\ 1\end{pmatrix}$ (6.77)

which are eigen vectors (spinors) for spin-up and spin-down states (pure states):

| ↑>spin-up state ; and | ↓> spin-down state respectively. Thus you may write

$|m_s>_+ = |+\frac{1}{2}> = \begin{pmatrix}1\\ 0\end{pmatrix} = |\uparrow>$ (spin-up state);

and $|m_s>_- = |-\frac{1}{2}> = \begin{pmatrix}0\\ 1\end{pmatrix} = |\downarrow>$ (spin-down state) (6.78)

Using eqns (6.65a) and (6.71) in this basis, you may readily write all the components of the spin operator as

$\hat{S}_x = \begin{pmatrix}0 & \frac{\hbar}{2}\\ \frac{\hbar}{2} & 0\end{pmatrix}$; $\hat{S}_y = \begin{pmatrix}0 & \frac{-i\hbar}{2}\\ \frac{i\hbar}{2} & 0\end{pmatrix}$; $\hat{S}_x = \begin{pmatrix}\frac{\hbar}{2} & 0\\ 0 & -\frac{\hbar}{2}\end{pmatrix}$ (6.79)

Using these relations you may readily verify the relation

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix}$$

which follows from eqn. (6.76) also. Both eigen values of this matrix for operator $\hat{S}^2$ are equal and hence the corresponding eigen vectors given by eqns. (6.77) are degenerate eigen states of this operator. It is obvious from equation (6.79) that eigen values of operators $\hat{S}_x$ and $\hat{S}_y$ are also $+\frac{\hbar}{2}$and $-\frac{\hbar}{2}$. The normalized eigen vectors of operator $\hat{S}_x$ corresponding to theseeigenvalues may readily be obtained as

$$\chi_{1+} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \text{and} \chi_{1-} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \qquad (6.80)$$

Similarly, you may obtain the eigenvectors of the operator $\hat{S}_y$ in the following form

$$\chi_{2+} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix} \text{and} \chi_{2-} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix} \qquad (6.81)$$

Since eigen vectors χ_+ and χ_- of spin operator $\hat{S}_z$, as given by eqns.(6.77), constitute the eigen basis of spin-space, any two- component state -vector in this space may be written as linear combination of these eigen vectors. For instance, you may readily write

$$\chi_{1+} = \frac{1}{\sqrt{2}}\chi_+ + \frac{1}{\sqrt{2}}\chi_- ;\chi_{1-} = \frac{1}{\sqrt{2}}\chi_+ - \frac{1}{\sqrt{2}}\chi_- \qquad (6.82)$$

$$\text{and}\chi_{2+} = \frac{1}{\sqrt{2}}\chi_+ + \frac{i}{\sqrt{2}}\chi_- ;\chi_{2-} = \frac{1}{\sqrt{2}}\chi_+ - \frac{i}{\sqrt{2}}\chi_- \qquad (6.83)$$

In general any spin eigen vector $\alpha = \begin{pmatrix}\alpha_+\\\alpha_-\end{pmatrix}$ may be written in terms of these spin-up and spin-down spinors as

$$\alpha = \alpha_+\chi_+ + \alpha_-\chi_- = \alpha_+|\uparrow> + \alpha_-|\downarrow> \qquad (6.84)$$

In an assembly of spin-1/2 particles, some of particles are spin-up and others are spin-down and then the spinor is the linear combination of $\chi_+$and χ_-. Furthermore, 2x2 unit matrix $\hat{I}$, and Pauli matrices $\sigma_x, \sigma_y$and $\sigma_z$are linearly independent and constitute the complete set in spin-space and hence any 2x2 matrix $\hat{A}$can be written as their linear combination:

$$\hat{A} = a_0\hat{I} + a_1\sigma_x + a_2\sigma_y + a_3\sigma_z \qquad (6.85)$$

Spin of a particle is a degree of freedom additional to the spatial degree of freedom. It is independent of the spatial degrees of freedom and hence you can simultaneously specify the exactly the spin state and the spatial state of a particle. In other words, all operators referring to the spatial degrees of freedom commute with those referring the spin degrees of freedom;

$[\hat{S},\hat{r}] = 0;\ [\hat{S},\hat{p}] = 0;\ [\hat{S},\hat{L}] = 0$etc (6.86)

where$\hat{p}$ is the linear momentum operator and $\hat{L}$is the orbital angular momentum operator which will be discussed in details in the next unit. For the particle of spin-1/2, the totaleigen state can be completely specified as the dot product of the spatial eigen state and the spin eigen state:

$|total> = |space> \otimes |spin>$ (6.87)

If we choose Z-axis as spin orientation direction, then the total eigen state of electron is determined by giving, for all $\hat{r}$,both $\Psi_\uparrow(\hat{r})$ and $\Psi_\downarrow(\hat{r})$ which are amplitudes for finding the particle at $\hat{r}$ with its spin- up and spin- down respectively.

Thus in general, the true wave function of the system of identical particles can be written as the product of spatial function $\Phi\ (r_1, r_{2,} \ldots\ldots r_N)$ (a solution of Schrodinger equation (6.3)) and the function χ depending on spin variables:

$\Psi(q_1, q_2, \ldots\ldots q_N) = \Phi\ (r_1, r_{2,} \ldots\ldots r_N)\ \chi(s_1, s_2, \ldots\ldots s_N)$ (6.88)

For this type of wave function the symmetry requirement under permuatation refer to the complete wave function since a permutation of particles corresponds to both, the space and the spin variables. Thus the necessary symmetry of wave function (symmetric for bosons and anti-symmetric for fermions) can be ensured for several combinations of Φ and χ which may have different symmetries under permutations of the appropriate coordinates.

EXAMPLES

Ex.6.6: Prove the followingidentity for any two vectors**A**and **B**
$(\boldsymbol{\sigma}.\boldsymbol{A})\ (\boldsymbol{\sigma}.\boldsymbol{B}) = (\boldsymbol{A}.\boldsymbol{B}) + i\boldsymbol{\sigma}.(\boldsymbol{A}\times\boldsymbol{B})$ (6.89)

Solution.LHS =$(\boldsymbol{\sigma}.\boldsymbol{A})\ (\boldsymbol{\sigma}.\boldsymbol{B}) = (\sigma_x A_x + \sigma_y A_y + \sigma_z A_z)\ (\sigma_x B_x + \sigma_y B_y + \sigma_z B_z)$

$$= \sigma_x^2 A_x B_x + \sigma_y^2 A_y B_y + \sigma_z^2 A_z B_z + \sigma_x\sigma_y A_x B_y + \sigma_y\sigma_x A_y B_x$$

$$+\sigma_y\sigma_z A_y B_z + \sigma_z\sigma_y A_z B_y + \sigma_x\sigma_z A_x B_z + \sigma_z\sigma_x A_z B_x$$

Using the following properties of Pauli matrices in this equation

$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \hat{I}and\sigma_y\sigma_z = -\sigma_z\sigma_y = i\sigma_x$etc,

you may readily get

LHS= $A_x B_x + A_y B_y + A_z B_z + i\sigma_x(A_y B_z - A_z B_y) + i\sigma_y(A_z B_x - A_x B_z) + i\sigma_z(A_x B_y - A_y B_x)$

$= (\boldsymbol{A}.\boldsymbol{B}) + i\boldsymbol{\sigma}.(\boldsymbol{A}\times\boldsymbol{B})$ = RHS

Ex. 6.7: Show that the shift operators

$\sigma_+ = \sigma_x + i\,\sigma_y$and= $\sigma_- = \sigma_x - i\,\sigma_y$

cannot be diagonalized. What happens when these operators are applied on spinorsχ_+ and χ_- ?

Solution: Using Pauli matrices of eqns.(6.71) you may readily get

$$\sigma_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \text{and} \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \qquad (6.90)$$

which are not Hermitian since ${\sigma_+}^\dagger = \sigma_-$ and ${\sigma_-}^\dagger = \sigma_+$

Matrices of eqns. (6.90) cannot be made diagonal with any choice of diagonalizing matrix. If matrices given by eqns.(6,90) are applied on spinor χ_+ you will get

$\sigma_+\chi_+ = 0$and$\sigma_-\chi_+ = 2\chi_-$

Similarly, on applying these matrices on the spinor χ_- you will get

$\sigma_+\chi_- = 2\chi_+$and$\sigma_-\chi_- = 0$

showing that operator σ_+ raises the spin- down to spin-up and the operator σ_- lowers the spin-up to spin-sown. Thus these operators are called raising and lowering operators respectively in the spin-space.

Ex. 6.8 Show that the operators

$$\hat{P}_+ = \frac{1}{2}\,(\hat{I} + \sigma_z)\text{and}\hat{P}_- = \frac{1}{2}\,(\hat{I} - \sigma_z) \qquad (6.91)$$

are idempotent operators and they suppress either the spinor χ_+ or χ_- in a state of mixed spin orientation where $\hat{I}$ is 2x2 unit matrix.

Solution: Substituting relation (6.63a) in to given operators, you may write

$\hat{P}_+ = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}and\hat{P}_- = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$ which obviously satisfy the following conditions

${\hat{P}_+}^2 = \hat{P}_+and{\hat{P}_-}^2 = \hat{P}_-$

Which show that these given operators are idempotent operators. When applied to Hilbert vectors (spinors)$\chi_+$and χ_- these operators give

$\hat{P}_+\chi_+ = \chi_+$; $\hat{P}_+\chi_- = 0$

and$\hat{P}_-\chi_+ = 0$; $\hat{P}_-\chi_- = \chi_-$ (6.92)

Thus when applied on a state of mixed spin orientation in the state $a\chi_+ + b\chi_-$, these operators give

$\hat{P}_+(a\chi_+ + b\chi_-) = a\chi_+and\hat{P}_-\ (a\chi_+ + b\chi_-) = b\chi_-$

Showing that these operators suppress the spinors χ_-an$d\ \chi_+$ respectively leaving the projection of the state vector upon one of the basic directions in Hilbert space. Consequently, these operators may also be called projection operators.

SELF ASSESMENT QUESTIONS (SAQ)

Q.7 Find thenormalized eigen vectors of the operator $\boldsymbol{\sigma}.\hat{\boldsymbol{n}}$**,** where $\hat{\boldsymbol{n}}$is unit vectorin an arbitrary direction in space.

Q.8 Show that the only matrix which commutes with Pauli matrices is a scalar matrix (scaler multiple of unit matrix).

Q.9 Show that Pauli matrices are all traceless, square of each of them is unity and all of them are mutually anti-commuting.

6.11 SUMMARY

In this unit you have learnt the fundamental indistinguishability of identical particles and its main consequences and you have seen thatthewave functions of Identical Particles are either totally symmetrical or totally antisymmetric depending on whether the identical particles are bosons or fermions respectively. You have also seen that the identical particles with symmetric states (bosons) follow Bose-Einstein Statisticswhile those with anti-symmetric states (fermions) follow Fermi-Dirac Statistics. You have also seen that the distinguishable particles follow classical Maxwell Boltzmann Statistics. You have proved the Pauli's exclusion principle for the system of fermion and studied its consequences. You have learnt in details that the elementary particles have intrinsic angular momenta (spins) besides their spatial (orbital) angular momenta. You have constructed the spin angular momentum operators for all the types of identical elementary particles,obtained their eigen values and eigen states, and learnt that the eigen states of the particles with integral spins are all symmetrical and those of half odd integral spins are all anti-symmetric under the permutations of particles. You have learnt the Stern- Gerlach experiment and the interpretations of its results in terms of the hypothesis of Uhlenbec and Goudsmit incorporating the spin-1/2 of electron. You have also learnt the Pauli theory of electron spin in terms of Pauli matrices and represented Spin operatorsinterms of these matrices. Undertaking the study of spin-space you have obtained the eigen states of spin operators for electron in terms of Hilbert eigen states (spinors) in this spin-space. You have also obtained the whole algebra of Pauli matrices and the resulting spin quantum numbers and finally developed the total eigen state of an elementary particle as the product of its spatial state and spin- state and then described the symmetries of the resulting states of identical particles of different types (fermions and bosons). Eight examples of solved innovative problems have been learnt and nine self- assessment questions (SAQ) , based on different topics discussed in this unit, have been solved.

6.12GLOSSARY (KEY WORDS);

Identical Particles; Symmetric eigen state; anti-symmetric wave function; distinguishability; bosons; fermions; intrinsic angular momentum, spin; spinor; Pauli matrices; Stern-Gerlac experiment; spin angular momentum; Pauli exclusion principle; spin-operators; Bose- Einstein statistics; Fermi-Dirac statistics. Maxwell- Boltzmann statistics; exchange operators; permutations.

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TERMINAL QUESTIONS

(A) Short Answer Type:

Q,1 What are the values of $[\sigma^2, \sigma_x]$; $[\sigma^2, \sigma_y]$; and $[\sigma^2, \sigma_z]$, where σ_x, σ_y and σ_z are Pauli matrices?.

Q.2 What is the value of $[\sigma_x, \sigma_y]$, where $\sigma_x and \sigma_y$are first two Pauli matrices?.

Q.3 What is the value of $\sigma_x\sigma_y + \sigma_y\sigma_x$, where $\sigma_x and \sigma_y$are first two Pauli matrices?.

Q.4 What is the value of $[\hat{P}_{ij}, \hat{H}]$, where $\hat{P}_{ij}$ is the exchange operator for the system of identical particles and $\hat{H}$ is the Hamiltonian operator of the system?.

Q.5 If $\alpha \; and \; \beta$ are single particle spin states of spin-1/2 identical particles, write the three symmetric spin states corresponding to three projections (1, 0,-1 of the total spin S=1 of these particles.

Q.6 In the previous problem, write the antisymmetric state corresponding to total spin zero.

Q.7 For a system of two identical particles each of spin-I, find the ratio of number of symmetricand anti- symmetric spin states.

Q.8 Show that $\{\sigma_j, \sigma_k\} = 2\delta_{ij}$, where $\sigma_j$and σ_k are Pauli matrices

Q.9 Show that $\boldsymbol{\sigma}^2 = 3$

Q.10 Prove that Pauli matrices are unitary

(B) Long Answer Type:

Q.1 Prove that $\sigma_j\sigma_k = \delta_{jk} + i\,\varepsilon_{jkl}\sigma_l$ where σ_j, σ_k and $\sigma_l$are Pauli matrices and other symbols have their usual meaning.

Q.2 Show that three Pauli matrices together with 2X2 unit matrix form the complete basis of an algebra.

Q.3 Show that the operator $(\boldsymbol{\sigma_1}\,.\,\boldsymbol{\sigma_2})^n$ for two particles, each of spin-1/2, can be linearly expressed in terms of $\boldsymbol{\sigma_1}\,.\,\boldsymbol{\sigma_2}$

Q.4Show that $\boldsymbol{\sigma} \times \boldsymbol{\sigma} = 2i\boldsymbol{\sigma}$

Q.5 Show that
(a) $(\sigma_3, \sigma_+) = 2\sigma_+$
(b) $(\sigma_3, \sigma_-) = -2\sigma_-$,
where $\sigma_\pm = \sigma_x \pm i\sigma_y$

Q.6 Show that $(\sigma_+, \sigma_-) = 4\sigma_z$

Q.7 Two identical non-interacting particles are in an isotropic harmonic oscillator potential. Show that the degeneracies of tree lowest energy levels are 1,12,39 if the particles have spin-1/2
Q.8 Consider two non-interacting particles in a one-dimensional potential oscillator potential $V = \frac{1}{2}\,kx^2$ and in the same spin states and find the eigen functions if the particles are
(a) distinguishable
(b) identical bosons
(c) identical fermions

Q.9 For the angular momentum operator $\hat{J}$,prove the identity

$[\hat{J}_x^2, \hat{J}_y^2] = [\hat{J}_y^2, \hat{J}_z^2] = [\hat{J}_z^2, \hat{J}_x^2]$and show that all these commutators are zero in states for j=0, ½, or 1

Q.10 (a) Define particle exchange operator and prove that its eigen values are ± 1.
(b) Obtain the spin wave functions of the system of two electrons and classify them according to their symmetries. Show that these wave functions are the eigen functions of the operators $\hat{S}^2$and $\hat{S}_z$.

(C) Numerical Type

Q.1 A particle with spin-1/2 is in a state with a definite value $s_z = 1/2$. Show that the probabilities of possible values of components of spin along an axis-z' at an angle θ to the z-axis are $\omega_+ = cos^2\frac{\theta}{2}$ and $\omega_- = sin^2\frac{\theta}{2}$, where $\omega_\pm$are probabilities of $s_z = \pm\frac{1}{2}$ respectively.

Q.2 From the first principle determine the eigen states of total spin angular momentum obtained by adding the spin angular momenta of two spin-1/2 particles.

Q.3 Construct the eigen functions of $\hat{S}^2$ and $\hat{S}_z$ for a system of three particles of spin-1/2 each.

Q.4 Show that the wave function of a j=1 state formed from two spin less particles in p-state is anti-symmetric in the coordinates of the two particles.

Q 5. Show that every unitary 2x2 matrix with determinant +1 has the form cos$\theta + i\boldsymbol{\sigma}.\hat{n}$ where θ and the components of unit vector $\hat{n}$ are suitably chosen parameters.

Q.6for a system of spin -1/2, find the eigen values and eigen vectors of the operator $\hat{S}_x + \hat{S}_y$. When the system is found to be in the state corresponding to the larger eigen value of this operator, find the probability that the measurement of $\hat{S}_z$yields$\frac{\hbar}{2}$.

Q.7 Determine the number of energy levels with different values of total spin S, for a system of N identical particles with spin-1/2.

Q.8 For Pauli spin matrices, prove that (a) $\exp\left(i\hat{n}.\boldsymbol{\sigma}\frac{\emptyset}{2}\right) = \cos\frac{\emptyset}{2} + i\hat{n}.\boldsymbol{\sigma}\, sin\frac{\emptyset}{\mathbf{2}}(b)(\boldsymbol{\sigma_1}.\boldsymbol{\sigma_2})^2 + 2(\boldsymbol{\sigma_1}.\boldsymbol{\sigma_2}) = 3$

Q.9 Write four linearly independent spin states for a pair of electrons and then construct the four normalized eigen functions for the operators $((\widehat{S}_1 + \hat{S}_z)^2$ and $\hat{S}_{1z} + \hat{S}_{2z}$

Q. 10 In the $\hat{S}_z$-eigen basis, find the eigen vectors of particle whose spin projections are precisely $\pm\frac{1}{2}\hbar$ along the x-axis. If the is in a quantum state in which its projection is precisely $\frac{1}{2}\hbar$ along x-axis, find the probability of finding it with its projection $\frac{1}{2}\hbar$ along z-axis.

ANSWERS

Self-Assessment Questions:

Q.4: $(N_1!\ N_2! \dots \dots . N_{n!}.)/\sqrt{N!}$

Q.6: $\chi_{\pm}^{(n)} = \frac{1}{\sqrt{2(1\pm n_z}} \{(1 \pm n_z)\chi_+ \pm (n_x + in_y)\chi_-\}$

Terminal Questions

(A) Short Answer Type:

Q.1 All zero; Q.2 $2i\sigma_z$; Q.3 Zero; Q.4 Zero; Q.5 $\alpha(1)\alpha(2)$; $\beta(1)\beta(2)$; $\alpha(1)\beta(2) + \alpha(2)\beta(1)$ Q.6$\alpha(1)\beta(2) - \alpha(2)\beta(1)$ Q.7 $\frac{I+1}{I}$

(B) Long Answer Type

Q.10$\chi_+(1)\,\chi_+(2)$; $\chi_-(1)\,\chi_-(2)$; $\{\chi_+(1)\chi_-(2) + \{\chi_+(2)\chi_-(1)\}$(symmetric) and $\{\chi_+(1)\chi_-(2) - \{\chi_+(2)\chi_-(1)\}$ (anti-symmetric)

(C) Numerical Type

Q.2 Triplet states: | ↑↑> ; $\frac{1}{\sqrt{2}}$[| ↑↓> +|↓↑>]; | ↓↓> and singlet state: $\frac{1}{\sqrt{2}}$[| ↑↓> −|↓↑>]

Q.3

$|s=\frac{3}{2},m_s=\frac{3}{2}>=\chi_+(1)\chi_+(2)\chi_+(3)=|\frac{3}{2},\frac{3}{2}>$: $|\frac{3}{2},\frac{1}{2}>=\frac{1}{\sqrt{3}}[\chi_+(1)\chi_+(2)\chi_-(3)+\chi_+(1)\chi_-(2)\chi_+(3)+\chi_-(1)\chi_+(2)\chi_+(3)]$

$|\frac{3}{2},\frac{-1}{2}>=\frac{1}{\sqrt{3}}[\chi_-(1)\chi_-(2)\chi_+(3)+\chi_-(1)\chi_+(2)\chi_-(3)+\chi_+(1)\chi_-(2)\chi_-(3)]$ $|\frac{3}{2},-\frac{3}{2}>=\chi_-(1)\chi_-(2)\chi_-(3)$ For double eigen value s=1/2: symmetric doublets

$|\frac{1}{2},\frac{1}{2}>_1=\frac{1}{\sqrt{6}}[\chi_+(1)\{\chi_+(2)\chi_-(3)+\chi_-(2)\chi_+(3)\}-2\chi_-(1)\chi_+(2)\chi_+(3)]|\frac{1}{2},-\frac{1}{2}>_1=\frac{1}{\sqrt{6}}[\chi_-(1)\{\chi_+(2)\chi_-(3)+\chi_-(2)\chi_+(3)\}-2\chi_+(1)\chi_-(2)\chi_-(3)]$ and anti-symmetric doublets

$|\frac{1}{2},\frac{1}{2}>_2=\frac{1}{\sqrt{2}}\chi_+(1)[\chi_+(2)\chi_-(3)-\chi_-(2)\chi_+(3)]|\frac{1}{2},-\frac{1}{2}>_2=\frac{1}{\sqrt{2}}\chi_-(1)[\chi_-(2)\chi_+(3)-\chi_+(2)\chi_-(3)]$

Q.7 For a given value of S : n(S)=$\frac{N!(2S=1)}{\left(\frac{1}{2}N+S+1\right)!\left(\frac{N}{2}-S\right)!}$

Total number of different energy level

$n=\sum_S n(S)=\frac{N!}{(\frac{N}{2}!)^2}$for even N

and $n=\frac{N!}{\left(\frac{N}{2}+\frac{1}{2}\right)!\left(\frac{N}{2}-\frac{1}{2}\right)!}$ for N odd

UNIT-7: ORBITAL ANGULAR MOMENTUM

Structure:

7.1 INTRODUCTION

The simplicity which the physicist have to expect of Nature, has been sought almost exclusively in terms of symmetries rather than detailed dynamics. Based on this idea of symmetry man, since his awakening, had tried to comprehend order, beauty and perfection in most diversified phenomena of Nature. By making the use of symmetric properties of a physical system one can make certain predictions more conveniently than by going through the detailed calculations. Under the set of symmetric transformations, the Lagrangian and the resulting dynamical equations of the physical system remain unaltered. Some symmetries, like spatial and temporal translations and spatial and temporal rotations are the exact symmetries (any violation of which has never been observed) while other symmetries, like space-reflections are only approximate (which is followed by some physical systems and violated by others).All these symmetries are space-time dependent and hence they are called the external symmetries. Beside these space-time dependent symmetries, physical systems follow some internal symmetries which do not depend on external spatial-temporal degrees of freedom but these symmetries depend on internal degrees of freedom (like spin, charge, isospin, strangeness, baryon number and charm etc,) Other striking fact of nature, besides the symmetry properties, is that besides many properties of physical system that continuously change with time, the few properties remain invariant. These constant properties appear in so many different physical systems that these properties are among the most fundamental laws of physics, known as conservation laws. Some of these laws, like conservation of energy, conservation of linear momentum and the conservation of angular momentum, are exact conservation laws while some others, like conservation of parity, are only approximate. The connectionsbetween symmetries and conservation laws of physical system, the apparently unrelated properties, was first established in classical mechanics by Jacobi when he showed that the invariance of the Lagrangian of a Physical system under spatial translations implies the conservation of its linear momentum and its invariance under the spatial rotations (rotations about a spatial coordinate-axis) implies the conservation of its angular momentum(rather, orbital angular momentum). A little later Schutz derived the conservation of energy from the invariance of Lagrangian under time translations. Then Herglotz gave a complete discussion of ten constants of motionassociated withthe invariance of Lagrangian (i.e. invariance of the physical system) under the group of Inhomogeneous Lorentz Transformations (Poincare group) consisting of time translation, three spatial translations, three spatial rotations and three pure Lorentz transformations (space-time rotations). In the Hamiltonian formulation, whenever a conservation law holds good for a physical system, the Hamiltonian of the system remains invariant under the corresponding group of transformations. In other words, every conservation law is a consequence of a symmetry possessed by the physical systems. The converse of it is not necessarily true as even if Hamiltonian of the system remains invariant under a group of transformations, there may not be a related conservation law. For instance, a physical system is invariant under time reversal ($\rightarrow -t$)but there is no corresponding conservation law. Then there had been a question, unanswered for some time, that what type of symmetries do lead to conservation laws and what type of symmetries do not. Then Wigner showed that all the symmetries of quantum mechanical statescan be chosen so as to correspond to either unitaryor anti-unitary operators. It is the unitary operator which is associated with a conservation law. For instance, the operators associated with four space-time translations and space-time rotations (three rotations about spatial axes by real angles and three rotations by imaginary angles in spatial-temporal planes like x-t, y-t and z-t) are all unitary operators and hence all these symmetric transformations lead to the corresponding conservation laws. On the other hand, the operator associated to time reversalis anti-unitary and hence it does not lead to a conservation law. However if the Hamiltonian of a physical system is invariant under an anti-unitary transformation, it has other consequences which may be verified experimentally.

This unit is devoted to symmetries with respect to rotations (about spatial coordinate axes as well as rotations in spin- space) which implies the conservation of angular momentum operators. Here you will study the angular momentum operators (the operators corresponding to orbital angular momentum, spin angular momentum, and total angular momentum) through the commutation rules for their components as incorporated in earlier unit (unit-6). In this unit the eigen values and eigen states of these angular momentum operators will be obtained and the rules of combination of two or more angular momenta will be derived in terms of Clebsch-Gordan Coefficients.

7.2 LEARNING OBJECTIVES

After reading this unit we will able to understand:

- Angular Momentum and Rotational symmetries
- Angular Momentum Operator
- Commutation of Components of Angular Momentum Operator
- Orbital Angular Momentum Operator and Its Commutation
- Eigen Values and Eigen Functions of Orbital Angular Momentum Operator
- Bohr Magnetron
- Total Angular Momentum Operator
- Addition of Two Angular Momentum Operators
- Clebsch-Gordan Coefficients and Their properties

7.3 DEFINITION OFORBITAL ANGULAR MOMENTUM OPERATOR

You know from classical mechanics that the angular momentum vector of a particle is given as **L=rxp,** where **r** and **p** are respectively the position and momentum vectors for the particle. In wave mechanics this vector is written as a linear Hermitian operator on replacing the dynamicalvariables**r** and **p** by the corresponding operators. Thus you can write the Cartesian components of this vector operator$\hat{L}$as

$\hat{L}_x = \hat{L}_1 = -i\,\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$; $\hat{L}_y = \hat{L}_2 = -i\,\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$;

and $\hat{L}_z = \hat{L}_3 = -i\,\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$

(7.1) or in general $\hat{L}_j = -i\,\hbar\varepsilon_{jkl}x_k\,\frac{\partial}{\partial x_l}(j,k,l = 1,2,3)$, where ε_{jkl}has the value +1 if the indices $jkl$are even permutations of 1,2,3 and -1for odd permutations of 1,2,3 and zero if two of the indices are equal. Using the fundamental commutation rules of components of the operators $\hat{x}$and $\hat{p}$you may readily get the following commutation relations for the components of angular operator, given by eqns. (6.1):

$[\hat{L}_j, \hat{L}_k] = i\,\hbar\varepsilon_{jkl}\hat{L}_l$ (7.2)

Using this relation, you may readily have

$[\hat{L}^2, \hat{L}] = 0$ (7.3)

where$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ (7.4).

This relation (7.3) shows that though the components of angular momentum operator $\hat{L}$ do not commute mutually, they commute with $\hat{L}^2$.

You know that central force is derivable from the potential that depends only on the distance r of the moving particle from a fixed point (usually the coordinate origin) and the Hamiltonian for such a problem is

$H_{cf} = \frac{p^2}{2m} + V(r)$ (7.5)

Classically, since this central force has no torque about its origin, the angular momentum **L** =**rxp** is conserved. This property is equally valid in wave mechanics where central force Hamiltonian operator corresponding to eqn.(7.5) may be written as

$\hat{H}_{cf} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$ (7.5a)

and you may readily write $\hat{L}^2 = r^2p^2 + \hbar^2\frac{\partial}{\partial r}\,(r^2\frac{\partial}{\partial r})$ (7.5b)

This$\hat{L}^2$ obviously commutes with kinetic energy $T = \frac{p^2}{2m}$ and the potential $V(r)$ for central force and hence you may readily write

$[\hat{L}^2, \hat{H}_{cf}] = 0and[\hat{L}, \hat{H}_{cf}] = 0$, (7.6)

ensuring the conservation of angular momentum in central force problem. These equations reveal an important difference between classical and quantum mechanical formulations of angular momentum. In classical mechanics the three components of angular momentum are the consequence of rotation in three planes in three dimensional space and the classical rotational symmetry leads to the conservation of all the three components separately. On the other hand, though eqns. (7.6) show the commutation between Hamiltonian and all the three components of angular momentum operator, these components do not commute among themselves and hence no more than component, $\hat{L}_j$, of angular momentum operator can be a constant of motion. Another difference between classical and quantum cases is that in classical mechanics one is concerned only withsuch angular momenta which are associated with space time description while in quantum mechanics a wider conceptual basis is used which includes those angular momenta also that do not have classical analogue, like the intrinsic spin and iso-spin of elementary particles. The angular momentum associated with operators defined by eqns. (7.1),is called orbital angular momentum, the definition of which has been borrowed from classical mechanics as the constant of motion in three dimensional ordinary space.

7.4 EIGEN VALUES AND EIGEN VECTORS OF ORBITAL ANGULAR MOMENTUM

Angular momentum operator $\hat{L}$, defined by eqns. (7.1), is closely related to the rotation of the system and if the system has rotational symmetry, then the eigen states of central force Hamiltonian, $\hat{H}_{cf}$, are the simultaneous eigen states of $\hat{L}^2$ and the operator associated with one well defined component of $\hat{L}$, say $\hat{L}_z$. These states have well defined eigen values of the operators $\hat{L}^2, and\ \hat{L}_z$. You have already studied these states in third unit of your quantum mechanics course, where you have obtained the solution of three dimensional Schrodinger equation in spherical coordinate system $(r, \theta, \emptyset)$ in the following form

$$\Psi(r, \theta, \emptyset) = R(r) Y_l^{m_l}(\theta, \emptyset) = \Psi_{n,l,m_l}(\theta, \emptyset), \qquad (7.7)$$

with$R(r)$ as radial part and $Y_l^m(\theta, \emptyset)$as spherical harmonics introduced in the third unit of this course such that

$$\hat{H}_{cf} \Psi_{n,l,m_l}(\theta, \emptyset) = E_{nl} \Psi_{n,l,m_l}(\theta, \emptyset) \qquad (7.8)$$

$$\hat{L}^2 \Psi_{n,l,m_l}(\theta, \emptyset) = \hbar^2 l(l+1) \Psi_{n,l,m_l}(\theta, \emptyset) \qquad (7.8a)$$

and$\hat{L}_z \Psi_{n,l,m_l}(\theta, \emptyset) = m_l \hbar \Psi_{n,l,m_l}(\theta, \emptyset),$ (7.8b)

where $E_{nl}$are energy eigen values corresponding to considered eigen states of $\hat{H}_{cf.}$ In these equations l is orbital quantum number and m_l is magnetic quantum numbers. Allowed values of these quantum numbers are

$l = 0,1,2, \dots\dots\dots\dots$, and $m_l = -l, -l+1, \dots\dots\dots, l-1, l)$ (7.9)

where half odd integral values of $j\ in$ the corresponding operator of general angular momentum operator $\hat{J}^2$, in eqn. (6.47) of section 6.7 of previous unit-6, have been ignored in the allowed values of l in eqn. (7.9) due to the condition of single valued-ness of the wave function $\Psi_{n,l,m_l}(\theta, \emptyset)$with respect to the angle $\emptyset$ i.e.

$\Psi_{n,l,m_l}(\theta,\emptyset+2\pi)=\Psi_{n,l,m_l}(\theta,\emptyset)$ (7.10)

The central force eigen functions $\Psi_{n,l,m_l}(\theta,\emptyset)$may also be written eigenkets$|n,l,m_l >$ and then eigen value equations (7.8), (7.8a) and (7.8b) may be written as

$\hat{H}_{cf}|n,l,m_l >= E_{nl}|n,l,m_l >$;

$\hat{L}^2|n,l,m_l > = \hbar^2 l(l+1)|n,l,m_l >$; (7.11)

$\hat{L}_z|n,l,m_l >= m_l\hbar|n,l,m_l >$where$l$ and m_l are given by (7.9).

These are the eigen values and eigen vectors of operators $\hat{L}^2, and\ \hat{L}_z$ $c$orresponding to the energy eigen states for central force problem. You will get an alternate derivation of these values of orbital and magnetic quantum numbers in the following sections.

7.5 ROTATIONAL SYMMETRY AND ORBITAL ANGULAR MOMENTUM

It is the result of isotropy of space (equivalence in all directions) which leads to the invariance of the properties of closed systems under rotation (rotational symmetry). Classically, a rotation is specified by an axis of rotation and an angle of rotation. The positive sense of rotation is determined by the well-known right handed screw rule. The rotation of a physical system within coordinate axes fixed in space is an active transformation while the rotation of coordinate system with physical system fixed in space is a passive transformation. Let us first consider herethe active point of rotating the physical system in fixed coordinate system. An infinitesimal rotation of the system may be denoted by the vector $\vec{\emptyset}$, length of which is equal to the infinitesimal angle of rotation $\delta\emptyset$ and the direction of which is along the axis of rotation. Under such a rotation the radius vector is transformed according to

$\boldsymbol{r}' = \boldsymbol{r} + \delta\vec{\emptyset} \times \boldsymbol{r} = \boldsymbol{r} + \boldsymbol{dr}$(7.12)You may readily prove that the infinitesimal rotations commute to the first order of infinitesimals. Assuming that the function $\psi(\boldsymbol{r})$ is continuous and differentiable, the value of ψ at point $\boldsymbol{r}'$may be written to the first order in $\boldsymbol{dr}$as

$$\psi(\boldsymbol{r}') = \psi(\boldsymbol{r}) + \boldsymbol{dr}.\boldsymbol{\nabla}\,\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}) + (\delta\vec{\emptyset} \times \boldsymbol{r}).\boldsymbol{\nabla}\,\psi(\boldsymbol{r})$$

$= \psi(\boldsymbol{r}) + \delta\vec{\emptyset}.(\boldsymbol{r} \times \boldsymbol{\nabla})\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}) + \frac{i}{\hbar}(\delta\vec{\emptyset}.\hat{L})\psi(\boldsymbol{r}),$ (7.13)where we have usedeqns (7.1)This equation gives

$\psi(\boldsymbol{r}') - \psi(\boldsymbol{r}) = d\psi = \frac{i}{\hbar}(\delta\vec{\emptyset}.\hat{L})\psi(\boldsymbol{r})$which when integrated gives the final result for the finite rotation $\vec{\emptyset}$ **:**

$\psi(\boldsymbol{r}')$ =exp($\frac{i}{\hbar}\vec{\emptyset}.\hat{L})\psi(\boldsymbol{r})$ = exp ($\frac{i}{\hbar}\phi\hat{n}.\hat{L})\psi(\boldsymbol{r})$(7.13a)where$\hat{n}$ is unit vector along the axis of rotation i.e. $\vec{\emptyset} = \phi\hat{n}$. It shows that from $\psi(\boldsymbol{r})$you may know$\psi(\boldsymbol{r}')$provided you know the orbital angular momentum operator $\hat{L}$ of the system about the axis of rotation. Equation (7.13) may also be written as

$\psi(\boldsymbol{r}') = R_{\hat{n}}(\phi)\psi(\boldsymbol{r})$(7.13a)

where$R_{\hat{n}}(\phi)$ = exp ($\frac{i}{\hbar}\phi\hat{n}.\hat{L}$) (7.14)
is the rotation matrix associated with the orbital angular momentum operator $\hat{L}$. The inverse operation of eqn.(7.13) may be readily written as

$\psi(\boldsymbol{r})$ = exp ($-\frac{i}{\hbar}\phi\hat{n}.\hat{L})\psi(\boldsymbol{r}')$(7.13b)

When the coordinate system is rotated by keeping the physical system fixed (passive point of view) and the coordinate system S' is obtained from S by rotation about the axis $\hat{n}$ by an angle $-\delta\vec{\emptyset}$, then you have

$\boldsymbol{r}' = \boldsymbol{r} + \delta\vec{\emptyset} \times \boldsymbol{r} = \boldsymbol{r} + \delta\emptyset(\hat{n} \times \boldsymbol{r})$where$\boldsymbol{r}$is the coordinate in S and $\boldsymbol{r}'$is that in S' for the same physical point. If an observer in S defines the state of the system as $\psi(\boldsymbol{r})$and the observer in S' defines it as $\psi'(\boldsymbol{r}')$then $\psi(\boldsymbol{r}) = \psi'(\boldsymbol{r}')$because both observersmeasure the same amplitude at particular physical point. Then according to eqn. (7.13), you may write

$\psi'(\boldsymbol{r}') = [1 + \frac{i}{\hbar}(\delta\emptyset.\hat{n}).\hat{L}]\psi'(\boldsymbol{r})$and for finite rotation you have

$\psi'(\boldsymbol{r}') = [1 + \frac{i}{\hbar}(\emptyset\,\hat{n}.\hat{L})]\psi'(\boldsymbol{r})or\psi'(\boldsymbol{r})$ = exp$\left[-\frac{i}{\hbar}(\emptyset\,\hat{n}.\hat{L})\right]\psi'(\boldsymbol{r}')$ = exp$\left[-\frac{i}{\hbar}(\emptyset\,\hat{n}.\hat{L})\right]\psi(\boldsymbol{r})$
(7.15) or $\psi'(\boldsymbol{r}) = R_{\emptyset}^{\hat{n}}\psi(\boldsymbol{r})$
(7.15a) where $R_{\emptyset}^{\hat{n}}$ = exp$\left[-\frac{i}{\hbar}(\emptyset\,\hat{n}.\hat{L})\right]$
(7.15b)

It is clear from eqns. (7.14) and (7.15b) that the generator of transformations of a rotation or the operator of an infinitesimal rotation around an axis $\hat{n}$ is determined by the component of orbital angular momentum operator along that axis. Comparison of these equations also show that a rotation of the coordinate axis around a unit vector $\hat{n}$ over an angle $\emptyset$ is equivalent to a rotation of the system over $-\emptyset$ around the same axis. From eqn. (7.15b) we may write the following operator of an infinitesimal rotation $\vec{\emptyset}$ **:**

$\hat{R}_{\delta\emptyset} = 1 - \frac{i}{\hbar}(\delta\vec{\emptyset}.\hat{L})$(7.16)

Using this result, you may transform the eigen value equation

$\hat{H}\,\psi = E\,\psi$ or $\hat{H}'\psi' = E\,\psi' = \hat{H}\psi'$
under the rotation $\hat{R}_{\delta\emptyset}$ where the invariance of Hamiltonian in rotations has beenused. This equation may be written as

$$\hat{H}\hat{R}_{\delta\emptyset}\ \psi = E\hat{R}_{\delta\emptyset}\ \psi$$

or $R_{\delta\emptyset}^{-1}\hat{H}\hat{R}_{\delta\emptyset} = E\,\psi = \hat{H}\,\psi$

or $\hat{H} = R_{\delta\emptyset}^{-1}\hat{H}\hat{R}_{\delta\emptyset}$

or $[1-\frac{i}{\hbar}(\hat{n}.\hat{L})\delta\emptyset]\hat{H} = \hat{H}[1-\frac{i}{\hbar}(\hat{n}.\hat{L})\delta\emptyset]$

or $(\hat{n}.\hat{L})\hat{H} = \hat{H}(\hat{n}.\hat{L})$

Choosing $\hat{n}$ along z-axis, this equation gives

$$[\hat{H}\,,\hat{L}_z] = 0$$

which is the same result as given by second of eqns. (7.6). It shows that the invariance of Hamiltonian operator under infinitesimal rotation is visualized through the commutation of Hamiltonian with the component of orbital angular momentum operator along the axis of rotation. It also implies that in a centrally symmetric field the component of orbital angular momentum operator along an arbitrary direction ($\hat{n}$) is constant of motion. In an axially symmetric field Hamiltonian is invariant under rotation around the axis of symmetry and hence the component of orbital angular momentum operator along that direction is constant.

EXAMPLES

Ex. 7.1 Using the relation $\hat{P}_r = i\,\hbar[\frac{\partial}{\partial r}+\frac{1}{r}]$, prove that $\frac{\hat{P}^2}{2m} = \frac{\hat{P}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2}$,
where $\hat{L}$ is orbital angular momentum operator.

Solution: Using eqn.(7.5b) you have

$\hat{L}^2 = r^2\hat{P}^2 + \hbar^2\frac{\partial}{\partial r}\,(r^2\frac{\partial}{\partial r})$. (i)

From the given relation you may readily write

$\hat{P}_r{}^2\Psi = -\hbar^2[\frac{\partial}{\partial r}+\frac{1}{r}]\left[\frac{\partial}{\partial r}+\frac{1}{r}\right]\Psi = -\hbar^2\left[\frac{\partial^2\Psi}{\partial r^2}+\frac{2}{r}\frac{\partial\Psi}{\partial r}\right] = -\hbar^2[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)]$which gives
$\frac{\hat{P}_r^2}{2m} = -\frac{\hbar^2}{2m}\,[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)]$

Substitute this relation in eqn.(i) then you will get

$\hat{L}^2 = r^2\hat{P}^2 - r^2\hat{P}_r{}^2$ which gives $\frac{\hat{P}^2}{2m} = \frac{\hat{P}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2}$ which is the required result.

Ex. 7.2 Show that any quantum mechanical operator $\hat{F}$ transforms under infinitesimal rotation $\delta\emptyset$ into

$\hat{F}' = \hat{U}\hat{F}\,\hat{U}^\dagger$(ii)

where $\hat{U}$ is an unitary operator given as

$$\hat{U} = \hat{I} - \frac{i}{\hbar}(\delta\vec{\emptyset}.\hat{L}) \qquad \text{(iii)}$$

and hence derive the commutation rules for $((\hat{L}_i, \hat{x}_k); (\hat{L}_i, \hat{p}_k)$ and $(\hat{L}_i, \hat{L}_k)$.

Solution: From eqn. (7.13) it is obvious that every state vector ψ or $\emptyset$ transforms into state vector $\psi' = \hat{U}\psi$ or $\emptyset' = \hat{U}\emptyset$ funder the infinitesimal rotation where $\hat{U}$ is given by eqn.(iii). But the expectation value of any quantum mechanical operator is independent of the choice of coordinates and hence you may write

$< \psi'|\hat{F}'|\emptyset' > = < \psi|\hat{F}|\,\emptyset >$(iv)

Or $< \hat{U}\,\psi\,|\hat{F}'|\hat{U}\,\emptyset > = < \psi|\hat{F}|\,\emptyset >$

i.e. $< \psi|\hat{U}^\dagger\hat{F}'\hat{U}|\emptyset > = < \psi|\hat{F}|\,\emptyset >$

which gives $\hat{U}^\dagger\hat{F}'\hat{U} = \hat{F}$ which may readily be written in the required form given by relation (ii) proving the first part of the problem.

Now substituting relation (iii) into relation (ii), you may write

$$\hat{F}' = \hat{F} - \frac{i}{\hbar}\delta\vec{\emptyset}.[\hat{L}, \hat{F}] \qquad \text{(v)}$$

where only first order terms of the infinitesimal $\delta\vec{\emptyset}$ have been retained. You may now choose $\hat{F}$ to be the operator corresponding to rectangular coordinates $x = r_1, y = r_2, z = r_3$ and then eqn. (v) will reduce to

$\hat{r}'_j = \hat{r}_j - \frac{i}{\hbar}\delta\vec{\emptyset}.[\hat{L}, \hat{r}_j]$(vi)

Comparing this relation with eqn. (7.12), you may readily get

$$[\hat{L}_j, \hat{r}_k] = i\,\hbar\varepsilon_{jkl}\hat{r}_l \qquad \text{(vii)}$$

As for the components of every vector operator the transformation under the rotation is the same as given by eqn. (7.12) and hence the same commutation rules must be satisfied by the components of linear momentum operator and the angular momentum operator and thus you may readily write

$[\hat{L}_j, \hat{p}_k] = i\,\hbar\varepsilon_{jkl}\hat{p}_land[\hat{L}_j, \hat{L}_k] = i\,\hbar\varepsilon_{jkl}\hat{L}_l$ (viii)

‘which are the requires commutation rules.

SELF ASSESMENT QUESTIONS (SAQ)

Q. 7.1. Show that orbital angular momentum operator commutes with the potential energy of a central force problem

Q. 7.2 A system is in the state $\emptyset_{lm}$, an eigen state of the orbital angular momentum operators $\hat{L}^2$and $\hat{L}_z$. Calculate $<\hat{L}_x>$and $<\hat{L}_x^2>$.

7.6 TOTAL ANGULAR MOMENTUM OPERATOR

Total angular momentum of a particle is composed of its orbital angular momentum discussed in earlier section and its intrinsic spin angular momentum (which does not have a classical analogue), discussed in previous unit-6. Thus total angular momentum operator is written as

$$\hat{J} = \hat{L} + \hat{S} \tag{7.17}$$

You have seen in unit-6 that the components of spin angular momentum operator also satisfy the same commutation rules as given by eqn. (7.2) for the components of orbital angular momentum operator:

$$[\hat{S}_j,\ \hat{S}_k] = i\,\hbar\varepsilon_{jkl}\hat{S}_l \tag{7.18}$$

You have also seen in unit-6 that these operators also satisfy the similar commutation rule as given by eqn.(7.3) for orbital angular momentum operator i.e.

$[\hat{S}^2, \hat{S}] = 0$or in particular manner$[\hat{S}^2, \hat{S}_z] = 0$ (7.19)

Furthermore, all operators referring to spatial degree of freedom commute with those referringto spin degree of freedom i.e.,

$$[\hat{S}, \hat{r}] = 0;\ \ [\hat{S}, \hat{p}] = 0;\ \ [\hat{S}, \hat{L}] = 0, etc \tag{7.20}$$

In view of the commutations, given by eqns.(7.2), (7.3), (7.18), (7.19) and (7.20), it is clear that the total angular momentum operators, given by qn. (7.17), is the Hermitian operators associated with observables and its components obey the following commutation relations

$[\hat{J}_x, \hat{J}_y] = i\,\hbar \hat{J}_z$(and other cyclic orders)

or in general $[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k, \quad (i, j, k = 1,2,3)$ (7.21)

Defining the square of angular momentum operator as

$J^2 = J_x^2 + J_y^2 + J_z^2,$ (7.22)

you may readily be show that

$[\hat{J}, \hat{J}^2] = 0$ (7.22a)

Equation (7.21) shows that the components of angular momentum operator $\hat{J}$ do not commute among themselves and hence you cannot have a common eigen basis for all these components. On the other hand eqn. (7.21) enables you to form a complete set of common eigen functions of J^2 and one of the components say $\hat{J}_z$.

7.6.1Eigen Values of Total Angular Momentum Operator

Let the vector $|j, m_j>$ be the common eigen vector of the commuting operators $\hat{J}^2$and $\hat{J}_z$ with the corresponding eigen values $\lambda_j\,\hbar^2$ and $\lambda_m\,\hbar$ respectively:

$\hat{J}^2|j, m_j> = \lambda_j\,\hbar^2\,|j, m_j>$ (7.23)

and$\hat{J}_z|j, m_j> = \lambda_m\,\hbar|j, m_j>$ (7.23a)

In view of eqn. (7.22), the operator $\hat{J}^2$ is positive definite and hence its eigen values $\lambda_j\,\hbar^2$ should be positive definite i.e., λ_j should be positive definite. You may also verify this property of λ_j from Hermitian nature of operator $\hat{J}_l$ and the fact that for any state $|\alpha>$ the quantity $<\alpha|\hat{J}^2|\alpha>$ may be written as norm of vector $\hat{J}_l\,|\alpha>$ i.e. it is positive definite. Thus you have

$$\lambda_j = \frac{<j,m_j|\hat{J}^2|j,m_j>}{\hbar^2} \geq 0 \qquad (7.24)$$

In view of eqn.(7.22), you may write

$<j, m_j|\hat{J}^2|j, m_j> = <\hat{J}^2> \geq <\hat{J}_z^2>$(7.25)

or$\lambda_j \geq \lambda_m{}^2 \geq 0$ (7.26)

For mathematical convenience you may introduce the non-Hermitian operators

$\hat{J}_+ = \hat{J}_x + i\hat{J}_y$ and $\hat{J}_- = \hat{J}_x - i\hat{J}_y$ (7.27)

Then you

may readily get

$\hat{J}^2 = \frac{1}{2}[\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+] + \hat{J}_z^2$; (7.28)

$\hat{J}_x = \frac{1}{2}[\hat{J}_+ + \hat{J}_-]$; (7.28a)

$\hat{J}_y = -\frac{i}{2}[\hat{J}_+ - \hat{J}_-]$ (7.28b)

Using relations (7.21), (7.27) and (7.28), you may readily get

$[\hat{J}^2, \hat{J}_\pm] = 0; \quad [\hat{J}_z, \hat{J}_+] = \hbar\hat{J}_+; \; [\hat{J}_z, \hat{J}_-] = -\hbar\hat{J}_-;$

$[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z; \; [\hat{J}^2, \hat{J}_z] = 0; \; [\hat{J}^2, \hat{J}_x] = 0; [\hat{J}^2, \hat{J}_y] = 0;$ (7.29)

Thus the three operators $\hat{J}_+, \hat{J}_-$ and $\hat{J}_z$ completely define the angular momentum operator $\hat{J}$.

You may readily obtain following relations also

$\hat{J}_-\hat{J}_+ = \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z = \hat{J}^2 - \hat{J}_z(\hat{J}_z + \hbar)$, (7.30)

and $\hat{J}_+\hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z = \hat{J}^2 - \hat{J}_z(\hat{J}_z - \hbar)$ (7.30a)

These relations may be combined to give

$\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ = 2[\hat{J}^2 - \hat{J}_z^2]$; (7.30b)

$\hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+ = 2\hbar\hat{J}_z$ (7.30c)

Appling $\hat{J}_+$ and $\hat{J}_-$ on eqn. (7.23), you will get

$$\hat{J}_\pm\hat{J}^2|\, j, m_j > = \hbar^2\lambda_j \hat{J}_\pm|\, j, m_j >$$

Or $\hat{J}^2\{\hat{J}_\pm|\, j, m_j >\} = \hbar^2\lambda_j\{\hat{J}_\pm|\, j, m_j >\}$, (7.31)

which shows that $\hat{J}_\pm|\, j, m_j >$ is also an eigen state of $\hat{J}^2$ corresponding to the same eigen value $\hbar^2\lambda_j$. Similarly on applying $\hat{J}_\pm$ on eqn.(7.23a), you will get

$\hat{J}_z\{\hat{J}_\pm|\, j, m_j >\} = (\lambda_m \pm 1)\hbar\{\hat{J}_\pm|\, j, m_j >\}$, (7.31a) which shows that the states $\hat{J}_+|\, j, m_j >$ and $\hat{J}_-|\, j, m_j >$ are the eigen vectors of $\hat{J}_z$ corresponding to eigen values $(\lambda_m + 1)\,\hbar$ and $(\lambda_m - 1)\,\hbar$ respectively. Thus you may write

$\hat{J}_+|\, j, m_j > = C_+|j, m_j + 1 >$, (7.32)

and $\hat{J}_-|\, j, m_j > = C_-|\, j, m_j - 1 >$ (7.32a)

with C_+ and C_- as constants.

Now from eqn.(7.30), you may readily get

$$< j, m_j|\hat{J}_-\hat{J}_+\,|j, m_j > = < j, m_j|\hat{J}^2|j, m_j > - < j, m_j|\hat{J}_z^2|j, m_j > - \hbar < j, m_j|\hat{J}_z|j, m_j >$$

Keeping in mind that $\hat{J}_+^\dagger = \hat{J}_-$ and using eqn.(7.23a), you may write this equation as

$$|\hat{J}_+|\, j, m_j > |^2 = \{\lambda_j - \lambda_m\,(\lambda_m + 1)\}\hbar^2$$

On the other hand, under normalization condition eqn. (7.32) gives

$$|\hat{J}_+|\, j, m_j > |^2 = |C_+|^2$$

Comparing these equations you may readily get

$$C_+ = [\{\lambda_j - \lambda_m\,(\lambda_m + 1)\}\,\hbar^2]^{\frac{1}{2}}$$

and hence eqn. (7.32) may be written as

$\hat{J}_+|\, j, m_j > = \hbar\{\lambda_j - \lambda_m\,(\lambda_m + 1)\}^{\frac{1}{2}}\,|j, m_j + 1 >$ (7.33)

Similarly, eqn. (7.32a) may be written as

$\hat{J}_-|\, j, m_j > = \hbar\{\lambda_j - \lambda_m\,(\lambda_m - 1)\}^{\frac{1}{2}}\,|j, m_j - 1 >$ (7.33a)

These eqns. (7.33) and (7.33a) respectively show that the operator $\hat{J}_+$ raises the λ_m eigen value of $\hat{J}_z$ by unity and operator $\hat{J}_-$ lowers it by unity. Therefore these operators are respectively called raising and lowering operators and consequently the spectrum of eigen values of operator $\hat{J}_z$ is integrally spaced.

Combining eqns. (7.33) and (7.33a), you may write

$\hat{J}_\pm|\, j, m_j > = \hbar\{\lambda_j - \lambda_m\,(\lambda_m \pm 1)\}^{\frac{1}{2}}\,|j, m_j \pm 1 >$, (7.33b)

which shows that by repeated applications of $\hat{J}_\pm$ you may have

$J_{\pm}^{p} \mid j, m_j > \propto |j, m_j \pm p >$ where p is any positive integer. But according to eqn. (7.26), the maximum value of λ_m^2 is bounded and hence maximum value of p is restricted with the conditions that

$\hat{J}_{+} \mid j, m_{j_{max}} > = 0$ (7.34)
and $\hat{J}_{-} \mid j, m_{j_{min}} > = 0$ (7.34a)

which show that after attaining maximum value of m_j in the eigen value of $\hat{J}_z$ the operator $\hat{J}_+$ cannot raise it further and after lowering it to the minimum value of m_j, the operator $\hat{J}_-$ cannot lower it further. Since the spectrum of operator $\hat{J}_z$ is integrally spaced, you may readily write

$m_{j_{max}} - m_{j_{min}} = a\ positive\ integer\ including\ zero$ (7.34b)

Under the condition (7.34), eqn. (7.33) gives

$\lambda_j = \lambda_{m\,max} (\lambda_{m\,max} + 1)$ (7.34c)
and under condition (7.34a) eqn. (7.33a) gives

$\lambda_j = \lambda_{m\,min} (\lambda_{m\,min} - 1)$ (7.34d)

These conditions (7.34c) and (7.34d) lead to

$\lambda_{m\,max} = -\lambda_{m\,min} = \lambda_{m\,0}$ (7.34e)

Thus integrally spaced eigen values λ_m are symmetrical with respect to zero and are bounded by $\lambda_{m\,0}$ as

$-\lambda_{m\,0}, -\lambda_{m\,0} + 1, \dots\dots\dots.\lambda_{m\,0} - 1, \lambda_{m\,0}$ (7.34f)

and it is possible to have these integrally spaced valuesonly when $\lambda_{m\,0}$ is either integral or half integral:

$\lambda_{m\,0} = j$ (integral or half integral) (7.35)

Then $\lambda_m = m_j$ is integral or half integral according to the value of j. Values of (7.34f) then become

$-j \le m_j \le j$ (7.36)

or $m_j = -j, -j+1, \dots\dots, +j$ (7.36a)

where $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots\dots..\infty$ (7.37)

Using eqns. (7.34c), (7.34e) and (7.35) you may readily get

$\lambda_j = j(j+1)$ (7.38)

It is clear from eqn. (7.36)thatλ_j is the maximum value of projection of angular momentum $\hat{J}$on z-axis. Thus the maximum eigen value of $\hat{J}_z$is $j\hbar$. The eigen values of operator $\hat{J}^2$are given as $j(J+1)\hbar^2$and for a given value of $j$there are $(2j+1)$eigen values of operator $\hat{J}_z$corresponding to $(2j+1)$values of m_j givenby eqn. (7.36a).

7.6.2 Eigen Vectors Of Total Angular Momentum Operator

You have seen that eigen values of operator $\hat{J}^2$ are $j(J+1)\hbar^2$ and for a given value of j there $(2j+1)$ eigen values$m_j\hbar$of operator $\hat{J}_z$. Consequently, for a given value of j thereare $(2j+1)$ linearly independent vectors $|j, m_j>$ which are simultaneous eigen vectors of angular momentum operators $\hat{J}^2$ and $\hat{J}_z$. From any of these eigen vectors others can be constructed by the repeated operations of operators $\hat{J}_+$ and $\hat{J}_-$ according to eqns. (7.33) and (7.33a) respectively, which may be written as

$$\hat{J}_+|j, m_j> = \hbar\{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}}|j, m_j+1>$$

and$$\hat{J}_-|j, m_j> = \hbar\{(j+m_j)(j-m_j+1)\}^{\frac{1}{2}}|j, m_j+1> \qquad (7.39)$$

In particular from eqns. (7.34) and (7.34a) you mat write

$$\hat{J}_+|j, j> = 0 \text{and} \hat{J}_-|j, -j> = 0, \qquad (7.39a)$$

showing that the operation of$\hat{J}_+$ on the state with maximum value $j$of m_j gives zero and the operation of$\hat{J}_-$ on the state with minimum value $-j$ of m_j gives zero.

The simultaneous eigen vectors $|j, m_j>$of the angular momentum operators, constitute an eigen basis for a $(2j+1)$-dimensional subspace of the Hilbert space of the system, where operators $\hat{J}^2$ and $\hat{J}_z$ are represented by Hermitian matrices with rows and columns labelled by $(2j+1)$ values of m_j :

$$(\hat{J}^2)_{m'_j m_j} = < j, m_j|\hat{J}^2|j, m_j> = j(j+1)\hbar^2\delta_{m'_j m_j}$$

and$$(\hat{J}_z)_{m'_j m_j} = < j, m_j|\hat{J}_z|j, m_j> = m_j\hbar\delta_{m'_j m_j} \qquad (7.40)$$

Then using eqns. (7.29), you may readily write

$$(\hat{J}_\pm)_{m'_j m_j} = < j, m_j|\hat{J}_\pm|j, m_j> = \{(j \mp m_j)(j \pm m_j + 1\}^{\frac{1}{2}}\hbar\delta_{m'_j m_j} \qquad (7.40a)$$

In other words you may have the following matrix representations of these operators in the basis constituted by eigen states $|j, m_j>$

$\hat{J}^2 = j(j+1)\,\hbar^2 \hat{I}$ (7.41)

and $\hat{J}_z = m_j\,\hbar \hat{I}$ (7.41a)

showing that matrices representing operators $\hat{J}^2$ and $\hat{J}_z$ are diagonal in this representation. Allowed values of j and m_j of these equations are given by eqns.(7.37) and (7.36a) respectively. These results have been derived by using the commutation relations

$$[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k, \quad (i, j, k = 1,2,3)$$

and $[\hat{J}^2, \hat{J}_z] = 0$ as given by eqns. (7.21) and (7.22a). The similar relations are satisfied by the components of orbital momentum operator $\hat{L}$ defined in section -7.3 and the components of intrinsic spin angular momentum operator $\hat{S}$, defined in earlier unit -6. The energy eigen values and eigen vectors of the orbital angular momentum operator have been obtained in section-7.4 and those of the spin operators have been obtained in the previous unit-6, where the relations corresponding to eigen value equations (7.41) and (7.41a) have been respectively obtained as given by eqns. (7.11) and (6.62). In view of these results the result corresponding to eqns. (7.40a) may be readily written as

$(\hat{L}_\pm)_{m'_j m_j} = < l, m_l|\hat{L}_\pm|\, l, m_l > = \{(l \mp m_l)(\, l \pm m_l + 1\}^{\frac{1}{2}}\,\hbar\delta_{m'_l m_l}$ (7.42)

with $l = 0,1,2, \ldots\ldots\infty$ and $-l \le m_l \le l$,
where the half integral values of l have been excluded due to the single valuedness of its eigen functions as shown by eqn. (7.10) since the orbital angular momentum operator has classical analogue. On the contrary, the operator $\hat{S}$ has no classical analogue and hence half integral eigen value for this operator is allowed. In view of eqn. (7.17) the half integral values are allowed in eqn. (7.37). In view of definition (7.17) of total angular momentum operator $\hat{J}$, the eigen state vectors $|\, j, m_j >$ may be written as

$$|\, j, m_j > = |total> = |space> \bigotimes |spin> = |space>|spin>$$

or $|total> = |n, l, m_l, m_s> = |n, l, m_l> \otimes |m_s> = |n, l, m_l>|m_s>$ (7.43)

State vectors $|n, l, m_l>$ are the simultaneous eigen vectors of Hamiltonian operator $\hat{H}_{cf}$ for central force problems and the orbital angular momentum operator. These state vectors satisfy eqns. (7.11) and the spin eigen states $|m_s>$ have been introduced in previous unit-6. Thus, in view of the conditions (7.17) and (7.20), eigen vectors of eqn. (7.43) are simultaneous eigenfunctions of the Hamiltonian operator $\hat{H}_{cf}$, orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ and intrinsic spin angular momentum operators $\hat{S}^2$ and $\hat{S}_z$ with the corresponding eigen

values given by

$\hat{H}_{cf}|n, l, m_l, m_s >= E_{nl}|n, l, m_l, m_s >$;

$\hat{L}^2|n, l, m_l, m_s >= l(l+1)\hbar^2|n, l, m_l, m_s >$;

$\hat{L}_z|n, l, m_l, m_s >= m_l\,\hbar|n, l, m_l, m_s >$;

$\hat{S}^2|n, l, m_l, m_s >= s(s+1)\hbar^2|n, l, m_l, m_s >$;

and$\hat{S}_z|n, l, m_l, m_s >= m_s\,\hbar|n, l, m_l, m_s >$; (7.44)

where$l = 0,1,2, \dots\dots$; $m_l = -l, -l+1, \dots\dots, l$; $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots.$; $s = -s, -s+1, .., s$

EXAMPLES

Ex. 7.3 Determine the eigen values of angular momentum operator obtained by adding two orbital angular momentum operators $\hat{L}_1$ and $\hat{L}_2$.

Solution: If you are given the simultaneouseigen function $Y_{l_1}^{m_1}$ of the operators $\hat{L}_1^2$and $\hat{L}_{1z}$ and the eigen functions $Y_{l_2}^{m_2}$ of the operators $\hat{L}_2^2$and $\hat{L}_{2z}$, then you can form $(2l_1+1)(2l_2+1)$ product wave functions $Y_{l_1}^{m_1}Y_{l_2}^{m_2}$, for $-l_1 \le m_1 \le l_1$ and $-l_2 \le m_2 \le l_2$. These eigen states may be classified by the eigen values of

$$\hat{J}_z = \hat{L}_{1z} + \hat{L}_{2z}$$

which are given by $(m_1 + m_2)\,\hbar = m\hbar$, where $-(l_1 + l_2) \le m \le (l_1 + l_2)$. Different linear combinations of the functions with same m value will belong to different j values. The highest state has the total angular momentum $l_1 + l_2$ for which you may have

$$\hat{J}^2 Y_{l_1}^{m_1}Y_{l_2}^{m_2} = \hbar^2[\,l_1(l_1+1) + l_2(l_2+1)]Y_{l_1}^{m_1}Y_{l_2}^{m_2}$$

The product $Y_{l_1}^{m_1}Y_{l_2}^{m_2}$ can be decomposed into eigen states of $\hat{J}^2$ with the correspongingeigen values $j(j+1)\,\hbar^2$ where j can have the values $l_1 + l_2, l_1 + l_2 - 1, \dots\dots.|l_1 - l_2|$.

Ex. 7.4 How do the operators $\hat{J}_x$ and $\hat{J}_y$ operate on the simultaneous eigen states of operators $\hat{J}^2$ and $\hat{J}_z$ where $\hat{J}$ is the total angular momentum operator?

Solution: Simultaneous eigenfunctions of the operators $\hat{J}^2$ and $\hat{J}_z$ are $|\,j, m_j>$with the corresponding eigen values given by eqns. (7.41) and (7.41a). These eigen functions constitute the eigen basis in which the matrix elements of operators$\hat{J}^2$ and $\hat{J}_z$ are given by equations (7.40). In this eigen basis the matrix elements of the raising and lowering operators $\hat{J}_\pm$ are given by eqns.(7.40a). The operators $\hat{J}_x$ and $\hat{J}_y$ are given by eqns. (7,28a) and (7.28b) respectively in terms of these operators ($\hat{J}_\pm$). Substituting relations (7.39) in eqn.(7.28a), you may readily get

$\hat{J}_x| j,m_j >= \frac{1}{2}[\hbar\{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}} |j,m_j+1>$

$+\hbar(j+m_j)(j-m_j+1)\}^{\frac{1}{2}} |j,m_j+1>]$ which gives the operation of the operator $\hat{J}_x$ on the simultaneous eigen functions of the operators $\hat{J}^2$ and $\hat{J}_z$. Similarly, on substituting relations (7.39) into eqn. (7.28b), you may readily get

$\hat{J}_y| j,m_j >= \frac{1}{2i}[\hbar\{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}} |j,m_j+1>$

$-\hbar(j+m_j)(j-m_j+1)\}^{\frac{1}{2}} |j,m_j+1>]$

which gives the operation of the operator $\hat{J}_y$ on the simultaneous eigen functions of the operators $\hat{J}^2$ and $\hat{J}_z$.

SELF ASSESSMENT QUESTIONS (SAQ)

Q.7.3. Find the transformation of an spinor under the rotation.

Q.7. 4.An electron has orbital angular momentum $\hat{L}$ in addition to the intrinsic spin momentum $\hat{S} = \frac{1}{2}\hat{\sigma}$. Show that the projection operator to the state $j = l + \frac{1}{2}$ is $\frac{(l+1)+L.\sigma}{(2l+1)}$.

7.7 ADDITION OF TWO ANGULAR MOMENTA (C-G COEFFICIENTS)

Consider a system with angular momentum $\boldsymbol{J_1}$ and a second system with angular momentum $\boldsymbol{J_2}$then classically, the total angular momentum of the combined system will be

$$\boldsymbol{J} = \boldsymbol{J_1} + \boldsymbol{J_2}$$

In quantum mechanics the situation is not that simple because here you become concerned with the eigen values and eigen states of the total angular momentum operator when you have one system in a state with angular momentum quantum numbers $j = j_1$ and $m_s = m_1$ and a second system with angular momentum quantum numbers $j = j_2$ and $m_s = m_2$. Aparticular case has been described by eqn. (7.17) by combining orbital angular momentum operator $\hat{L}$ and spin angular momentum operator $\hat{S}$ into total angular momentum operator $\hat{J}$. In a more general case you consider the addition of two mutually commuting angular momentum operators $\hat{J}_1 and\, \hat{J}_2$ and construct the eigen states of the total system in which the squares and z-components of both these angular momentum operators have well defined eigen values (in view of their mutual commutation). Designate any such state as $|j_1 j_2 m_1, m_2>$and then you may readily write

$\hat{J}_1^2|j_1 j_2 m_1, m_2> = j_1(j_1+1)\hbar^2|j_1 j_2 m_1, m_2>;$

$\hat{J}_{1z}|j_1 j_2 m_1, m_2> = m_1\,\hbar|j_1 j_2 m_1, m_2>;$

$$\hat{J}_2^2|j_1j_2m_1,m_2>= j_2(j_2+1)\hbar^2|j_1j_2m_1,m_2>;$$

$$\hat{J}_{2z}|j_1j_2m_1,m_2>= m_2\,\hbar|j_1j_2m_1,m_2> \qquad (7.45)$$

In these equations the quantum numbers specifying eigen values of Hamiltonian have been suppressed.Such simultaneous eigen states of the operaors$\hat{J}_1^2,\hat{J}_{1z};\hat{J}_2^2,\hat{J}_{2z}$ can be written as the following direct product of kets$|j_1\,m_1>$ and $|j_2m_2>$ as generalization of eqn. (7.43):

$$|j_1j_2m_1,m_2>= |j_1\,m_1>|j_2m_2> \qquad (7.46)$$

These are $(2j_1+1)(2j_2+1)$ different eigen states for fixed j_1 and j_2 which differ in the values of $m_1$and m_2.

In view of the commutation rules (7.21) for the components of the operators $\hat{J}_1 and\, \hat{J}_2$ respectively and the fact that the different components of the operator $\hat{J}_1$ commutes with all the components of the operator $\hat{J}_2$, the components of the total angular momentum operator$\hat{J}$ must satisfy the commutation rules (7.21) and also the following ones with $\hat{J}_1^2$ and $\hat{J}_2^2$:

$$[\hat{J}_1^2,\hat{J}_z]=[\hat{J}_2^2,\hat{J}_z]=[\hat{J}^2,\hat{J}_1^2]=[\hat{J}^2,\hat{J}_2^2]=0 \qquad (7.47)$$

However, $\hat{J}^2$ does not commute with $\hat{J}_{1z}$and $\hat{J}_{2z}$. In view of these facts you can think of the simultaneous eigen states of the operators $\hat{J}^2$, $\hat{J}_z$,$\hat{J}_1^2$ and $\hat{J}_2^2$. Designate such states as $|j_1j_2\,jm>$. Then you may readily write the following eigen value equations

$$\hat{J}^2|j_1j_2\,jm>=j(j+1)\hbar^2|j_1j_2\,jm>;$$

$$\hat{J}_z|j_1j_2\,jm>=m\,\hbar|j_1j_2\,jm>;$$

$$\hat{J}_1^2|j_1j_2\,jm>= j_1(j_1+1)\hbar^2|j_1j_2\,jm>;$$

$$\hat{J}_2^2|j_1j_2\,jm>=j_2(j_2+1)\hbar^2|j_1j_2\,jm> \quad (7.48)$$

It is obvious from eqns. (7.45) and (7.48) that sets of states $|j_1j_2m_1,m_2>$ and $|j_1j_2\,jm>$ constitute two different basis in the same Hilbert space. Thus the problem of addition of two angular momenta in quantum mechanics reduces to find out the ways to express states $|j_1j_2\,jm>$ as linear combination of states $|j_1j_2m_1,m_2>$ and vice-versa.

Using The completeness property of the basis $|j_1j_2m_1m_2>$, you can readily write

$$|j_1j_2\,jm>= \sum_{m_1m_2}|j_1j_2m_1,m_2><j_1j_2m_1m_2|j_1j_2\,jm> \qquad (7.49)$$

where summation has beentaken over $m_1 and\ m_2$since you have assumed $j_1\ and\ j_2$ having fixed values. In this relation the coefficients $<j_1j_2m_1m_2|j_1j_2\,jm>$ determine the contribution of state $|j_1j_2m_1,m_2>$ given by eqn.(7.46) to the state $|j_1j_2\,jm>$ which simultaneously specify square of total angular momentum, its z-component, and squares of angular momenta $\hat{J}_1 and\, \hat{J}_2$. These coefficients are called Clebsh-Gordon coefficients of Wigner coefficients which may be designated as

$C^{j_1,j_2,j}_{m_1,m_2,m} = < j_1 j_2 m_1 m_2 | j_1 j_2\, jm > = |m_1 m_2 > |jm >,$ (7.50)

where it is understood that j_1 *and* j_2 are the maximum values of m_1*and* m_2 and hence these symbols have been dropped in right hand side of eqn. (7.50).Then eqn. (7.49) may be written as

$|jm > = \sum_{m_1 m_2} C^{j_1,j_2,j}_{m_1,m_2,m} |j_1 m_1 > |j_2 m_2 >$ (7.51)

where you have used relation (7.46). It shows that Clebsh-Gordon coefficients$C^{j_1,j_2,j}_{m_1,m_2,m}$ are the matrices of transformation from the representation, where z-components of angular momenta $\hat{J}_1$*a*nd $\hat{J}_2$ are given, to a representation where total angular momentum $\hat{J}$ and its z-component $\hat{J}_z$ are given.

Using relation, $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$, you may readily write

$$\hat{J}_z | j_1 j_2\, jm > = m\,\hbar | j_1 j_2\, jm >$$

and$\hat{J}_z | j_1 j_2\, jm > = (\hat{J}_{1z} + \hat{J}_{2z})\, | j_1 j_2\, jm > = (m_1 + m_2)\hbar | j_1 j_2\, jm >$

Combining these two equations, you may readily get

$$(m - m_1 - m_2)\hbar | j_1 j_2\, jm > = 0$$

Using relation (7.51), this equation may be written as

$$(m - m_1 - m_2)\,\hbar \sum_{m_1 m_2} C^{j_1,j_2,j}_{m_1,m_2,m} | j_1 j_2 m_1, m_2 > = 0$$

But $| j_1 j_2 m_1, m_2 >$ are linearly independent vectors, and hence this equation leads to

$C^{j_1,j_2,j}_{m_1,m_2,m} = 0form \neq (m_1 + m_2)$

Thus Clebsch-Gordon coefficient, defined by eqn. (7.50), vanishes unless

$m = m_1 + m_2$ (7.52)

and hence in eqns. (7.49) and (7.51) you can take summation only on m_2(or m_1)once $m$is given.

Now operating the state of eqn. (7.49) by the operators $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$and using eqns. (5.39), you may readily get the following recurrence relations for C-G coefficients

$$\sqrt{(j \pm m)(j \mp m + 1)}\, C^{j_1,j_2,j}_{m_1,m_2,m\mp 1} = \sqrt{(j_1 \pm m_1 + 1)(j_1 \mp m_1)}\, C^{j_1,j_2,j}_{m_1 \pm 1,m_2,m}$$

$$+\sqrt{(j_2 \pm m_2 + 1)(j_2 \mp m_2)}\, C^{j_1,j_2,j}_{m_1,m_2 \pm 1,m} , \quad (7.53)$$

whereorthonormality of the states have been kept in mind. Now you substitute $m_1 = j_1$ and $m = j$ in the upper part of this equation (i.e. for $\hat{J}_+$) and have the value $m_2 = j - j_1 - 1$ using relation (7.52). Then you will readily get

$$\sqrt{2j}\, C^{j_1,j_2,j}_{j_1,j-j_1-1,j-1} = \sqrt{(j_2 - j + j_1 + 1)(j_2 + j - j_1)}\, C^{j_1,j_2,j}_{j_1,j-j_1,j} \quad (7.54)$$

Similarly, in the lower part of eqn. (7.53) (I.e. for $\hat{J}_-$), you set $m_1 = j_1$, $m_2 = j - j_1$ and $m = j - 1$ and get the following recurrence relation

$$\sqrt{2j}\, C^{j_1,j_2,j}_{j_1,j-j_1,j} = \sqrt{2j_1}\, C^{j_1,j_2,j}_{j_1-1,j-j_1,j-1} + \sqrt{(j_2 + j - j_1)(j_2 - j + j_1 + 1)}\, C^{j_1,j_2,j}_{j_1,j-j_1-1,j-1} \quad (7.54a)$$

Eqn.(7.54) gives C-G coefficient $C^{j_1,j_2,j}_{j_1,j-j_1-1,j-1}$ if the C-G coefficient $C^{j_1,j_2,j}_{j_1,j-j_1,j}$ is known and subsequently eqn. (7.54a) can be used to get C-G coefficient$C^{j_1,j_2,j}_{j_1-1,j-j_1,j-1}$ from these two coefficients. Repeating this procedure by using recurrence relation (7.53), you may get all the C-G coefficients for fixed values of j_1, j_2 *and* j in terms of just one of them (i.e. $C^{j_1,j_2,j}_{j_1,j-j_1,j}$)which is non-vanishing only if $-j_2 \le j - j_1 \le j_2$, since $-j_2 \le m_2 \le j_2$. It gives

$$j_1 - j_2 \le j \le j_1 + j_2 \text{ for } j_1 \ge j_2 \quad (7.55)$$

From recurrence relation (7.53) you could equally well have expressed all these C-G coefficients in terms of $C^{j_1,j_2,j}_{j_1-j_2,j_2,j}$ which is non-vanishing only when$-j_1 \le j - j_2 \le j_1$ corresponding to $-j_1 \le m_1 \le j_1$. This condition gives

$$j_2 - j_1 \le j \le j_1 + j_2 \text{ for } j_2 \ge j_1 \quad (7.55a)$$

Combining relations (7.55) and (7.55a), you may readily write

$$|j_1 - j_2| \le j \le j_1 + j_2 \quad (7.55b)$$

which is the triangle rule obeyed by the possible values of j showing that the three numbers j_1, j_2 and j must constitute the three sides of a triangle for the non-vanishing values of the concerned C-G coefficients. If this condition is not satisfied, these C-G coefficients automatically vanish.

It is obvious that

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1) \quad (7.56)$$

which is the number of linearly independent functions defined by eqn.(7.46). Thus for fixed values of j_1 and j_2, eqn. (7.49) gives a completely new basis in $(2j_1 + 1)(2j_2 + 1)$dimensional vector space spanned by the vectors . $|j_1 j_2\, jm >$.

C-G coefficients $C^{j_1,j_2,j}_{m_1,m_2,m}$can be written as square matrices with number of rows and columns equal to $(2j_2 + 1)$ for $j_1 > j_2$ and $(2j_1 + 1)$ for $j_2 > j_1$ .Since the largest values of $m_1$and $m_2$are $j_1\, and j_2$ respectively, the largest possible value of m is $m_1 + m_2$ and largest value of j is $j_1 + j_2$. For such a case when $m_1 = j_1$ and $m_2 = j_2$ the summation in eqn.(7.51) reduces to a single term and you have

$|j_1 + j_2 , m_1 + m_2 > = \quad |j_1 + j_2 , j_1 + j_2 > = \; C^{j_1,j_2,j_1 + j_2}_{j_1,j_2 ,j_1 + j_2} |j_1 j_1 > |j_2 j_2 >$which gives

$C^{j_1,j_2,j_1 + j_2}_{j_1,j_2 ,j_1 + j_2} = 1$ (normalization condition) (7.57)

Thus you have $|j_1 + j_2 , j_1 + j_2 > = |j_1 j_1 > |j_2 j_2 >$.

Now applying the operator $\hat{J}_- = \hat{J}_{1-} + \hat{J}_{2-}$ on this equation and using eqn. (7.33a) you may readily get

$$|j_1 + j_2 , j_1 + j_2 - 1 > = \sqrt{\frac{j_1}{j_1 + j_2}} |j_1 , j_1 - 1 > |j_2 , j_2 > + \sqrt{\frac{j_2}{j_1 + j_2}} |j_1 , j_1 > |j_2 , j_2 - 1 \quad (7.58)$$

You may also write this equation as follows by using eqn. (7.51)

$$|j_1 + j_2 , j_1 + j_2 - 1 > = C^{j_1,j_2,j_1 + j_2}_{j_1-1,j_2 ,j_1 + j_2 -1} |j_1 , j_1 - 1 > |j_2 , j_2 >$$

$$+ C^{j_1,j_2,j_1 + j_2}_{j_1,j_2 -1,j_1 + j_2 -1} |j_1 , j_1 > |j_2 , j_2 - 1 > \qquad (7.58a)$$

Comparing these equations (7.58) and (7.58a), you may readily get

$$C^{j_1,j_2,j_1 + j_2}_{j_1-1,j_2 ,j_1 + j_2 -1} = \sqrt{\frac{j_1}{j_1 + j_2}}$$

and$C^{j_1,j_2,j_1 + j_2}_{j_1,j_2 -1,j_1 + j_2 -1} = \sqrt{\frac{j_2}{j_1 + j_2}}$

Continuation of this process would give all C-G coefficients for which $j = j_1 + j_2$.

Similarly you may readily get

$$C^{j_1,j_2,j_1 + j_2 -1}_{j_1 -1,j_2 ,j_1 + j_2 -1} = \sqrt{\frac{j_2}{j_1 + j_2}}$$

and$C^{j_1,j_2,j_1+j_2-1}_{j_1,j_2-1,j_1+j_2-1} = -\sqrt{\frac{j_1}{j_1+j_2}}$

7.8 PROPERTIES OF C-G COEFFICIENTS

7.8.1 Symmetry Properties

The following symmetry properties of C-G coefficients may be readily verified from their recurrence relations

(a) $C^{j_1,j_2,j}_{m_1,m_2,m} = C^{j_1,j_2,j}_{-m_2,-m_1,-m}$ (7.60)

(b) $C^{j_1,j_2,j}_{m_1,m_2,m} = (-1)^{j_1+j_2-1} C^{j_2,j_1,j}_{m_2,m_1,m}$ (7.60a)

(c) $C^{j_1,j_2,j}_{m_1,m_2,m} = (-1)^{j_1-m_1} (\frac{2j+1}{2j_2+1})^{\frac{1}{2}} C^{j_1,j,j_2}_{m_1,-m,-m_2}$ (7.60b)

(d) $C^{j_1,j_2,j}_{m_1,m_2,m} = (-1)^{j_2+m_2} (\frac{2j+1}{2j_2+1})^{\frac{1}{2}} C^{j,j_2,j_1}_{-m,m_2,-m_1}$ (7.60c

7.8.2 Orthogonality Properties

C-G coefficients obey the simple orthogonality relations.

Proof: Since the states $|j_1 j_2 jm>$ constitute a basis, you may write

$$|j_1 j_2 jm> = \sum_{j,m} |j_1 j_2 jm> < j_1 j_2 jm | j_1 j_2 m_1 m_2>;$$

$< j_1 j_2 m'_1 m'_2 | j_1 j_2 m_1 m_2 > = \sum_{jm} [< j_1 j_2 m'_1 m'_2 | j_1 j_2 jm > < j_1 j_2 jm | j_1 j_2 m_1 m_2 >$,

where $m = m_1 + m_2$. Here left hand side vanishes unless $m'_1 = m_1$and $m'_2 = m_2$. Thus you have

$< j_1 j_2 m'_1 m'_2 | j_1 j_2 jm > < j_1 j_2 jm | j_1 j_2 m_1 m_2 > = \delta_{m_1 m'_1} \delta_{m_2 m'_2}$ (7.61)

According to recurrence relation (7.53), C-G coefficients are all real numbers if one of them is chosen real by the proper choice of phase.. Thus you may readily have

$< j_1 j_2 jm | j_1 j_2 m_1 m_2 > = < j_1 j_2 m_1 m_2 | j_1 j_2 jm >$

Then eqn.(7.61) reduces to the following orthogonality condition of C-G coefficients:

$\sum_{jm} C^{j_1,j_2,j}_{m'_1,m'_2,m} C^{j_1,j_2,j}_{m_1,m_2,m} = \delta_{m_1 m'_1} \delta_{m_2 m'_2}$ (7.62)

Similarly, from eqn. (7.49) you may readily get

$\sum_{m_1,m_2} C^{j_1,j_2,j}_{m_1,m_2,m} C^{j_1,j_2,j'}_{m_1,m_2,m'} = \delta_{jj'}\delta_{mm'}$ (7.62a)

Equations (7.62) and (7.62a) give the orthogonality properties of C-G coefficients.

Sometimes, it is convenient to use Wigner's 3-j symbols in place of C-G coefficients. These symbols are defined as

$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \frac{1}{\sqrt{2j_3+!}} C^{j_1,j_2,j_3}_{m_1,m_2,-m_3}$ (7.63)

These symbols high degree of symmetry and they are non-vanishing only when the following conditions are satisfied

$m_1 + m_2 + m_3 = 0$ (7.63a)

and$|j_1 - j_2| \leq j \leq j_1 + j_2$ (7.63b)

EXAMPLES

Ex. 7.5 Find the C-G coefficients for addition of spin-1/2 to the orbital angular momentum operator and find the corresponding eigen states.

Solution: For constructing the eigen states of

$\hat{J} = \hat{L} + \hat{S}$, (i)

we need the required C-G coefficients. In the special case for $l = 0$, i.e. for $j_1 = 0$, only possible j values are $\frac{1}{2}$ hence for the trivial case ($j_1 = 0, j = \frac{1}{2}, j_2 = \frac{1}{2}$), we have the trivial C-G coefficients

$$C^{0,\frac{1}{2},\frac{1}{2}}_{m_1,m_2,m} = \delta_{m,(m_1+m_2)}$$

For $j_1 = 1, j_2 = \frac{1}{2}$ $(i.e.\ s)$, the possible j values are given by
$1 - \frac{1}{2} \leq j \leq 1 + \frac{1}{2}$
or $j = j_1 \pm \frac{1}{2}$, since there is only one state with $m = l + \frac{1}{2}$, you may write

$$|1, \frac{1}{2}, m_1 = 1, m_2 = \frac{1}{2} > = |1, \frac{1}{2}, 1 + \frac{1}{2}, 1 + \frac{1}{2} >$$

Comparing it with eqn. (7.51), you may readily write

$C^{l,\frac{1}{2},l+\frac{1}{2}}_{\frac{1}{2},\frac{1}{2},1+\frac{1}{2}} = 1$ (ii)

From eqn. (7.53) you may readily write

$$C^{l,\frac{1}{2},l+\frac{1}{2}}_{m-\frac{1}{2},\frac{1}{2},m} = \sqrt{\frac{l+m+\frac{1}{2}}{l+m+\frac{3}{2}}}\, C^{l,\frac{1}{2},l+\frac{1}{2}}_{m+\frac{1}{2},\frac{1}{2},m+1}$$

Iterating it and using relation (ii), you may readily have

$C^{l,\frac{1}{2},l+\frac{1}{2}}_{m-\frac{1}{2},\frac{1}{2},m} = \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$ (iii)

In general you may write

$C^{l,\frac{1}{2},l+\frac{1}{2}}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \sqrt{\frac{l\pm m+\frac{1}{2}}{2l+1}}$, (iv)

and$C^{l,\frac{1}{2},l-\frac{1}{2}}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \mp\sqrt{\frac{l\mp m+\frac{1}{2}}{2l+1}}$ (v)

These are the required C-G coefficients which enables you to find the eigen states $|n,l,j,m_j>$ of the total angular momentum operator given by eqn. (i) for $s=\frac{1}{2}$:

$$\left|n,l,j,m_j> =\right|n,l,l\pm\frac{1}{2},m> = \frac{1}{\sqrt{2l+1}}\ [(l\pm m+\frac{1}{2})^{\frac{1}{2}}\,|n,l,m-\frac{1}{2},\frac{1}{2}>$$

$\mp(l\mp m+\frac{1}{2})^{\frac{1}{2}}\,|n,l,m+\frac{1}{2},-\frac{1}{2}>]$(vi)

which are required eigen states. Substituting $l=1$ in eqns. (iv) and (v), you may readily get the values of C-G coefficients for p-states of electron. Then these states may be readily obtained from eqn. (vi) by substituting$l=1$.

Ex. 7.6 Obtain the states of $\hat{S}=\hat{S}_1+\hat{S}_2$ by using the method of C-G coefficients for addition of two angular momenta.

Solution: For two spin-1/2 particles the direct product spin space,

$$|s,m_s>=|s_1,m_{s1}>|s_2,m_{s2}>,$$

of the composite system is four dimensional and particle representation-space is spanned by the following eigen vectors of S_{1z} and S_{2z} :

$\chi_+(1)\,\chi_+(2);\ \chi_-(1)\,\chi_-(2);\ \chi_+(1)\chi_-(2);\ \chi_-(1)\chi_+(2)$ (i)

which have been introduced in previous umit-6.

Setting $l = 1/2$ in eqns. (iv)and (v) of previous example EX. 7.5, you may write

$$C^{\frac{1}{2},\frac{1}{2},1}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \sqrt{\frac{1\pm m}{2}};\quad C^{\frac{1}{2},\frac{1}{2},0}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \mp\sqrt{\frac{1\mp m}{2}} \qquad \text{(ii)}$$

Using these relations you may readily get the following values of concerned non-zero C-G coefficients:

$$C^{\frac{1}{2},\frac{1}{2},1}_{\frac{1}{2},\frac{1}{2},1} = 1;\ C^{\frac{1}{2},\frac{1}{2},1}_{-\frac{1}{2},\frac{1}{2},0} = \frac{1}{\sqrt{2}};\ C^{\frac{1}{2},\frac{1}{2},1}_{\frac{1}{2},-\frac{1}{2},0} = \frac{1}{\sqrt{2}};\ C^{\frac{1}{2},\frac{1}{2},1}_{\frac{-1}{2},-\frac{1}{2},-1} = 1;\ C^{\frac{1}{2},\frac{1}{2},0}_{\frac{1}{2},-\frac{1}{2},0} = \frac{1}{\sqrt{2}};\ C^{\frac{1}{2},\frac{1}{2},0}_{\frac{-1}{2},\frac{1}{2},0} = -\frac{1}{\sqrt{2}} \ \text{(iii)}$$

Then you may readily write

$$|\tfrac{1}{2}\tfrac{1}{2}00> = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)] \quad \text{(iv)}$$

$$|\tfrac{1}{2}\tfrac{1}{2}11> = \chi_+(1)\,\chi_+(2) \ \text{(v)}$$

$$|\tfrac{1}{2}\tfrac{1}{2}10> = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2)]\text{(vi)}$$

$$|\tfrac{1}{2}\tfrac{1}{2}1-1> = \chi_-(1)\,\chi_-(2) \qquad \text{(vii)}$$

where the state given in eqn. (iv) is singlet corresponding to $s = 0$ and the three states given by eqns. (v), (vi) and (vii), corresponding to $s = 1$,are the triplets with eigen values of $\hat{S}_z$given by ħ,0 – ħ respectively.

SELF ASSESSMENT QUESTIONS

Q.7.5: Using relations (iv) and (v) of Ex. 7.5, find the values of C-G coefficients:

$$C^{1,\frac{1}{2},\frac{3}{2}}_{1,-\frac{1}{2},\frac{1}{2}};\qquad C^{1,\frac{1}{2},\frac{3}{2}}_{-1,\frac{1}{2},-\frac{1}{2}};\ C^{1,\frac{1}{2},\frac{3}{2}}_{0,\frac{1}{2},\frac{1}{2}};C^{1,\frac{1}{2},\frac{3}{2}}_{0,-\frac{1}{2},-\frac{1}{2}} \text{ and } C^{1,\frac{1}{2},\frac{3}{2}}_{-1,-\frac{1}{2},-\frac{3}{2}}$$

Q.7.6. Prove that

$$\text{(a) } C^{j,1,j}_{j,0,j} = \sqrt{\frac{j}{j+1}};\quad \text{(b)}\quad C^{j,2,j}_{j,0,j} = \sqrt{\frac{j(2j-1)}{(j+1)(2j+3)}}$$

Q.7.

7Using (iv) and (v) of Ex. 7.5, prove that

$C^{1,\frac{1}{2},\frac{1}{2}}_{1,-\frac{1}{2},\frac{1}{2}} = -C^{1,\frac{1}{2},\frac{1}{2}}_{-1,\frac{1}{2},-\frac{1}{2}} = \sqrt{\frac{2}{3}}$

Q7.8 Find the values of the following C-G Coefficients

$C^{1,\frac{1}{2},\frac{1}{2}}_{0,\frac{1}{2},\frac{1}{2}}$; $C^{1,\frac{1}{2},\frac{1}{2}}_{-1,-\frac{1}{2},\frac{1}{2}}$;$C^{1,\frac{1}{2},\frac{1}{2}}_{1,-\frac{1}{2},-\frac{1}{2}}$ and $C^{1,\frac{1}{2},\frac{1}{2}}_{0,-\frac{1}{2},-\frac{1}{2}}$

7.8 SUMMARY

In this unit you have undertaken the study of symmetries with respect to rotations about spatial coordinate axes as well as the rotations in spin-space, which implies the conservations of orbital angular momentum and intrinsic spin angular momentum. You have studied herewith the angular momentum operators (the operators corresponding to orbital angular momentum, spin angular momentum and the total angular momentum)

through the commutation rules for their components as incorporated in earlier unit (unit-6). In this unit the eigen values and eigen states of these angular momentum operators havebeen obtained and the rules of combination of two angular momenta have been derived in terms of Clebsch-Gordan Coefficients and Wigner's 3-j symbols. Starting with the commutation rules of the components of orbital angular momentum operator among themselves and also with the Hamiltonian of central force problem, you have derived the eigen values and corresponding eigen functions of the orbital angular momentum operator and learnt its invariance under the infinitesimal rotations about space-coordinates. You have also constructed the total angular momentum operator by adding the orbital angular momentum operator and spin angular momentum operator and derived its eigen values and corresponding eigen vectors. Undertaking the study of addition of two angular momentum operators in this unit, you have also derived C-G coefficients for obtaining the eigen functions of the combination of two angular momentum operators. In this unit you have also studied the symmetry properties and orthogonality of C-G coefficients.

7.9 GLOSSARY (KEY WORDS)

Symmetries and Conservation Laws; Orbital Angular Momentum Operator; Rotational Symmetries; Eigen Values ; Eigen Functions; Hilbert Space; Eigen -Basis; Spinors; Total Angular Momentum Operator; Spin Angular Momentum Operator; Orthogonality; Ortho-normality; Triangle- Rule; Addition of Angular momenta; Clebsch-Gordan Coefficients; Wigner's 3-j Symbols.

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TERMINAL QUESTIONS

A) Short Answer Type:

Q.1 Write the values of the following C-G coefficients

(a) $C^{1,\frac{1}{2},\frac{1}{2}}_{0,\frac{1}{2},-\frac{1}{2}}$; (b) $C^{1,\frac{1}{2},\frac{1}{2}}_{1,\frac{1}{2},\frac{1}{2}}$; (c) $C^{1,\frac{1}{2},\frac{1}{2}}_{1,-\frac{1}{2},-\frac{1}{2}}$ (d) $C^{1,\frac{1}{2},\frac{1}{2}}_{1,\frac{1}{2},-\frac{1}{2}}$

Q.2 Show that

$$C^{1,\frac{1}{2},\frac{3}{2}}_{1,-\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{0,-\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{0,\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{-1,-\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{-1,\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{-1,-\frac{1}{2},\frac{3}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{1,\frac{1}{2},\frac{1}{2}} = 0$$

Q.3 Find values of $C^{1,\frac{1}{2},\frac{3}{2}}_{0,-\frac{1}{2},\frac{1}{2}}$; $C^{1,\frac{1}{2},\frac{3}{2}}_{-1,\frac{1}{2},\frac{1}{2}}$; $C^{1,\frac{1}{2},\frac{3}{2}}_{-1,-\frac{1}{2},\frac{1}{2}}$ and $C^{1,\frac{1}{2},\frac{3}{2}}_{-1,\frac{1}{2},-\frac{3}{2}}$

Q.4 Show that $C^{1,\frac{1}{2},\frac{3}{2}}_{1,-\frac{1}{2},\frac{1}{2}} = C^{1,\frac{1}{2},\frac{3}{2}}_{-1,\frac{1}{2},-\frac{1}{2}} = -C^{1,\frac{1}{2},\frac{1}{2}}_{0,\frac{1}{2},\frac{1}{2}} = {}^{1}/_{\sqrt{3}}$

Q.5 Show that in a state $\emptyset$ with well-defined eigenvalues of $\hat{J}_z$ the average values of $\hat{J}_x$ and $\hat{J}_y$ are zero

Q.6 Write the matrices representing $\hat{J}_\pm$ for the quantum number $j = 1$

Q. 7 Represent the operators $\hat{J}_x$ and $\hat{J}_y$ in the basis corresponding to $j = 1$

Q.8Show that every matrix representative of a component of $\boldsymbol{J}$ which satisfies

$\boldsymbol{J} \times \boldsymbol{J} = i\,\hbar\,\boldsymbol{J}$has zero trace**.**

Q.9 Show that the vector $|j_1 m_1 > |j_2 m_2 >$ is an eigen vector of $\hat{J}^2$ only for particular values of m_1 and m_2.

Q.10 Show that magnetic quantum number cannot exceed the orbital quantum number.

B) Long Answer Type

Q. 1Obtain the matrix elements of the matrices representing the operators $\hat{J}_+ \hat{J}_-, \hat{J}_x\ and\ \hat{J}_y$ in space spanned by the simultaneous egien vectors $|jm_j >$ of the operators $\hat{J}^2$and $\hat{J}_z$.

Q.2 If $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ are operators representing the components of orbital angular momentum, show that if $\emptyset_{l,m_l}$ is an eigen function of $\hat{L}_z$ corresponding to eigen value $m_l\,\hbar$, then $\hat{L}_\pm\, \emptyset_{l,m_l} = \widehat{(L_x} \pm i\hat{L}_y)\emptyset_{l,m_l}$ are also the eigen functions of $\hat{L}_z$ with the corresponding eigen values $(m_l \pm 1)\,\hbar$ respectively.

Q.3 Deduce the following commutation rules for angular momentum operators:

(i) $[\hat{J}^2, \hat{J}_\pm] = 0$ (ii) $[\hat{J}_z, \hat{J}_\pm] = \pm\hat{J}_\pm$ (iii) $[\hat{J}_+ \hat{J}_-] = 2\hbar\hat{J}_z$

Show that $\hat{J}_\pm|j, m_j >= [j(j+1) - m_j(m_j \pm 1)]^{\frac{1}{2}}\hbar|j, m_j \pm 1 >$

where$|j, m_j >$ is an eigen function of the operator $\hat{J}_z$ with the corresponding eigen value $m_j\hbar$.

Q.4 Determine the eigen function of angular momentum operator obtained by adding two orbital angular momentaL_1 and L_2.

Q.5 Find the eigen functions for addition of two angular momenta to give the zero total angular momentum

Q.6 Find the transformation of spinor under rotation about an axis $\vec{\emptyset}$ which rotates the unit vector $\hat{m}$into unit vector $\hat{n}$ such that

$$\hat{n} = \hat{m} + \delta\vec{\emptyset} \times \hat{m}$$

Q.7 Orbital angular momentum operator $\hat{L}$ and spin angular momentum $\hat{S}$ commute. Show that $\hat{J} = \hat{L} + \hat{S}$ commutes with $\hat{L}.\hat{S}$ and $\hat{L}^2$

Q.8. Find the matrices representatives of the operators $\hat{J}^2$;$\hat{J}_z$; $\hat{J}_+$ and $\hat{J}_-$in

the basis corresponding to $j = \frac{3}{2}$

Q.9 In the previous problem, find the matrices representing operators $\hat{J}_x$ *and* $\hat{J}_y$.

Q.10Show that the operator $\hat{\pi} = \hat{\sigma}\,.\hat{p}$ anti-commutes with the operator $\hat{M} = \hat{\sigma}.\hat{L} + \hbar\hat{I}$

Numerical Type

Q.1 Find the inverse of matrices representing the operators $\hat{J}_x, \hat{J}_y, \hat{J}_z$ and $\hat{J}^2$ in the eigen basis corresponding to j=1.

Q.2 If the operators associated to components of orbital angular momentum satisfy the commutation relation $[\hat{L}_x, \hat{L}_y] = i\,\hbar\hat{L}_z$, express these operators in polar coordinates and show that the eigen values of the operator $\hat{L}_z$ are integral multiples of ħ.

Q.3. In the previous problem obtain the polar forms of $\hat{L}_+$ and $\hat{L}_-$

Q.4 Prove that $[\hat{J}_z^2, \hat{J}_x^2] = [\hat{J}_y^2, \hat{J}_z^2] = [\hat{J}_x^2, \hat{J}_y^2]$ and show that all these commutators are zero in the eigen states corresponding to j=0,1,or ½.

Q.5Show that

(a) An operator which commutes with $\hat{J}_x$ *and* $\hat{J}_y$, commutes with $\hat{J}_z$ also.

(b) Angular momentum of a particle is 3/2 means the length of angular momentum vector is $\sqrt{\frac{15}{4}}\hbar$

(c) $tr\,\hat{J}_k = 0$ for k=1,2,3

Q. 6 Show that

(a) $\hat{L}_+ Y_l^{m_l}(\theta,\varphi) = \hbar\{(l-m_l)(l+m_l+1)\}^2 Y_l^{m_l+1}(\theta,\varphi)$

(b) $\hat{L}_- Y_l^{m_l}(\theta,\varphi) = \hbar\{(l+m_l)(l-m_l+1)\}^2 Y_l^{m_l-1}(\theta,\varphi)$

where$Y_l^{m_l}(\theta,\varphi)$ are spherical harmonics and $\hat{L}_\pm = \hat{L}_x \pm \hat{L}_y$

Q.7 If eigen functions of the orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ corresponding to quantum numbers l= 1 and $m_l = 1,0,-1$ are $\emptyset_1, \emptyset_0$ and $\emptyset_{-1}$ respectively then show that eigen functions of $\hat{L}_x$ corresponding to eigen values

$\hbar, 0, -\hbar$ are $\frac{1}{2}(\emptyset_1 + \sqrt{2}\emptyset_0 + \emptyset_{-1})$;$\frac{1}{2}(\emptyset_1 - \emptyset_{-1})$ and $\frac{1}{2}(\emptyset_1 - \sqrt{2}\emptyset_0 + \emptyset_{-1})$ respectively.

Q.8. Calculate from the first principle the C-G coefficients for $j_1 = 1$ and $j_2 = \frac{1}{2}$ and then write the wave functions for the p-states of an electron ($l = 1, s = 1/2$) for$j = \frac{3}{2}$ ($m_j = \frac{3}{2}, \frac{1}{2}. -\frac{1}{2}, -\frac{3}{2}$) and for $j = \frac{1}{2}$ ($m_j = \frac{1}{2}. -\frac{1}{2}$)

Q.9 Show that:

(a) $\hat{J}_\pm \hat{J}_\mp = \hat{J}^2 - \hat{J}_z(\hat{J}_z \mp \hbar\hat{I})$

(b) $[\hat{J}_z, \hat{J}_\pm^n] = \pm n\,\hbar\,\hat{J}_\pm^n$

(c) $\hat{J}^2 = \frac{1}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+) + \hat{J}_z^2$

Q.10 Show that the operator$\hat{L}.\hat{S}$ has the eigen values 3/2 and -1

in the p-states of an electron and verify that:

$(\hat{L}.\hat{S})|\frac{3}{2}, m > = \frac{1}{2}\,|\frac{3}{2}, m >and(\hat{L}.\hat{S})|\frac{1}{2}, m > = -|\frac{1}{2}, m >$

Q.11 Show that the following expression gives the effect of spin operator on a vector wave function of a particle of spin-1/2:

$$\Psi_{n,l,l\pm\frac{1}{2},m}(r,\theta,\emptyset) = \frac{R_{nl}(r)}{\sqrt{2l+1}}\begin{pmatrix}\sqrt{\left(l \pm m + \frac{1}{2}\right)}\, Y_l^{m-\frac{1}{2}}(\theta,\emptyset) \\ \sqrt{\left(l \mp m + \frac{1}{2}\right)}\, Y_l^{m+\frac{1}{2}}(\theta,\emptyset)\end{pmatrix}$$

where$R_{nl}(r)$ in the radial part and n is the principal quantum number.

ANSWERS

(a) SELF ASSESSMENT QUESTIONS

Q7.2: 0; $\frac{1}{2}\{l(l+1) - m_l^2\}$ Q.7.3: $|\hat{n}\uparrow> = e^{-\frac{i}{\hbar}\hat{J}\delta\emptyset}\,|\hat{m}\uparrow>$;$|\hat{n}\downarrow> = e^{-\frac{i}{\hbar}\hat{J}\delta\emptyset}\,|\hat{m}\downarrow>$

Q 7.5: $\frac{1}{\sqrt{3}}$; $\frac{1}{\sqrt{3}}$; $\frac{2}{\sqrt{3}}$; $\frac{2}{\sqrt{3}}$ and 1 Q 7.8: $-\frac{1}{\sqrt{3}}$; 0; 0;$\frac{1}{\sqrt{3}}$

(b) TERMINAL QUESTIONS

A) Short Answer Type

Q.1: All zeros; Q.3: All zeros;

Q. 6: $\hat{J}_+ = \hbar\begin{pmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{pmatrix}$;$\hat{J}_- = \hbar\begin{pmatrix}0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{pmatrix}$

Q. 7: $\hat{J}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}$;$\hat{J}_y = \frac{i\hbar}{\sqrt{2}}\begin{pmatrix}0 & -1 & 0\\ 1 & 0 & -1\\ 0 & 1 & 0\end{pmatrix}$

B) Long Answer Type

Q.1:$(\hat{J}_+)_{m'_j m_j} = \{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}}\hbar\delta_{m'_j m_j+1}$;

$$(\hat{J}_-)_{m'_j m_j} = \{(j+m_j)(j-m_j+1)\}^{\frac{1}{2}}\,\hbar\delta_{m'_j m_j-1}$$

$$(\hat{J}_x)_{m'_j m_j} = \frac{1}{2}\{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}}\hbar\delta_{m'_j m_j+1}$$

$$+\frac{1}{2}\{(j+m_j)(j-m_j+1)\}^{\frac{1}{2}}\,\hbar\delta_{m'_j m_j-1}$$

$$(\hat{J}_y)_{m'_j m_j} = \frac{-i}{2}\{(j-m_j)(j+m_j+1)\}^{\frac{1}{2}}\hbar\delta_{m'_j m_j+1}$$

$$+\frac{i}{2}\{(j+m_j)(j-m_j+1)\}^{\frac{1}{2}}\hbar\delta_{m'_j m_j-1}$$

Q.4: $|jm> = \sum_{m_1 m_2} C^{l_1,l_2,j}_{m_1,m_2,m}|l_1 m_1>|l_2 m_2>$

Q.5: $\frac{1}{\sqrt{2j_1+1}}\sum_{m_1}(-1)^{j_1-m}\psi^{(1)}_{j_1,m_1}\,\psi^{(2)}_{j_1,-m_1}$

Q.6: $|\hat{n}\uparrow> = e^{-\frac{i}{\hbar}\hat{J}\delta\emptyset}\,|\widehat{m}\uparrow>$; $|\hat{n}\downarrow> = e^{-\frac{i}{\hbar}\hat{J}\delta\emptyset}\,|\widehat{m}\downarrow>$

Q.8: $\hat{J}^2 = \frac{15}{4}\hbar^2\hat{I}$; $\hat{J}_z = \frac{3}{2}\hbar\hat{I}$, where $\hat{I}$ is unit matrix of order 4X4

$$\hat{J}_+ = \hbar\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix};\ \hat{J}_- = \hbar\begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

Q.9: $$\hat{J}_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix};\hat{J}_y = \frac{1}{2i}\hbar\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

C) Numerical Type:

Q.1: Inverses of $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$; $(\hat{J}^2)^{-1} = \frac{1}{2\hbar^2}\hat{I}$, where $\hat{I}$ is 3X3 unit matrix

Q.2 $\hat{L}_x = i\,\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\emptyset\frac{\partial}{\partial\emptyset})$; $\hat{L}_y = i\,\hbar(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\emptyset\frac{\partial}{\partial\emptyset})$;

and $\hat{L}_z = -i\hbar\frac{\partial}{\partial\emptyset}$

Q.3: $\hat{L}_\pm = \hbar e^{\pm i\emptyset}(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\emptyset})$

Q.8: For j=3/2, $C^{1,\frac{1}{2},\frac{3}{2}}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \sqrt{\frac{3\pm 2m}{6}}$,where m=3/2,1/2,-1/2,-3/2;

for j=1/2, $C^{1,\frac{1}{2},\frac{1}{2}}_{m\mp\frac{1}{2},\pm\frac{1}{2},m} = \mp\sqrt{\frac{3\mp 2m}{6}}$, where m=1/2, -1/2.

UNIT 8 Approximation methods

Structure

8.1 Introduction

The basic idea of perturbation is taken from classical mechanics; in quantum mechanics as in classical mechanics exactly solvable problems are rare and in one must frequently resort to approximation. Various methods of approximate solution of the wave equation have been devised, leading to the more or less accurate approximate evaluation of energy values and wave function. These methods the first and in many respect the most interesting is simple wave mechanical perturbation theory developed bySchroedinger in 1926.

Perturbation theories are of two types:

(i) Time independent or stationary perturbation theory
(ii) Time dependent perturbation theory

These theories can be used for solving some important problems.

8.2 Stationary or Time independent Perturbation Theory

The stationary or time independent theory helps in finding the change in the energy levels and eigen functions of a system caused by a small disturbance. In such cases, the Hamiltonian can be broken up into two parts,one of which is large and represent a system for which the schroedinger equation can be solved exactly, while other part is small and can be treated as perturbation term.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly, however, the arrangement of energy levels remains the same. Mathematically, it can be said that the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may by constant or it may by constant or it may be a function of both the space and momentum co-ordinates.

In other words, the Hamiltonian H in the Schroedinger wave equationcan be written as sum of two parts; one of these parts $H^{(0)}$corresponds to unperturbed Hamiltonian and the other part $H^{(1)}$corresponding to perturbation effect. It means the perturbed Hamiltonian can be represented as

$$H = H^{(0)} + H^{(1)} \qquad (1)$$

In the perturbed state the schroedinger wave equation can be written as

$$H\psi = E\psi \qquad (2)$$

Where Hamiltonian H represents the operator

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right) \quad (3)$$

In the equation (2) E is the eigen value and ψ is eigen function of the operator.

Let $\psi_n^{(0)}$ and $E_n^{(0)}$ are the orthonormal eigen function and eigen values of unperturbed Hamiltonian $H^{(0}$respectively i.e.

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} (4)$$

8.2 .1 Perturbation theory for Non-degenerate Case

Consider non degenerate system that is the system for which there is one eigen function corresponding to each energy level or eigen value. In case there are two or more eigen functions corresponding to one energy level the system is regarded as degenerate system

The Schroedinger wave equation for a perturbed state can be represented as follows:

$$H\psi = E\psi \qquad (1)$$

Where H Hamiltonian the operator is given by

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right) \qquad (2)$$

In the stationary state of the system , the Hamiltonian H does not depend upon time and it is possible to expand H in terms of some parameter λ , given the expression:

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} (3)$$

Where the energy associated with $H^{(0)}$ is large compared with that associated with $H^{(1)}$.

Consider the eigenvalues and eigenfunctions of the unperturbed problem be $E_1^{(0)}$,$E_2^{(0)}$,……,$E_n^{(0)}$,…,and $\psi_1^{(0)}$, $\psi_2^{(0)}$…,.$\psi_n^{(0)}$,…….respected.Its means

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \text{where } n = 1,2,3,\ldots,n \qquad (4)$$

The equation represent (4) is regarded as the wave equation for the unperturbed system and $E_n^{(0)}$ represented the energy of the n^th^ level of the system.

The eigenfunctionψ_n for the perturbed system must satisfy the equation

$$H\psi_n = E_n\psi_n \qquad (5)$$

Now let us consider the effect of perturbation. The application of perturbation does not cause large changes; hence the energy values and wave function for the perturbed system will have very small difference from the unperturbed system. Now expand the energy E and the wave function ψ for perturbed system in terms of λ as given below :

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\ldots\ldots\ldots \qquad (6)$$

$\psi_{n=}\,\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots\ldots\ldots\ldots\ldots\ldots$ (7)

Where $E_n^{(1)}, E_n^{(2)}, \ldots\ldots$ and $\psi_n^{(1)}, \psi_n^{(2)}, \ldots\ldots$ are quantities to be determined.

Now substituting (6) and (7) in equation (5), we get

$(H^{(0)} + \lambda H^{(1)})\ (\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots)$ (8)

Or $H^{(0)}\psi_n^{(0)} + \lambda(H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)}) + \lambda^2(H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)}) + \ldots\ldots = E_n^{(0)}\psi_n^{(0)} + \lambda(E_n^{(0)} + E_n^{(1)}\psi_n^{(0)}) + \lambda^2(E_n^{(0)}\psi_n^{(2)} + E_n^{(2)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$ (9)

Equation (9) should be satisfied for all values of λ,the coefficient of the same power of λ on both sides of this equation must be equal. Its means

$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ (10)

$H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$ (11)

$(H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(2)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$ (12)

This equation (10),(11) and (12) represent unperturbed, first order perturbation and second order perturbation equation respectively.

8.3 First order perturbation

8.3.1 Evaluation of first order energy E_n^1 : The first order perturbation equation can be expressed as follows:

$$H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$$

To solve above s equation can be use the expansion theorem. The unknown function $\psi_n^{(1)}$ can be expanded in terms of the known functions

$\psi_1^{(0)}, \psi_2^{(0)}, \psi_3^{(0)}, \ldots\ldots \psi_m^{(0)}, \ldots\ldots$ as

$\psi_n^{(1)} = \sum_{m=0}^{\infty} C_m\psi_m^{(0)}$ (13)

Now solve equation (11) to evaluate the perturbation of the first order.

On substituting equation (13) in equation (11), we get

$\sum_m C_m H^{(0)}\psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = \sum_m C_m E_n^{(0)}\psi_m^{(0)} + E_n^{(1)}\psi_n^{(0)}$ (14)

Now $H^{(0)}\psi_m^{(0)} = E_m^{(1)}\psi_m^{(0)}$

$\sum_m C_m E_m^{(0)}\psi_m^{(0)} - \sum_m C_m E_n^{(0)}\psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)}$

Or $\quad \sum_m^m C_m\,[\,E_m^{(0)} - E_n^{(0)}]\,\psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)}$ (15)

On multiplying (15) by $\psi_n^{(0)}$ and integrating over the space variable, we get

$$\int \sum_m \psi_n^{(0)*}\, C_m[E_m^{(0)} - E_n^{(0)}]\,\psi_m^{(0)} d\tau + \int \psi_n^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau = \int E_n^{(1)}\psi_n^{(0)*}\,\psi_n^{(0)} d\tau \quad (16)$$

The function $\psi_n^{(0)}$from a complete orthogonal set if they have been normalized

$$\int \psi_1^{(0)*}\psi_j^{(0)} d\tau = 0, if\ i \neq j \quad (17)$$

$=1$,if $i = j$

Using equation (17) in equation (16), we get

$0 + \int \psi_n^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau = E_n^{(1)}$

$$E_n^{(1)} = \int \psi_n^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau \quad (18)$$

The first order perturbation of the energy eigenvalue is given by the equation (18).

8.3.2 Evaluation of first order wave function $\psi_n^{(1)}$.

On multiplying equation (15) by $\psi_m^{(0)*}$ and integrating over all space

$$\int \sum_m C_m[E_m^{(0)} - E_n^{(0)}]\psi_m^{(0)*}\psi_m^{(0)} d\tau + \int \psi_m^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau = \int E_n^{(1)}\psi_m^{(0)*}\,\psi_n^{(0)}\, d\tau \quad (19)$$

Using condition (17), of the orthonormal set we get

$$C_m[E_m^{(0)} - E_n^{(0)}] + \int \psi_m^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau = 0$$

Or $\quad C_m = \frac{\int \psi_m^{(0)*} H^{(1)}\psi_n^{(0)} d\tau}{[E_m^{(0)} - E_n^{(0)}]}$, m$\neq n$ (20)

It means the first order energy and wave functions by the following equation :

$$E_{n=}E_n^{(0)} + \lambda \int \psi_m^{(0)*}\, H^{(1)}\psi_n^{(0)} d\tau \quad (21)$$

And $\quad \psi_{n=}\psi_n^{(0)}$- λ$\sum_{m=0}^{\infty\prime} \frac{\int \psi_m^{(0)*} H^{(1)}\psi_n^{(0)} d\tau}{[E_m^{(0)} - E_n^{(0)}]}$ (22)

$\sum{}'$indicates the omission of the term having m = n

Q1. For the harmonic oscillator, $V = \frac{1}{2}kx^2$, the energy eigenvalues are $E_n = \left[n + \frac{1}{2}\right] h\omega$. For a small charge in k, the spring constant εk, find the first order perturbation in energy.

Sol. $V = V^0 + V^1$

$V^0 = \frac{1}{2}kx^2,$

$V = \frac{1}{2}[k + \varepsilon k]x^2$

So, $V' = \frac{1}{2}kx^2$

If $|n>$ are the eigenkets of the unperturbed Hamiltonian

$$H|n=E_n|n >$$

Where $E_n = \left[n + \frac{1}{2}\right] h\omega.$

$$E_n^1 =< |H'|n >$$

$$=\frac{1}{2}\ \varepsilon k < n|x^2|n >$$

Using creation and annihilation operator, x may be written as

$$\mathrm{x} = \sqrt{\frac{\hbar}{2m\omega}(\mathrm{a} + \mathrm{a}^+)}$$

$$x^2 = \frac{\hbar}{2m\omega}(a^+ + a^+a + aa^+ + a^{+^2})$$

When the expectation with respect to $|n>$,only a^+a and aa^+ will be contribute.

$$< n|x^2|n >= \frac{\hbar}{2m\omega}[< n|a^+a|]n > +< n|aa^+|a^{+^2}]$$

$$=\frac{\hbar}{2m\omega}[\sqrt{n} < n|a^+|n - 1 > +\sqrt{n+1}<\left|\sqrt{n+1}\right| < n|a|n + 1 >]$$

$$=\frac{\hbar}{2m\omega}[\sqrt{n}\sqrt{n} + \sqrt{n+1}\sqrt{n+1}]$$

$$=\frac{\hbar}{2m\omega}[2n + 1]$$

Therefore,$E_n^1 = \frac{\varepsilon k}{2}\frac{\hbar}{m\omega}\left[n+\frac{1}{2}\right]$

$=\frac{\hbar\omega\varepsilon}{2}\left[n+\frac{1}{2}\right]$

In fact, the exact energy eigenvalue would be

$$E_n = \frac{\hbar\omega'}{}\left[n+\frac{1}{2}\right]$$

$$\omega' = \sqrt{\frac{k(1+\varepsilon)}{m}} = \quad (1+\varepsilon)^{1/2}$$

$$=\omega(1+\frac{\varepsilon}{2})=\omega+\frac{\varepsilon}{2}$$

$E_n = \omega\hbar\left[n+\frac{1}{2}\right]+\frac{\hbar\varepsilon\omega}{2}\left[n+\frac{1}{2}\right]+$……….

Which agree up to first order.

Self Assessment Question

Q2. Consider the isotopic three-dimensional harmonic oscillator. Discuss the effect of the perturbation.

$H' = \lambda x^2 yz$on the ground state.

8.4 Second order perturbation

8.4.1 Evaluation of second order energy E_n^2 :

Let us consider the unknown function $\psi_n^{(2)}$ can be expanded in terms of the known function $\psi_m^{(0)}$ as given by the following expression:

$$\psi_n^{(2)} = \sum_m g_m \psi_m^{(0)} \tag{23}$$

On substituting equations (23) and (13) in equation (12) , we get

$$\sum_m g_m H^{(0)}\psi_m^{(0)} + \sum_m C_m H^{(1)}\psi_m^{(0)} = \sum_m g_m E_n^{(0)}\psi_m^{(0)} + \sum_m C_m E_n^{(1)}\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)} \tag{24}$$

Or

$$\sum_m g_m[E_m^{(0)} - E_n^{(0)}] \ \ \psi_m^{(0)} = \sum_m C_m \, [E_n^{(1)} - H^{(1)}]\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)} \tag{25}$$

On multiplying equation (25) by $\psi_n^{(0)*}$ and integrating over the space variable, we get

$$\int \sum_m g_m[E_m^{(0)} - E_n^{(0)}] \ \ \psi_n^{(0)*}\psi_m^{(0)} \, d\tau =$$
$$\int \sum_m \psi_n^{(0)*} C_m \, [E_n^{(1)} - H^{(1)}] \ X \, \psi_m^{(0)} \, d\tau + \int E_n^{(2)}\psi_n^{(0)*}\psi_n^{(0)} \, d\tau$$
(26)

Using orthonormal condition from equation (17) we get

$$0 = -\sum_m C_m \ \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)} \ d\tau + E_n^{(2)}$$

$$\text{Or } E_n^{(2)} = \sum_m C_m \ \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)} \ \ d\tau \tag{27}$$

Substituting the value of C_m , we get

$$E_n^{(2)} = -\sum{}' \frac{\int \psi_m^{(0)*} \, H^{(1)}\psi_m^{(0)} d\tau \ \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)}}{[E_m^{(0)} - E_n^{(0)}]} \ d\tau$$

Or

$$E_n^{(2)} = \sum_m{}' \frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} d\tau \ \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)}}{[E_n^{(0)} - E_m^{(0)}]} d\tau \tag{28}$$

8.4.2 Evaluation of second order wave function $\psi_n^{(2)}$:

On multiplying equation (25) by $\psi_m^{(0)*}$ (m$\neq n$) and integrating, we get

$$\sum_m g_m \int [E_m^{(0)} - E_n^{(0)}] \psi_m^{(0)*}\psi_m^{(0)} \, d\tau = \sum_m C_m \int \psi_m^{(0)*} [E_n^{(0)} - H^{(1)}]\psi_m^{(0)} \, d\tau + \int E_n^{(2)} \psi_m^{(0)*}\psi_n^{(0)} \, d\tau \tag{29}$$

$$\text{Or } g_m \int [E_m^{(0)} - E_n^{(0)}] = \sum_m C_m \, (E_n^{(1)} - \int \psi_m^{(0)*} \, H^1 \psi_m^{(0)} \,) \ d\tau$$

$$g_m = \sum_m \ \frac{C_m}{[E_m^{(0)} - E_n^{(0)}]} (E_n^{(1)} - \int \psi_m^{(0)*} \, H^1 \psi_m^{(0)} \,) \ \ d\tau \tag{30}$$

Now we can calculate the second order perturbed wave function if the value of g_m from equation (30) in equation (23).

Q3. Find the second order correction to the energy due to a perturbation $\boldsymbol{H' = \alpha\delta(x - \frac{a}{2})}$ at the centre of a infinite square well.

Sol. The unperturbed energy eigenvalues are

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

And Eigen functions are $\psi_n^0 = \sqrt{\frac{2}{a}} sin\frac{n\pi x}{a}$

The second order correction to the energy is

$$E_n^2 = \sum_k \frac{|<\psi_k^0|H'|\psi_n^0>|^2}{E_n^o - E_k^0}$$

$$= \frac{4}{a^2}\int \frac{\left|sin\frac{k\pi x}{a}\alpha\delta(x - \frac{a}{2})sin\frac{n\pi x}{a}dx\right|}{\frac{\pi^2\hbar^2}{2ma^2}(n2 \quad - k^2)}$$

$$= \frac{4}{a^2}\frac{2m^2a^2\alpha^2}{\pi^2\hbar^2}\sum\nolimits_k \frac{sin^2\frac{k\pi}{2}sin^2\frac{n\pi}{2}}{n^2-k^2}$$

$$= \frac{8}{a^2}\frac{m^2a^2\alpha^2}{\pi^2\hbar^2}sin\frac{n\pi}{2}\left(\frac{1}{n^2-1} + \frac{1}{n^2-9} + \frac{1}{n^2-25} + \cdots \ldots.\right)$$

8.5 PERTURBED HARMONIC OSCILLATOR

The perturbation energy term is proportional to x. Let the Hamiltonian of one-dimensional harmonic oscillator be given as

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 + \frac{1}{2}bx \qquad \ldots\ldots.. (1)$$

$$H = H_0 + H'$$

Where H_0 is unperturbed Hamiltonian and H' is first order perturbation, such that

$$H_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \text{and} H' = \frac{1}{2}bx \qquad \ldots\ldots.. (2)$$

i.e. unperturbed equation for H_0 can be solved very easily by Schrodinger method.

$$H_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

The unperturbed Schrödinger equation is

$$H_0\psi_n = E_n\psi_n$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2}+\frac{1}{2}kx^2\psi_n = E_n\psi_n$$

$\frac{\partial^2\psi_n}{\partial x^2}+\frac{2m}{\hbar^2}\left(E_n-\frac{1}{2}kx^2\right)\psi_n = 0$ …….. (3)

This is simple harmonic oscillator equation having the energy values

$E_n = \left(n+\frac{1}{2}\right)\hbar\omega, \quad n = 0,1,2 \dots\dots$ …….. (4)

Where ω is the angular frequency of oscillations given by

$$\omega = \sqrt{\frac{k}{m}}$$

Equation (4) gives eigen values of unperturbed harmonic oscillator

$E_0 = \frac{1}{2}\hbar\omega$(for n= 0)

$E_1 = \frac{3}{2}\hbar\omega$(for n= 1)

…………

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

Ist order perturbation energy

$$E' = < m|H'|m >$$

$$E' = < \psi_0(x)|H'|\psi_0(x) >$$

Where $\psi_0(x) = N_0 e^{-\alpha^2x^2/2}$

Where $N_0 = \sqrt{\frac{\alpha}{\sqrt{x}}}$ and $\alpha^4 = \frac{mk}{\hbar^2}$

But we have $H' = \frac{1}{2}bx$

$$E' = < \psi_0|H'|\psi_0 > = < \psi_0\left|\frac{1}{2}bx\right|\psi_0 >$$

$$= \int N_0 e^{-\alpha^2x^2/2}.\frac{1}{2}bxN_0e^{-\alpha^2x^2/2}\,dx$$

$$= \frac{1}{2}b\,N_0^2\int e^{-\alpha^2x^2}xdx = 0$$

Since $$\int e^{-x^2} x dx = 0$$

We should remember that if function H' in E' is odd like x, x^3, x^5,….., then E' will be zero definitely. *Hence Ist order energy E' is zero.*

8.6 ZEEMAN EFFECT (WITHOUT ELECTRON SPIN)

The change in the energy levels of an atom when it is placed in uniform external magnetic field is called the Zeeman Effect.

Let us consider that the field strength B is applied on a hydrogen atom, so that an electron of reduced mass μ carrying the charge '-e' is moving in a field whose vector potential is **A.** The magnetic induction **B** in terms of vector potential **A** can be written as

$$\mathbf{B} = \text{curl } \mathbf{A} = \nabla \times \mathbf{A}$$

Then the constant magnetic potential **A** in terms of magnetic induction **B** can be expressed as

$\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r})$------------- (1)

[Since $\mathbf{B} \times \mathbf{r} = \boldsymbol{\nabla} \times \mathbf{A} \times \mathbf{r} (\mathbf{for B} = \nabla \times \mathbf{A})$

$$= (\boldsymbol{\nabla}.\boldsymbol{r})\boldsymbol{A} - (\boldsymbol{A}.\boldsymbol{\nabla})\boldsymbol{r} = \mathbf{3}\boldsymbol{A} - \boldsymbol{A} = \mathbf{2}\boldsymbol{A}$$

Therefore, $\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r})$

The classical Hamiltonian of a particle of mass μ carrying charge –e and moving in field of vector potential **A** may be expressed as

$$H(p, r) = \frac{1}{2\mu}(p + eA)^2 + V(r)$$

$$= \frac{p^2}{2\mu} + V(\boldsymbol{r}) + \frac{e}{2\mu}(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p}) + \frac{e^2}{2\mu}\boldsymbol{A}^2$$

$$= H^0 + H' + H''$$

Where $H^0 = \frac{p^2}{2\mu} + V(\boldsymbol{r})$ is the unperturbed Hamiltonian

$$H' = \frac{e}{2\mu}(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p})$$

$$H'' = \frac{e^2}{2\mu}\boldsymbol{A}^2$$

Ist order Zeeman effect:

For weak fields the second order perturbation term H'' containing $\boldsymbol{A}^2$ may be neglected and hence the perturbed Hamiltonian takes the form

$$\mathrm{H}= H^0 + H' = \frac{\boldsymbol{p}^2}{2\mu} + V(\boldsymbol{r}) + \frac{e}{2\mu}(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p}) \qquad \text{------------- (2)}$$

Writing $\boldsymbol{p} \rightarrow \widehat{\boldsymbol{p}} = \frac{\hbar}{i}\nabla$

And keeping in mind the vector identity

div (**A** ψ) = ψ div **A** + **A.** ∇ψ

$$\nabla.(\mathbf{A}\,\psi) = (\nabla.\mathbf{A})\psi + \mathbf{A}.\nabla\psi$$

We note $(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p})\psi = \left(\frac{\hbar}{i}\nabla.\boldsymbol{A} + \boldsymbol{A}.\frac{\hbar}{i}\nabla\right)\psi$

$$= \frac{\hbar}{i}\nabla.(\boldsymbol{A}\psi) + \frac{\hbar}{i}\mathbf{A}.\nabla\psi$$

$$= \frac{\hbar}{i}\{(\nabla.\boldsymbol{A})\psi + \mathbf{A}.\nabla\psi\} + \frac{\hbar}{i}\mathbf{A}.\nabla\psi$$

$$= \frac{\hbar}{i}[(\nabla.\boldsymbol{A})\psi + 2\mathbf{A}.\nabla\psi] \qquad \text{----------- (3)}$$

Also $\nabla.A = \nabla.\left[\frac{1}{2}(B \times r)\right] = \frac{1}{2}\nabla.(B \times r)$

Also using the identity vector identity

div (a× b) = b. curl a- a. curl b we get

$$\nabla.A = \frac{1}{2}[r \times \nabla \times B - B.\nabla \times r] = 0$$

Since $\nabla \times B = 0$ and $\nabla \times r = 0$ --------- (4a)

And $A.\nabla\psi = \frac{1}{2}(B \times r).\nabla\psi = \frac{1}{2}\,\mathrm{B}.(\mathrm{r} \times \nabla)\psi$ --------- (4b)

Using (4a) and (4b) equation (3) gives

$$(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p})\psi = \frac{\hbar}{i}[0 + 2.\frac{1}{2}\,\mathrm{B}.(\mathrm{r} \times \nabla)\psi]$$

$$= B.\left(r \times \frac{\hbar}{i}\nabla\right)\psi = B.(r \times p)\psi$$

$= \mathrm{B.L}\,\psi$

$(\boldsymbol{p}.\boldsymbol{A} + \boldsymbol{A}.\boldsymbol{p}) = \mathrm{B.L}$

The energy eigen function of the unperturbed H-atom are usually chosen to be eigen state of $L_z$with eigen values $m\hbar, m$being magnetic quantum number. It is customary for convenience to chose magnetic field along Z-axis then B.L = B L_z

First order energy correction

$$E' =< n|H'|n >=< n\left|\frac{e}{2\mu}\, BL_z\right|n >$$

$= \frac{e}{2\mu}\, Bm\hbar < n|n >= m\frac{e\hbar}{2\mu}\, B$ --------- (5)

can take for (2*l*+1) values since m varies from - *l* to +*l*

The selection rule permits only those transitions in which magnetic quantum number m changes by 0 or ±1. This selection rule coupled with expression (5) is sufficient to explain the spectrum of normal Zeeman effect. As an example we consider the transitions between two states with *l*=2 and *l*=1, (i.e. between *d* and *p*-states) shown in fig 1.

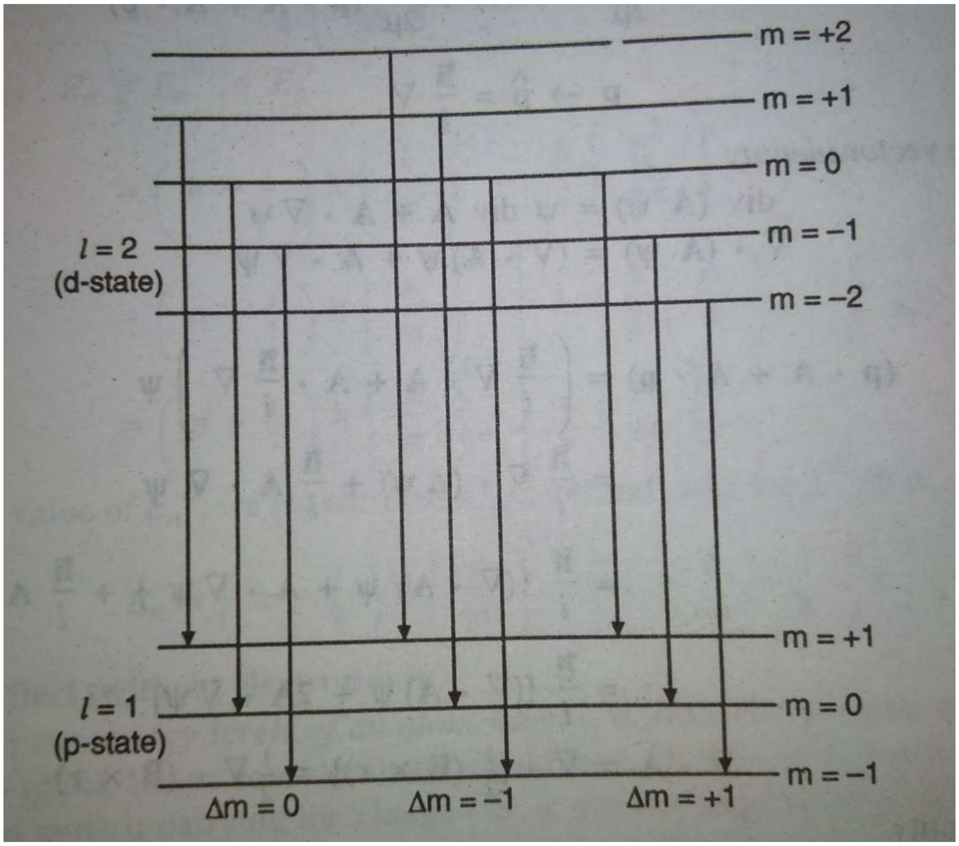


Fig. 1 The three lines observed are a superposition of several transitions.

The Second Order Zeeman Effect: If the magnetic field applied is large, then the term $\frac{e^2A^2}{2\mu}$ cannot be neglected.

If we consider again the field **B** along Z-axis, then according to expression A=$\frac{1}{2}(B \times r)$, the components of **A** are given as

$$A_x = -\frac{1}{2}\, B.y\,, A_y = -\frac{1}{2}\, B.x \; and \; A_z = 0$$

So that the *second order perturbation term in Hamiltonian*

$$H" = \frac{e^2A^2}{2\mu} = \frac{e^2}{2\mu}\left(A_x^2 + A_y^2 + A_z^2\right) = \frac{e^2}{8\mu}B^2(x^2 + y^2)$$

$$= \frac{e^2}{8\mu}B^2(x^2 + y^2)_n$$

where suffix *n* indicates the energy in nth state.

If we consider the state to be spherically symmetrical,

then$x^2 = y^2 = z^2 = \frac{r^2}{3}$

then the average value of energy

$$< H" >= \frac{e^2B^2}{2\mu} < x^2 + y^2 >_n = \frac{e^2B^2}{8\mu} . \frac{2}{3} < r^2 >_n$$

For ground state of hydrogen atom

$\psi_n = \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0}$,where$a_0 = \frac{\hbar^2}{me^2} = 0.529\, \dot{A}$

$$\therefore \quad < r^2 >_{n=1} = \int \psi^* \, r^2 \psi \; d\tau$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0} r^2 . \frac{1}{\sqrt{(\pi a_0^3)}} e^{-r/a_0} r^2 dr \; sin\theta \;\; d\theta \; d\emptyset$$

$$= \frac{1}{\pi a_0^3} . 4\pi \int_0^\infty r^4 e^{-2r/a_0} dr = \frac{4}{a_0^3} \times \frac{3}{4} a_0^5 = 3a_0^2$$

$$\therefore \qquad < H" >= \frac{e^2B^2}{8\mu} . \frac{2}{3} . \; 3a_0^2 = \frac{e^2B^2}{4\mu} a_0^2$$

More generally it can be shown that for a state with quantum number *nlm* in hydrogen like atom with nuclear charge Z

$$< r^2 >_{nlm} = \frac{a_0^2 n^4}{Z^2}\left\{1+\frac{3}{2}\left(1-\frac{l(l+1)-\frac{1}{3}}{n^2}\right)\right\}$$

For large value of n i.e. for highly excited states, this is proportional to n^4.

Therefore the general expression foe the effect of term containing A^2 on the energy of state of *nlm*is

$$< H" > = \frac{e^2A^2}{2\mu} = \frac{e^2B^2}{8\mu}\frac{2}{3} < r^2 >_{nlm}$$

$$= \frac{e^2B^2}{8\mu}\frac{2}{3}\frac{a_0^2 n^4}{Z^2}\left\{1+\frac{3}{2}\left(1-\frac{l(l+1)-\frac{1}{3}}{n^2}\right)\right\}$$

This equation gives second order Zeeman Effect under the selection rule $\Delta l = \pm l$.

So far we have not considered the effect of electron spin. The complete and generalized solution can be found by taking the spin contribution as well. The resulting effect gives rise so called anomalous *Zeeman Effect.*

8.7 STARK EFFECT

The splitting of energy levels of an atom caused by a uniform external electric field E is called **Stark Effect.** It was observing Balmer lines of hydrogen with an electric field of strength 10^5 volt/cm.

Let us choose the unperturbed initial states with a direction of the perturbing electric field along the z-axis and use the eigen states of L_z.

The force on electron of charge (q= -e, e being positive quantity) in an electric field of strength **E** is

$\mathbf{F}_e = q\mathbf{E} = - e\,\mathbf{E}$

As field is along z-axis, therefore extra-energy of electron in electric field= $\mathbf{F}_e z = - e Ez$

The Schrödinger equation for this case is

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left(W + \frac{Ze^2}{r} + eEz\right)\psi = 0 \qquad \text{--------- (1)}$$

Where W is total energy and $-\frac{Ze^2}{r} - eEz$ is potential energy of electron in atom.

Equation (1) may be written as

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} - eEz\right)\psi = W\psi$$

$$(H_0 + H')\,\psi = W\psi \qquad \text{--------- (2)}$$

Where the unperturbed Hamiltonian;

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

And the first order perturbed Hamiltonian term

$$H' = -e\,Ez$$

If we use polar co-ordinates (r, θ), then z = r cos θ

And so $$H' = -e\,Ez = -eEr\,cos\theta$$

e being again a positive quantity.

Here the potential energy is spherically symmetric.

Ist Order Stark effect in General state of Hydrogen Atom:

The ground state of H- atom is specified by
n= 1, *l*= 0, *m*= 0

The ground state (*n*= 1, *l*= 0, *m*= 0) of hydrogen atom is *non- degenerate state* and the corresponding spherically symmetric function is given by

$$\psi_{100} = R_{10}(r)Y_{100}(\theta,\phi) = \frac{1}{\sqrt{(\pi a_0^3)}}e^{-r/a_0}$$

where$a_0 = \frac{\hbar^2}{\mu e^2}$ is radius of Bohr's first orbit.

The first order perturbation energy correction is given by

$$E' = \int \psi_{100}^* H' \psi_{100} d\tau$$

$$= \iiint \frac{1}{\sqrt{(\pi a_0^3)}}e^{-r/a_0}(-eEr\,cos\theta)\frac{1}{\sqrt{(\pi a_0^3)}}e^{-r/a_0}\,r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= -\frac{eE}{\pi a_0^3}\int_0^\infty r^3\,e^{-r/a_0}dr\int_0^\pi sin\theta\,cos\theta\,d\theta\int_0^{2\pi} d\phi = 0$$

Since $\int_0^\pi sin\theta\,cos\theta\,d\theta = 0$

Thus **for ground state of hydrogen there is no first order Stark effect.**

Ist Order Stark effect in First Excited State:

Let us now consider the first excited state n= 2 for Hydrogen atom. Since *n*=2, therefore *l*=0, 1 and *m* =1, 0,-1 and hence the quantum number (*l, m*) can have the following combinations. i.e., (0, 0), (1, 0), (1, 1) and (1, -1)

Thus the wave-function $\psi_{nlm}$is four fold degenerate i.e., the wave-function $\psi_{200}, \psi_{210}, \psi_{211}\ and \psi_{2,1,-1}$ all have same energy.

Let us calculate the elements of the secular determinant, we have

$$\psi_{200} = \frac{1}{\sqrt{(32\pi a_0^3)}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

$$\psi_{210} = \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0}\ cos\theta\right)e^{-r/2a_0}$$

$$\psi_{211} = \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0\sqrt{2}}\ sin\theta\ e^{i\phi}\right)e^{-r/2a_0}$$

$$\psi_{2,1,-1} = \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0\sqrt{2}}\ sin\theta\ e^{i\phi}\right)e^{-r/2a_0}$$

$$\therefore \qquad < 0,0\,|H'|0,0 >= \int \psi_{200}^*\, H'\psi_{200} d\tau = 0$$

The non-vanishing elements of H' are

$$< 1,0\,|H'|0,0 >=< 0,0\,|H'|1,0 >_*$$

$$= \int \psi_{210}^*\,(-eEr\ cos\theta)\psi_{200} d\tau$$

$$= -\iiint \frac{1}{\sqrt{(32\pi a_0^3)}}\left(\frac{r}{a_0}\ cos\theta\right)e^{-r/2a_0}\,(eEr\ cos\theta).\frac{1}{\sqrt{(32\pi a_0^3)}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\,r^2 dr \sin\theta\ d\theta\ d\phi$$

$$= -\frac{eE}{32\pi a_0^4}\int_0^\infty \left(2-\frac{r}{a_0}\right).r^4 e^{-r/2a_0} dr \int_0^\pi cos^2\theta\ sin\theta\ d\theta\ \int_0^{2\pi} d\phi$$

We have $\int_0^\pi cos^2\theta\ sin\theta\ d\theta = -\frac{1}{3}[cos^3\theta]_0^\pi = \frac{2}{3}$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^\infty \left(2-\frac{r}{a_0}\right).r^4 e^{-r/2a_0}dr = -72\, a_0^5$$

Using above results we get

$$< 1,0\,|H'|0,0 >=< 0,0\,|H'|1,0 >_*$$

$$= -\frac{eE}{32\pi a_0^4}\left(-72\, a_0^5\right).\left(\frac{2}{3}\right).2\pi$$

$$= 3e\,Ea_0$$

The splitting of energy level as shown in fig.2. The electric potential energy of a dipole moment **p** is – **p. E**

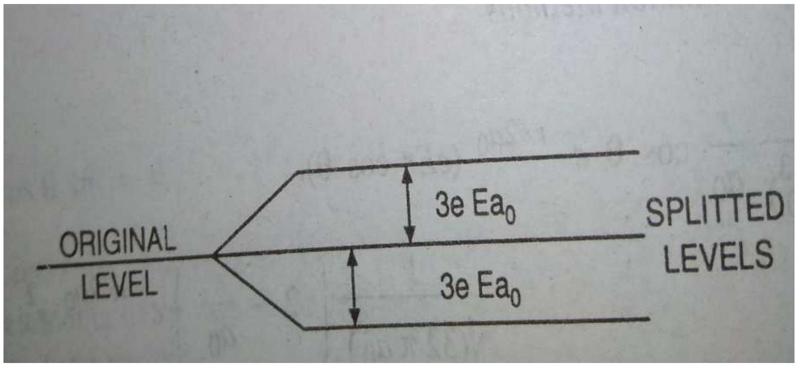


Fig 2. First order splitting of energy level

8.8 VARIATION METHOD

The variation method is especially applicable for the interest in chemical problems. In special cases variation method can be extended to the state of the system other than the lowest one. The variation method may also be applied to the lowest state of the given resultant angular momentum and of given electron spin multiplicity.

The expectation value of energy in normalized state ψ is given by

$$< E > = \int \psi^* H \psi\, d\tau \qquad \text{------- (1)}$$

If we choose the wave function ψ as variable function, then the integral (1) is known as variation integral and gives an upper limit to the energy E_0 of the lowest state of the system. The function ψ is the variation function.

If the variation function ψ equal to the function ψ_0 of the lowest state, then energy E will be equal to E_0

$$< E > = \int \psi_0^* H \psi_0 d\tau = E_0 \qquad \text{------- (2)}$$

If $\psi \neq \psi_0$, then by expansion theorem ψ may be expanded in term of a complete set of orthogonal functions ϕ_0, ϕ_1, ϕ_2……obtaining

$\psi = \sum_n a_n b_n \;\; with \;\; \sum_n a_n \, a_n * \; = 1 \qquad and \;\; H\phi_n = \mathrm{E}_n\phi_n$ ------- (3)

Substituting this in equation (1), we get

$< E >= \; \sum_n a_n^* \, a_m \int \phi_n^* \; H\phi_m d\tau$ ------- (4)

$$H\phi_m = E_m\phi_m$$

$$< E >= \sum\nolimits_n a_n^* \, a_m \int \phi_n^* \; E_m\phi_m d\tau$$

$$< E >= \sum\nolimits_n a_n^* \, a_m \, E_m \int \phi_n^* \; \phi_m d\tau$$

$$= \sum_n a_n^* \, a_m \, E_m\delta_{mn}$$

Therefore, $< E >= \; \sum_n a_n^* \, a_m \, E_n$ [since $\delta_{mn} = 1$ for m= n

= 0 for m≠ n]

$= \sum_n |a_n|^2 \, E_n$ ------- (5)

Subtracting ground state energy E_0 from both sides, we get

$< E > -E_0 = \; \sum_n |a_n|^2 \; (E_n - E_0)$ ------- (6)

As $|a_n|^2$ is positive and $E_n \geq E_0$ (always) for all values of n; therefore RHS is positive or zero. Thus we have proved that $< E >$ is always upper limit to E_0 i.e.

$$< E >= E_0$$

This theorem is the basis of the variation method for the calculation of the approximate eigen value of the system.

Q4.For a harmonic oscillator,using a Gaussian wave function as atrial wave function, estimates the ground state energy.

Sol.$\psi = Ae^{-bx^2}$is atrial function. A is a normalization constant.

$$\int_{-\infty}^{+\infty} |\psi|^2 \; dx = 1$$

Or A=$\left(\frac{2b}{\pi}\right)^{1/4}$

We calculate $< \psi|H|\psi >$

Or$\int A^2 \, e^{-bx^2} \left(\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m}{2}\omega^2 x^2\right) e^{-bx^2} dx$

$= A^2 \int\{-\frac{\hbar^2}{2m}(-2b+4b^2x^2)e^{-bx^2} + \frac{m\omega^2}{2}x^2e^{-bx^2}dx$

$=A^2\int_{-\infty}^{-\infty}\frac{\hbar^2}{2m}e^{-2bx^2}dx + A^2\left[\frac{-4b^2\hbar^2}{2m}+\frac{m\omega^2}{2}\right]\int_{-\infty}^{+\infty}x^2\,e^{-2bx^2}dx$

$=A^2\frac{\hbar^2}{2m}\sqrt{\frac{\pi}{2b}} + A^2\left(\frac{-2b^2\hbar^2}{2m}+\frac{m\omega^2}{2}\right)2\sqrt{\frac{\pi}{2b}}\frac{1}{2b}$

$=\sqrt{\frac{2b}{\pi}}\frac{\hbar^2}{m}\sqrt{\frac{\pi}{2b}} + \sqrt{\frac{2b}{\pi}}\sqrt{\frac{\pi}{2b}}\frac{1}{4b}\left(\frac{-2b^2\hbar^2}{m}+\frac{m\omega^2}{2}\right)$

$=\frac{\hbar^2 b}{m} - \frac{-b\hbar^2}{2m} + \frac{m\omega^2}{8b}$

<H> = $\frac{\hbar^2 b}{m} + \frac{m\omega^2}{8b}$

Minimize <H> with respect to b

$$\frac{\partial < H >}{\partial b} = 0$$

$$\frac{\hbar^2}{2m} - \frac{m\omega^2}{8b} = 0$$

Or $b^2 = \frac{m^2\omega^2}{4\hbar^2}$

$$b \quad = \frac{m\omega}{2\hbar}$$

<H>min=$\frac{\hbar\omega}{2}$

$$E_g \leq \frac{\hbar\omega}{2}$$

For this trial function, we get the exact answer.

Self Assessment Question

Q5. Use the Gaussian trial function to obtain the lowest upper bound for the potential V= $\alpha|x|$.

8.9 WKB APPROXIMATION

WKB Approximation is a final type of time independent approximate calculations. It applies to only situations in which the potential energy is slowly varying function of position.

A slowly changing potential means the variation of potential energy V(r) slightly over several wavelength of the particles as shown in fig 3.

The de- Broglie wavelength associated with a particle moving with energy E in a region of potential V is

$\lambda = \frac{h}{p} = \frac{h}{[2m(E-V)]^{1/2}}$ ------- (1)

$$\frac{1}{2}mv^2 = E - V$$
$$m^2v^2 = 2m(E - V)$$
$$p = mv = \sqrt{[2m(E - V)]}$$

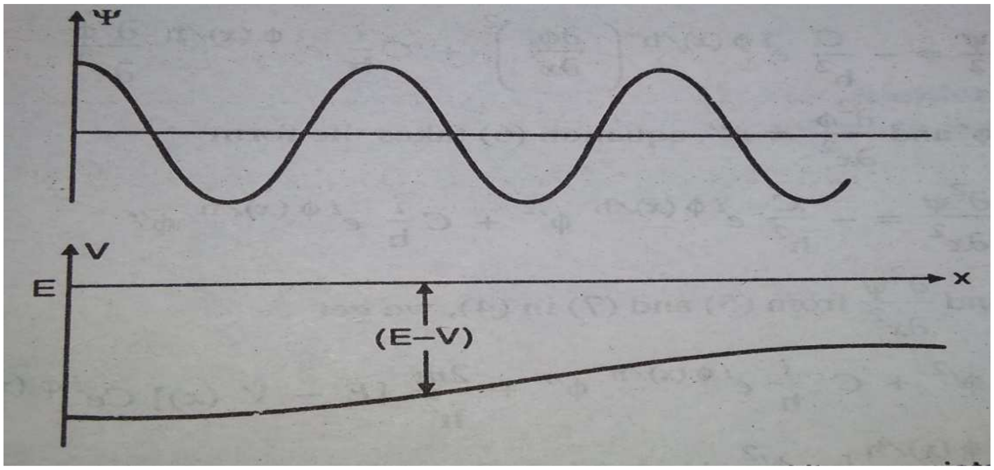


Fig. 3" Slowly changing" one-dimensional potential and its associated wavefunction

The propagation constant

$k = \frac{2\pi}{\lambda} = \frac{[2m(E-V)]^{1/2}}{\hbar}$ ------- (2)

Mathematically slowly varying potential can be expressed by conditions

$$\left|\frac{1}{k^2}\frac{dk}{dx}\right| < 1$$

Substituting value of k from (1), we get

$\frac{\hbar m\,|\frac{\partial V}{\partial x}|}{[2m(E-V)]^{3/2}} < 1\ or\ \frac{\lambda\frac{\partial V}{\partial x}}{4\pi(E-V)} < 1$ ------- (3)

This equation gives the validity of W.K.B approximation.

Principle of the Method: W.K.B. method consists in introducing an expansion in the powers of $\hbar$ and neglecting the terms in higher order of $\hbar$. Thus, Schrodinger equation reduced in its classical limits.

Let ψ(x) be the wave function satisfying Schrodinger's equation

$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0$ ------- (4)

Let the solution of equation (4) be of the form

$\psi = Ce^{i\phi(x)/\hbar}$ ------- (5)

Where C is a constant, $\phi(x)$ is an undetermined function of x

$$\frac{\partial\psi}{\partial x} = C\frac{i}{\hbar}e^{i\phi(x)/\hbar}.\frac{\partial\phi}{\partial x}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}.\left(\frac{\partial\phi}{\partial x}\right)^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}.\frac{\partial^2\phi}{\partial x^2} \qquad \text{------- (6)}$$

Now substituting $\frac{\partial\phi}{\partial x} = \phi'$ and $\frac{\partial^2\phi}{\partial x^2} = \phi''$ in equation (6)

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}.\phi'^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}.\phi'' \qquad \text{------- (7)}$$

Substituting values of ψ and $\frac{\partial^2\psi}{\partial x^2}$ from (5) and (7) in (4)

$$-\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}.\phi'^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}.\phi'' + \frac{2m}{\hbar^2}[E - V(x)]Ce^{i\phi(x)/\hbar} = 0$$

$$\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}.[-\phi'^2 + i\hbar\,\phi'' + 2m[E - V(x)] = 0$$

As $\psi = Ce^{i\phi(x)/\hbar} \neq 0$

$$[i\hbar\phi'' - \phi'^2 + 2m[E - V(x)] = 0 \qquad \text{------- (8)}$$

To get the approximate solution of (8) we apply W.K.B method and hence expand $\phi(x)$ in the power of $\hbar$

$$\phi(x) = \phi_0(x) + \hbar\phi_1(x) + \frac{\hbar^2}{2!}\phi_2(x) + \cdots \qquad \text{------- (9)}$$

where the subscript ϕ's are independent of $\hbar$.

Differentiating equation (6), we get

$$\left.\begin{aligned} \phi'(x) &= \phi_0{}'(x) + \hbar\phi_{1'}(x) + \frac{\hbar^2}{2}\phi_2{}'(x) + \cdots \\ \phi''(x) &= \phi_0{}''(x) + \hbar\phi''_1(x) + \frac{\hbar^2}{2!}\phi''_2(x) + \cdots \end{aligned}\right\} \qquad \text{------- (10)}$$

Substituting values of ϕ' and ϕ'' from (10) in equation (8), we get

$$i\hbar\left[\phi_0{}''(x) + \hbar\phi''_1(x) + \frac{\hbar^2}{2!}\phi''_2(x) + \cdots\right] - \left[\phi_0{}'(x) + \hbar\phi_{1'}(x) + \frac{\hbar^2}{2}\phi_2{}'(x) + \cdots\right]^2 +$$

$$2m[E - V(x)] = 0$$

Collecting coefficient of various powers of $\hbar$

$$[2m(E - V)] - \phi_0{}'^2] + \hbar[i\phi_0{}'' - 2\phi_0{}'\phi_{1'}] + \hbar^2[i\phi''_1 - \phi_{1'}{}^2 - \phi_0{}'\phi_2{}'] = 0 \qquad \text{------- (11)}$$

In order that equation (11) may hold identically in $\hbar$, the coefficient of each power of $\hbar$ must vanih separately. This requirement leads to the following series of equations

$2m(E - V)] - \phi_0{}'^2 = 0$ (a)

$$i\phi_0'' - 2\phi_0'\phi_{1'} = 0 \qquad \text{(b)} \qquad \text{-------} \ (12)$$

$$i\phi''_1 - {\phi_{1'}}^2 - \phi_0'\phi_2' = 0 \qquad \text{(c)}$$

and so on.
These equations may be solved successively. That is, the first equation defines ϕ_0 in terms of | (E−V) |, the second equation defines ϕ_1 in terms of ϕ_0, the third defines ϕ_2 in terms of ϕ_1 and ϕ_0 etc.

From equation (12 a), we obtain

$$\phi_0' = \pm\sqrt{[2m(E - V)]} \qquad \text{-------} \ (13)$$

Integration of above equation yields

$$\phi_0 = \int_{x_0}^{x} \pm\sqrt{[2m(E - V)]}\ dx \qquad \text{-------} \ (14)$$

Where x_0 is an arbitrary fixed value of x

From equation (12 b), we obtain

$$\phi'_1 = \frac{i\phi_0''}{2\phi_0'}$$

Integration of above equation yields

$$\phi_1 = \frac{i}{2}\log\phi_0' + C_1 \qquad \text{-------} \ (15)$$

where C_1 is the integration constant. This result is inconvenient if ϕ_0' is negative. Therefore keeping in mind that the logarithm of a negative function differs only an arbitrary constant from the logarithm of the absolute value of the function, we replace equation (15) by

$$\phi_1 = \frac{i}{2}\log|\phi_0'| + C_2 \qquad \text{-------} \ (16)$$

where C_2 is an arbitrary constant.

Similarly

$$\phi_2 = \frac{1}{2}\frac{m\left(\frac{\partial V}{\partial x}\right)}{[2m(E-V)]^{3/2}} - \frac{1}{4}\int_{x_0}^{x}\frac{m^2\left(\frac{\partial V}{\partial x}\right)}{[2m(E-V)^3]^{5/2}} \qquad \text{-------} \ (17)$$

From equation (16) we see that ϕ_1 is represented as a logarithm of $|\phi_0'|$, therefore it is not, in general, small compared with ϕ_0. Consequently ϕ_0 and ϕ_1 both must retained. On the other hand from equation (17) we see that ϕ_2 will be small whenever $\partial V/\partial x$ is small and (E−V) is not too close to zero. Further it can be seen easily that the smallness of the higher approximations ($\phi_3, \phi_4 \ldots etc$) requires the smallness of all derivatives of V. Thus the W.K.B. approximation will be suitable in case where V is a sufficiently smooth and slowly varying function of position.

Thus the approximation W.K.B. solution of equation (8) may be expressed in the form

$$\phi = \phi_0(x) + \frac{i}{2}\log|\phi_0'| \qquad \text{-------} \ (18)$$

Assuming constant C_2 is absorbed in $\phi_0(x)$

Substituting value $\phi(x)$ from (18) in equation (5) and rearranging the result, we finally get the approximation solution ψ_{app} of equation (4) in the form

$$\psi_{app} = C\,\{2m|E - V(x)|\}^{-1/4} exp\left[\pm\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[2m(E-V)]}\ dx\right] \qquad \text{------- (19)}$$

where C remains arbitrary. The two solution contained in (19) and differing in the sign of the exponent are linearly independent and hence the approximate general solution, according to W.K.B approximation,

$$\psi_{app} = C\,\{2m|E - V(x)|\}^{-1/4}\begin{bmatrix} A\ exp\left(\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[2m(E-V)]}\ dx\right) \\ +B\ exp\left(-\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[2m(E-V)]}\ dx\right)\end{bmatrix} \qquad \text{------- (20)}$$

where A and B are arbitrary constants. The positive exponential corresponds to a wave moving in the positive direction and the negative exponential corresponds to a wave moving in the negative direction. For the special case when V(x) is a constant, these reduce respectively to the plane waves

$\exp(ipx/\hbar)$and$\exp(-\,ipx/\hbar)$

The alternative form of equations (20) may be expressed as

$$\psi_{app} = C\,\{2m|E - V(x)|\}^{-1/4} cos\left(\frac{i}{\hbar}\int_{x_0}^{x}\sqrt{[2m(E-V)]}\ dx + \theta\right) \qquad \text{------- (21)}$$

where C and θ are arbitrary constants.

The approximate solutions (20) and (21) of Schrodinger equation are usually called W.K.B ψ- functions.

8.10 FERMI GOLDEN RULE

The transition rate and probability of observing the system in a state *k* after applying a perturbation to *l* from the constant first-order perturbation doesn't allow for the feedback between quantum states, so it turns out to be most useful in cases where we are interested just the rate of leaving a state. This question shows up commonly when we calculate the transition probability not to an individual eigen state, but a distribution of eigen states. Often the set of eigen states form a continuum of accepting states, for instance, vibration relaxation or ionization.

Transfer to a set of continuum (or bath) states forms the basis for a describing irreversible relaxation. You can think of the material Hamiltonian for our problem being partitioned into two portions, $H = H_S + H_B + V_{SB}(t)$, where you are interested in the loss of amplitude in the H_S states as it leaks into H_B . Qualitatively, you expect deterministic, oscillatory feedback between discrete quantum states. However, the amplitude of one discrete state coupled to a continuum will decay due to destructive interferences between the oscillating frequencies for each member of the continuum.

So, using the same ideas as before, let's calculate the transition probability from *l* to a distribution of final states: P_k.

$P_k = |b_k|^2$ Probability of observing amplitude in discrete eigen state of H_0

$\rho(E_k)$: Density of states—units in $1/E_k$, describes distribution of final states—all eigen states of H_0

we start in a state *l* , the total transition probability is a sum of probabilities

$$\overline{P_k} = \sum_k P_k$$

We are just interested in the rate of leaving *l* and occupying any state *k* or for a continuous distribution:

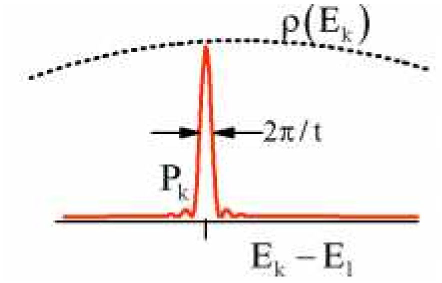
$$\overline{P}_k = \int dE_k\ \rho(E_k)\, P_k$$

For a constant perturbation:

$$\overline{P}_k = \int dE_k\ \rho(E_k)\, 4|V_{k\ell}|^2\, \frac{\sin^2\left((E_k - E_\ell)t/2\hbar\right)}{|E_k - E_\ell|^2}$$

Now, let's make two assumptions to evaluate this expression:

1) ρ(E_k) varies slowly with frequency and there is a continuum of final states. (By slow what we are saying is that the observation point t is relatively long).
2) The matrix element V_{kl} is invariant across the final states.



These assumptions allow those variables to be factored out of integral

$$\overline{P}_k = \rho|V_{k\ell}|^2 \int_{-\infty}^{+\infty} dE_k\ 4\, \frac{\sin^2(E_k - E_\ell)t/2\hbar}{(E_k - E_\ell)^2}$$

Here, we have chosen the limits $-\infty \rightarrow +\infty$ since ρ(E_k) is broad relative to P_k. Using the identity

$$\int_{-\infty}^{+\infty} d\Delta\, \frac{\sin^2 a\Delta}{\Delta^2} = a\pi$$

with $a = t/\hbar$ we have

$$\overline{P}_k = \frac{2\pi}{\hbar}\, \rho |V_{k\ell}|^2\, t$$

The total transition probability is linearly proportional to time. For relaxation processes, we will be concerned with the transition rate, $\overline{w_{kl}}$

$$\bar{w}_{k\ell} = \frac{\partial \overline{P}_{k\ell}}{\partial t}$$

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar}\rho\left|V_{k\ell}\right|^2$$

Remember that P_k is centered sharply at $E_k = E_l$. So although ρ is a constant, we usually write in terms of ρ $(E_k = E_l)$ or more commonly in terms of $\delta\,(E_k - E_l)$

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar}\rho\left(E_k = E_\ell\right)\left|V_{k\ell}\right|^2$$

$$w_{k\ell} = \frac{2\pi}{\hbar}\left|V_{k\ell}\right|^2\delta\left(E_k - E_\ell\right) \qquad \bar{w}_{k\ell} = \int dE_k\,\rho\left(E_k\right)w_{k\ell}$$

This expression is known as Fermi's Golden Rule.

8.11 Summary

Time independent theory or stationary is concerned with finding changings in the energy levels and eigen function of system when a small disturbance is applied.If the potential energy is disturbed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

The change in the energy levels of an atom when it is placed in uniform external magnetic field,is called the Zeeman effect. The splitting of energy levels of an atom caused by a uniform external field E is called Stark-Effect. Stark observing Balmer lines of hydrogenwith an electric field of strength 10^5volt/cm. The energy shift of stark effect by perturbation theory.

Generally the solution of schrodinger's equation gives the energy eigenvalues but it is difficult to solve it in a closed from except for some special cases. Finding the ground state energy, the variation method provides an upper limit in the ground state energy

8.12Glossary

Perturbation	a deviation of a system
Degenerate	having lost the physical
Transition	the process or a period of changing from one state or condition to another
Discrete	distinct, separate
Relaxation	the state of being free from tension and anxiety
Harmonic	a component frequency of an oscillation or wave

Anomalous	non typical,abnormal
Orthogonal	statistically independent
Continuum	a continuous nonspatial whole or extent or succession in which no part
Approximate	almost correct but completely accurate

8.13 References

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3. V. Devanathan, Quantum Mechanics, Narosa Publishing House, New Delhi.

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5. David J. Griffiths, Introduction of Quantum mechanics

8.14 Suggested Reading

1. Landau and Lifschitz "Quantum Mechanics"
2. Nielsen & Chuang: "Quantum Computation and Quantum Information"
3. “Principle of Quantum Mechanics”by Ramamurti Shankar

8.15 Terminals questions

Long Answer type

Q1. What do you mean by perturbation theory? Discuss the perturbation theory for non-degenerate levels in first orders.

Q2. Discuss the general theory of the variation principle.

Q3. Describe W.K.B. approximation method and give an application of this method.

Q4. Discuss the general theory of the Fermi Golden Rule.

Q5. Describe the general theory on one-dimensional harmonic oscillator.

Q6. What do you mean by Zeeman Effect? Explain the theory on 1st order and 2nd order Zeeman Effect.

Q7. Write the short note on

(a) Perturbation of harmonic oscillator
(b) First order Stark effect in H atom.

Numerical type

Q1.Suppose a perturbation $H' = \alpha\delta(x - \frac{a}{2})$ is put in the centre of an infinite square well,

$$V(x)= \begin{cases} 0, & 0 < x < a \\ \infty, & elsewhere \end{cases}$$

Find the first order correction to the energies and ψ_n^1.

Q2. For the Hamiltonian

$$H = \frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$$

Where, $\delta(x)$ is a delta function, find the estimate for the ground state energy.

Objective answer type

Q1. In the harmonic oscillator problem we consider a small perturbation bx,the first order energy correction to the nth energy level is

(a) $\frac{1}{2}(n+\frac{1}{2})\frac{\hbar\omega}{mb}$ (b) $\frac{1}{2}\hbar\omega b$

(c) $(n+\frac{1}{2})\hbar\omega b$ (d) 0

Q2.Consider a two dimensional harmonic oscillator with a perturbation $H' = bx_1x_2$, the first order correction to the energy is

(a) $\frac{\lambda\hbar}{2m\omega}$ (b) $-\frac{\lambda\hbar}{2m\omega}$

(c) $\pm\frac{\lambda\hbar}{2m\omega}$ (d) 0

Q3.Zeeman effect is

(a) The change in energy levels of an atom when it is placed in uniform external field

(b) The change in energy levels of an atom when placed in non-uniform external field
(c) The change in energy levels of an atom when placed in external electric field
(d) The change in energy levels of an atom when placed in non –uniform field

Q4. A one –dimensional harmonic oscillator of mass m,charge q and classical amplitude a is kept in an electric field of strength E along x. First order change in ground and first excited state are respectively.

(a) 0,$\frac{qEa}{2}$ (b) 0,qEa (c)0,0 (d) $\frac{qEa}{\alpha}$,qEa

Q5. The degree of degeneracy for three dimensional isotropic harmonic oscillators

(a) n^2 (b) (2n+1) (c) $\frac{1}{2}$ (2n+1) (2n+2) (d) $\frac{1}{2}$ (n+1)(n+2)

Q6. The WKB approximation is valid, when

(a) $\frac{\hbar m\left|\frac{\partial V}{\partial x}\right|}{2m(E-V)^{\frac{3}{2}}} > 1$ **(b)**$\frac{\hbar m\left|\frac{\partial V}{\partial x}\right|}{\{2m(E-V)\}^{\frac{3}{2}}} > 1$ (c)$\frac{\hbar m\left|\frac{\partial V}{\partial x}\right|}{2m(E-V)^{\frac{3}{2}}} \leq 1$ (d)$\frac{\hbar m\left|\frac{\partial V}{\partial x}\right|}{2m(E-V)^{\frac{3}{2}}} < 1$

Q7. The first order perturbed Hamiltonian, when an external uniform electric field $\vec{E}$ is applied to the z-axis on an atom is

(a) H'=eEz (b)H'= - eEz (c)$H' = \frac{eZ}{E}$ (d) $H' = -\frac{eZ}{E}$

Q8.consider a harmonic oscillator of the form $H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2x^2$.If it is subjected to a time independent perturbation λ(xP+Px), where λ is real.The first order correction to the nth energy state is

(a) Zero (b) λħ (c)λ^2ħ (d) $\frac{\lambda^2\hbar}{\omega}$)

Q9. A quantum harmonic oscillator is in energy eigenstate$|n\rangle$.A time independent perturbation 1λ$(a^ta)^2$ acts on the particle, where λ is a constant of suitable dimensions and a anda^t are lowering and raising operator respectively. Then ,the first order energy shift is given by

(a) λn (b) $\lambda^2 n$ (c) λn^2 (d) $(\lambda n)^2$

Q10.When a perturbation of cx^3 is applied in the Hamiltonian of harmonic oscillation, the shift in first order energy is

(a)Zero (b) $\frac{3}{4}c(\frac{\hbar\omega}{k})^2$ (c)$\frac{1}{2}c(\frac{\hbar\omega}{k})^2$ (d) $c(\frac{\hbar\omega}{k})$

8.16 Answers

1(d) 2(c) 3(a) 4(d) 5(d) 6(d) 7(b) 8(a) 9(b) 10(a)

UNIT 9 Elementary theory of scattering

Structure

9.1 Introduction

If a beam of particle of any kind is directed at matter the particle will be deflected from their original path due to their collision with the particle of matter which they encounter. The scattering experiments with atom and nuclei have given very useful information about the forces and interaction between the scattered particle and the target materials.

In some collisions, the energy of incident particle does not change after interaction, such collisions are called elastic collision and such scattering is called elastic scattering.

In some collisions, the energy of incident particle change after interaction. Such collisions are termed as inelasting collision and such scattering are termed as inelasting scattering.

9.2 Classical theory of scattering

In order to treat scattering problem quantum mechanically, the motion of a particle cannot be describe accurately by involving classical orbits; but one must use wave packet whose average coordinate give the classical orbits. It means the scattering has to be described by wave functions which are solutions of the Schrödinger equation but not by particle trajectories which are solutions of classical equation of motion.

These conditions under which classical theory become inadequate and quantum theory become necessary can easily obtained. When the classical theory is applied, one must be able without seriously changing any significant result to get this classical description by forming a wave packet. But in most of the case the angle of scattering is obtained from the magnitude of force in the neighborhood of the distance of closed approach. Its indicate that wave packet has to narrower than this distance otherwise no method is available which make one to sure that the particle gets experienced a definite predictable force which become possible to calculate deflection in a classical way. To obtain get the condition of validity roughly of classical approximation, its assumed that the distance of closed approach is of the same order of magnitude as the collision parameter b. In order to from a wave packet smaller than b,it is necessary to use the range of wavelength $\leq$ b. From uncertainty principle,

$$\Delta x \, \Delta p \geq \hbar/2$$

Its mean that the momentum of the incident particle should be greater than $\approx \hbar/2b$.In defining the position of this packet, that the momentum of a particle becomes uncertain by a quantity much greater than $\delta p \approx \hbar/2b$. This uncertainty will make the angle of deflection to be uncertain by a quantity which is much greater than $\delta p/p$. Therefore the classical description will hold only if this uncertainly $\delta p/p$ is much smaller than the deflection itself otherwise the entire calculation of deflection by classical methods will be meaningless .This mean that the uncertainty in momentum must be much smaller than the net momentum which gets transferred (Δp) during the collision i.e.

$$\frac{\delta\,\mathrm{p}}{p} \approx \frac{\hbar/2b}{\Delta\,\mathrm{p}} = \frac{\hbar}{2b\Delta\,\mathrm{p}} \;=\leq\; 1$$

To get the value of Δ p must be obtained by using classical orbits theory. Large angles of scattering the calculation of Δ p is rather complicated, but for small angle of scattering use classical perturbation theory. This theory is applicable only when the scattering angle is large compared with quantum fluctuations, but small compared with π.

Calculate the value of Δ p in the following way:

Let us consider momentum p of the particle moving x direction under a force .when the particle is scattered and obtain Y component of momentum. If θ is the angle of deflection, then

$$\sin\theta = \frac{p_y}{p}$$

If $F_y$be the force along y- axis, then $p_{y = \int_{-\infty}^{+\infty} F_{Y\,dt}}$

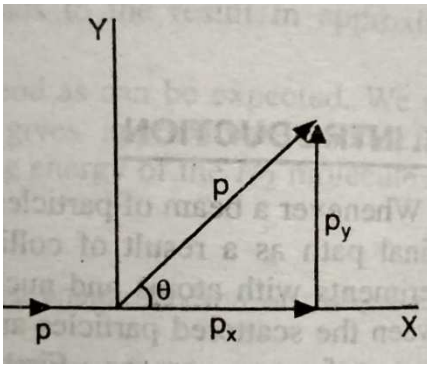


Fig. 1

If the force is spherically symmetric, then $F_{Y = \frac{y}{r}F}$

where F is the total force.

$$p_{y = \int_{-\infty}^{+\infty} \frac{y}{r}F(r)dt}$$

As an approximation, it may be considered that y = b, x = v i.e. dx = vdt

So that $r = \sqrt{(x^2 + y^2)} \approx \sqrt{(x^2 + b^2)}$ and $dt = \frac{dx}{v}$

Thus the momentum transferred

$$\Delta p = p_{y = \int_{-\infty}^{+\infty} \frac{b}{r}F(r)\frac{dx}{v}}$$

$$= \frac{b}{v}\int_{-\infty}^{+\infty} \frac{F(r)}{r}\,dx$$

Thus the classical description will be valid whenever

$$\frac{\delta\,\mathrm{p}}{\Delta p} < 1 \; or \; \frac{\Delta\,\mathrm{p}}{\delta p} > 1$$

i.e.

$$\frac{\Delta p}{\hbar/_{2b}} = \frac{2b^2}{\hbar v}\int_{-\infty}^{+\infty}\frac{F(r)}{r}\,dx > 1(\text{ for small deflections})$$

9.3 Scattering cross section

Scattering cross section used to dealing with the collision of a beam of particle with scattering centre. It is measured of the probability that the particle will get scattered as it traverse as given thickness of matter dx. In scattering, each molecule offers the on-coming particle a target area πd^2,where d represents the diameter of the molecules. This target area will be representing that cross section of the region within which there occurs a collision which can viewed along the direction of motion of the beam of molecule. This is where the name scattering cross-section comes from. The results of the collision experiments are expressed by means of cross section and are directly related to the asymptotic behavior of the stationary solutions of the Schrodinger's equation.

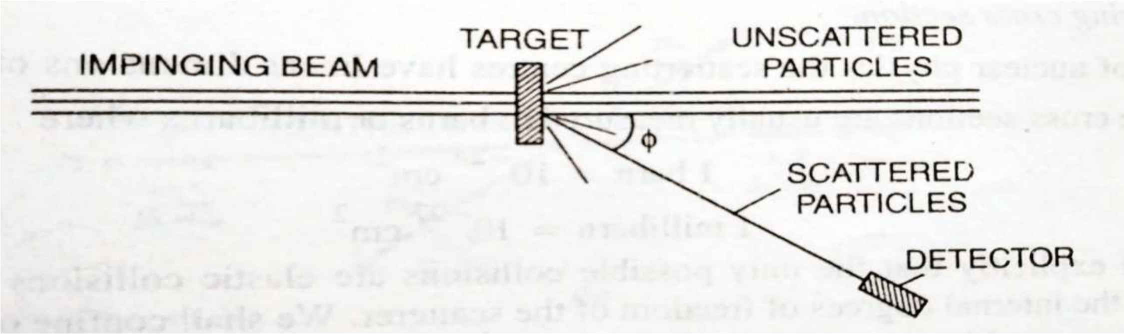


Fig. 2

To define the cross-section considers a typical experiment in which a target is struck by a beam of mono-energetic particles and the scattered particles are counted with the aid of a detector (fig.2). Let J be the magnitude of the incident flux i.e. the number of incident particles crossing per unit time a unit surface area placed perpendicular to the direction of incident beam and at rest respect to the target. If ρ is the number of particles per unit volume in the incident beam and v is the velocity of the incident particles, then

$J = \rho v$

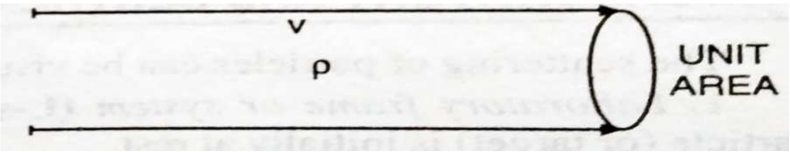


Fig. 3

If ρ is small (under the conditions of the experiment) that the mutual interaction of the incident particles can be neglected, then they undergo their collisions independently of each other. If n is the number of particles scattered per unit time into a solid angle dω located in the direction (θ, ϕ) then n is directly proportional to the incident current i.e.

$$n \propto J\, d\omega$$

$$n = \Sigma(\omega)\, J\, d\omega$$

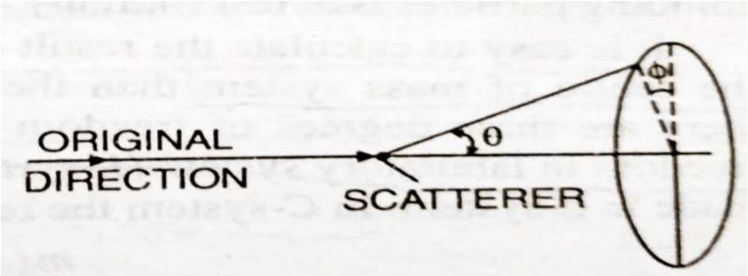


Fig.4

where Σ(ω) is a constant of proportionality which has dimension of source area and is characteristic parameter of the collision of particle with target. It is known as *scattering cross-section of the particle and the target in the direction ω(θ, ϕ).*

9.3.1 Differential Scattering Cross-section: Let us consider the target to be made up of a large number N of atomic or nuclear scattering centers and the distances between these atoms or nuclei are sufficiently large with respect to the wavelength of the incident particles as is observed in most practical cases. Then each scattering centers acts as it were alone. Moreover, if the target is sufficiently thin, so that one may neglect multiple scattering; then n is directly proportional to N also i.e.

$$n \propto N$$

So in this case $n \propto NJ\, d\omega$

$$= \sigma(\omega)\, NJ\, d\omega$$

Again σ (ω), the constant of proportionality, has the dimensions of surface area and is called the scattering cross-section of the particle by the scattering centre in the direction ω(θ, ϕ) or briefly the *differential scattering cross-section.*

Total Scattering Cross-section: The total number of particles scattered in unit time is obtained by integrating n over all angles. It is equal to

$$N_{\text{total}} = \int \sigma(\omega)\, NJ\, d\omega = NJ\sigma_{\text{total}}$$

where $\sigma_{\text{total}} = \int \sigma(\omega) d\omega$

is the *total scattering cross section.*

9.4 Scattering amplitude

In wave mechanics, an incident beam of particles is represented by a plane wave in an incident channel. Let us consider the scattering of a particle of mass *m* by a central potential V(**r**) such that V(**r**) tends to zero more rapidly than 1/r as r→∞.

Let E be the energy and $p = \hbar\boldsymbol{k}$ the initial momentum of the particle where **k** is the wave – vector. The Schrodinger equation for the central potential V(**r**) is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_k(\boldsymbol{r}) = E\psi_k(\boldsymbol{r}) \qquad \text{---------} (1)$$

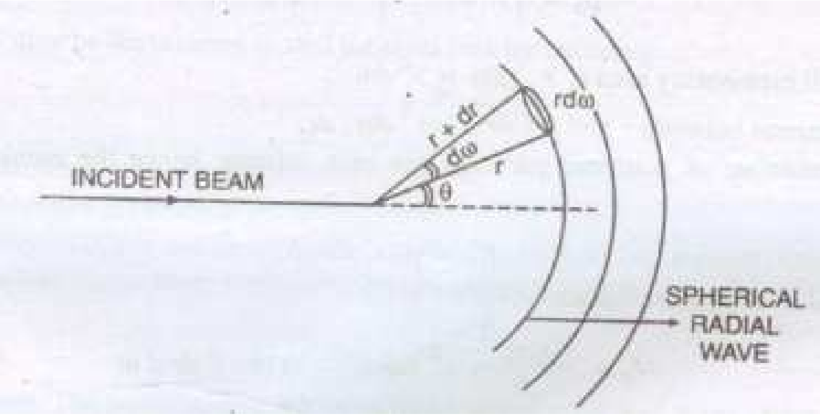


Fig. 5

The wave function ψ_k may be written as a function of θ;ϕ and radial distance r between the two particles, i.e.

$$\psi_k = \psi_k(r, \theta, \phi)$$

The scattering is determined by the asymptotic form of $\psi_k(r, \theta, \phi)$ in the region where V=0, when the colliding particles are far apart (or r→∞). We want to represent such that it contains two parts, one representing an incident wave and the other representing a scattered radially outgoing wave i.e.

$$\psi_k(r,\theta,\phi) = \lim_{r\to\infty} e^{\boldsymbol{ik.r}} + f(\omega)\frac{e^{ikr}}{r} \qquad \text{---------} (2)$$

Let us assume that one and only one solution of this type exists for each value of **k**. We shall call this solution, the stationary scattering wave vector **k.** The two terms of the asymptotic form are easily interpreted if we remember the definition of current density vector

$$J = \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) \qquad \text{---------} (3)$$

The plane wave term $e^{\boldsymbol{ik.r}}$ represents a wave of unit density and of current density $\frac{\hbar\boldsymbol{k}}{m}$. Retaining only the lowest order in r, the term $\frac{f(\omega)}{r}e^{\boldsymbol{ik.r}}$ represents a wave of density $\frac{|f(\omega)|^2}{r^2}$ and of current density $\frac{|f(\omega)|^2}{r^2}\frac{\hbar\boldsymbol{k}}{m}$ directed along the direction ω towards increasing r (outgoing-wave). In fact, since the effect of the potential V(**r**) can be neglected in the asymptotic region, therefore according to classical approximation we can interpret the term $e^{\boldsymbol{ik.r}}$ as a beam of monoenergetic particles of momentum $\hbar\boldsymbol{k}$and of density 1, representing the incident beam $\frac{f(\omega)}{r}e^{\boldsymbol{ik.r}}$ is interpreted as a beam of particles emitted radially from the scattering centre and represents a beam of the scattered particles.

In accordance with this interpretation we can calculate the number of particles emitted per unit time into the solid angle dωlocated in the direction ω.

The scattering wave-function is $\frac{f(\omega)}{r}e^{\boldsymbol{ik.r}}$; hence density of scattered particles

$$\rho_s = |f(\omega)\frac{e^{ik.r}}{r}|^2 = \frac{|f(\omega)|^2}{r^2} \qquad \text{--------} (4)$$

From fig. small elementary area = r.rdω = $r^2 d\omega$

The volume element between r and r+dr = $r^2 d\omega.dr$

As ρ_s in the number of scattered particles per unit volume, hence the number of particles in this elementary volume

$$N_s = \rho_s r^2 d\omega.dr$$

Substituting value of ρ_s from equation (4), we get

$$N_s = \frac{|f(\omega)|^2}{r^2} r^2 d\omega.dr = |f(\omega)|^2 dr\, d\omega \qquad \text{--------} (5)$$

The number of scattered particles per unit time

$$\frac{dN_s}{dt} = |f(\omega)|^2\, d\omega\frac{dr}{dt} = |f(\omega)|^2\, d\omega\, v = |f(\omega)|^2\, d\omega.\frac{\hbar\boldsymbol{k}}{m}$$

$= |_{f(\omega)}|^2 \frac{\hbar \boldsymbol{k}}{m}\, d\omega$ -------- (6)

If J is the current density, then J=ρv -------- (7)

Since beam of particles is travelling in the same direction with velocity v. The flux of the beam is the number of particles crossing unit area (perpendicular to the beam) per unit time. These are number of particles in a volume of unit cross-section and length v

But ρ =1 for incident particles.

$$J = v = \frac{\hbar \boldsymbol{k}}{m} \qquad \text{-------- (8)}$$

Also if σ(ω) is the scattering cross-section, then number of particles scattered in solid angle $d\omega$ per unit time.

$= J\sigma(\omega)d\omega = \frac{\hbar \boldsymbol{k}}{m} . \sigma(\omega)d\omega$ [using (8)] -------- (9)

Comparing equations (6) and (9) we get

$$\frac{\hbar \boldsymbol{k}}{m} . \sigma(\omega)d\omega = |_{f(\omega)}|^2 \frac{\hbar \boldsymbol{k}}{m}\, d\omega$$

$\sigma(\omega)d\omega = |_{f(\omega)}|^2$ -------- (10)

Here $f(\omega)$ is called the *scattering amplitude*

Hence the total scattering cross section is

$\sigma_{total} = \int |_{f(\omega)}|^2 d\omega$ -------- (11)

The wave function ψ_k may be normalized by making

$$\int \psi_k{}^{*}\psi_k \, d\tau = 1$$

or$\int |_{\psi_k}|^2 d\tau = 1$ -------- (12)

over a large box that have periodic boundary conditions

Therefore for finding out the normalization constant A, we must take the wave function as

$\psi_k = \lim_{r \to \infty} A[e^{i\boldsymbol{k}.\boldsymbol{r}} + f(\omega)\frac{e^{ikr}}{r}]$ -------- (13)

The wave-function may be normalized to unit incident flux by choosing

$$A = \frac{1}{v^{1/2}} = \left(\frac{m}{\hbar k}\right)^{1/2}$$

But for simplicity we often choose A equal to unity.

The argument given above is incorrect for two reasons:

(i) The current density vector is not simply the sum of the current of the incident plane wave and that of the scattered wave. We must add to these contributions, the interaction term

$$e^{ik.r} \; and \; f(\omega)\frac{e^{ikr}}{r}$$

in the foregoing treatment. The interfaces between incident and scattered waves have been deliberately ignored.

(ii) The representation of the physical situation by the stationary wave

$$\psi_k(r)e^{iEt/\hbar} \qquad \text{-------- (14)}$$

in an idealization. In reality each particle participating in the scattering process must be represented by a wave-packet formed by superposition of the stationary wave.

9.5 Quantum theory of Scattering

In the quantum theory of scattering, we imagine an incident plane wave,ψ(z) = Ae^{ikz}, travelling in the z-direction, which encounters a scattering potential, producing an outgoing spherical wave. We will look for solution to the Schrödinger equation of the general

$$\Psi(\mathrm{r},\theta) \approx \mathrm{A}\left\{\mathrm{e}^{\mathrm{ikz}} + \mathrm{f}(\theta)\frac{\mathrm{e}^{\mathrm{ikr}}}{\mathrm{r}}\right\}, \qquad \text{for larger}$$

(The spherical wave must carry a factor of $1/r$, because this portion of $|\psi|^2$ must go like $1/r^2$ to conserve probability). The wave number k is related to the energy of the incident particles in the usual way:

$$\mathrm{k} = \frac{\sqrt{2\mathrm{mE}}}{\hbar}$$

(As before, I shall assume the target is azimuthally symmetrical; in the more general case the amplitude f of the outgoing spherical wave could depend on ϕ as well θ).

The whole problem is to determine the scattering amplitude f(θ); it tells you probability of scattering in a given direction θ, and hence related to the differential cross-section. The probability that the incident particle, travelling at speed *v*, passes through the infinitesimal area dσ, in time dt,

$$dP = |\psi_{incident}|^2 dV = |A|^2 (vdt) d\sigma$$

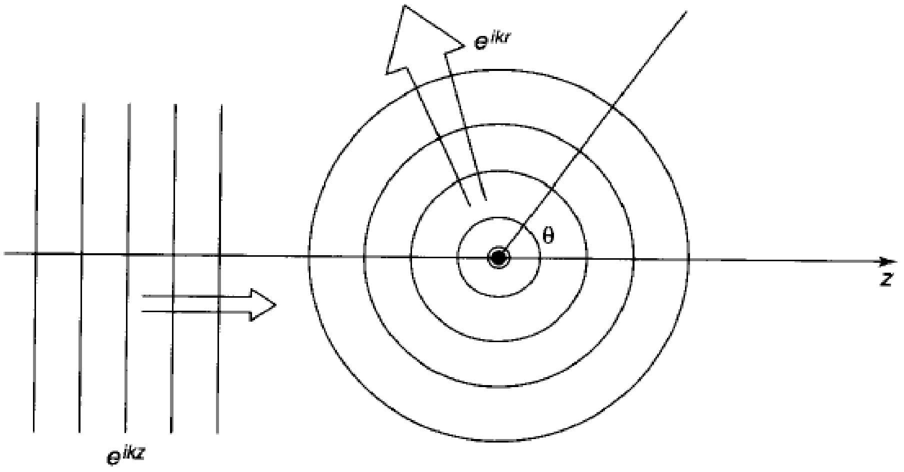


Fig. 6 Scattering of waves; incoming plane wave generates outgoing spherical waves.

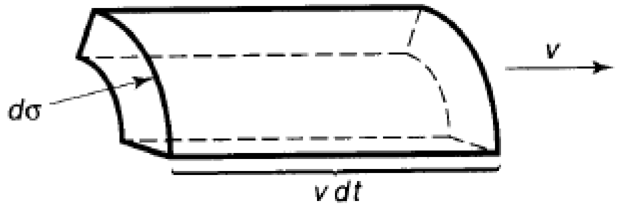


Fig.7 The volume dV of incident beam that passes through area dσ in time dt

But this is probability that the particle later emerges into the corresponding solid angle dΩ

$$dP = |\psi_{scattered}|^2 dV = \frac{|A|^2 |f|^2}{r^2} (vdt) r^2 d\Omega$$

From which it follows that= $|f|^2 \; d\Omega$, so

$$\boxed{D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2}$$

The differential cross section is equal to the absolute square of the scattering amplitude.

9.6 Partial Wave

The Schrodinger equation for a spherically symmetrical potential V(r) admits the separable solutions

$$\psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi)$$

Where Y_l^m is a spherical harmonic and $u(r) = rR(r)$ satisfies the “radial equation”

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

At very large r the potential goes to zero, and the centrifugal term is negligible, so

$$\frac{d^2u}{dr^2} \approx -k^2u$$

The general solution is

$$u(r) = Ce^{ikr} + De^{-ikr};$$

The first term represents an outgoing spherical wave, and the second an incoming one–for the scattered wave, we evidently want D = 0. At very large r, then,

$$R(r) \approx \frac{e^{ikr}}{r}$$

That’s for very large r (more precisely, for $kr \gg 1$; in optics it would be called the radiation zone). As in one-dimensional scattering theory, we assume that the potential is “localized”, in the sense that exterior to some finite scattering region it is essentially zero. In the intermediate region (where V can be ignored but the centrifugal term cannot), the radial equation becomes

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = -k^2u$$

And the general solution is a linear combination of spherical Bessel functions

$$u(r) = Arj_l(kr) + Brn_l(kr)$$

However, neither j_l(which is something like a sine function) nor n_l(which is a sort of generalized cosine function) represents an outgoing (or an incoming) wave. The linear combinations analogous to e^{ikr} and e^{-ikr}; these are known as spherical Hankel functions:

$$h_l^{(1)}(x) = j_l(x) + in_l(x);\ \ h_l^{(2)}(x) = j_l(x) - in_l(x)$$

The first few spherical Hankel functions are listed in table. At larger r, $h_l^{(1)}(kr)$(the “Hankel function of the first kind”) goes like e^{ikr}/r, whereas $h_l^{(2)}(kr)$(the “Hankel function of the second kind") goes like$e^{-ikr}/r;$for outgoing waves we evidently need spherical Hankel functions of the first kind:

$$R(r) = Ch_l^{(1)}(kr)$$

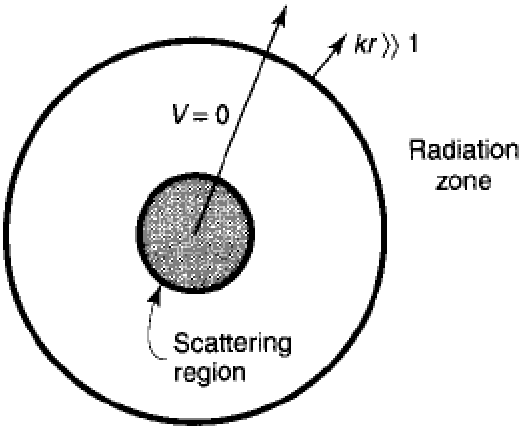


Fig.8 Scattering from a localized potential: the scattering region (shaded)the intermediate region (where V= 0), and the radiation zone (where kr>> 1)

Thus, the exact wave function, in the exterior region [where V(r) = 0], is

$$\psi(r,\theta,\phi) = A\left\{e^{ikz} + \sum_{l,m} C_{l,m} h_l^{(1)}(kr) Y_l^m(\theta,\phi)\right\}.$$

Now, for very large r, the Hankel function goes like $(-i)^{l+1}\, e^{ikr}/r$ (Table), so

$\psi(r,\theta,\phi) \approx A\left\{e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r}\right\},$

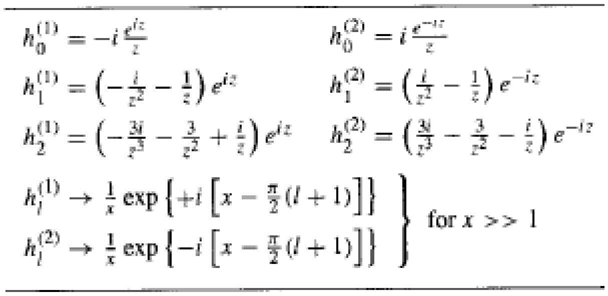
Where

$$f(\theta,\phi) = \frac{1}{k}\sum_{l,m}(-i)^{l+1} C_{l,m} Y_l^m(\theta,\phi)$$

This confirms more rigorously the general structure postulated and tells us how to compute the scattering amplitude, f(θ,ϕ), in terms of the partial wave amplitude. Evidently, the differential cross section is

$$D(\theta,\phi) = |f(\theta,\phi)|^2 = \frac{1}{k^2}\sum_{l,m}\sum_{l',m'}(i)^{l-l'} C_{l,m}^{*} C_{l',m'} (Y_l^m)^{*} Y_{l'}^{m'},$$

Table: Spherical Hankel function $h_l^{(1)}(x)$ and $h_l^{(2)}(x)$



$h_0^{(1)} = -i\frac{e^{iz}}{z}$	$h_0^{(2)} = i\frac{e^{-iz}}{z}$
$h_1^{(1)} = \left(-\frac{i}{z^2} - \frac{1}{z}\right)e^{iz}$	$h_1^{(2)} = \left(\frac{i}{z^2} - \frac{1}{z}\right)e^{-iz}$
$h_2^{(1)} = \left(-\frac{3i}{z^3} - \frac{3}{z^2} + \frac{i}{z}\right)e^{iz}$	$h_2^{(2)} = \left(\frac{3i}{z^3} - \frac{3}{z^2} - \frac{i}{z}\right)e^{-iz}$

$$\left.\begin{array}{l} h_l^{(1)} \to \frac{1}{x}\exp\left\{+i\left[x - \frac{\pi}{2}(l+1)\right]\right\} \\ h_l^{(2)} \to \frac{1}{x}\exp\left\{-i\left[x - \frac{\pi}{2}(l+1)\right]\right\} \end{array}\right\} \text{for } x >> 1$$

And the total cross section is

$$\sigma = \frac{1}{k^2}\sum_{l,m}\sum_{l',m'}(i)^{l-l'}C^*_{l,m}C_{l',m'}\int (Y_l^m)^* Y_{l'}^{m'}\, d\Omega = \frac{1}{k^2}\sum_{l,m}|C_{l,m}|^2$$

If V is independent of ϕ, then only terms with m=0 survive (remember $Y_l^m \approx e^{im\phi}$)

$$Y_l^0(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}P_l(cos\theta)$$

Where P_l is the lth Legendre polynomial. The exact wave function in the exterior region is

$$\boxed{\psi(r,\theta) = A\left\{e^{ikz} + \sum_{l=0}^{\infty}\sqrt{\frac{2l+1}{4\pi}}C_l h_l^{(1)}(kr)P_l(\cos\theta)\right\};}$$

The scattering amplitude is

$$\boxed{f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(-i)^{l+1}\sqrt{\frac{2l+1}{4\pi}}C_l P_l(\cos\theta);}$$

The total cross-section is

$$\sigma = \frac{1}{k^2}\sum_{l=0}^{\infty}|C_l|^2$$

9.7 Born Approximation

Suppose V(r_0) is localized about r_0= 0 that is, the potential drops to zero outside some finite region and we want to calculate ψ(r) at points far away from the scattering center. Then |r|>>|r_0| for all points that contribute to the integral form in equation

$$|r - r_0|^2 = r^2 + r_0^2 - 2r.r_0 \cong r^2\left(1 - 2\frac{r.r_0}{r^2}\right) \qquad \text{---------} (1)$$

And hence

$$|r - r_0| \cong r - \hat{r}.r_0 \qquad \text{--------} (2)$$

Let

$$k = k\hat{r}; \qquad \text{---------} (3)$$

Then

$$e^{ik|r-r_0|} \cong e^{ikr}e^{-ik.r_0}\text{---------} (4)$$

And therefore

$$\frac{e^{ik|r-\boldsymbol{r_0}|}}{|r-\boldsymbol{r_0}|} \cong \frac{e^{ikr}}{r}e^{-ik.\boldsymbol{r_0}}\text{---------} (5)$$

In the denominator we can afford to make the more radical approximation |r- r_0|≈r_0; in the exponent we need to keep the next term.

In the case of scattering, we want

$$\psi_0(r) = Ae^{ikz}$$

representing an incident plane wave. For the large r, then.

$$\psi(r) \cong Ae^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-ik.r_0}V(r_0)\psi(r_0)d^3r_0\text{---------} (6)$$

This is in the staandard form. We can read off the scattering amplitude:

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2 A}\int e^{-ik.r_0}V(r_0)\psi(r_0)d^3r_0 \qquad \text{---------} (7)$$

Suppose the incoming wave is not substantially altered by potential; then

$$\psi(r_0) \approx \psi_0(r_0) = Ae^{ikz_0} = Ae^{ik'r_0}\text{--------} (8)$$

where $k' = k\hat{z}$,

This would be the exact wave function, if V were zero; it is essentially a weak potential approximation. In the Born approximation, then

$$f(\theta,\phi) \cong -\frac{m}{2\pi\hbar^2}\int e^{i(\boldsymbol{k}'-\boldsymbol{k}).r_0}V(r_0)d^3r_0 \text{-------- (9)}$$

In particular, for low energy (long wavelength) scattering, the exponential factor is essentially constant over the scattering region and the Born approximation simplifies to

$f(\theta,\phi) \cong -\frac{m}{2\pi\hbar^2}\int V(r)d^3r$ (low energy)--------- (10)

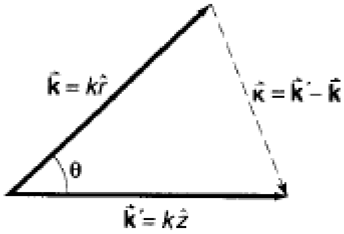


Fig.9Two wave vector in the Born approximation: k points in the incident direction, k′ in the scattered direction

For a spherically symmetrical potential, V(**r**) = V(r), the Born approximation again reduces to a simpler form.

$\kappa = k' - k$,--------- (11)

And let the polar axis for the $r_0$integral lies along k, so that

$(k' - k).r_0 = \kappa r_0 cos\theta_0$-------- (12)

Then

$f(\theta) \cong -\frac{m}{2\pi\hbar^2}\int e^{i\kappa r_0 cos\theta_0}V(r_0)r_0^2 sin\theta_0 dr_0\, d\theta_0 d\phi_0$-------- (13)

Dropping the subscript on r, then

$f(\theta) \cong -\frac{2m}{\hbar^2\kappa}\int_0^\infty rV(r)\sin(\kappa r)\,dr,$ (spherical symmetry)

The angular dependence of f is carried by k

$$\kappa = 2k\sin(\theta/2)$$

9.8 Phase Shift

The total scattering cross section is given by

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)sin^2\delta_l$$

The above equation represents the cross section of *l*th partial wave and $\delta_l$represents the phase shift of *l*th partial wave

The cross section gets vanished when δ_l = 0 or π and the value of cross section becomes maximum when the value of $\delta_l = \pm\frac{\pi}{2}, \pm\frac{3\pi}{2}, etc.$

We have

$$\text{R(r)=lim}_{r\to\infty}\frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

It is coming from R(r) →Aj_l(kr)

Thus, δ_l represents the difference in phase between the asymptotic from actual radial function R(r) and the radial function j_l(kr) in the absence of scattering potential i.e., V=0

Now j_l(kr) becomes maximum if r ≈ $\frac{1}{k}$, thus for the value of r (we select "a") r ≈ a ≈ $\frac{1}{k}$, we obtain higher order phase difference because V gets vanished beyond a, i.e., r >a.

The phase shift becomes very small when a <$\frac{1}{k}$. Hence the summation $\sum_{l=0}^{\infty}$ will beequal to the summation of few terms such as $\sum_{l=0}^{l=ak}$.

Calculation of$\boldsymbol{\delta_l}$. It becomes possible to calculate the value of δ_l by applying the boundary condition for the continuity of $R_l$at r=a in the region r <a and r> a

$$\left(\frac{1}{R_l}\frac{dR_l}{dr}\right)_{r>a} | \text{ at r=0 } \left(\frac{1}{R_l}\frac{dR_l}{dR}\right)_{r>a} | \text{ at r=a}$$

$$R_l = A_l(cos\delta_l j_l(kr) - sin\delta_l \eta_l(kr)$$

$$\left(\frac{1}{R_l}\frac{dR_l(r)}{dr}\right)_{r>a} | \text{ at r=a}$$

$$= \text{k}\left[\frac{cos\delta_l j_l'(ka) - sin\delta_l j_l'(ka)}{cos\delta_l j_l(ka) - sin\delta_l j_l(ka)}\right]_{r>a>}$$

Suppose $\left(\frac{1}{R_l}\frac{dR_l}{dr}\right)_{r>a}$ | at r= a= γ_l

Soγ_l= k$\left[\frac{j_l'(ka)-tan\delta_l\eta_l'(ka)}{j_l(ka)-\tan\delta_l\eta_l(ka)}\right]$

$$\tan\delta_l = \left[\frac{kj_l'(ka)-\gamma_l j_l(ka)}{k\eta_l'(ka)-\gamma_l\eta_l(ka)}\right] \qquad \text{---------} \ (1)$$

where$j_l'(ka) = j_{l-1}(ka) - \frac{l+1}{ka}j_l(ka)$

$$\eta_l'(ka) = \eta_{l-1}(ka) - \frac{l+1}{ka}\eta_l(ka)$$

In the above equations, γ_l represents the ratio of the slope to the value of the interior wave equation.

It becomes possible at once to get an approximate value of $\delta_l$provided the value of l is large and δ_l is expected to be small. In such a case, $\gamma_l$will not be much different from the ratio of the slope to the value of the solution in the absence of a scattering potential, so that it becomes possible to put

γ'=k $\left(\frac{j_l'(ka)}{j_l(ka)} + \varepsilon_l\right)$

As

$$|\varepsilon_l| \ll \frac{|j_l'(ka)|}{|j_l(ka)|} \qquad \text{---------} \ (2)$$

By changing j_l' into$j_l$into Eq. 1, we get

$$\tan\delta_l = \left[\frac{\varepsilon_l(ka)^2 j_l^2(ka)}{\varepsilon_l(ka)^2 j_l(ka)\eta_l-1}\right] \qquad \text{---------} \ (3)$$

The above is still exact

If the power series equation for j_l is used when l>>$(ka)^2$and the value of j_l is used in terms of sine and cosine, the inequality Eq. 2 becomes as follows

$$|\varepsilon_l| \ll \frac{1}{(ka)} \ \text{---------} \ (4)$$

And Eq. (3) on approximation becomes as follow:

$$\delta_l = \frac{\varepsilon_{l(ka)^{2l+2}}}{[(2l+1)!]^2} = -\frac{\varepsilon_{l(ka)^{2l+2}2^{2l}(l!)^2}}{(2l+1)!}$$

By using Stirling's formula, we obtain

$$log|_{\delta_l}| \approx \ log|\varepsilon_l| = 2l[\log(ka) + 1 + log2] - logl$$

Some explanatory remarks about δ_k are as follows:

(i) It follows that for an attractive field X(r) gets shifted inward relative to $X_{kr}(r)$ and for a repulsive field X(r) gets shifted outward relative to other function. i.e.,
$\delta_l > 0$for attractive field
$\delta_l < 0$for repulsive field

(ii) Classically, $l\hbar = pp$ where pp represents the momentum of the particle and ρ the impact parameter. The summation of *l* for the partial wave *l*=0,1… has been found to be equivalent to the integration of all values of the impact parameter in the classical theory.

(iii) When the values of k and *l*are large, it is possible to calculate the phase shift by the Born approximation. Thus, we get

$$\delta_i \cong -\frac{1}{2k} U(r_0) r_0$$

Where $r_0$represents the classical distance of closet approach. For large *l*, r_0 becomes ρ, the ≅ impact parameter. The series for total cross section behaves like as follows:

$$\sigma \propto \sum (2l+1)\delta_l^2 = \frac{1}{4}\int_0^\infty dp\rho^3 U^2(\rho)$$

As $l\hbar = p\rho = \hbar k\rho$

In order that this may get converged U(r) should decrease with distance at a rate greater than $\frac{1}{r^2}$

(iv) For the scattering amplitude in the forward direction, f(0) will take the following form:

$$f(0) \propto \sum (2l+1)\delta_l \rightarrow k\int_0^\infty d\rho\rho^2 U(\rho)$$

In order that it may get converted $U(\rho)$ should decrease with distance faster than $\frac{1}{r^3}$

(v) For low energy scattering by a potential of the asymptotic form c/r^n, the variations of the phase shifts for various *l*are as follows:

$$\delta_l \propto k^{2l+1} \text{for} \quad 2l < n-3$$

$$\delta_l \ \propto k^{2l+1} logk \qquad \text{for} \quad 2l = n-3$$

$\delta_l \ \propto \ k^{n-2}for2l > n-3$

Aliter. It follows that the total S-wave (i.e.,l=0) scattering cross-section is given as follows:

$$\sigma_s = \frac{4\pi}{k^2} sin^2\delta$$

$$= \pi \left(\frac{2\ sin\delta}{k}\right)^2$$

In case of classically hard sphere scattering, the total cross-section may be given as follows:

$\sigma = \pi a^2$

where a represents the radius of hard sphere

Here $\left(\frac{2 \sin\delta}{k}\right)$ represents the effective radius of the target.

The scattering cross section gets vanished for $\delta_l = 0$ or 180°and the cross section becomesmaximum for the value of $\delta_l = \pm\frac{1}{2}\pi, \pm\frac{3}{2}\pi$ etc.

$Sin\delta < 1$

$$\sigma_s < \frac{4\pi}{k^2}$$

Thus, it represents upper limit of scattering. A simple case for which δ can be solved exactly has been found to be that of the S-wave scattering from hard sphere scattering by a hard sphere

Scattering by a hard sphere

But $\mathcal{X}(r) = rR(r)$

For $r > a,\ V(r) = 0$

$$E = \frac{\hbar^2 k^2}{2m}$$

Now general equation may be written as:

$$\frac{d^2\mathcal{X}}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right]\mathcal{X} = 0$$

$$U(r) = \frac{2\mu V(r)}{\hbar^2} \to 0 \qquad as\, r > a$$

And $\frac{l(l+1)}{r^2} = 0 \quad for \quad l = 0$

Thus, $\left(\frac{d^2}{dr^2} + k^2\right)\mathcal{X}(r) = 0$

The solution of above equation must be as follows:

$$R(r) = \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{\pi} + \delta\right)$$

$$\mathcal{X}(r) = rR(r) = \frac{A_l}{k}\frac{e^{(ikr - il\pi/2 + i\delta)} - e^{(-ikr + il\pi/2 - i\delta)}}{2i}$$

$$= \frac{A_l}{2ik}e^{-i\delta}\left(e^{2i\delta}\, e^{ikr}\, e^{-il\pi/2} - e^{-ikr}\, e^{il\pi/2}\right)$$

But $A_l = e^{i\delta}$ $and\ l = 0$

So $\mathcal{X}(r) = \frac{e^{2i\delta}\, e^{-ikr} - e^{ikr}}{2ik}$

From the boundary condition, function, and

$$\mathcal{X}(r) = 0 \quad at \quad r \geq a$$

On substituting $\mathcal{X}(a) = 0$ in the above relation, we obtain

$$0 = \frac{e^{2i\delta}\, e^{-ika} - e^{ika}}{2ik}$$

Thus, $\delta = -ka$

And total S-wave scattering may be given as follows:

$$\sigma_s = \frac{4\pi}{k^2} sin^2 ka$$

For extreme low energy limit, we obtain

$$ka \leq 1$$

It means that only S-wave scattering is taking place and this is equal to total scattering. Thus,

$$\sigma \cong \frac{4\pi}{k^2}(ka)^2 = 4\pi a^2$$

In classical way it has been found to be πa^2 only. Thus, it becomes large by factor 4 for the same radius. Hence, for low energy particles the cross-section becomes 4 times the geometrical cross-section of the rigid sphere.

9.9 Summary

Scattering theory is very important both to the experimentalist as well as the theoretical physicist. A thorough understanding of scattering is indispensable in the study of interaction of atoms, nuclei and particle.The result of scattering are mainly expressed in terms of a cross section.Scattering cross section used to dealing with the collision of a beam of particle with scattering center. It is measured of the probability that the particle will get scattered as it traverse as given thickness of matter.Where the Born approximation fails, use some other method. One such method is the method of partial waves. This method is applicable to spherically symmetric potentials. For such potentials, the angular momentum is a constant of motion. It is advantageous to expand the solution in terms of angular momentum eigenfunctions.

9.10 Glossary

Collision – to hit something violently

Inelastic- lacking flexibility

Scattering- refract or diffract

Transverse- acting or lying

Incident- falling on or striking something

Interaction- exchange

Imagine- assume

Symmetrical- arrangement of part

Intermediate- coming between two things in time

Approximate- close to

9.11References

1. P.M. Mathews and K. Venkatesan, A Text book of Quantum Mechanics, Tata McGraw-Hill, NewDelhi.

2. L.I. Schiff, Quantum Mechanics, 3rd Edition, International Student Edition, McGraw-Hill.

3. V. Devanathan, Quantum Mechanics, Narosa Publishing House, New Delhi.

4. SatyaPrakash, Advanced Quantum mechanics

5. David J. Griffiths, Introduction of Quantum mechanics

9.12 Suggested Reading

1. Landau and Lifschitz "Quantum Mechanics"
2. Nielsen & Chuang: "Quantum Computation and Quantum Information"
3. “Principle of Quantum Mechanics”by Ramamurti Shankar

9.13 Terminals questions

Long Answer type

Q1.What do you understand by scattering cross-section? Deduce an expression for the scattering cross-section of particles by a spherically symmetric potential. Explain the significance of the “phase shift” terms appearing in the formula.

Q2. Give the theory of Born approximation in scattering.

Q3. Find a general expression for the phase shift produced by scattering potential $V(r) = A/r^2$ where $A>0$.

Q4. Calculate the scattering amplitude for a central potential in the first Born approximation.

Q5. Describe and discuss the method of partial waves for an elastic scattering. Give the interpretation of phase-shift.

Q6. Define the scattering cross-section. Describe the method of partial waves for scattering.

Q7. What is meant by differential scattering cross-section, the total scattering cross-section and the scattering amplitude?

Q8. Write short notes on

(a) Classical theory of scattering
(b) Quantum theory of scattering

Objective answer type

Q1. The differential cross-section $\sigma(\theta, \phi)$ will be equal to

(b) $|f(\theta, \phi)|$ (b) $\frac{|f(\theta, \phi|^2}{2}$

(c) $|f(\theta, \phi|^2$ (d) $f(\theta, \phi$

Q2.Scattering cross-section for coulomb potential using Born approximation is directly proportional to

(a) $sin^4\theta$ (b) $cos^4\theta$

(c) $cosec^4\theta$ (d) $cosec^4\frac{\theta}{2}$

Q3.Born approximation is vaild only when

(a) Total wave function is different from incident wave function
(b) Total wave function is not generally different from the incident wave function
(c) Always applicable
(d) None of theses

Q4 For scattering on a hard sphere of radius R,in classical physics the different scattering cross-section is given by

(a)πR^2 (b)$\frac{\pi R^2}{2}$ (c)$\frac{R^2}{2}$ (d) $\frac{R^2}{4}$

Q5. If scattering amplitude $f(\theta) = e^{+\left(\theta+\frac{\pi}{4}\right)i}$,then total scattering cross-section is

(a) $\sqrt{\frac{2\pi}{k}}$ (b) $\frac{\pi}{2\sqrt{2k}}$ (c)$\frac{2\sqrt{2\pi}}{k}$ (d)$\frac{2\pi}{\sqrt{2k}}$

Q6. Which of the following is /are correct?

(a) Scattering amplitude for bose particle = amplitude direct +amplitude exchanged

(b) Scattering amplitude for Fermi particle = amplitude direct- amplitude exchanged

(c) For bose and Fermi particle scattering amplitude = amplitude direct + amplitude exchanged

(d) Nose of these

Q7. The scattering amplitude in partial wave analysis is given by

$$f(\theta) = cos2 + i\,2\sin\left(\theta + \frac{\pi}{2}\right)$$

Propagation constant is k = π

The value of imaginary part at θ=0 is

(a) 2 (b) 4 (c) 1 (d) 0

Q8. In Q7 the total scattering cross section is given by

(a) 4 (b) 8 (c) 10 (d) 12

Q9.Which of the following is /are correct for partial wave analysis?

(a) This method is applied when born approximation failed
(b) It is used only antisymmetric potentials
(c) It is used only symmetric potential
(d) All of the above

Q10. For scattering on a hard sphere of radius R. The δ_0- wave phase is given by

(a) $\delta_0 = KR$ (b)$\delta_0 = -KR$ (c) δ_0=2KR (d)$\delta_0 = -2KR$ 12

Answers

1(c) 2(d) 3(b) 4(d) 5(c) 6(a,b) 7(a) 8(b) 9(a,c) 10(b)