UNIT-1

LESSON – I - EMERGENCE OF QUANTUM MECHANICS

Objective

Presentation of brief review of classical concepts and their limitations in understanding the sub-microscopic realm of atoms and their constituents and new concepts put forward to eliminate the limitations thus leading to the consequent emergence of quantum mechanics.

1.1.1 Introduction

Towards the end of nineteenth century classical mechanics, constituting Lagrangian – Hamiltonian formulation of Newtonian Mechanics, proved to be successful in explaining the motion and interactions of material objects and most of the related experimental findings. Maxwell's Electromagnetic (EM) theory was equally successful in predicting and analyzing the behaviour of radiant energy. Therefore many scientists believed that classical mechanics and EM theory together provided physics with elegant and unquestionable fundamental laws.

In the classical picture, the position and path of a particle are sharply defined whereas the radiation (EM-field) exists over a region of space. These classical pictures of particles and radiation are mutually exclusive. But experiments in the beginning of the twentieth century gave firm evidence for the existence of the wave-like behaviour of particles (electron diffraction experiments of Davisson and Germer – 1927; G.P. Thomson-1928) and the particle like behaviour of radiation (Photoelectric effect-1905; Compton effect-1923). This dual nature of matter and radiation and allied phenomena of micro-particle world could not be explained by the classical pictures. This inability of classical physics necessitated a new branch of physics, called Quantum Mechanics.

Historical development of any branch of science, more so theoretical physics like Quantum Mechanics, involves two main stages:

(i) accumulation of experimental facts, discovery of semi-empirical laws, development of preliminary hypothesis and theories.

(ii)discovery of general laws which provide a basis for interpreting a large number of phenomena.

1.1.2 Black Body Radiation:

The failure of classical laws was first felt acutely in their inability to account for the experimentally observed energy distribution (energy density Vs wavelength or frequency) in the continuous spectrum of black body radiation.

A black body is one, which absorbs all the radiation it receives. The best example is an isothermal cavity with a small aperture into which radiation from outside is admitted and trapped. In such a container, radiation bounces around inside the cavity and eventually comes into thermal equilibrium at the temperature of the cavity. The properties of the black body radiation depend solely on the temperature (T) of the black body.

For analyzing the radiation (EM waves in the cavity), it was treated as a superposition of normal modes characteristic of the cavity. In each normal mode, field was assumed to vary with time simple harmonically and accordingly each mode was considered equivalent to a simple harmonic oscillator. Thus the absorption of radiation by the walls of the cavity was treated as equivalent to a transfer of energy to the walls by the oscillators and the emission was the reverse process.

According to classical physics, oscillators emit or absorb energy in a continuous fashion. Rayleigh-Jeans law was rigorously derived on the basis of classical physics. Average energy density $\rho(\upsilon)\,d\upsilon$ of the black body radiation in the frequency range υ and $\upsilon+d\upsilon$ was derived to be

$$\rho\,(\upsilon)\,d\upsilon = \frac{8\pi\upsilon^2}{c^3}\,kT\,d\upsilon \qquad (1.1.1)$$

where ‘c’ is the velocity of light and ‘k’ is the Boltzmann constant.

This law agreed with experiment only for small values of υ (fig.1.1.1).

Also a serious fundamental difficulty became apparent; there would be according to this formula a disproportionate amount of energy radiant in very high frequency radiations like x-rays and γ-rays - an event known as the ultraviolet catastrophe. But such a phenomenon has never been observed.

In an effort to remove these difficulties, Planck (1900) hits upon a formula

$$\rho\,(\upsilon)\,d\upsilon = \left(\frac{8\pi\upsilon^2}{c^3}\right)\frac{h\upsilon}{e^{h\upsilon/kT}-1}d\upsilon \qquad (1.1.2)$$

where h = 6,626 x 10^{-34} Js is called the Planck’s constant.

S.N.Bose (1924) derived Planck’s equation using a statistical approach based entirely on the idea that radiation is made up of tiny particles (quanta or photons). It derives the black body radiation entirely in quantum terms without using the idea of EM radiation at all. Thus, Bose secured strong mathematical footing for the quantum theory of light.

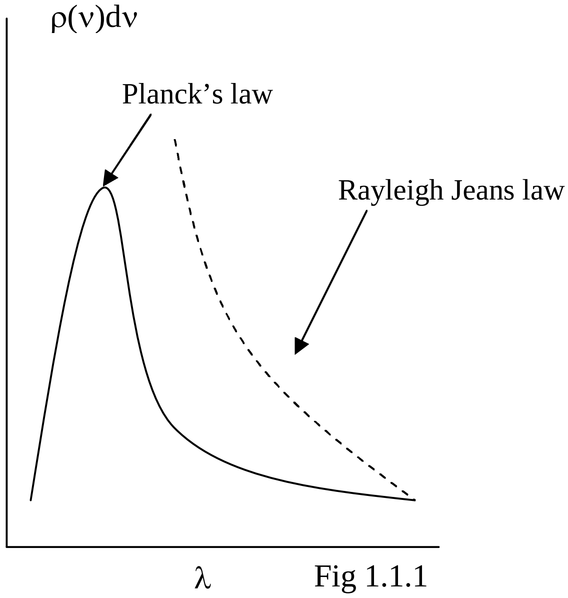

Fig 1.1.1

This expression is in agreement with the experiment for all frequencies. But when he developed a theoretical justification for such a formula he was forced to make a startling non-classical assumption that the energy states of an oscillator must be an integral multiple of the constant h and frequency υ of the radiation it emits. If E represents the smallest permissible energy change, Planck's famous quantum equation is

$E = h\upsilon$ (or) $E = nh\upsilon$ (n=1,2,3…..)

It follows that the oscillator cannot slowly radiate energy as the classical electrodynamics requires, for it would then be led into states other than the allowed ones. Therefore radiation is not emitted continuously but in discrete bundles (or) packets of radiant energy equal to $h\upsilon$. These bundles (or) packets of radiant energy are called **Quanta**. The light quantum is given the name **Photon** by the American physical chemist Gilbert Lewis in 1926. It is obvious however that, quanta of different frequencies have different sizes (energies). Planck thought at first that his hypothesis applied only to the radiating object (or oscillator) and possibly to the emitted radiation in their immediate neighbourhood. However this initiated a series of events which changed our whole concept of interaction of EM radiation with matter.

1.1.3 Photoelectric Effect

Classical physics received another jolt in the explanation of the photoelectric effect.When radiation falls on certain materials, electrons are emitted. This effect is called photoelectric effect.

If E_o is the energy required to separate an electron from the metal surface, v is the electron's velocity after separation and E is the energy of the absorbed light, then

$$\frac{1}{2}\,mv^2 = E - E_o \qquad (1.1..3)$$

According to classical EM theory, E depends on the square of the amplitude (or) intensity of the incident radiation. Therefore the velocity of the photoelectrons should increase with increasing intensity of incident radiation. But experiments proved that the intensity increases only the number of photoelectrons released but not their velocity. Further for any particular material, there is a minimum frequency of the radiation called the threshold frequency, below which no photoelectrons are emitted. The existence of the threshold frequency also could not be explained from classical laws.

In 1905, Einstein proposed a daring simple explanation by further developing the quantization of energy concept by assuming that

(i) the quantization phenomenon was a property of the radiation itself. (ii) the quantization process applied to both absorption and emission of the radiation (iii) the energy bundles (or photons) preserve their identity throughout their life.

Accordingly, each photon carries an amount of energy equal to $h\upsilon$. The equation (T) can be written as

$$\frac{1}{2}\,mv^2 = h\upsilon - h\upsilon_o \quad \text{where } E_o = h\upsilon_o \qquad (1.1.4)$$

His interpretation of the threshold frequency was that a quanta of light below threshold frequency (υ_o) does not have enough energy to remove an electron. The quanta above the frequency ($\upsilon > \upsilon_o$) possess the required energy. Intensity increases the number of photons and hence the number of photoelectrons but not the energy of the photons and the K.E of photoelectrons. This interpretation is a great success to **Quantum Theory**.

1.1.4 Compton Effect

The explanation of the phenomenon of X-ray scattering, like that of energy distribution of Black Body Radiation, necessitated the rejection of the classical concept of continuous energy distribution of radiation. The experimental evidences strongly supported the Quantum ideas of the particle aspects of radiation.

According to classical ideas, when X-rays are incident on a scatterer, the electric vector of the incident waves accelerates the electrons in the scatterer. According to electrodynamics, an accelerated charge radiates energy. Consequently, the electrons radiate energy due to the forced oscillations under the action of the incident X-ray beam. Therefore we expect the scattered radiation to have the same wavelength as the incident radiation (coherent scattering). But according to experimental evidence, the scattered radiation, in addition to the unmodified incident radiation, consists of intense long wavelength component (incoherent scattering). This is explained by **Compton** using **Quantum Theory**. This incoherent X-rays scattering is called **Compton Effect**.

Energy distribution of Black Body Radiation was explained by Planck with a radical postulate that radiation is emitted in bundles (photons). Photoelectric effect was explained by Einstein with the extension of the idea of photon and the assumption that the photon preserves its identity during propagation and interaction with matter.

Einstein’s mass energy relation ($E = mc^2$) endows the photon ($E = h\upsilon$) with a mass $m = h\upsilon/c^2$. The concept that photons behave as particles through out their life with more concrete particle aspects like momentum ($p = mc = h\upsilon/c = h/\lambda$) was put forward by Compton to explain incoherent x-ray scattering known as Compton effect.

Based on these ideas, Compton derived the equation

$$\Delta\lambda = \frac{h}{m_e c}(1-\cos\alpha) \qquad (1.1.5)$$

where $\Delta\lambda$ is the difference between the unmodified incident radiation and modified scattered radiation and α is the angle of scattering.

When $\alpha = 90^o$, $\Delta\lambda = \frac{h}{m_e c}$. It is called **Compton Wavelength** and is equal to 0.0242 Å. This corresponds to the energy of 0.51 MeV.

The theoretical predictions were verified in scattering experiments conducted with carbon and Molybdenum K_α radiation. The results of the Compton Effect provide a good evidence of the particle concept of photon and also a good check of theory of Relativity.

1.1.5 Photon

It is quite interesting to have a glimpse at the historical development of the concept of a novel idea 'photon'. The idea of photon, the particle of radiation (light) originates more directly from Albert Einstein's work (1905) on the photoelectric work. However many years passed by before establishing the physical reality of the photons and they were only given this name in 1926 by Gilbert Lewis.

The primary reason for the delay was the lack of direct and accurate experimental confirmation of Einstein's ideas. In 1905, the experimental data of photoelectric effect, on which Einstein had based his idea was not sufficiently accurate to exclude the possibility of other theoretical explanations of photoelectric effect and there was no other evidence in favour of Einstein's idea. Einstein himself, as late as 1911, expressed that "I insist on the provisional nature of this concept which does not seem reconcilable with the experimentally verified consequences of the wave theory".

Robert Millikan, who provided the accurate experiments needed to prove the correctness of Einstein's idea was, ironically, motivated by a strong desire to prove them wrong. Finally Einstein's idea was proved and in Millikan's words "I spent ten years of my life testing that 1905 equation of Einstein's and contrary to all my expectations, I was compelled in 1915 to assert its unambiguous verifications in spite of its unreasonableness". After Millikan's work, momentum associated with quantum of light was envisaged. Only in 1923 Arthur Compton's investigations of Compton Effect asserted that EM quanta behave exactly like particles, exchanging both energy and momentum in collisions with electrons.

To complete the story of the photon, it is a boson with zero mass and spin 1. It obeys Bose-Einstein statistics. Every second, nearly about 1000 billion photons of sunlight fall on a pinhead.

1.1.6 Hydrogen Atomic Spectrum

An important development of Quantum Physics started in 1913, when Bohr theoretically derived the well-known Ritz-Rydberg empirical relation for the wave number

$$\bar{\upsilon} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \qquad (1.1.6)$$

where R is the Rydberg constant. For different spectral series 'm' takes on different integral values, whereas for different lines within a series 'n' takes a different integral values. For example m = 2 and n = 3,4,5,…. for the popular **Balmer's series**.

Bohr's theory is based on the following postulates:

1. The electron of the hydrogen atom moves about the nucleus (the proton) in certain circular orbits (stationary states) without radiating energy.
2. The allowed stationary states are such that the angular momentum of the electron is equal to the integral multiple of $h/2\pi$ ($I\omega = n\hbar$, $n = 1,2,3,\ldots$).
3. When an electron makes a transition from a state of energy E_i to a state of energy E_f (where $E_i > E_f$) electromagnetic radiation (photon) of frequency $\upsilon = (E_i - E_f)/h$ is emitted.

In his theory Bohr retained the concept of Rutherford's nuclear model of the atom with a central heavy proton and a revolving electron. Classical electrodynamics predicts that the orbital electron should radiate energy because of its acceleration and slowly spiral into the nucleus. But to account for the stability of the hydrogen atom, Bohr postulated stationary non-radiating orbits. According to classical physics, the electron should emit radiation of frequency, which is equal to the orbital frequency of the electron. This is not in agreement with the experiments. To rectify this defect, Bohr formulated his third postulate, $\upsilon = (E_i - E_f)/h$.

1.1.7 Old Quantum Theory

Planck-Einstein photon theory, Bohr theory and their numerous variations generally go under the name **Old Quantum Theory.**

In addition to the spectrum of hydrogen, Bohr's theory could explain the **Stark and Zeeman effects**. A semi-quantitative description of the energy levels of multi-electron atoms was also given. However, adhoc selection rules forbidding transitions between certain energy levels were required in the explanation of Zeeman and Stark effects and also the spectra of multi-electron atoms. Though the frequencies of the spectral lines were explained by the old quantum theory, the calculation of their intensities could not be attempted. For this purpose an adhoc rule called the **Correspondence Principle** was to be put forward by Bohr in 1918. This principle was based on the fact that Bohr's spectral frequency in the limit of large quantum numbers asymptotically equals the actual orbital frequency of the electron, which would be radiated according to the classical electrodynamics. Based on this it is postulated that for the states of the atom associated with large quantum numbers, actual radiation intensity may approach that given by the application of the classical electrodynamics. There is still another ambiguity in the classical intensity calculation for a transition, for the intensity computed differed for the two states involved and we don't know how much contribution of each state is to be taken. Further, a number of experimental observations like dispersion could not be properly explained. Besides these practical difficulties, there are important conceptual difficulties.

The existence of discrete stationary states was experimentally verified. But as long as the classical picture of **well-defined particle orbits** is retained, it remains incomprehensible why certain orbits should be completely stable and other not allowed to exist at all. This perplexing question was responsible in part for the ultimate realization that particle states at microscopic level are not describable in terms of well defined orbits but must be pictured in terms of some kind of waves.

1.1.8 Wave-particle Duality

Old Quantum Theory visualized radiation as a stream of photons. This theory was successful in explaining Photoelectric Effect, Compton Effect etc. However it in no way invalidated the old well-tested wave theory of light, which was very successful in the explanation of the phenomena like interference and diffraction. Thus radiation is to be sometimes treated as particles and some times as waves. This **paradox** is called **wave-particle duality**.

Based on the symmetry of nature, de Broglie (1925) postulated that micro-particles like electrons should also have wave properties. This was experimentally confirmed by the electron diffraction experiments of Davisson-Germer (1927), Kikuchi (1928) and G.P.Thomson (1928). In these experiments, electrons were diffracted by crystal lattices as waves would be. The wave-particle duality therefore was not something limited to radiation but appeared to be a more general phenomenon: particles under certain circumstances behave like waves and radiation (waves) may have certain particle properties.

To understand the diffraction pattern of electrons or photons and at the same time to resolve the wave-particle duality, the electron (or) photon is to be treated as a particle whereas the laws of the motion in the micro-world are wavelike in character. The wave here plays the role of probability amplitude in the probability distribution of the particles. This description leads to an important limitation that no physical measurements are capable of providing information of unlimited precision about the simultaneous values of position and momentum of a particle. This is the famous uncertainty principle of Heisenberg: $\Delta x \ \Delta p_x \geq \hbar/2$**.**

Uncertainty principle is the heart and soul of Quantum Mechanics and therefore it is worthwhile to understand the principle through a thought experiment (gedanken experiment). Thought experiment is one, which is not intended to be carried out as a practical reality, but it is ‘all in mind’. The idea is that by using our understanding of the laws of Physics, we can construct imaginary experiments and predict their outcomes, thereby highlighting features of those laws, which may not be obvious at the first sight.

Heisenberg's gamma microscope set up to measure the position of electron is one such experiment. As shown in the figure-2, a gamma-ray photon (frequency = υ and momentum = $h\upsilon/c$) from a source collides with the electron.

The electron (mass = m) recoils with velocity 'v' at an angle 'ψ' from the initial direction (say x – direction) and the photon bounces into the microscope (with changed momentum = $h\upsilon^{/}/c$) at an angle **Φ.** Accordingly, the momentum along the X-axis (p_x) transferred to the electron is given as

$p_x = mv\cos\psi = h\upsilon/c - (h\upsilon^{/}/c)\cos\Phi$

The photon may enter the objective of the microscope along path OA or OB. Therefore **Φ** varies from $(90 - \theta)$ to $(90 + \theta)$ where θ is the angle between the path of the photon entering the microscope and the axis of the microscope. Therefore p_x can have a range of values indicated below:

$h\upsilon/c - (h\upsilon^{/}/c)\cos(90 - \theta) < p_x < h\upsilon/c - (h\upsilon^{/}/c)\cos(90 + \theta)$

$\Rightarrow h\upsilon/c - (h\upsilon^{/}/c)\sin\theta < p_x < h\upsilon/c + (h\upsilon^{/}/c)\sin\theta$

Therefore, the possible variation in p_x, namely Δp_x, is

$\Delta p_x = (2h\upsilon^{/}/c)\sin\theta = (2h/\lambda^{/})\sin\theta$

This Δp_x is the uncertainty in the value p_x. In the determination of the position of the electron, the resolving power of the microscope plays an important role.

Resolving power $= \Delta x = \lambda^{/}/(2\sin\theta)$.

This is the minimum distance, between two points in the field of view, which can be distinguished as separate. Therefore, if Δx is less, the accuracy in measurement of position of the electron is more. For this purpose, we have to use gamma rays of lower wavelength or higher frequency. It is evident that Δx is the uncertainty of the position of the electron. From the

equations for Δp_x and Δx, it is obvious that as the wavelength of the gamma photon increases, Δx increases and Δp_x decreases and vice-versa. The product of the uncertainties

$\Delta x\,\Delta p_x \approx [\lambda^{/}/(2\sin\theta)]\,(2h/\lambda^{/})\sin\theta = h$

From the accurate theoretical derivation, presented in the next lesson, it can be proved that $\Delta x \ \Delta p_x \geq \hbar/2$.

1.1.9 Quantum Mechanics

The major difficulty with the old quantum theory was the lack of coherence in the structure of the principles. Problems were first solved by the classical laws of motion and later quantum conditions were added, instead of being an integral part of it. For this reason, the old quantum theory was finally abandoned in favour of what is known as New Quantum Theory or Quantum Mechanics. In this theory, instead of starting with classical laws of motion and adding quantum conditions as an after thought, the classical concepts are abandoned almost entirely. The theory is developed to give as natural consequences of it the quantization, dual nature, uncertainty principle and other important features of them.

Heisenberg, argued that most of the conceptual difficulties were because the old quantum theory was built on quantities like electron orbits and quantum jumps which cannot be experimentally observed. Therefore he felt that the new quantum theory should be built on nothing but **observable** physical quantities like frequencies and intensities of spectral lines. With this background, Heisenberg (1925) developed his new mechanics (Matrix Mechanics) with the help of powerful mathematical tools like Fourier analysis and Matrix theory. Physicists have hardly acquainted with matrix mechanics before another mechanics (Wave Mechanics) was formulated by Schrodinger (1926). The essential feature of his theory is the incorporation of the expression for the deBroglie wavelength into the general classical wave equation. Subsequently, it was shown that the matrix mechanics and wave mechanics are mathematically equivalent and lead to the same results. Now, both matrix mechanics and wave mechanics together go under the more general name **Quantum Mechanics**. Dirac developed his own operator techniques, which further enriched quantum mechanics.

Summary of lesson

The limitations of the laws of classical physics to explain the phenomena of Black Body Radiation, Photoelectric Effect, Compton Effect and Hydrogen Atomic Spectrum have been outlined. New concepts like

Planck's quantization, Wave-particle Duality and Uncertainty Principle, which emerged to overcome the limitations, have been explained. The consequent emergence of the new branch of physics, namely Quantum Mechanics has been explained.

Key terminology

Planck's quantization – Black body radiation – Compton effect – Compton wavelength – Quantum – Photon – Bohr model – Wave-particle duality – Uncertainty principle – Matrix mechanics – Wave mechanics – Quantum Mechanics.

Self assessment questions

(i) Explain the term's Black body radiation and ultraviolet catastrophe.

(ii) What is the revolutionary idea put forward by Planck to explain Black Body Radiation?

(iii) Compare laws of Black body radiation formulated by Rayleigh-Jeans and Planck.

(iv) Give Einstein's explanation of Photoelectric effect.

(v) What is the role of Compton Effect in the formulation of the particle aspect of radiation?

(vi) Explain wave-particle duality.

(vii) What is the relation between thought experiment of gamma microscope and uncertainty principle?

(viii) Differentiate between classical physics, old quantum theory and quantum mechanics.

REFERENCE BOOKS

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2. Advanced Quantum Mechanics – Rajput B S (Pragati Prakashan, Meerut)
3. Quantum Mechanics – Chatwal G R and Anand S K (Himalaya Pub. House, Bombay)

UNIT - 1

LESSON - II - OPERATOR ALGEBRA

Objective

Introduction and explanation of various operators like linear and Hermitian operators which are useful for the foundation of the basic structure of Quantum Mechanics and their algebra.

1.2.1 Introduction

Quantum Mechanics was developed by eminent scientists who had strong foundation in both physics and mathematics. Modern approach treats quantum mechanics as a new subject with its own set of postulates. The development of the theory is based on mathematical techniques using operators. Operator algebra follows the general laws of commutation, association and distribution with respect to addition. But multiplication is not necessarily commutative, as is with matrices. It is of interest to understand operators and the related algebra for understanding the **Foundations of Quantum Mechanics,** given in the next lesson.

1.2.2 Operators

An operator is a mathematical quantity which operating on any function transforms it into another. Generally, operators are indicated by symbols with a caret over them as $\hat{A}$. If $\hat{A}$ is an operator which operates on function ‘f ’ and converts into another function ‘g’, this process is represented as

$$\hat{A} f = g. \qquad (1.2.1)$$

Example-1

Some common operators are given below:

(i) addition operator : $\hat{A} = 4 +$ (ii) differential operator : $\hat{B} = \frac{d}{dx}$

(iii) integral operator : $\hat{C} = \int dx$ (iv) square root operator : $\hat{D} = \sqrt{\ }$

(v) multiplication operator : $\hat{E} = x \, x$ (or) simply $\hat{E} = x$

Accordingly, if we take $f = x^2$, we have

(i) $\hat{A}f = 4 + f = 4 + x^2$ **(ii)** $\hat{B}f = \frac{d(x^2)}{dx} = 2x$

(iii) $\hat{C}f = \int x^2 \, dx = x^3/3$ **(iv)** $\hat{D}f = \sqrt{x^2} = x$

(v) $\hat{E}f = x(x^2) = x^3$

1.2.3 Linear Operators

An operator $\hat{A}$ is said to be linear if it has the following characteristics:

$$\left.\begin{aligned} \hat{A}(f_1 + f_2) &= \hat{A}f_1 + \hat{A}f_2 \\ \hat{A}(cf) &= c\,\hat{A}(f) \end{aligned}\right\} \qquad (1.2.2)$$

where c is a constant and f, f_1,f_2 are arbitrary functions

Conditions in equation - 2 can collectively be written as

$$\hat{A}(c_1f_1 + c_2f_2) = c_1(\hat{A}f_1) + c_2(\hat{A}f_2) \qquad (1.2.3)$$

where c_1, c_2 are constants and f_1, f_2 are arbitrary functions. This equation implies that a linear combination of two (or more) functions, say f_1 and f_2, is converted into some linear combination of $\hat{A}f_1$ and $\hat{A}f_2$.

Example-2

(i) $\frac{d}{dx}$ is a linear operator, since

$$\frac{d}{dx}\ (c_1f_1 + c_2f_2) = c_1\frac{df_1}{dx} + c_2\frac{df_2}{dx}$$

(ii) $\sqrt{\ }$ is a non-linear operator, since

$\sqrt{9+16}$ is not equal to $\sqrt{9} + \sqrt{16} = 3 + 4 = 7$, but equal to $\sqrt{25} = 5$

1.2.4 Anti-linear Operators

If an operator follows the relation

$$\left.\begin{aligned} \hat{A}\,(f_1 + f_2) &= \hat{A}f_1 + \hat{A}f_2 \\ \hat{A}(cf) &= c^*\,\hat{A}(f) \end{aligned}\right\} \qquad (1.2.4)$$

$$\text{(or)}\quad \hat{A}\,(c_1f_1 + c_2f_2) = c_1^*\,(\hat{A}f_1) + c_2^*\,(\hat{A}f_2) \qquad (1.2.5)$$

where c_1^* and c_2^* are the complex conjugates of the constants c_1 and c_2, then $\hat{A}$ is called an anti-linear operator.

Complex conjugation operator is an example of the anti-linear operator. If $\hat{T}$ is a complex conjugation operator, then $\hat{T}$ (cf) = $c^*\hat{T}$ f.

1.2.5 Operator Equations

Consider the operators $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x$. To understand the result of $\hat{A}\hat{B}$, let it operate on an arbitrary function f. The order of operations by convention is always from right.

$$\hat{A}\hat{B}f = \frac{d}{dx}x\,f = \frac{d}{dx}(x\,f) = \frac{dx}{dx}f + x\frac{df}{dx} = 1\,.\,f + x\frac{df}{dx} = (1 + x\frac{d}{dx})\,f$$

$$\Rightarrow \frac{d}{dx} \; x\,\mathrm{f} \;=\; (1 + x\,\frac{d}{dx}\,)\,\mathrm{f}$$

If the arbitrary function ‘f ’ is removed from both the sides

$$\frac{d}{dx}x \;=\; (1 + x\,\frac{d}{dx}\,) \qquad (1.2.6)$$

Equations of this type are called operator equations. The full meaning of the operator equations can be demonstrated only when they operate on functions.

Example-3

Prove the operator equation $\left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial}{\partial x} - x\right) = \frac{\partial^2}{\partial x^2} - x^2 - 1.$

Let LHS expression operate on an arbitrary function *f*. Then

$$\left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial}{\partial x} - x\right) f \;=\; \left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial f}{\partial x} - xf\right)$$

$$= \frac{\partial^2}{\partial x^2}f - \frac{\partial}{\partial x}(xf) + x\,\frac{\partial}{\partial x}\,f - x^2 f \;=\; \frac{\partial^2}{\partial x^2}f - \frac{\partial x}{\partial x}\,f \; - x\,\frac{\partial}{\partial x}\,f + x\,\frac{\partial}{\partial x}\,f \; - \; x^2 f$$

$$= \frac{\partial^2}{\partial x^2}f - f - x\,\frac{\partial}{\partial x}\,f + x\,\frac{\partial}{\partial x}\,f \; - \; x^2 f \;=\; \frac{\partial^2}{\partial x^2}f - \; x^2 f \; - f = \left[\frac{\partial^2}{\partial x^2} \; - \; x^2 \; - 1 \quad \mathrm{f}\right]$$

On removing **f** on both the sides, we have

$$\left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial}{\partial x} - x\right) \;=\; \frac{\partial^2}{\partial x^2} - x^2 - 1.$$

1.2.6 Eigenvalues and Eigenfunctions

If an operator, operating on any function, converts it into some function and a multiplicative constant, then the equation representing the operation is called an eigenvalue equation. For example

$$\hat{A}\,\varphi_n \;=\; a_n\,\varphi_n \qquad (1.2.7)$$

is called an eigenvalue equation. In this equation φ_n are called the eigenfunctions of the operator Â and the corresponding eigenvalues are a_n.

Example-4

If $\hat{A} = \frac{\partial^2}{\partial x^2}$ and $\varphi_n = \sin nx$, we have

$$\frac{\partial^2}{\partial x^2}(\sin nx) = -n^2 \sin nx$$

Here $a_n = -n^2$ are eigenvalues corresponding to the eigenfunctions $\sin nx$

1.2.7 Degenerate eigenvalues and Degree of degeneracy

Let us consider an eigenvalue equation

$$\hat{A}\psi_{l,m,n} = (l^2 + m^2 + n^2)\,\psi_{l,m,n} \qquad (1.2.8)$$

where $\psi_{l,m,n}$ are the eigenfunctions of the operator Â and

$a_{l,m,n} = (l^2 + m^2 + n^2)$ are the corresponding eigen values.

For the case when l = 1, m = 1 and n = 1, $\psi_{1,1,1}$ is the eigenfunction and $a_{1,1,1} = (1 + 1 + 1) = 3$ is the eigen value. This eigenvalue corresponding to only one distinct eigenfunction is said to be non-degenerate. Now, let us consider the eigenfunctions $\psi_{2,1,1}$, $\psi_{1,2,1}$ $\psi_{1,1,2}$. All these eigenfunctions have the same eigenvalue

$$a_{l,m,n} = a_{2,1,1} = a_{1,2,1} = a_{1,1,2} = (l^2 + m^2 + n^2) = 6$$

It means that there are three distinct eigenfunctions $\psi_{2,1,1}$, $\psi_{1,2,1}$ and $\psi_{1,1,2}$ for one distinct eigenvalue $a_{l,m,n} = 6$. Similarly, in many eigenvalue problems, several distinct or linearly independent eigenfunctions may belong to the same eigenvalue. In such cases, the eigenvalue is said to be degenerate and the number of linearly independent eigenfunctions is the degree of degeneracy. In the example cited above, the degeneracy is three.

Note: The eigenfunctions in the set $\{ \varphi_n \}$ are said to be linearly independent, if no relation $c_1 \varphi_1 + c_2 \varphi_2 + \ldots + c_n \varphi_n$ exists between them, except the trivial one with

$c_1 = c_2 = \ldots = c_n = 0$.

1.2.8 Ortho-normality of Eigenfunctions

Consider a set of eigenfunctions $\{ \varphi_n \}$. The eigenfunctions are said to be ortho-gonal, if

$$\int \varphi_m^*(x) \; \varphi_n(x)\, dx = 0, \text{ (for } m \neq n)$$

They are said to be normalized, if

$$\int \varphi_n^*(x) \; \varphi_n(x)\, dx = 1$$

The set of eigenfunctions are said to be ortho-normal (i.e., both orthogonal and normalized), if

$$\int \varphi_m^*(x) \; \varphi_n(x)\, dx = \delta_{mn} \qquad (1.2.9)$$

$$\text{where } \delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

The limits of integration, to be used, shall indicate the region over which the eigen-functions are expected to be valid.

Example-5

Check the ortho-normality of the eigenfunctions $\varphi_n(x) = B \sin (n\pi x/a)$,

where $\mathbf{B} = \sqrt{2/a}$ in the range $x = 0$ to $x = a$.

(i) $\varphi_n(x)$ are orthogonal, if $I = \int_0^a \varphi_m^*(x)\ \varphi_n(x)\, dx = 0$

In the present problem $I = B^2 \int_0^a \sin(m\pi x/a)\sin(n\pi x/a)\, dx$

$$= (B^2/2)\int_0^a \left[\cos\{(m-n)\pi x/a\} - \cos\{(m+n)\pi x/a\}\right] dx$$

$$= \left[(B^2 a/(m-n)2\pi\right]\sin(m-n)\pi x/a\,\Big|_{x=0}^{x=a} - \left[(B^2 a/(m+n)2\pi\right]\sin(m+n)\pi x/a\,\Big|_{x=0}^{x=a} = 0$$

Hence $\varphi_n(x)$ are orthogonal.

(ii) $\varphi_n(x)$ are normalized, if $I = \int_0^a \varphi_n^*(x)\ \varphi_n(x)\, dx = 1$

In the present problem, $I = (\sqrt{2/a})^2 \int_0^a \sin(n\pi x/a)\sin(n\pi x/a)\, dx$

$$= (2/a)\int_0^a \sin^2(n\pi x/a)\, dx = (1/a)\int_0^a [1-\cos(2n\pi x/a)]\, dx$$

$$= (1/a)\int_0^a dx - (1/a)\int_0^a \cos(2n\pi x/a)\, dx$$

$$= (1/a)\,[x]_{x=0}^{x=a} - (1/a)(a/2n\pi)[\sin(2n\pi x/a)]_{x=0}^{x=a} = (1/a)\,a - 0 = 1$$

Hence $\varphi_n(x)$ are normalized

The results of (i) and (ii) together prove that $\{\varphi_n(x)\}$ are orthonormal.

1.2.9 Commuting Operators

Two operators $\hat{A}$ and $\hat{B}$ are said to be commuting operators,

if $\hat{A}\hat{B} = \hat{B}\hat{A}$. By this we mean that $\hat{A}\hat{B} f = \hat{B}\hat{A} f$ for any arbitrary function f ; the difference $(\hat{A}\hat{B} - \hat{B}\hat{A})$ is called the commutator of $\hat{A}$ and $\hat{B}$. A bracket notation is used to denote the commutator as

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \qquad (1.2.10)$$

In this notation, $\hat{A}$ and $\hat{B}$ are said to commute with each other if $[\hat{A},\hat{B}] = 0$

Theorem (1)

If two operators $\hat{A}$ and $\hat{B}$ commute, they share a common set of eigenfunctions.

Proof:

Since $\hat{A}$ and $\hat{B}$ commute, $\hat{A}\hat{B} = \hat{B}\hat{A}$ (i)

Let the operator $\hat{A}$ has a set of eigenfunctions $\{\varphi_n\}$ with eigenvalues a_n

$\therefore \hat{A}\varphi_n = a_n\varphi_n$ (ii)

Operating with $\hat{B}$ from left on both sides, we have

$\hat{B}\hat{A}\varphi_n = \hat{B}(a_n\varphi_n) = a_n(\hat{B}\varphi_n)$ (iii)

Since $\hat{A}\hat{B} = \hat{B}\hat{A}$, the LHS can be written as $\hat{A}\hat{B}\varphi_n$ and therefore equation (iii) becomes

$\hat{A}(\hat{B}\varphi_n) = a_n(\hat{B}\varphi_n)$ (iv)

This equation indicates that the operator $\hat{A}$ has an eigenfunction $(\hat{B}\varphi_n)$ with the eigenvalue a_n. But according to our assumption (equation ii), $\hat{A}$ has an eigenfunction φ_n with the same eigenvalue a_n. If this eigenvalue is non-degenerate $\hat{B}\varphi_n$ must be equal to φ_n except for a constant multiple. Therefore $\hat{B}\varphi_n =$ constant x φ_n. Indicating the constant by b_n, we have

$\hat{B}\varphi_n = b_n\varphi_n$ (v)

This shows that $\hat{B}$ also possesses the same eigenfunctions $\{\varphi_n\}$ which $\hat{A}$ also possesses. Hence $\hat{A}$ and $\hat{B}$, the commuting operators share a common set of eigenfunctions.

Theorem 2

If two operators $\hat{A}$ and $\hat{B}$ possess the same set of eigenfunctions, prove that the operators commute.

Proof

This theorem, in fact, is the converse of the previous theorem. Let the common set of eigenfunctions possessed by $\hat{A}$ and $\hat{B}$ are $\varphi_n(x)$ with eigenvalues a_n and b_n respectively.

Therefore $\hat{A}\,\varphi_n = a_n\varphi_n$ (vi)

$\hat{B}\,\varphi_n = b_n\varphi_n$ (vii)

Operating from left on both sides of equation (vii) by $\hat{A}$, we have

$\hat{A}(\hat{B}\,\varphi_n) = \hat{A}(b_n\,\varphi_n) = b_n\,\hat{A}(\varphi_n) = b_n\,a_n\,\varphi_n$ (viii)

Similarly, operating from left, on both sides of equation (vi) by $\hat{B}$**,** we have

$\hat{B}(\hat{A}\,\varphi_n) = \hat{B}(a_n\varphi_n) = a_n\hat{B}(\varphi_n) = a_nb_n\,\varphi_n$ (ix)

From equations (viii) and (ix), we have

$(\hat{A}\hat{B} - \hat{B}\hat{A})\,\varphi_n = (b_n\,a_n - a_nb_n)\,\varphi_n$ (x)

RHS of equation (x) is zero, since a_n and b_n are constants and commute with each other.

$\therefore (\hat{A}\hat{B} - \hat{B}\hat{A})\,\varphi_n = 0$

$\Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} = 0$ or $[\hat{A},\hat{B}] = 0$ Hence $\hat{A}$ and $\hat{B}$ commute.

Theorem 3

Show that $[\hat{A}\,\hat{B},\ \hat{C}] = \hat{A}\,[\hat{B},\ \hat{C}] + [\hat{A},\ \hat{C}]\ \hat{B}$

Proof

$\text{LHS} = \hat{A}\,\hat{B}\,\hat{C} - \hat{C}\,\hat{A}\,\hat{B}$

Subtracting and adding the same factor $\hat{A}\,\hat{C}\,\hat{B}$,

$\text{LHS} = \hat{A}\,\hat{B}\,\hat{C} - \hat{A}\,\hat{C}\,\hat{B} + \hat{A}\,\hat{C}\,\hat{B} - \hat{C}\,\hat{A}\,\hat{B} = \hat{A}(\hat{B}\,\hat{C} - \hat{C}\,\hat{B}) + (\hat{A}\,\hat{C} - \hat{C}\,\hat{A})\hat{B}$

$= \hat{A}\,[\hat{B},\ \hat{C}] + [\hat{A},\ \hat{C}]\ \hat{B} = \text{RHS}$

Hence the theorem is proved.

Theorem 4

If $\hat{A}$ and $\hat{B}$ are two operators each of which commute with their commutator $[\hat{A},\hat{B}]$, prove that

$[\hat{A}^{n},\hat{B}] = n\ \hat{A}^{n-1}[\hat{A},\hat{B}]$.

Proof:

$\text{LHS} = [\hat{A}^{n},\hat{B}] = [\hat{A}\ \hat{A}^{n-1},\hat{B}] = \hat{A}\ [\hat{A}^{n-1},\hat{B}] + [\hat{A},\hat{B}]\ \hat{A}^{n-1}$

$= \hat{A}\ [\hat{A}\ \hat{A}^{n-2},\hat{B}] + [\hat{A},\hat{B}]\ \hat{A}^{n-1} = \hat{A}\ \{\hat{A}\ [\hat{A}^{n-2},\hat{B}] + [\hat{A},\hat{B}]\ \hat{A}^{n-2}\} + [\hat{A},\hat{B}]\ \hat{A}^{n-1}$

$= \hat{A}^{2}\ [\hat{A}^{n-2},\hat{B}] + \hat{A}\ [\hat{A},\hat{B}]\ \hat{A}^{n-2} + [\hat{A},\hat{B}]\ \hat{A}^{n-1}$

Since $\hat{A}$ commutes with $[\hat{A},\hat{B}]$,the second term equals

$[\hat{A},\hat{B}]\hat{A}\ \hat{A}^{n-2} = [\hat{A},\hat{B}]\hat{A}^{n-1}$ since

$\hat{A}\ [\hat{A},\hat{B}]\ \hat{A}^{n-2} = [\hat{A},\hat{B}]\hat{A}\ \hat{A}^{n-2} = [\hat{A},\hat{B}]\hat{A}^{n-1}$

$\therefore\ \text{LHS} = \hat{A}^{2}\ [\hat{A}^{n-2},\hat{B}] + 2\,[\hat{A},\hat{B}]\ \hat{A}^{n-1}$

Repeating the process (n-2) times, we have

LHS = $\hat{A}^n\ [\hat{A}^{n-n}, \hat{B}] + n\, [\hat{A}, \hat{B}]\ \hat{A}^{n-1} = \hat{A}^n\ [\hat{A}^o, \hat{B}] + n\ \hat{A}^{n-1} [\hat{A}, \hat{B}]$

(since $\hat{A}$ and hence the powers of $\hat{A}$ commute with $[\hat{A}, \hat{B}]$)

using $\hat{A}^o = 1$ and $[1, \hat{B}] = 0$, since 1 commutes with $\hat{B}$,

$\therefore$ LHS = n $\hat{A}^{n-1} [\hat{A}, \hat{B}]$ = RHS, hence proved.

1.2.10 Hermitian Operators

Hermitian operators are very important in the development of Quantum Mechanics. Therefore, it is necessary to understand the essential features of this class of operators.

If, for any two arbitrary eigenfunctions $\varphi_m (x)$ and $\varphi_n (x)$,

$$\int \varphi_m^* \hat{A}\, \varphi_n\, dx = \int (\hat{A}^\dagger \varphi_m)^* \varphi_n\, dx \qquad (1.2.11)$$

then $\hat{A}^\dagger$ is called the adjoint of the operator $\hat{A}$. If $\hat{A} = \hat{A}^\dagger$, then the operator $\hat{A}$ is called the self-adjoint or Hermitian operator. Thus a Hermitian Operator is defined according to the following equation:

$$\int \varphi_m^* \hat{A}\, \varphi_n\, dx = \int (\hat{A}\, \varphi_m)^* \varphi_n\, dx \qquad (1.2.12)$$

Properties

(i) The eigenfunctions of a Hermitian operator are real.

(ii) Any two eigenfunctions which belong to two different eigenvalues of a Hermitian operator are orthogonal.

Proof:

In the case of operator $\hat{A}$, consider two eigenfunctions φ_m and φ_n with eigenvalues a_m and a_n respectively.

$$\hat{A}\ \varphi_m = a_m\ \varphi_m \tag{1.2.13}$$

$$\hat{A}\ \varphi_n = a_n\ \varphi_n \tag{1.2.14}$$

Multiplying equation-14 with φ_m^* and equation-13 by φ_n^* from left and integrating,

$$\int \varphi_m^*\ \hat{A}\ \varphi_n\, dx = a_n \int \varphi_m^*\ \varphi_n\, dx \tag{1.2.15}$$

$$\int \varphi_n^*\ \hat{A}\ \varphi_m\, dx = a_m \int \varphi_n^*\ \varphi_m\ dx \tag{1.2. 16}$$

Taking the complex conjugation of equation-16, we have

$$\int (\hat{A}\ \varphi_m)^*\ \varphi_n\, dx = a_m^* \int \varphi_m^*\ \varphi_n\ dx \tag{1.2.17}$$

Using the Hermitian property of operator $\hat{A}$(equation-12), LHS of equations-15 and 17 are equal; hence the RHS must also be equal. Therefore,

$$a_n \int \varphi_m^*\ \varphi_n\, dx = a_m^* \int \varphi_m^*\ \varphi_n\ dx \tag{1.2.18}$$

If we consider the case **n = m**, the above equation becomes

$$a_m \int \varphi_m^*\ \varphi_m\, dx = a_m^* \int \varphi_m^*\ \varphi_m\ dx \tag{1.2.19}$$

From the above equations, it is obvious that $a_m = a_m^*$ and hence a_m = real. This proves the first property that the eigenfunctions of a Hermitian Operator are real.

Using $a_m^* = a_m$ and rewriting equation-18, we have

$$(a_n - a_m) \int \varphi_m^*\ \varphi_n\ dx = 0 \tag{1.2. 20}$$

For two different eigenvalues, i.e., for $(a_n - a_m) \neq 0$, we have

$$\int \varphi_m^* \varphi_n \, dx = 0$$

This is the condition for orthogonality of φ_m and φ_n and this proves the second property.

Note:

(i) In the case of matrix operators, a matrix (M) is said to be Hermitian, if it is equal to its transpose conjugate $(M^\dagger)$ **:** $(M^\dagger) = M$.

(ii) M is said to be unitary, if $M^\dagger = M^{-1}$, where M^{-1} is the inverse of M

(iii)M is said to be orthogonal, if $M^T = M^{-1}$, where M^T is the transpose of M.

Summary of lesson

Various classes of operators like linear, anti-linear, commuting and Hermitian operators have been introduced. Their properties and algebra have been illustrated with examples. The concepts of degenerate eigenvalues and degree of degeneracy have been explained. Thus, the basic knowledge of operators and their algebra, necessary for laying the foundations of Quantum Mechanics, have been presented with examples and illustrations.

Key terminology Operator – Linear operator – Anti-linear operator – Operator equation – Eigenvalues – Eigenfunctions – Degeneracy – Orthogonality – Normalisation – Commuting operators – Commutator – Hermitian operator.

Self assessment questions

(i) Explain linear and anti-linear operators with examples.

(ii) Prove the operator equation $\left(\frac{\partial}{\partial x} - x\right) \left(\frac{\partial}{\partial x} + x\right) = \frac{\partial^2}{\partial x^2} - x^2 + 1$.

(iii) Evaluate the commutator $[\hat{A}\ \hat{B}]$, if $\hat{A}$ = x and $\hat{B} = -i\hbar\dfrac{d}{dx}$

(iv) What are the eigenfunctions and eigenvalues of the operator $\dfrac{\partial^2}{\partial x^2}$?

(v) What is degeneracy? Explain with an example.

(vi) Determine the normalisation constant for the eigenfunction

$\psi_n(x) = B \sin(n\pi x/a)$, in the range x = 0 to a

(vii) State and prove the properties of a Hermitian operator.

(viii) Prove that $[\hat{A}, \hat{B}\,\hat{C}] = [\hat{A}, \hat{B}]\,\hat{C} + \hat{B}\,[\hat{A}, \hat{C}]$.

(ix) Show that $[\hat{A}, [\hat{B}, \hat{C}] + [\hat{C}, [\hat{A}, \hat{B}] + [\hat{B}, [\hat{C}, \hat{A}]] = 0$

Reference books

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2. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York).
3. Introduction to Quantum Mechanics – Mathews P T (Mc Graw Hill Book Co., New York).

UNIT - 1

LESSON - III - FOUNDATIONS OF QUANTUM MECHANICS

Objective

Formulation of the principles of the basic foundations of quantum mechanics, their interpretation and explanation.

1.3.1 Introduction

Schrodinger developed a wave equation governing the behaviour of material particles, utilising the concept of wave nature of matter introduced by de Broglie. Historically, first a simple method of reasoning was used to arrive at the Schrodinger equation for a free non-relativistic particle and generalise the equation for a particle subject to forces. Then comprehensive foundation of quantum mechanics was however laid based on a set of fundamental postulates. Necessary details of the foundations, along with elegant Dirac's Bra-Ket notation, are dealt in this chapter so as to facilitate their application in the succeeding chapters.

1.3.2 Deduction of the Schrodinger Equation

(i) Time dependent equation

For a free particle of mass m, moving in x – direction , with a momentum p, and energy E, is given as

$$E = p^2/(2m) \qquad (1.3.1)$$

Based on the de Broglie hypothesis,

wave length (λ) of particle of momentum p, is given as $\lambda = h/p$

$$p = h/\lambda = \hbar k \quad \text{and} \quad E = h\upsilon = \hbar\omega \qquad (1.3.2)$$

Propagation constant $k = 2\pi/\lambda$

From equations .1.3.1 and 1.3. 2, we have

$$\hbar\omega = \hbar^2k^2/(2m) \qquad (1.3.3)$$

The possible functions to represent such harmonic waves are

cos (kx – ωt), sin (kx – ωt), or their linear combinations:

$$\therefore \psi(x, t) = a \cos(kx - \omega t) + b \sin(kx - \omega t) \qquad (1.3.4)$$

The common differential equations for such waves are

$$\frac{\partial \psi}{\partial t} = -(\omega/k)\frac{\partial \psi}{\partial x}; \qquad \frac{\partial^2 \psi}{\partial t^2} = (\omega/k)^2 \frac{\partial^2 \psi}{\partial x^2} \qquad (1.3.5)$$

The authenticity of these equations can be checked by substituting in equation-1.3.5, the expressions for ψ (x, t) from equation-1.3.4.

It is obvious from equation 1.3.2 that ω/k = E/p = p/(2m) and therefore the differential equations in equation-1.3.5, represent particles of a particular momentum p.

However, we need an equation to represent free particles of all momenta. It can be observed that unlike ω/k, the term ω/k^2 is independent of p, since

$\omega/k^2 = \hbar/(2m)$. With this in view, ψ (x, t) of equation-1.3.4, suggests a differential equation involving first order time derivative $\frac{\partial \psi}{\partial t}$ and second order space derivative $\frac{\partial^2 \psi}{\partial x^2}$. Using equation-1.3.4, we obtain

$$\frac{\partial \psi}{\partial t} = -\omega\,[\,-a \sin(kx - \omega t) + b \cos(kx - \omega t)$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\,[a \cos(kx - \omega t) + b \sin(kx - \omega t)\,]$$

In the above equations, if b = ai we get the differential equation connecting them as $\frac{\partial \psi}{\partial t} = (i\omega/k^2)\frac{\partial^2 \psi}{\partial x^2}$. Substituting from equation-1.3.3, $\omega/k^2 = \hbar/(2m)$, we have

$$\frac{\partial \psi}{\partial t} = (i\,\hbar/2m)\frac{\partial^2 \psi}{\partial x^2}\,.$$

$$\Rightarrow i\,\hbar\,\frac{\partial \psi(x,t)}{\partial t} = -\,(\hbar^2/2m)\,\frac{\partial^2 \psi(x,t)}{\partial x^2} \qquad (1.3.6)$$

This is the Schrodinger equation for a free particle in one dimension. A comparisons of 1.3.1 and 1.3.6 suggest that the Schrodinger equation can easily be deduced if we replace the energy E and momentum p in the equation-1.3.1 with differential operators $E \rightarrow i\hbar\,\frac{\partial}{\partial t}$ and $p \rightarrow -\,i\hbar\frac{\partial}{\partial x}$.

If a force F_x is acting on a particle, the body possesses potential energy V (x) given according to the relation $F_x = -\,\frac{\partial V(x,t)}{\partial x}$. Accordingly, the total energy E of the particle of mass m, momentum p and potential energy V(x,t) is given as

$$E = \frac{p^2}{2m} + V(x,t) \qquad (1.3.7)$$

With the correspondences $E \rightarrow i\hbar\,\frac{\partial}{\partial t}$ and $p \rightarrow -\,i\hbar\frac{\partial}{\partial x}$ in equation-1.3.7, we get the following Schrodinger equation for a particle having both K.E and P.E:

$$i\,\hbar\,\frac{\partial \psi(x,t)}{\partial t} = -\,(\hbar^2/2m)\,\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\,\psi(x,t) \qquad (1.3.8)$$

In 3D, this equation becomes

$$i\hbar\,\frac{\partial \psi}{\partial t} = [\,\hbar^2/(2m)\,]\,\nabla^2\psi + V\,\psi \qquad (1.3.9)$$

The Schrodinger time dependent equations (equations 1.3.6, 1.3.8 and 1.3.9) deduced here are based on merely trial and error methods depending on assumptions based on past experience. Thus, the procedure is simply heuristic.

(ii) **Time independent equation**

A lucid heuristic procedure to develop the non-relativistic time independent Schrodinger equation is to incorporate de Broglie wavelength of the particle in the general wave equation. The usual wave equation is

$$\frac{1}{v^2}\frac{\partial^2\psi(x,t)}{\partial t^2} - \frac{\partial^2\psi(x,t)}{\partial x^2} = 0 \qquad (1.3.10)$$

For stationary waves $\psi(x,t) = \psi(x)\, e^{i\omega t} = \psi(x)\, e^{2\pi i\upsilon t}$

Substituting, this in the above equation, we obtain

$$\frac{1}{v^2}(2\,\pi\, i\,\upsilon)^2\, \psi(x)\, e^{2\pi i\upsilon t} - e^{2\pi i\upsilon t}\frac{d^2\psi(x)}{dx^2} = 0$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \qquad (1.3.11)$$

It is well known that the de Broglie relation for wave length λ, of a particle of momentum p is given as $\lambda = h/p$. On substituting this value of λ in the above equation, we obtain

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2 p^2}{h^2}\psi(x) = 0 \qquad (1.3.12)$$

But, $p^2 = 2m\,(E\text{-}v)$

$$\therefore \frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2 2m(E-V)}{h^2}\psi(x) = 0$$

$$\Rightarrow \frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi(x) = 0 \text{ (or) } \frac{d^2\psi(x)}{dx^2} + \frac{2m(E-V)}{\hbar^2}\psi(x) = 0 \qquad (1.3.13)$$

This is the time independent one-dimensional Schrodinger equation of a particle. In 3-D, it can be written as

$$\nabla^2\psi + (2m/\hbar^2)(E-V)\,\psi = 0 \qquad (1.3.14)$$

However, the foundations of a new subject like Quantum Mechanics must be based firmly on a self-consistent comprehensive framework. For this purpose, Schrodinger formulated postulates, popularly called Schrodinger postulates. They encompass the Schrodinger equation also as will be seen in the next section.

1.3.3 Schrodinger's Postulates

The postulates of any theory are a set of fundamental statements, which cannot be explained in terms of more fundamental concepts. Therefore, one should not try to understand the postulates. One should rather believe them and draw conclusions from them. The conclusions are then tested by experiment and if they are confirmed, the belief in the postulates is justified.

The second point, which should be kept in mind, is the ease with which a postulate may be made to appear reasonable depends on how readily it relates to every day experiences. In quantum mechanics, the postulates are about atomic and molecular properties and these are in general quite far from everyday experience. Consequently, the postulates may also in this sense be difficult to understand.

The main point to keep in mind is that the postulates are justified only by their ability to predict and correlate experimental facts and their general applicability. With this background in mind, we introduce the basic postulates of quantum mechanics.

1. Any state of a dynamical system of N-particles is described as fully as possible by a function ψ $(q_1, q_2, ..., q_{3N}, t)$ such that the quantity $\psi * \psi \, dq$ is proportional to the probability that the variables lie in a volume element dq at a specific time t. The concise form of $\psi (q_1, q_2, ... q_{3N}, t)$ is $\psi (q,t)$ and is generally called the Wave Function or State Function. It may be either complex or negative but guarantees real and positive probability.

   The following are its important properties

   (i) It is finite and single-valued

   (ii) The function and its first derivative should be continuous.

   (iii) It should have an integrable square.

2. For every observable physical quantity, there exists a corresponding linear Hermitian Operator. The classical expression for an observable is first to be written in terms of its cartesian coordinates (q), momenta (p) and time (t).

Then the following operator correspondences for p, q, t are used to get the operator expressions

$A_{op} = A\ (q_{op}, p_{op,}\ t_{op})$ where

$$q_{op} = \hat{q} \rightarrow q\ ;\ p_{op} = \hat{p}_q = -\,i\hbar \frac{\partial}{\partial q}\ ;\ t_{op} = \hat{t} \rightarrow t$$

3. The State Function ψ (q, t) satisfies the quation

$$H_{op}\ \psi(q, t) = i\,\hbar\ \frac{\partial}{\partial t}\psi(q,t)$$

where H_{op} (q,t) is the Hamiltonian operator of the system.

This equation is called the **Schrodinger's time-dependent equation**.

4. If for a set of identical systems in a state ψ_n (q, t), the state function is an eigenfunction of the operator corresponding to an observable, then the successive measurements will give the same value of the observable.

Accordingly, if $\hat{A}\,\psi_n$ (q, t) = a_n (q, t), we will get the same result a_n if we perform a series of a measurements of an observable quantity on different members of the identical system set. If $\hat{H}\ \psi_n$ (q, t) = $E_n\ \psi$ (q, t) and if this is to be consistent with the Schrodinger's time dependent equation

$$i\,\hbar\ \frac{\partial}{\partial t}\psi(q,t) \ = \ \hat{H}\,\psi\ (q, t),$$

then ψ (q, t) must be of the form $\boldsymbol{\psi\ (q, t) = \psi\ (q)\ e^{-iEt/\hbar}}$ where ψ (q) is the solution of the equation H ψ (q) = E ψ (q).

This equation is called the **Schrodinger's time-independent or Stationary State equation**.

5. If for a set of identical systems in a state ψ_n (q, t), the state function is not equal to the eigenfunction of the operator corresponding to a physical observable, then the successive measurements will not give the same value but a range of values for the observable physical quantity. The average of a large number of these measurements is called the expectation value.

$$\overline{A} = < \hat{A} > = \frac{\int \psi_n^* \hat{A} \psi_n \, dq}{\int \psi_n^* \psi_n \, dq}$$

This is consistent with the previous postulate.

1.3.4 Wave function : Interpretation and Properties

Interpretation

(i) Wave function ψ (q, t) describes as fully as possible the state of a particle (or a system).

(ii) ψ (q, t) of a particle is a measure of its presence and we do not expect the particle in the region where $\psi = 0$.

(iii) Since ψ (q, t) can be negative or complex, it cannot directly be a measure of the presence of the particle. Therefore, $|\psi(q, t)|^2 \, d\tau$ can be interpreted as the probability of finding the particle in the volume element $d\tau$ around q. Accordingly, $\psi^*\psi = |\psi|^2$ is the probability density and is denoted as ρ.

(iv) Since the probability of finding a particle anywhere in the space is unity,

$\int \rho \, d\tau = \int \psi^*\psi \, d\tau = \int |\psi|^2 \, d\tau = 1.$

Whenever this integral exists, ψ is said to be normalised. If ψ is normalised at t = 0, it remains normalised at all times, indicating $\frac{\partial}{\partial t} \int \rho \, dt = 0.$

(v) The probability interpretation of ψ can be made consistent, only if it is possible to define a probability current density $\vec{j}$ which together with probability density

$\rho = \psi^*\psi$ satisfies

$$\frac{\partial \rho}{\partial t} + \nabla . \vec{j} = 0 \qquad (1.3.15)$$

as in the case of the conservation of matter in hydro-dynamics, or conservation of charge in electro-dynamics. In fact, a relation of the form (equation-1.3.15) can easily be deduced from the Schrodinger's wave equation and its complex conjugate

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \psi + V(q)\psi \qquad (1.3.16)$$

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \psi^* + V(q)\psi^* \qquad (1.3.17)$$

Multiplying equation-1.3.16 from left by ψ^* and equation-1.3.17 from right by ψ and subtracting, we get

$$\frac{\partial \psi^* \psi}{\partial t} + \frac{\hbar}{2mi} \nabla . [\psi^* \nabla \psi - (\nabla \psi^*)\psi] = 0 \qquad (1.3.18)$$

This is of the form of equation-1.3.15, if we identify

$$\rho = \psi^* \psi \text{ and } \vec{j} = \frac{\hbar}{2mi}[\psi^* \nabla \psi - (\nabla \psi^*)\psi] \qquad (1.3.19)$$

Properties

For the probability interpretation to hold good, ψ must have the following properties (or admissibility conditions):

(i) ψ should be finite.

(ii) ψ must be single valued.

(iii) ψ must be square integrable.

(iv) ψ and $\frac{\partial \psi}{\partial q}$ should be continuous functions of q for all q. The continuity of $\frac{\partial \psi}{\partial q}$ is due to the implicit assumption that **V(q)** is a continuous function of q, except perhaps for a certain number of finite discontinuities.

1.3.5 Dirac's Bra and Ket notation

Any state of a dynamical system is described as fully as possible by a wave function or state function ψ (q, t) in Schrodinger's picture. This function can be expressed as a linear combination of a complete ortho-normal set of basis functions. If the variable takes a continuous range of values, the state function is continuous. However, if the variable takes discrete values, it is convenient to use matrix notation to represent the state function and the linear operators, which operate on it.

Therefore, it is desirable to develop a mathematical structure, which contains all these concepts in a comprehensive unified way. In this formalism, the values of the state function are considered as projections (or components) of a vector ψ. This vector is generally called the state vector. For two vectors, in a linear vector space, a scalar product is defined as follows:

$$\left.\begin{array}{l} \text{(i)} \quad (\psi_a, \psi_b) \geq 0(1.3) \\ \text{(ii)}(\psi_a,\psi_b)=(\psi_b,\psi_a)^* \\ \text{(iii)} \; (\psi_a, k_b \psi_b + k_c \psi_c) = k_b (\psi_a, \psi_b) + k_c (\psi_a, \psi_c) \\ \qquad (k_b \psi_b + k_c \psi_c, \psi_a) = k_b^* (\psi_b, \psi_a) + k_c^* (\psi_c, \psi_a) \end{array}\right\} \quad (1.3.20)$$

Obviously, the scalar product is linear with reference to post factor and anti-linear with reference to pre-factor.

Unitary linear vector space or simply unitary space is the linear vector space in which scalar product is defined. Hilbert space is a unitary space that is complete and the language of the Hilbert space suits better for the formulation of quantum mechanics. To avoid apparent asymmetry and to make the scalar product symmetrical with respect to post and pre-factors, Dirac proposed a new notation called 'Bra and Ket' notation. In this notation, two different vector spaces linear in themselves but related to each other anti-linearly are conceived. For example, the vector in the post factor in (ψ_a, ψ_b) is written as $|\psi_b\rangle$ or simply $|b\rangle$; the vector in the pre-factor is written as $\langle \psi_a|$ or simply $\langle a|$. The vector in the post-factor space, denoted by the symbol $|\ \rangle$, is called ket, whereas the vector in the pre-factor space, denoted by the symbol $\langle\ |$ is called bra. The scalar product in Dirac bra-ket notation is given as follows:

$(\psi_a, \psi_b) = \langle a, b \rangle = \langle b, a \rangle^*$

This relation implies that $|a\rangle^* = \langle a|$ and indicates that the ket space and the bra space are not independent of each other. They are said to be dual to each other.

A few common definitions are given below in Dirac's bra – ket notation:

(i) $\hat{A}$ is a Hermitian operator if $\langle a|\hat{A}|b\rangle = \langle b|\hat{A}|a\rangle^*$ (1.3.21)

(ii) Normalisation condition of ψ is given as $\langle \psi | \psi \rangle = 1$ (1.3.22)

If the state of a system at a particular time t is specified by ψ_a (q,t), it is denoted in bra-ket notation as $|a,t\rangle$. The expectation value

$\langle \hat{A} \rangle = \int\psi^* \hat{A}\ \psi\, d\tau / \int\psi^*\ \psi\, d\tau = \langle a, t|\hat{A}|a, t\rangle / \langle a, t | a, t\rangle$.

For normalised wave function, since $\langle a, t | a, t \rangle = 1$, expectation value is given as

$\langle \hat{A} \rangle = \langle a, t|\hat{A}|a, t\rangle$ (1.3.23)

(iii) Unit operator is denoted as

$\sum_i |a^i\rangle\langle a^i| = 1$ (1.3.24)

Note In two dimensions (X-Y axis system), the unit vectors $\hat{i}$ and $\hat{j}$ are often represented as $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$.

These can be expressed as $|i\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ and

$\langle i| = (1\ \ 0)$. Similarly, $|j\rangle = \begin{pmatrix}0\\1\end{pmatrix}$ and $\langle j| = (0\ \ 1)$. Accordingly,

$| i \rangle \langle i | + | j \rangle \langle j | = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (1 \quad 0) + \begin{pmatrix} 0 \\ 1 \end{pmatrix} (0 \quad 1) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ = unit matrix

This can be expressed more generally in n – dimensions as

$\sum_i | a^i \rangle \langle a^i | = 1$ which is a common relation for unit operator.

Representation

In Dirac's bra-ket notation, an operator can be represented by a matrix. For example, consider an ortho-normal set of basis vectors $\{| a^i \rangle\}$ in terms of which the operator $\hat{B}$ is to be represented. Let $\hat{B}$ operate on $| a^i \rangle$ and give another vector $|\chi^i \rangle$. This $|\chi^i \rangle$ can in turn be expanded as a linear combination of the basis vectors $|a^i \rangle$.

$$\therefore \hat{B} |a^i \rangle = |\chi^i \rangle = \sum_j b_{ji} |a^j \rangle$$

where b_{ji} are expansion coefficients. Operating from left on both sides with $\langle a^j |$,
we have

$$\langle a^j | \hat{B} |a^i \rangle = \langle a^j | \sum_j b_{ji} |a^j \rangle = \langle a^j | a^j \rangle b_{ji} = b_{ji}$$

since $\langle a^j | a^i \rangle = \delta_{ji}$, because of ortho-normality

$$\therefore b_{ji} = \langle a^j | \hat{B} |a^i \rangle \qquad (1.3.25)$$

From the above equation, it is obvious that the operator $\hat{B}$ is represented by a square matrix whose elements are b_{ji}.

1.3.6 Expectation value and Equation of motion

Let a large number of observations be made on the position of a particle having a specified normalised wave function ψ_a (q,t) or state vector $|q,t \rangle$. After each experiment, the particle is so prepared as to have the same wave function. According, to probability interpretation, we don't get the same result each time.

Therefore, we have to take the mean or average value of all the observed values. The result, according to Quantum Mechanics (postulate –V) is expected to be $\int \psi_a^*(q,t)\,\hat{x}\,\psi_a(q,t)\,d\tau$, where $\hat{x}$ is the position operator and $d\tau$ is the volume element. This is also called the expectation value of the position variable and is often denoted as $\langle \hat{x} \rangle$. Likewise, for any physical observable A, the expectation value, for a normalised state vector, is given by the relation

$$\langle \hat{A} \rangle = \int \psi_a^*(q,t)\ \hat{A}\ \psi_a(q,t)\,d\tau, \qquad = \langle a, t\,|\hat{A}\,|\,a, t\,\rangle \tag{1.3.26}$$

A better insight of a physical quantity can be had, if we study the time rate of change of that quantity. The physical quantity is represented in its real form, as an average value [$\bar{A}$ = $\langle \hat{A} \rangle$]. Accordingly, $\bar{A} = \langle \hat{A} \rangle = \langle a, t\,|\hat{A}\,|\,a, t\,\rangle$. Now, the time rate of change in this average (expectation value) is given by

$$\frac{d\bar{A}}{dt} = \frac{d}{dt} < \text{a, t}\,|\,\hat{\text{A}}\,|\text{a, t} > = \left[\frac{\partial}{\partial \text{t}} < a,t\,|\right]\hat{\text{A}}\,|\text{a, t} > + < \text{a, t}\,|\,\frac{\partial\hat{\text{A}}}{\partial \text{t}}|\text{a, t} > + < \text{a, t}\,|\,\hat{\text{A}}\left[\frac{\partial}{\partial \text{t}}\,|\,a,t >\right] \tag{1.3.27}$$

Using in the above equation the Schrodinger time-dependent equation and its Hermitian adjoint, namely

$$\hat{H}\,|\,a,t >= i\hbar\frac{\partial}{\partial t}\,|\,a,t > \quad \text{and} \quad < a,t\,|\,\hat{H} = -i\hbar\frac{\partial}{\partial t} < a,t\,| \tag{1.3. 28}$$

we have

$$\frac{d\bar{A}}{dt} =< a,t\,|\,\frac{\partial\hat{A}}{\partial t}\,|\,a,t > + \frac{1}{i\hbar} < a,t\,|\,\hat{A}\hat{H} - \hat{H}\hat{A}\,|\,a,t > \tag{1.3.29}$$

Defining $\overline{\dfrac{dA}{dt}} = \dfrac{d(\bar{A})}{dt}$, the above equation can be written as

$$\frac{\overline{dA}}{dt} = \frac{\overline{\partial A}}{\partial t} + \frac{1}{i\hbar}\overline{[A, H]} \qquad (1.3.30)$$

This can also be expressed, in the operator form, as

$$\frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + \frac{1}{i\hbar}[\hat{A}, \hat{H}] \qquad (1.3.31)$$

If $\hat{A}$ does not explicitly depend on time, the equation of motion becomes

$$\frac{d\hat{A}}{dt} = \frac{1}{i\hbar}[\hat{A}, \hat{H}] \qquad (1.3.32)$$

1.3.7 Ehrenfest's Theorem

In Quantum Mechanics, as already explained, the equation of motion deals with the time rate of change in the expectation value of the operator ($\hat{A}$) which represents a physical variable (A).

$$\frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + \frac{1}{i\hbar}[\hat{A}, \hat{H}]$$

This is of the same form as the classical equation of motion of the physical variable (A), in the poisson bracket form $\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$, if we identify the quantum mechanical poisson bracket as $\frac{1}{i\hbar}[\hat{A}, \hat{H}] \to \{A, H\}$.

This statement that "the expectation values of operator $\langle \hat{A} \rangle$ obey the same equation of motion in quantum mechanics as the dynamical variables A in classical mechanics" goes in literature as the general statement of Ehrenfest's theorem. Physically this statement implies that an infinitesimally small quantum wave packet is well approximated by classical mechanics.

Specifically, the following equations constitute Ehrenfest's theorem:

$$\langle \hat{p} \rangle = m \frac{d}{dt} \langle \hat{x} \rangle \qquad (1.3.33)$$

$$\frac{d}{dt}\langle \hat{p} \rangle = -\langle \frac{\partial \hat{V}}{\partial x} \rangle \qquad (1.3.34)$$

(i) **Proof of $\langle \hat{p} \rangle = m \frac{d}{dt} \langle \hat{x} \rangle$**

Using equation of motion $\frac{d\hat{A}}{dt} = \frac{1}{i\hbar}[\hat{A}, \hat{H}]$ and observing that H = $p^2/(2m)$ + V(x) we obtain

$$\frac{d}{dt}\langle \hat{x} \rangle = \frac{1}{i\hbar} < [\hat{x}, \frac{\hat{p}^2}{2m} + \hat{V}(x)] > \;=\; \frac{1}{i\hbar} < [\hat{x}, \frac{\hat{p}^2}{2m}] > \text{ since } \hat{x} \text{ and } \hat{V}(x) \text{ commute}$$

$$= (2mi\hbar)^{-1} \langle \{ [\hat{x}, \hat{p}]\, \hat{p} + \hat{p}\, [\hat{x}, \hat{p}] \} \rangle = (2mi\hbar)^{-1} \langle (i\hbar\, \hat{p} + \hat{p}\, \mathbf{i}\hbar) \rangle$$

$$= (2mi\hbar)^{-1} \langle (2i\hbar\, \hat{p}) \rangle = \langle \hat{p} \rangle / m \qquad \Rightarrow \langle \hat{p} \rangle = \mathbf{m} \frac{d}{dt} \langle \hat{x} \rangle$$

(ii) Proof of $\frac{d}{dt}\langle \hat{p} \rangle = -\langle \frac{\partial \hat{V}}{\partial x} \rangle$

$$\frac{d}{dt}\langle \hat{p} \rangle = \frac{1}{i\hbar} < [\hat{p}, \frac{\hat{p}^2}{2m} + \hat{V}(x)] > \;=\; (\mathbf{i}\hbar)^{-1} < [\hat{p}, \hat{V}(x)] > \text{since } \hat{p}\, and\, \frac{\hat{p}^2}{2m} \text{ commute}$$

$$= (\mathbf{i}\hbar)^{-1} < [-i\hbar \frac{\partial}{\partial x}, \hat{V}(x)] > \;=\; < -[\frac{\partial}{\partial x}, \hat{V}(x)] >$$

Let us study $[\frac{\partial}{\partial x}, \hat{V}(x)]\psi = \frac{\partial}{\partial x}\hat{V}(x)\,\psi - \hat{V}(x)\frac{\partial}{\partial x}\,\psi$

$$= (\frac{\partial}{\partial x}\hat{V}(x))\,\psi + \hat{V}(x)\frac{\partial}{\partial x}\,\psi - \hat{V}(x)\frac{\partial}{\partial x}\,\psi = (\frac{\partial}{\partial x}\hat{V}(x))\,\psi$$

$$\Rightarrow [\frac{\partial}{\partial x}, \hat{V}(x)] = \frac{\partial}{\partial x}\hat{V}(x)$$

$$\therefore \frac{d}{dt}\langle \hat{p} \rangle = \langle -[\frac{\partial}{\partial x}, \hat{V}(x)] \rangle = -\langle \frac{\partial \hat{V}}{\partial x} \rangle$$

1.3.8 Derivation of Uncertainty Principle

When a physical quantity assumes several values with various possibilities, it is usual to use the mean square deviation as a measure of the width of the probability distribution or the uncertainty in the value of the quantity. The uncertainty in an observable A, denoted as $(\Delta A)^2 = <\psi | (\hat{A} - \bar{A})^2 | \psi >$

(1.3.35)

where $(\hat{A} - \bar{A})$ is the operator corresponding to the deviation of A from its mean value. Let us consider simultaneous uncertainties in two observables, namely position x and momentum p_x in that direction. For this purpose, let us introduce corresponding operators

$$\hat{\alpha} = \hat{x} - \bar{x} \text{ and } \hat{\beta} = \hat{p}_x - \bar{p}_x \qquad (1.3.36)$$

where $\hat{x}$ and $\hat{p}_x$ are the position and momentum operators and $\bar{x}$ and $\bar{p}_x$ are the average values of the position and momentum (from a large number of measurements).

$$[\hat{\alpha}, \hat{\beta}] = (\hat{x} - \bar{x})(\hat{p}_x - \bar{p}_x) - (\hat{p}_x - \bar{p}_x)(\hat{x} - \bar{x}) = [\hat{x}, \hat{p}_x] = i\hbar \qquad (1.3.37)$$

Now let us consider a ket $|\varphi>$ and the dual bra $<\varphi|$ where

$|\varphi> = (\hat{\alpha} + i\lambda\hat{\beta})|\psi>$ and $<\varphi| = <\psi|(\hat{\alpha} + i\lambda\hat{\beta})^{\dagger}$ (1.3.38) In which λ is an arbitrary real parameter. Now, the scalar product

$$<\varphi|\varphi> = <\psi|(\hat{\alpha} + i\lambda\hat{\beta})^{\dagger}(\hat{\alpha} + i\lambda\hat{\beta})|\psi>$$

$$= <\psi|(\hat{\alpha} - i\lambda\hat{\beta})(\hat{\alpha} + i\lambda\hat{\beta})|\psi>$$

$$= <\psi|(\hat{\alpha}^2 + i\lambda[\hat{\alpha}, \hat{\beta}] + \lambda^2\hat{\beta}^2)|\psi> \geq 0 \qquad (1.3.39)$$

since the scalar product of non-zero vector $|\psi>$ is always greater than or equal to zero.

From equations 1.3.35 and 1.3.36, it is evident that

$$< \psi | \ \hat{\alpha}^2 \ | \psi > \ = < \psi | (\hat{x} - \bar{x})^2 | \psi > = (\Delta x)^2$$

$$< \psi | \ \hat{\beta}^2 \ | \psi > \ = < \psi | (\hat{p}_x - \bar{p}_x)^2 | \psi > = (\Delta p_x)^2$$

$$\therefore \ (\Delta \ x)^2 + i\lambda \ \ (i\hbar) + \lambda^2 \ (\Delta \ \ p_x)^2 \geq 0$$

$$\Rightarrow (\Delta x)^2 - \lambda \hbar + \lambda^2 (\Delta p_x)^2 \geq 0 \qquad (1.3.40)$$

Since λ is arbitrary, we will investigate for which value of λ, the LHS will be minimum. For this LHS should be differentiated with respect to λ and equated to zero.

$$\therefore -\lambda \hbar + \lambda^2 (\Delta p_x)^2 \ = \ 0 \ \Rightarrow - \hbar + 2\lambda (\Delta p_x)^2 = 0 \qquad (1.3.41)$$

$$\lambda = \hbar / [2 (\Delta p_x)^2] \qquad (1.3.42)$$

With this value of λ, equation – 1.3.40 yields

$$(\Delta x)^2 - \hbar^2 / [2 (\Delta p_x)^2] + \{ \hbar / [2 (\Delta p_x)^2] \}^2 (\Delta p_x)^2 = 0$$

$$\Rightarrow [(\Delta p_x) (\Delta x)]^2 = \ \hbar^2 / 4$$

$$(\Delta p_x) (\Delta x) \geq \hbar /2 \qquad (1.3.43))$$

This is the minimum uncertainty product.

SUMMARY OF LESSON

First a heuristic method of developing Schrodinger’s equation has been outlined. Then, the postulates of Schrodinger have been stated and explained. Probabilistic interpretation of wave function has been presented along with the admissibility condition of wave function. Dirac’s bra-ket notation has been put forward and expectation values and their time development have been studied. Ehrenfest’s theorem has been explained and proved using the equation of motion. Heisenberg’s uncertainty principle has been derived using operator techniques.

KEY TERMINOLOGY:

Schrodinger equation – Schrodinger postulates – State function – Dirac bra-ket notation – Ortho-normality – Hermitian Operator – Representation – Expectation values - Equation of Motion – Ehrenfest's theorem – Uncertainty principle.

SELF-ASSESSMENT QUESTIONS

(i) Develop heuristic method formulating Schrodinger's time-dependent equation.

(ii) Deduce from the classical wave equation, Schrodinger's time-independent equation.

(iii) State and explain Schrodinger's postulates.

(iv) Explain the interpretation of state function and its admissibility conditions.

(v) What is Dirac's bra-ket notation? Explain matrix representation of operators.

(vi) State and explain Ehrenfest's theorem. Derive any one of the relations

a) $\langle \hat{p} \rangle = m \frac{d}{dt} \langle \hat{x} \rangle$ b) $\frac{d}{dt} \langle \hat{p} \rangle = - \langle \frac{\partial \hat{V}}{\partial x} \rangle$

(vii) Derive Heisenberg's uncertainty principle.

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UNIT - 1

LESSON - IV- SOLUTIONS FOR SOME SIMPLE SYSTEMS

Objective

Application of Schrodinger’s equation to simple problems of a particle in a one-dimensional infinite and finite potential wells, rectangular box and a linear harmonic oscillator.

1.4.1 Introduction

We have learnt already the necessity of Quantum Mechanics and constructed the essential theoretical foundations. Now our aim is to apply the basic principles of Schrodinger’s equation to solve some simple problems like (i) particle in an one dimensional infinite potential well, (ii) particle in a rectangular box, (iii) particle in an one dimensional finite potential well, and (iv) particle in an one dimensional harmonic potential well. The examples are quite useful to illustrate the Schrodinger’s technique of analysis of the energy levels of a particle, which is under the influence of various potentials. It will be evident from the analysis how smoothly all the results emerge from the quantum mechanical theory without the necessity of any intermediate adhoc assumptions.

1.4.2 Particle in an infinitely deep potential well

Let us consider the problem of a particle of mass 'm' in a one-dimensional well of width 'a'. The potential is given as (Fig.4.1)

$V = 0 ; \quad 0 < x < a$

$V = \infty ; \quad \text{elsewhere} \qquad \ldots(1.4.1)$

The Hamiltonian is $H = p^2_x / 2m$

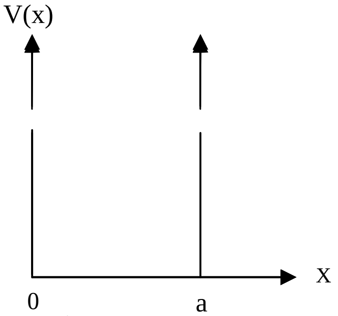

Figure-1.4.1

Hamiltonian operator $\hat{H} = \hat{p}_x^2 / 2m = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ …(1.4.2)

Therefore, using Schrodinger's equation $\hat{H}\psi = E\psi$,

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad \text{…(1.4.3)}$$

where $k^2 = 2mE / \hbar^2$

The solution is

$\psi(x) = A \sin kx + B \cos kx$ …(1.4.4)

Since the particle is confined to the box, $\psi(o) = \psi(a) = o$,

these conditions yield

$\psi(x) = A \sin(n\pi x/a)$ …(1.4.5)

where n = 1,2,3 --- and $ka = n\pi$

Therefore $k^2 a^2 = n^2\pi^2$ (or) $2mEa^2 / \hbar^2 = n^2\pi^2$

Hence $E_n = n^2 (h^2 / 8ma^2)$

Normalization of $\psi(x)$, namely

$$\int_0^a [\ A \sin(n\pi x/a)\ ]^2\, dx = 1, \text{yields } A = \sqrt{2/a}$$

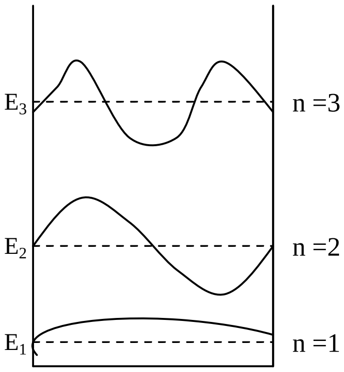

Fig 1.4.2

Eigenvalues and eigenfunctions

Energy of the particle in the infinitely deep potential well

$E_n = n^2 (h^2 / 8ma^2)$; n = 0,1,2…. …(1.4.6)

$\psi(x) = \sqrt{2/a}\,\sin(n\pi x/a)$ …(1.4. 7)

From the figure-2, depicting eigenfunctions and eigenvalues, it is evident that the number of nodes increases with increase in energy (eigenvalues) and hence wavelength decreases. This is in accordance with the de Broglie principle (x=h/p) which implies decrease of wavelength with the increase of momentum (or energy)

Average value of p_x

Let us consider the ground state with the energy E_1 and the state function ψ_1. The average value of p_x is given by

$$\bar{p}_x = <\hat{p}_x>_1 = \frac{\int \psi_1^* \hat{p}_x \psi_1 \, dx}{\int \psi_1^* \psi_1 \, dx} = \int \psi_1^* \hat{p}_x \psi_1 \, dx, \quad \ldots(1.4.8))$$

since $\int \psi_1^* \psi_1 \, dx = 1$ due to normalization

Using $\hat{p}_x = - i \hbar \frac{d}{dx}$, we have

$$< p_x > = - i\hbar \left(\frac{2}{a}\right) \int_0^a \sin\left(\frac{n \pi x}{a}\right) \frac{d}{dx} \sin \left(\frac{n\pi x}{a}\right) dx = 0 \quad \ldots(1.4.9)$$

Average value of p_x, evaluated from that of p_x^2

We know that $\hat{p}_x^2 \psi_1 = 2 m E_1 \psi_1$ …(1.4.10)

Since the state function is an eigenfunction of $\hat{p}_x^2$ the average value of p_x^2 is $2 m E_1$

From the average value of p^2_x if we evaluate the average value of p_x,

we have $(\hat{p}_x)_1 = \pm \sqrt{2 m E_1}$ (1.4.11)

This result is not inconsistent with the result of equation-1.4.8, because in a large number of observations, half of the results will be positive and other half will be negative leading to the effective value of zero for $(\bar{p}_x)_1$

Uncertainty Principle

For the particle in the well, we cannot give the exact position. But we can only say that it is in the box. That is, the uncertainty in the measurement of the position will be 'a'.

Since we have for the momentum $p_x = \pm\sqrt{2\ m\ E_1}$ the particle will have either $p_x = +\sqrt{2\ m\ E_1}$ or $p_x = -\sqrt{2\ m\ E_1}$

This leads to the uncertainty of $2\sqrt{2\ m\ E_1}$ in the momentum

$$\therefore \Delta x\, \Delta p_x = (a)\, 2\ \sqrt{2\ m\ E_1}\ = 2\ a\sqrt{2\ m.\ h^2/8ma^2} = h \qquad \ldots(1.4.12)$$

This is the minimum value. In the upper states the value will be **nh**. This is Heisenberg's uncertainty principle.

1.4.3 Particle in a Box

Let us consider the problem of a particle of mass 'M' in a three dimensional rectangular box of sides a, b, c. The potential function V (x, y, z) This is represented as follows:

V(x, y, z) = 0; (0<x<a; 0<y<b;0<z<c)

V(x, y, z) = ∞; elsewhere (1.4.13)

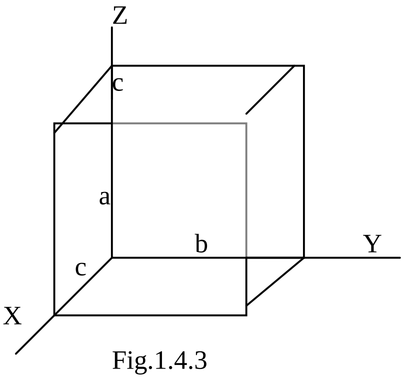

Fig.1.4.3

The Hamiltonian of the problem is

$$H = \frac{p_x^{\ 2}}{2M} + \frac{p_y^{\ 2}}{2M} + \frac{p_z^{\ 2}}{2M}$$

Hamiltonian operator

$$\hat{H} = \frac{1}{2M}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + \frac{1}{2M}\left(-i\hbar\frac{\partial}{\partial y}\right)^2 + \frac{1}{2M}\left(-i\hbar\frac{\partial}{\partial z}\right)^2$$

$$\Rightarrow\ \hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \qquad (1.4.14)$$

Therefore the Schrodinger time-independent (or stationary state equation

$\hat{H}\,\psi = E\,\psi$) becomes

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+k^2\psi=0, \quad \text{where } k^2 = 2ME/\hbar^2 \qquad (1.4.15)$$

Standard technique to solve the above eigenvalue equation is separable variable method. For this, we write ψ(x,y,z) as the product of three functions independent of each other as follows:

$$\Psi(x,y,z) = X(x)\, Y(y)\, Z(z) \qquad (1.4.\ 16)$$

Substituting this in equation-(!.4.15), we obtain

$$\left(\frac{d^2X}{dx^2}\right)YZ + X\frac{d^2Y}{dy^2}Z + XY\frac{d^2Z}{dz^2} + k^2\, XYZ = 0 \qquad (1.4.17)$$

Dividing by XYZ, the equation becomes

$$\frac{1}{X}\ \frac{d^2X}{dx^2} + \frac{1}{Y}\ \frac{d^2Y}{dy^2} + \frac{1}{Z}\ \frac{d^2Z}{dz^2} = -k^2 \qquad (1.4.18)$$

Each term on the LHS is independent of other terms and all of them put together are equal to a constant 'k'. Therefore, if one of the variables is changed, keeping the other two invariant, then also the sum must be constant. This is true only if each term on LHS is a constant by itself and is independent of the variables. Therefore, we can rewrite the equation-1.4.18 as follows:

$$\frac{1}{X}\ \frac{d^2X}{dx^2} = -k_1^2\ ;\quad \frac{1}{Y}\ \frac{d^2Y}{dy^2} = -k_2^2\ ;\quad \frac{1}{Z}\ \frac{d^2Z}{dz^2} = -k_3^2 \qquad (1.4.19)$$

where k_1^2, k_2^2, k_3^2 are constants such that $k^2 = k_1^2 + k_2^2 + k_3^2$ (1.420)

From, equation-1.4.19, we have

$$\frac{d^2X}{dx^2} + k_1^2\, X = 0;\quad \frac{d^2Y}{dy^2} + k_2^2\, Y = 0;\quad \frac{d^2Z}{dz^2} + k_3^2\, Z = 0 \qquad (1.4.21)$$

The solutions are as follows:

$$\left.\begin{aligned} X(x) &= A_1 \cos k_1x + B_1 \sin k_1x \\ Y(y) &= A_2 \cos k_2y + B_2 \sin k_2y \\ Z(z) &= A_3 \cos k_3z + B_3 \sin k_3z \end{aligned}\right\} \qquad (1.4.22\ )$$

Since the particle is confined to the box, 'ψ' must vanish at the surface of the infinite potential. This gives the boundary condition,

$\Psi = 0$, when x=0, y=0, z=0; x=a, y=b, z=c (1.4.23)

The condition $\psi = 0$ for x=0, y=0, z=0 results in the vanishing coefficients

($A_1 = A_2 = A_3 = 0$) of the cosine terms. The condition $\Psi = 0$ for x = a, y = b and

z = c gives (as in the case of the particle in an infinitely deep potential well

constrained to move along x-axis, which has already been dealt in the previous section)

$k_1a = \ell\,\pi$, $k_2b = m\,\pi$ and $k_3c = n\,\pi$ (1.4..24)

where ℓ,m,n are integers greater than zero (ℓ or m or n = 1,2,3,….)

We know that $k^2 = 2ME/\hbar^2$ and accordingly, using equations-1.4.20 and 1.4. 24, we have

$2ME/\hbar^2 = k_1^2 + k_2^2 + k_3^2$

$\Rightarrow E = \hbar^2/2M\,(k_1^2 + k_2^2 + k_3^2)$

$$= \frac{\hbar^2\pi^2}{2M}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right)$$

or $E_{\ell,m,n} = \frac{h^2}{8M}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right)$ (1.4..25)

The eigenfunctions $\psi_{\ell,m,n}$ are given as

$\psi_{\ell,m,n}(x,y,z) = N \sin(\ell\,\pi\,x/a)\,\sin(m\,\pi\,y/b)\,\sin(n\,\pi\,z/c)$ (1.4..26)

where $N = B_1B_2B_3$ is the normalisation constant.

The normalisation condition, $\int_0^a\int_0^b\int_0^c \psi^*\psi\,dx\,dy\,dz = 1$, can be written as

$$N^2\int_0^a\int_0^b\int_0^c \sin^2(\ell\,\pi\,x/a)\,\sin^2(m\,\pi\,y/b)\,\sin^2(n\,\pi\,z/c)\,dx\,dy\,dz = 1$$

$\Rightarrow N^2\,(a/2)(b/2)(c/2) = 1 \Rightarrow N^2\,(abc/8) = 1$

This gives $N = \sqrt{8/(abc)}$ and accordingly

$\psi_{\ell,m,n}$ (x,y,z) = $\sqrt{8/(abc)}$ sin (n π x/a) sin (n π y/b) sin (n π z/c) (1.4..27)

Equations-(1.4..25) and (1.4..27) give the expressions for the evaluation of eigenvalues and eigenfunctions.

Energy levels and degeneracy

The eigenvalues (or) energy values of the particle of mass 'M' in the box of sides a,b,c is given (equation-1.4.25) as follows:

$$E_{n,\ell,m} = \frac{h^2}{8M}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right) \qquad (1.4..28)$$

Where ℓ,m,n have integral values greater than zero.

These are called quantum numbers. For a special case of a cubic box

(a = b = c),

$$E_{n,\ell,m} = \frac{h^2}{8Ma^2}(\ell^2 + m^2 + n^2) \qquad (1.4..29)$$

(i) For the lowest quantum state (ℓ = m = n = 1),

$$E_{1,1,1} = \frac{h^2}{8Ma^2}(1 + 1 + 1) = \frac{3h^2}{8Ma^2} \qquad (1.4.30)$$

There is only one set of quantum numbers (ℓ,m,n) = (1,1,1) and hence one eigenfunction $\psi_{1,1,1}$ for this state. Therefore this energy state or eigenvalue is said to be non-degenerate.

(ii) Consider the next higher energy state with energy, $\frac{3h^2}{4Ma^2}$. For this eigenvalue or energy state there are three sets of quantum numbers (2,1,1), (1,2,1) and (1,1,2) which give the same energy. That is this energy state is associated with three eigenfunctions $\psi_{2,1,1}$, $\psi_{1,2,1}$ and $\psi_{1,1,2}$. Therefore the degeneracy of the state is three and the level is called three-fold degenerate.

Note: It is important to note here that if we reduce the symmetry of the potential field, the degeneracy is partially or fully removed. For example if a = b ≠ c, we observe that $E_{2,1,1} = E_{1,2,1} \neq E_{1,1,2}$ and the state is only doubly degenerate.

If a ≠ b ≠ c, as in the case of a rectangular box , it is obvious that $E_{2,1,1} \neq E_{1,2,1} \neq E_{1,1,2}$ and the state becomes non-degenerate.

1.4.4 Particle in an One-dimensional Finite Potential Well

Let us consider a particle of mass 'm' with energy 'E' moving in a potential field shown in figure-4 and is represented as follows:

$$\left.\begin{aligned} V(x) &= 0 \ ; \ 0<x<a \\ V(x) &= V_o \ ; \ x > a \\ V(x) &= V_o \ ; \ x < 0 \end{aligned}\right\} \qquad \ldots(1.4.31)$$

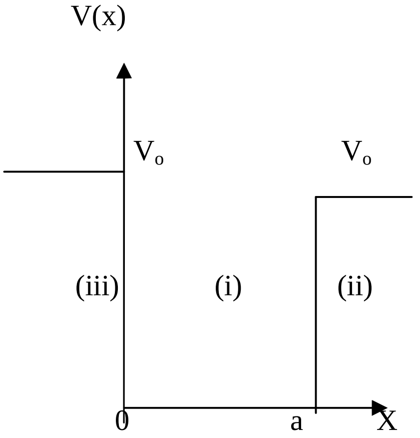

Figure-1.4..4

For the localised states (i.e., when $E < V_o$), Schrodinger's equations in the three zones are given as follows:

$$\left.\begin{aligned} \frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2}\psi_1 &= 0 \quad ; \quad 0 < x < a \\ \frac{d^2\psi_2}{dx^2} - \frac{2m(V_o - E)}{\hbar^2}\psi_2 &= 0 \quad ; \quad x > a \\ \frac{d^2\psi_3}{dx^2} - \frac{2m(V_o - E)}{\hbar^2}\psi_3 &= 0 \quad ; \quad x < 0 \end{aligned}\right\} \qquad (1.4.32)$$

The solutions, as usual, are as follows:

$$\left.\begin{aligned} \Psi_1(x) &= A_1 \cos k_1x + A_2 \sin k_1x \\ \Psi_2(x) &= B_1 e^{k_2x} + B_2 e^{-k_2x} \\ \Psi_3(x) &= C_1 e^{k_2x} + C_2 e^{-k_2x} \end{aligned}\right\} \qquad \ldots(1.4.33\ )$$

where $k_1^2 = \dfrac{2mE}{\hbar^2}$ and $k_2^2 = \dfrac{2m(V_o - E)}{\hbar^2}$ …(1.4.34)

In the second zone x takes positive values and therefore the term $B_1 e^{k_2 x} \rightarrow \infty$ as $x \rightarrow \infty$. Similarly, in the third zone, x takes negative values and therefore the term $C_2\ e^{-k_2 x} \rightarrow \infty$ as $x \rightarrow -\infty$. Accordingly, for wave functions to be finite as per the requirement of Schrodinger's postulates, the values of B_1 and C_2 must be made zero. This eliminates the terms $B_1 e^{k_2 x}$ and $C_2\ e^{-k_2 x}$ in the second and third zones. Therefore solutions in equation-1.4.33 become,

$$\left.\begin{aligned} \Psi_1(x) &= A_1 \cos k_1x + A_2 \sin k_1x \\ \Psi_2(x) &= B_2 e^{-k_2 x} \\ \Psi_3(x) &= C_1 e^{k_2 x} \end{aligned}\right\} \quad \ldots(1.4.35)$$

Continuity conditions of ψ and $\dfrac{d\psi}{dx}$ at x = 0 are

$$\Psi_1(0) = \Psi_3(0) \;;\; \left(\frac{d\psi_1}{dx}\right)_{x=0} = \left(\frac{d\psi_3}{dx}\right)_{x=0} \quad \ldots(1.4.36)$$

They yield the following results:

$A_1 = C_1$; $k_1A_2 = k_2C_1$ …(1.4.37)

The equation-1.4.37 gives $A_1/A_2 = k_1/k_2$ (1.4.38)

Continuity conditions of ψ and $\dfrac{d\psi}{dx}$ at x = a are

$$\Psi_1(a) = \Psi_2(a) \;;\; \left(\frac{d\psi_1}{dx}\right)_{x=a} = \left(\frac{d\psi_3}{dx}\right)_{x=a} \quad \ldots(1.4.39)$$

They yield the following relations:

$$\left.\begin{aligned} A_1 \cos k_1a + A_2 \sin k_1a &= B_2 e^{-k_2a} \\ -k_1A_1 \sin k_1a + k_1A_2 \cos k_1a &= -k_2B e^{-k_2a} \end{aligned}\right\} \quad (1.4.40)$$

Dividing the first by the second in equation –1.4. 40,

$$\frac{A_1 \cos k_1a + A_2 \sin k_1a}{-k_1A_1 \sin k_1a + k_1A_2 \cos k_1a} = \frac{B_2e^{-k_2a}}{-k_2B_2e^{-k_2a}} = -\frac{1}{k_2} \quad \ldots(1.4.41)$$

Dividing the numerator and denominator of the LHS by A_2 cos k_1a, we have

$$\frac{\dfrac{A_1}{A_2} + \tan k_1a}{-k_1\dfrac{A_1}{A_2}\tan k_1a + k_1} = -\frac{1}{k_2} \quad \ldots(1.4.42)$$

Substituting $(A_1/A_2) = (k_1/k_2)$ in the above equation, we obtain

$$\frac{\dfrac{k_1}{k_2} + \tan k_1a}{-\dfrac{k_1{}^2}{k_2}\tan k_1a + k_1} = -\frac{1}{k_2} \qquad \Rightarrow \quad \frac{k_1 + k_2 \tan k_1a}{-k_1{}^2 \tan k_1a + k_1k_2} = -\frac{1}{k_2}$$

$$\Rightarrow \quad k_1k_2 + k_2^2 \tan k_1a = k_1^2 \tan k_1a - k_1k_2$$

$$\Rightarrow \tan k_1a = \frac{2k_1k_2}{k_1{}^2 - k_2{}^2} \quad \ldots(1.4.43)$$

Substituting the values of k_1 and k_2 from equation-1.4.34,

$$\tan a \sqrt{\frac{2mE}{\hbar^2}} = \frac{2\sqrt{E(V_o - E)}}{2E - V_o} \quad (1.4.44\ \ )$$

Case (i) (when $V_o \rightarrow \infty$)

For $V_o \rightarrow \infty$, equation-1.4.44 becomes

$$\tan a \sqrt{\frac{2mE}{\hbar^2}} = 0 \quad \ldots(1.4.45)$$

This equation is valid if

$$a\sqrt{\frac{2mE}{\hbar^2}} = n\,\pi \;;\quad n = 1,2,3,\ldots \qquad \ldots(1.446)$$

$$\therefore (E_n)_{V_o\to\infty} = \frac{n_2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \quad \text{where } n = 1, 2, 3,\ldots \qquad \ldots(1.4.47)$$

This equation for energy levels tallies exactly with that of infinitely deep potential well, as expected.

Case (ii) (When V = V_o is finite)

General solution is obtained by graphical method by plotting (from equation-1.4.43) tan k_1a and $2k_1k_2 / (k_1^2 - k_2^2)$ on the same graph sheet as functions of k_1a. The intersections of the two curves give the allowed k_1 values and hence the allowed energy levels. From the graph the non-trivial values of k_1a are given by

$$k_1a < n\,\pi \;;\quad n = 1, 2, 3\ldots \qquad (1.4..48)$$

Squaring the equation and substituting

$$k_1^2 = \frac{2mE}{\hbar^2}, \text{ we have}$$

$$E_n < \frac{n^2h^2}{8ma^2} = (E_n)_{V_o=\infty} \qquad (1.4..49)$$

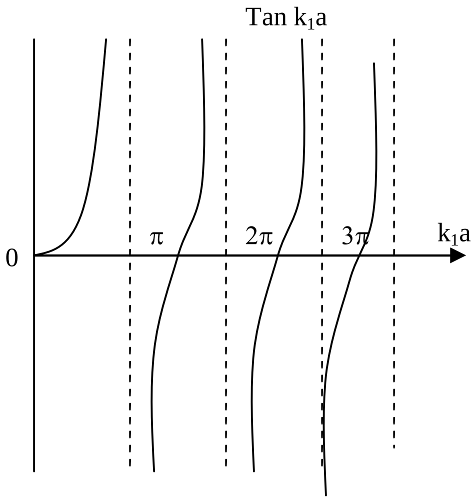

Fig 1.4. 5

From this equation, it is evident that the

Allowed energies of the particle in a finite potential well are similar to those of the one-dimensional box. They are however less than those of the one-dimensional box. The sequence of the eigenvalues is not changed..

For E > 0, the Schrodinger's equations-1.4.32 become

$$\left.\begin{aligned} \frac{d^2\psi_I}{dx^2} + k_I^{\,2}\,\psi_1 = 0 \\ \frac{d^2\psi_{II}}{dx^2} + k_{II}^{\,2}\,\psi_2 = 0 \\ \frac{d^2\psi_{III}}{dx^2} + k_{II}^{\,2}\,\psi_3 = 0 \end{aligned}\right\} \qquad . (1.4..50)$$

where $k_I^{\,2} = \frac{2mE}{\hbar^2}$ and $k_{II}^{\,2} = \frac{2m(E - V_o)}{\hbar^2}$

The solutions for all the equations are of the type e $^{\pm ikx}$ and hence they remain now zero even when x → ± ∞. Therefore the particle is not confined to any region of space (i.e., not localised). Further all solutions are possible and hence the spectrum is continuous. Classically, the particle in such a state (i.e., with E > V_o) approaching the well undergoes an instantaneous acceleration on reaching the edge of the well and equal retardation at the opposite edge. But is would keep on going with no probability of reflection. However, in quantum mechanics, the particle in such a state has a non-zero probability of its being reflected by the well.

1.4.5 Linear Harmonic Oscillator

Linear harmonic oscillator is a particle of mass ‘m’, vibrating under the influence of a restoring force which is directly proportional to its displacement ‘x’ from the equilibrium position (i.e., **F = -kx**). This simple model is of interest in the study of chemical bonds and molecular spectra. The vibrations of diatomic and polyatomic molecules and oscillations of other more complicated systems expressed in terms of their normal modes are a few problems that can be analysed on the basis of this model.

Polynomial Method**:**

The classical Hamiltonian of the linear harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad (1.4..51)$$

where ‘m’ is the mass and ‘k’ is the force constant. It is convenient to express it in terms of the classical vibrational frequency of the oscillator,

$$\upsilon = \omega/(2\pi) = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (1.4..52)$$

where ‘ω’ is the angular frequency and ‘υ’ is the linear frequency.

Since $k = m\,\omega^2$, we have $H = \frac{p^2}{2m} + \frac{1}{2} m\,\omega^2 x^2$ (1.4..53)

Then the time-independent Schrodinger’s equation ($\hat{H}\psi = E\psi$) becomes

$$\frac{\hat{p}^2\psi}{2m} + \frac{1}{2}m\omega^2\,\hat{x}^2\,\psi = E\psi \qquad (1.4..54)$$

With $\hat{p} \rightarrow -i\hbar\,\frac{d}{dx}$ and $\hat{x} \rightarrow x$, equation-1.4.54 becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2} m\,\omega^2 x^2\right)\psi = 0 \qquad (1.4..55)$$

Substituting, for simplicity,

$$\lambda = \frac{2m}{\hbar^2}E \quad \text{and} \quad \alpha = m\,\omega/\hbar \qquad (1.4..56)$$

we obtain $\frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2)\,\psi = 0$ (1.4..57)

For further simplification, substituting $\xi = \sqrt{\alpha}\;x$, we have

$$\frac{d^2\psi}{d^2\xi^2} + \left(\frac{\lambda}{\alpha} - \xi^2\right)\psi = 0 \qquad (1.4..58)$$

Asymptotic Solution

For large values of x and hence ξ, since $\xi^2 >> \frac{\lambda}{\alpha}$, equation-1.4.58, can be written as $\frac{d^2\psi}{d^2\xi^2} = \xi^2\,\psi$ (1.4..59)

Let us assume a solution $\psi = ce^{\pm\xi^2/2}$ (1.4..60)

and substitute it in equation-1.4.59

$$\text{LHS} = \frac{d^2\psi}{d^2\xi^2} = \frac{d^2}{d\xi^2}(ce^{\pm\xi^2/2}) = \frac{d}{d\xi}[ce^{\pm\xi^2/2}(\pm\xi)]$$

$$= \pm\ [ce^{\pm\xi^2/2} + ce^{\pm\xi^2/2}(\pm\xi)(\xi)]$$

$$= ce^{\pm\xi^2/2}(\xi^2 \pm 1) \qquad (1.4..61)$$

If we assume $\xi \rightarrow \infty$, the '1' in the expression $(\xi^2 \pm 1)$ can be ignored and therefore

$$\text{LHS} = ce^{\pm\xi^2/2}\xi^2 \quad = \quad \xi^2\psi \ = \ \text{RHS}$$

Therefore, $\psi = ce^{\pm\xi^2/2}$ (1.4..62)

is a valid solution of equation-1.4.59, when $\xi \rightarrow \infty$. This solution is called the asymptotic solution. Since, the positive sign leads to infinite values of ψ for large values of ξ, it is obvious that $ce^{\xi^2/2}$ is not finite and therefore is not an acceptable wave function. The only acceptable solution is

$$\psi = ce^{-\xi^2/2} \qquad (1.4..63)$$

It is well known that $\xi^n\, e^{-\xi^2/2}$ (1.4..64)

is square integrable for a finite 'n' over the total range of ξ from $-\infty$ to $+\infty$. Therefore,

$f(\xi)e^{-\xi^2/2}$ is square integrable when $f(\xi)$ is a polynomial in ξ terminating after a finite number of terms. Therefore, for a general solution of equation-1.4.58, we can assume

$$\psi = f(\xi)\, e^{-\xi^2/2} \qquad (1.4..65)$$

with the above substitution in equation-1.4.58, we obtain

$$\frac{d^2 f}{d\xi^2} - 2\xi \frac{df}{d\xi} + \left(\frac{\lambda}{\alpha} - 1\right) f = 0 \qquad (1.4..66)$$

Let us compare this equation with Hermite differential equation

$$f'' - 2\xi f' + 2nf = 0 \qquad (1.4..67)$$

This equation is identical to Hermite's equation, provided $\frac{\lambda}{\alpha} - 1 = 2n$ (1.4..68)

Polynomial solutions exist for n = 0, 1, 2,…..

$\therefore 2mE/\hbar^2 = (2n + 1)\, m\omega / \hbar$

$\Rightarrow E_n = (n + ½)\, \hbar\omega$ (1.4..69)

Even in the lowest level n = 0, the quantum mechanical oscillator still has energy $\hbar\omega / 2$. This is called the zero-point vibrational energy, which persists even at the absolute zero of temperature.

The existence of zero-point energy is in accordance with the uncertainty principle – for if the oscillator had zero energy, it would have zero momentum and would also be located at the position of the minimum potential energy thus enabling precise determination of position and momentum simultaneously.

Since $f(\xi)$ is identified with the Hermite polynomial $H(\xi)$, the eigen-functions of the linear harmonic oscillator are

$$\psi_n(x) = N_n e^{-\alpha x^2/2} H_n\left(\sqrt{\alpha}\, x\right) \quad ; \quad \text{where } N_n = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}}\right)^{1/2} \qquad (1.4.70)$$

and $$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}\left(e^{-x^2}\right) \qquad (1.4.71)$$

Vibrational Spectrum

Harmonic oscillator is an ideal model to explain the vibrations of a diatomic molecule. In Spectroscopy 'v' is generally used, instead of n, for vibrational quantum number. Accordingly, the vibrational energy is expressed as $E_v = (v + ½)\ \hbar\omega$. Conventionally, the vibrational energy is expressed in cm^{-1} units by dividing E_v with hc, where 'c' is the velocity of light and is denoted as G(v). Therefore,

$G(v) = E_v / hc = \boldsymbol{\omega_e (v + ½)}$, (1.4..72)

where $\omega_e = \hbar\omega / (hc) = \omega / (2\pi c)$ = vibrational frequency.

In the electronic spectrum of a diatomic molecule, if the selection rule $\Delta v = \pm 1$ is only taken, one band is predicted in the absorption spectrum because of the same energy difference between successive energy levels. But, practically, we observe a large number of bands. Therefore, a non-harmonic oscillator model is necessary to explain even the gross structure of the spectrum. For a harmonic oscillator, the selection rule is $\Delta v = 0, \pm 1, \pm 2, \ldots$ Accordingly, overtones can also be explained.

Eigenfunctions

The eigenfunctions (wave functions) of the harmonic oscillator are given by the relation, $\psi_n(x) = N_n e^{-\alpha x^2/2} H_n\left(\sqrt{\alpha}\, x\right)$**.** They are shown in the figure-6. As is seen in the figure normal state v = 0 corresponds to Gaussian function with the maximum probability in the middle. All other states with v > 0 have two peaks, which coincide with the extremes of classical range. In between, there are v nodes and (v-1) subsidiary peaks. These maxima diminish in amplitude and are crowded towards the centre of the range. The wave function and hence the wave mechanical probability density has large values just in the region of classical vibration, but that also some what outside this region the probability density is not negligible, although it falls off exponentially there. Thus, in wave mechanics the oscillator in a given energy level can reach, with a non-zero probability region that a classical oscillator of the same energy and the same force constant can never reach. While classically the oscillator stays for the greater part of the time at the turning points, wave mechanically for v ≠ 0, there is broad maximum of probability distribution in the neighbourhood of the classical turning points, but lying some what more towards the centre. In addition, for v > 0, there are other maxima of wave mechanical probability distribution between the two outer most maxima. No classical analogues exist for these maxima.

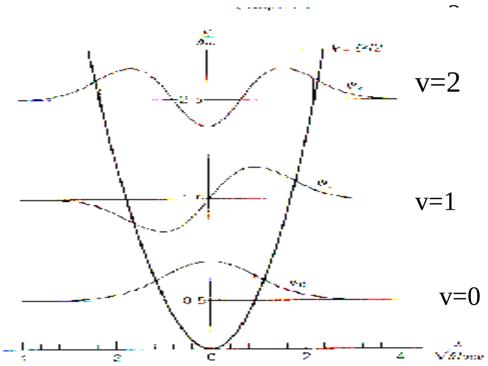

Fig 1.4.6 wave functions of linear harmonic oscillator

Summary of lesson

Schrodinger’s wave equation has been developed for a particle in a linear infinite potential well and also finite potential well. The eigenvalues have been solved and compared. Problem of a particle in three dimensions (in a rectangular box) has been solved and degeneracy explained. The eigenvalues and eigenfunctions of a linear harmonic oscillator have been derived and discussed.

Key terminology

Infinite Potential Well – Finite Potential Well – Localised States – Harmonic Potential – Degeneracy – Non-degenerate state – Asymptotic Solution – Hermite Polynomials.

Self assessment questions

(i). Solve the Schrodinger’s equation for a particle in a linear potential well of width ‘a’. Discuss the eigenvalues and eigenfunctions.

(ii) Solve the Schrodinger’s equation for a particle in an one-dimensional infinitely deep potential well. Deduce uncertainty principle.

(iii) Solve the Schrodinger’s equation for a particle in a rectangular box. Discuss the degeneracy of the energy levels.

(iv) Write the Schrodinger's equation for a particle in an one-dimensional finite potential well. Solve the equation for the localised states.

(v) Solve the Schrodinger's equation for a linear harmonic oscillator. Discuss the eigenvalues and eigenfunctions.

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UNIT - 1

LESSON - V - SYSTEMS WITH SPHERICAL SYMMETRY

Objective:

Determination and discussion of eigenvalues and eigenfunctions of rigid rotator and hydrogen atom.

1.5.1 Introduction

Systems with spherical symmetry are of great importance. Central force problems form an important class. These are forces, which are derivable from a potential that depends only on the distance 'r' of a moving particle from a fixed point. Accordingly, central potential V = V(r).

The Schrodinger's equation for a particle of mass 'm' under the influence of such a potential is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V (r)] \psi = 0 \qquad (1.5.1)$$

where $$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \qquad (1.5.2)$$

In this lesson, it is convenient to first study simpler cases of Rigid rotator with free axis and Rigid rotator with fixed axis (or plane rigid rotator), which possess no potential energy to reckon with and then analyse the problem of Hydrogen atom, which is a central force problem.

1.5.2 Rigid Rotator with Free Axis:

It is a system of two point masses (particles) m_1 and m_2 connected by a mass-less rigid rod of definite length 'r' and rotating about an axis passing through the centre of mass and normal to the plane containing the two masses.

If the two particles are constrained to remain in one plane, then the direction of rotation of the axis of the rotation is fixed and the system is called the rigid rotator with fixed axis. If there is no such constraint and if the plane of these two particles can move, then the axis of rotation is free to take any position in space. This system is called the rigid rotator with free axis. Ideal diatomic molecule without vibrations is the best example of the system.

For a rigid rotator, since r = constant, the term with $\frac{\partial}{\partial r}$ is zero. There is no potential energy. Therefore for a rigid rotator of reduced mass $\mu = m_1m_2 / (m_1 + m_2)$, the Schrodinger's equation is

$$\frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial}{\partial\theta}) \psi + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu E}{\hbar^2} \psi = 0$$

$$\Rightarrow \quad \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial\psi}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{2IE}{\hbar^2} \psi = 0 \qquad (1.5.3)$$

where I = momentum of Inertia = μr^2

It is a differential equation with two independent variables and so can easily be solved by the well-known method of separation of variables.

Using $\psi = \Theta(\theta)\Phi(\phi)$, $\frac{\sin^2\theta}{\Theta} \left[\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\frac{\sin\theta d\Theta}{d\theta} \right) + \frac{2IE\Theta}{\hbar^2} \right] = - \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$ (1.5.4)

Since each side is dependent on one variable only and is independent of the other, each side should be equal to the same constant (say m^2), which is independent of θ and ϕ.

$$\therefore \frac{d^2\Phi}{d\phi^2} = -m^2\Phi \qquad (1.5.5)$$

and $\frac{\sin^2\theta}{\Theta} \left[\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2IE\Theta}{\hbar^2} \right] = m^2$ (1.5.6)

Solution of equation-1.5.5 is

$$\Phi_m(\phi) = Ae^{im\phi} \qquad (1.5.7)$$

For $\Phi_m(\phi)$ to be single valued,

$$\Phi_m(\phi) = \Phi_m(\phi + 2\pi) \Rightarrow Ae^{im\phi} = Ae^{im(\phi + 2\pi)} \Rightarrow Ae^{im\phi} = Ae^{im\phi} e^{im2\pi}$$

Therefore, $e^{im2\pi} = 1$ and this is true if m = 0, ±1, ±2,….

Normalisation condition is given as

$$\int_0^{2\pi} \Phi_m^* \, \Phi_m \, d\phi = 1$$

$$\therefore A^2 \int_0^{2\pi} e^{-im\phi} \, e^{im\phi} \, d\phi = 1$$

$$\Rightarrow A^2 \int_0^{2\pi} d\phi = 1 \qquad \Rightarrow A^2 (2\pi) = 1 \Rightarrow A = \frac{1}{\sqrt{2\pi}}$$

$$\therefore \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}; \quad m = 0, \pm 1, \pm 2,\ldots \qquad (1.5.8)$$

Equation-1.5.6 can be rewritten as

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\frac{2IE}{\hbar^2} - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad (1.5.9)$$

This theta equation is identically equal to associated Legendre differential equation,

$$\text{if } \frac{2IE}{\hbar^2} = \ell(\ell + 1) \qquad (1.5.10)$$

According to the properties of associated Legendre differential equation, it has an acceptable polynomial solution only for integral value of 'ℓ' such that $\ell \geq |m|$. Therefore, from equation-1.5.10, the energy levels of the rigid rotator are given by the relation

$$\frac{2IE}{\hbar^2} = \ell(\ell + 1)$$

$$\text{(or) } E = \frac{\hbar^2}{2I} \ell(\ell + 1); \ \ell = 0, 1, 2\ldots \qquad (1.5.11)$$

Accordingly, the normalized $\Theta(\theta)$ are the associated Legendre polynomials

$\Theta_{\ell,m}(\theta)$ as given below:

$$\Theta(\theta) = \Theta_{l,m}(\theta) = \varepsilon \left(\frac{(2l+1)}{2} \frac{(l-|m|)\,!}{(l+|m|)\,!} \right)^{1/2} P_\ell^{|m|}(\cos\theta) \qquad (1.5.12)$$

where $\varepsilon = 1$, $m \le 0$; $\varepsilon = (-1)^m$, $m > 0$

$$P_\ell^{|m|}(\cos\theta) = \frac{(-1)^l}{2^l\, l!} (\sin\theta)^{|m|} \left(\frac{d}{d\cos\theta} \right)^{l+|m|} (\sin\theta)^{2\ell}$$

The total wave function is

$$\Psi_{\ell,m}(\theta,\phi) = \Theta_{\ell,m}(\theta)\,\Phi_m(\phi) = Y_{\ell.m}(\theta,\phi) \qquad (1.5.13)$$

Here $Y_{\ell,m}(\theta,\phi)$ are called spherical harmonics.

Rotational Spectrum

Rigid rotator model explains the rotational spectrum of a diatomic molecule, which occurs in the microwave and far infra-red regions. The rotational quantum number is generally denoted as ‘J’ in spectroscopy. Accordingly, the rotational energy is given as

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad \Rightarrow \quad E_J = \frac{h^2}{8\pi^2 I} J(J+1)\,; \quad J = 0,1,2\ldots..$$

Conventionally, the energy is expressed in cm $^{-1}$ units by dividing E_J by hc, where c is the velocity of light, and is denoted as F(J). Accordingly,

$$F(J) = E_J / hc = \frac{h^2}{8\pi^2 Ihc} J(J+1) = BJ(J+1), \text{ where}$$

$$e\ B = \frac{h}{8\pi^2 Ic}$$

$\therefore F(J) = BJ(J+1)$; $J = 0, 1, 2\ldots.$

The selection rule for transitions between various energy levels is **ΔJ = ± 1**. Accordingly, the rotational spectrum is equidistant with a separation of **2B** between successive lines, as can be seen in the energy level diagram (fig.1). From the spectrum, we can determine experimentally B value, then evaluate moment of inertia ‘ I ’ and hence (since $I = \mu r^2$) inter-nuclear distance (r).

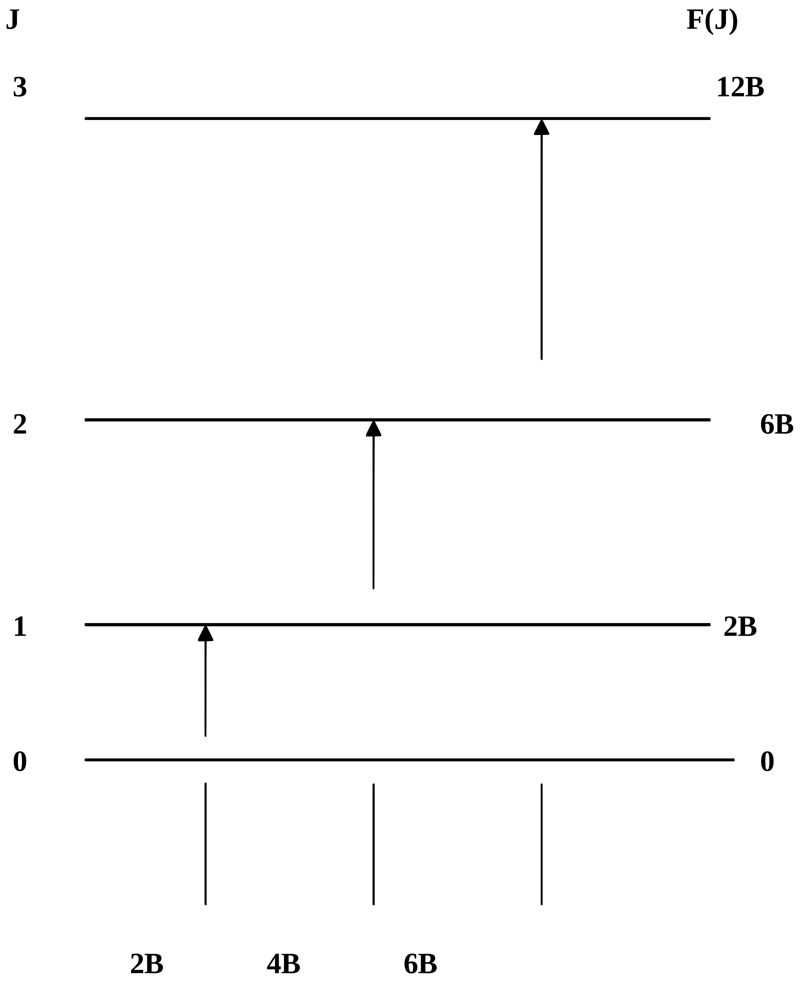


Figure-1.5.1

1.5.3 Rigid Rotator with Fixed Axis (or) Plane Rigid Rotator:

Plane rigid rotator is one, which is constrained to a plane. Let it be constrained to XY-plane. Then its axis is fixed with $\theta = 90^o$. Therefore in Schrodinger's equation-1.5.3, the terms with $\frac{\partial}{\partial\theta}$ will vanish and $\sin\theta = \sin 90^o = 1$. Accordingly, the equation-1.5.3 becomes

$$\frac{d^2\psi}{d\phi^2} + \frac{2IE}{\hbar^2}\ \psi = 0 \qquad (1.5.14)$$

If we substitute $\frac{2IE}{\hbar^2} = m^2$ (1.5.15)

equation-1.5.14 becomes $\frac{d^2\psi}{d\phi^2} + m^2\ \psi = 0$ (1.5.16)

The solution, obviously, is given by $\psi\ (\phi) = Ae^{im\phi}$

For it to be single valued, as already explained, m = 0, ±1, ±2,….

Further, the normalisation constant is $A = \frac{1}{\sqrt{2\pi}}$

Accordingly, the solution is

$$\psi_m\ (\phi) = \frac{1}{\sqrt{2\pi}}\ e^{im\phi}\ ; \qquad m = 0, \pm1, \pm2,\ldots. \qquad (1.5.17)$$

From equation-1.5.15, the eigenvalues are given by the relation

$$E = E_m = \frac{m^2\hbar^2}{2I}\ ; m = 0, \pm1, \pm2,\ldots. \qquad (1.5.18)$$

1.5.4 Hydrogen Atom

The problem of hydrogen atom, is a two-body problem (namely of the electron of mass 'm' and proton of mass 'M'). Since, we are not interested in translational motion of the atom as a whole, the centre of mass of the system is taken as the origin of the coordinate system. Since the system is centro-symmetric, it is most convenient to use spherical polar coordinates. The problem can be treated (as in the case of rigid rotator) as a single particle problem of reduced mass $\mu = \frac{mM}{m+M}$, with the radial coordinate 'r' which is equal to the distance between the electron and the nucleus. Potential energy of attraction between the electron and the nucleus is

$$V = \frac{-Ze^2}{r} \qquad (1.5.19)$$

(Here Z = 1 for H-atom. But for generality 'Z' is retained. The treatment, then, remains same for H-like ions He^+, Li^{++} etc. with appropriate μ)

Schrodinger's equation for H-atom is

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2}(E + \frac{Ze^2}{r})\psi = 0 \qquad (1.5.20)$$

$$\text{where } \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad (1.5.\ 21)$$

It is well known that the operator for the square of the orbital angular momentum

$$\hat{L}^2 = -\hbar^2 \qquad (1.5.22\ )$$

Using this in equation-1.5.21, we have $\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) - \frac{\hat{L}^2}{\hbar^2 r^2} \qquad (1.5.23)$$

$\hat{L}^2$ has eigenfunctions $Y_{\ell.m}(\theta,\phi)$ and eigenvalues $\ell(\ell+1)\hbar^2$

where $\ell = 0,1,2,\ldots$ and $\ell \geq |m|$.

$$\therefore \hat{L}^2 \ Y_l^m(\theta,\phi) = \ell(\ell+1)\hbar^2\, Y_l^m(\theta,\phi);\ \ell = 0,1,2,\ldots;\ \ell \geq |m| \qquad (1.5..24)$$

From equations 1.5.20 and 1.5.23,

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r}) - \frac{1}{\hbar^2 r^2}\hat{L}^2\psi + \frac{2\mu}{\hbar^2}(E + \frac{Ze^2}{r})\psi = 0 \qquad (1.5.25)$$

Using separable variable technique with $\psi(r,\theta,\phi) = N\,R(r)\,Y(\theta,\phi)$ (1.5.26)

$$\frac{1}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{2\mu r^2}{\hbar^2}(E + \frac{Ze^2}{r}) = \frac{1}{\hbar^2 Y}(\hat{L}^2\ Y) \qquad (1.5.27)$$

The LHS is dependent only on ‘r’ whereas the RHS is dependent only on θ and ϕ. But they are equal to each other. Therefore they must be independent of r, θ and ϕ; and each must be equal to a constant, say ‘λ’.

$$\therefore \frac{1}{\hbar^2 Y}(\hat{L}^2\, Y) = \lambda \Rightarrow \hat{L}^2\, Y(\theta,\phi) = \lambda\, \hbar^2\, Y(\theta,\phi)$$

We know already (equation-1.5.24) that $\lambda = \ell\,(\ell+1)$ with $\ell = 0,1,2,\ldots.$

Therefore equation-1.5.27 becomes

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{2\mu}{\hbar^2}[\,(E + \frac{Ze^2}{r}) - \frac{l(l+1)\hbar^2}{2\mu r^2}]\,R = 0 \qquad (1.5.28)$$

The term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ appears as an addition to the potential and can be considered as centrifugal potential since its negative gradient is equal to the centrifugal force experienced by a particle moving in an orbit of radius ‘r’ with angular momentum $\sqrt{l(l+1)\hbar^2}$. Alternatively, it may be looked upon as the K.E associated with the rotary part of the motion ($\hat{L}^2 / 2\, I$) where $I = \mu r^2$ is the moment of inertia.

Equation-1.5.28 can also be written as

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}[\,(E + \frac{Ze^2}{r}) - \frac{l(l+1)\hbar^2}{2\mu r^2}]\,R = 0 \qquad (1.5.29)$$

With the change of the variable as $\rho = \alpha r$, the above equation becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{r}\frac{dR}{d\rho} + [\,(\frac{2\mu E}{\alpha^2\hbar^2} + \frac{2\mu}{\hbar^2}\frac{Ze^2}{\rho\alpha}) - \frac{l(l+1)}{\rho^2}]\,R = 0 \qquad (1.5.30)$$

For bound states (E<0)

Let us introduce a new parameter n and also write ‘α’ in terms of other known constants as

$$\alpha = \frac{2}{\hbar}\sqrt{-2\mu E} \text{ and } n = \frac{2\mu Ze^2}{\hbar^2\alpha} \qquad (1.5.31)$$

With these parameters, equation-1.5.30 can be written as

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + [\frac{-1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}]\, R = 0 \qquad (1.5.32A)$$

(or) $$\frac{d^2}{d\rho^2}(\rho R) + [\frac{-1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}](\rho R) = 0 \qquad (1.5.32B)$$

The asymptotic solution (for $\rho \to \infty$) can be obtained using equation – 1.5.32(A):

$$\frac{d^2R}{d\rho^2} = \frac{R}{4} \Rightarrow R(\rho) \sim e^{-\rho/2} \qquad (1.5.33)$$

The asymptotic solution (for $\rho \to 0$) can be obtained using equation1.5.-32(B):

$$\frac{d^2}{d\rho^2}(\rho R) - \frac{l(l+1)}{\rho^2}(\rho R) = 0 \Rightarrow R(\rho) \sim \rho^{\ell} \qquad (1.5.34)$$

The correctness can be checked by back substitution

Therefore, the actual solutions for all values of ρ (or) r may be of the form

$$R(\rho) \sim f(\rho)\rho^{\ell} e^{-\rho/2} \qquad (1.5.35)$$

With this substitution in equation 1.5.32(A) or 1.5.32(B), we have

$$\rho\frac{d^2f}{d\rho^2} + (2\ell + 2 - \rho)\frac{df}{d\rho} + (n - \ell - 1) f = 0 \qquad (1.5.36)$$

This equation is similar to the Associated Laguere Differential Equation

$$\rho L'' + (p + 1 - \rho) L' + (q - p) L = 0 \qquad (1.5.37)$$

if $q = n + \ell$ and $p = 2\ell + 1$

(or) $(q - p) = (n - \ell - 1)$ and $(p + 1 - \rho) = (2\ell + 2 - \rho)$ (1.5.38)

This differential equation has a polynomial solution when q – p = +ve integer.

$\therefore n - \ell - 1$ = +ve integer (1.5.39)

Since $\ell = 0, 1, 2, \ldots$, from equation-1.5.39 we have $n = \ell + 1 = 1, 2, 3, \ldots$ (1.5.40)

From equation-1.5.31

$$E_n = \frac{-\hbar^2\alpha^2}{8\mu} = \frac{-\hbar^2}{8\mu}\left[\frac{2\mu Ze^2}{\hbar^2 n}\right]^2$$

$$\Rightarrow E_n = \frac{-2\pi^2\mu Z^2 e^4}{n^2h^2}\text{ ; n = 1,2,3….} \qquad (1.5.41)$$

These bound state energies are in accordance with those obtained from Bohr's theory. The wave functions are

$\Psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r)\, Y_l^m(\theta,\phi)$

where $R_{n,\ell}(r)$ are radial function and $Y_{\ell,m}(\theta, \phi)$ are spherical harmonics involving angular functions.

Note: The normalised radial wave functions are as follows:

$$R_{n,\ell}(r) = -\sqrt{\left(\frac{2Z}{na_o}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\left(\frac{2Zr}{na_o}\right)^l e^{-Zr/(na_o)}\, L_{n+l}^{2l+1}\left(\frac{2Zr}{na_o}\right)$$

where $L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1}[(n+l)!]^2\rho^k}{(n-l-1-k)!(2l+1+k)!}$ and

$a_o = \mu e^2/\hbar^2$ = Bohr's first orbit radius.

Degeneracy of eigenvalues

The energy levels (eigenvalues)

$$E_n = \frac{-2\pi^2\mu Z^2 e^4}{n^2h^2} \quad ; \quad n = 1,2,3….$$

For a particular value of n, there is only one specific eigenvalue as is predicted by Bohr theory. But there will be a number of eigenfunctions $\psi_{n,\ell,m}$. For a particular value of principal quantum number **n**, the orbital angular momentum quantum number **ℓ** takes the values ℓ = 0,1,2….n-1 and for each value of ℓ there are (2 ℓ +1) magnetic quantum numbers **m** from -ℓ to +ℓ. Therefore, the total number of eigenfunctions ($\psi_{n,\ell,m}$) for a particular eigenvalue

E_n is $\sum_{0}^{n-1}(2\ell + 1) = n^2$. Accordingly, degeneracy of each level is n^2.

Spin of the electron is not considered in the present case. If the spin is also taken into consideration, the degeneracy doubles ($2n^2$) because every s = ½ level has two sub levels depicted by $m_s = \pm$ ½. From this quantum mechanical theory of Hydrogen atom, intensities of spectral lines, selection rules, polarisation rules and other physical parameters are correctly predicted in addition to the positions of the energy levels (spectral lines).

Wave functions

Wave functions of hydrogen atom are $\Psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r)\, Y_l^m(\theta,\phi)$, where $R_{n,\ell}(r)$ are radial function and $Y_{\ell,m}(\theta, \phi)$ are spherical harmonics involving angular functions. To distinguish the three dimensional distribution $\Psi^*\Psi$, from the Bohr-Sommerfeld concept of an electron moving in a circular or elliptic orbit, the 3D distributions are called **orbitals**.

The orbitals are designated by the principal quantum number 'n' followed by a symbol signifying azimuthal quantum number ℓ (ℓ = 0,1, 2, 3,…→ s, p, d, f..). The value of the magnetic quantum number 'm' is added as a subscript to the symbol. For example the orbitals with n = 2, ℓ = 1 and m = +1, 0, -1 are denoted by $2p_+$, $2p_o$ and $2p_{-1}$.

Sometimes the orbitals (wavefunctions) are expressed in terms of Cartesian coordinates and these are expressed as subscripts instead of the values of 'm'. For example, since $\Psi_{n,1,0} \sim r\cos\theta = z$ (except for a numerical constant), $p_o \sim p_z$. It is difficult to pictorially represent the 3D probability densities in 2D figures. Therefore it is convenient to study separately the radial part

$R_{n,\ell}(r)$ and the angular part $Y_l^m(\theta,\phi)$.

Radial functions [$R_{n\ell}(r)$]

All $R_{n\ell}(r)$ contain a factor r^ℓ. So they are all zero at the origin except for states for which $\ell = 0$ (s-state). This leads to an important fact that s-states interact with the nuclear moments more strongly than other states. We know that $R^*R = R^2$ is the probability density of the electron at a particular r along a particular direction. More important is the radial probability density. D(r) = $4\pi r^2 R^2$ of an electron to be somewhere at a distance r, irrespective of the direction. D (r) (vs) r graphs for a few states are shown in figure-2.

The curves for 1s, 2p and 3d orbitals have one maximum only and it is interesting to note that these are at distances equal to the radii of the corresponding Bohr orbits ($r = n^2 a_o$). Other curves have more than one maxima but it is evident that the electron spends most of its time in the outermost zone. For a particular n, the maximum corresponding to a greater ℓ is closer to the nucleus.

Angular Functions [$Y_l^m(\theta,\phi)$]

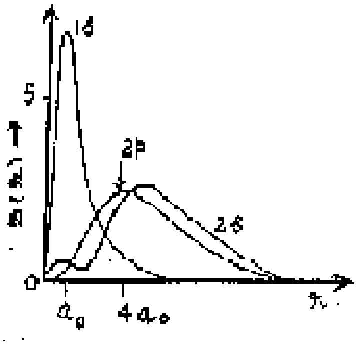
It is evident that the size of the orbital is determined by the radial function. The shape of it is determined by the angular function. Hence the angular function is of great importance in understanding the geometrical and other related properties of molecules. Y*Y is the angular probability density which is positive everywhere. However the angular function Y = ΘΦ will have different signs in different regions of space. The sign of the wave function is useful in discussing symmetry. Therefore we will depict, in figure-3 the diagrams of both the angular probability and angular probability density. In this diagram ΘΦ and $|\Theta\Phi|^2$ values are shown by solid and dotted lines respectively.

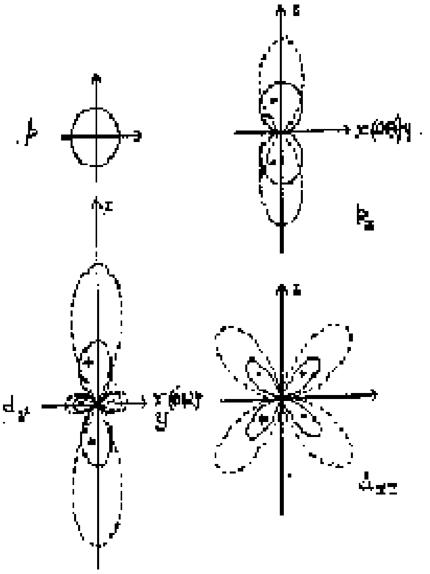
s – orbitals

For s-orbitals, $Y_{oo} = \dfrac{1}{\sqrt{4\pi}}$ and hence it is spherically symmetrical. This is represented by a **sphere** in 3D and in 2D by its cross-section, **the circle**.

p-orbitals

For the p_o (or p_z) orbital $Y_{1,0} = \sqrt{\dfrac{3}{4\pi}}\cos\theta$. This function will be maximum at θ = 0 and θ = π and vanishes at θ = π/2. On one side of the xy plane, it is +ve and on the other it is –ve. Such an orbital is said to be **anti-symmetric** with reference to reflection in the ‘xy’ plane.





For $p_{\pm 1}$ orbital, $Y_{1,\pm 1} \sim \sin\theta\, e^{\pm i\phi}$ except for a constant. For convenience a linear combination of these degenerate eigenfunctions, ($p_1 \pm p_{-1}$) are used to construct new orbitals designated as p_x and p_y ($p_x \sim r \sin\theta \cos\phi = x$ and

$p_y \sim r (\sin\theta \sin\phi = y)$. They have the same shape as p_z orbitals except that the maxima are along the x and y axes respectively.

d-orbitals

Similar procedures may be used for representing the **d-orbitals**.

The $d_o \sim (3\cos^2\theta - 1)$ orbitals are designated as $d_{2z^2-x^2-y^2} = d_{3z^2-r^2}$. This orbital has two large lobes along z axis and a small **"smoke-ring"** about the xy plane. Other four independent orthogonal orbitals are given by the linear combinations of $d_{\pm 2} \sim \sin^2\theta\, e^{\pm 2 i\phi}$ and $d_{\pm 1} \sim \sin\theta \cos\theta\, e^{\pm i\phi}$ orbitals. They are d_{xz}, d_{xy}, d_{yz} and $d_{x^2-y^2}$. Each of these orbitals has four equivalent lobes with two nodal planes separating them. The orbital $d_{x^2-y^2}$ differs from d_{xy} in that its lobes lie along the Cartesian axis x and y instead of making an angle of 45° with them.

Summary of lesson

The Schrodinger equation for rigid rotator with free axis has been formulated and solved. The resulting eigenvalues have been used to explain the rotational spectrum of diatomic molecules. Schrodinger equation of Plane rigid rotator has been solved. Schrodinger's analysis of the hydrogen atom has been presented. The degeneracy of the hydrogen energy levels has also been discussed.

Key terminology

Central force – Associated Legendre Polynomial – Spherical Harmonics – Plane Rigid Rotator – Rotational Spectrum – Hydrogen Atom – Associated Legendre Differential Equation – Asymptotic Solution – Degeneracy of Hydrogen Eigenvalues.

Self-assessment questions

(i) What is central potential? Write the Schrodinger equation for such a problem in spherical polar coordinates.

(ii) Explain rigid rotator model. Derive its eigenvalues and explain the rotational spectrum of a diatomic molecule.

(iii) Solve the Schrodinger equation of a rigid rotator with fixed axis.

(iv) Formulate the Schrodinger equation for hydrogen atom and separate the angular and radial parts.

(v) Solve the Schrodinger equation of H – atom and derive the eigenvalues.

(vi) Write the eigenvalues and eigenfunctions of hydrogen atom. Hence explain the degeneracy.

Reference books

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2. Advanced Quantum Mechanics – Rajput B S (Pragati Prakashan, Meerut).
3. Quantum Mechanics – Chatwal G R and Anand S K (Himalaya Pub. House, Bombay).

UNIT – 2

Lesson-VI - Time Independent Perturbation Theory

(For non-degenerate systems)

Objective of the lesson

In this section, the theory of time-independent perturbation is discussed. We consider the corresponding Schrodinger time -independent wave equation and obtain the expressions for 1st order and 2nd order energy and wave functions. The theory will be applied to some physical examples and evaluate the energy and wave function.

2.1.1Introduction

In the development of quantum mechanics, only very simple physical situations have been treated using schrodinger wave equation for which exact analytic solutions can be (found).In majority situations of physical interest, the exact solution of the schrodinger equation may have a quite complicated, rendering an analytic solution of the corresponding eigen value problem too difficult to obtain if not altogether impossible. In quantum mechanics, perturbation theory is an approximation scheme for describing such a complicated quantum system in terms of a simpler one. The main idea here is to start with a simple system and gradually turn on an additional perturbing Hamiltonian representing a weak disturbance to the system. As such Hamiltonian can be split into several terms, some of which may play by far the most significant role than others and such terms can be treated exactly to obtain analytic solution to the eigen value problem, and the effect of the rest of the terms can be estimated in an approximate way. Here are three important approximation methods, which are (i) perturbation method (ii) variation method (iii) the WKB method.

In order to develop the wave mechanical perturbation theory the basic idea is taken from the perturbation theory in classical mechanics, which is explained as follows. The motion of a planet in the solar system is essentially determined from the gravitational force of the sun. Of course the gravitational force of attraction of the other planets, though small still influences the motion of the planets in their orbits and as a result the orbit instead of being a closed ellipse is a slowly processing ellipse. The perturbation theory enables us to calculate these small changes. Similarly quantum mechanical systems can be treated with perturbation methods.

In the case of perturbation theory, these are two cases which can treated separately as (i) Time-dependent perturbation theory (ii) Time-independent perturbation theory. Further Time-independent perturbation theory is applied to degenerate and non-degenerate system separately.

The stationary perturbation theory concerns with finding the changes in energy levels and eigen functions of a system when a small disturbance is applied. In such cases, the Hamiltonian may be considered as spilt into two parts, one of them is a major part, which characterizes the system for which exact solution is obtained for the wave equation; while the second part is small and treated as perturbation.

2.1.2 Theory

Now, In this section we study the time-independent perturbation theory applied to a non-degenerate system. If one energy value or energy level is corresponding to only one wave function, then such a system is called as non-degenerate system.

We start with the schrodinger wave equation, which basically describes a single particle, for obtaining the energy values and eigen functions for the 1st order and 2nd order perturbations.

We begin with an unperturbed Hamiltonian $H^{(0)}$ which is also assumed to have no time dependence. It has known eigen functions arising from the time independent schrodinger equation which is written as.

$$H^{(o)}\psi_n^v = E_n^{(o)}\psi_{-n}^{-(o)} \text{ -- ------------(2.1.1)}$$

Where E_n^o is the energy of the nth level of the system and corresponding eigen function is $\psi_n^{(o)}$. This means eigen values and eigen /functions of the unperturbed problem is E_1^o,$E_2^{(1)}$,$E_3^{(0)}$…..$E_n^{(0)}$ and $\psi_1^{(0)}$, $\psi_2^{(0)}$, $\psi_3^{(0)}$…$\psi_m^{(0)}$ respectively.

For the perturbed system, the eigen function ψ_n satisfies the equation.

$H\Psi_n=E_n\Psi_n$ …………..(2.1.2)

Where E_n are the energy values of the modified Hamiltonian; representing the operator

$$\hat{H} = \left(\frac{-h^2}{2m} \nabla^2 + v \right) \text{……..(2.1.3)}$$

Let us assume that it is possible to expand H interms of some parameter, giving the expression.

$H=H^0 + \lambda H^{(1)}+ \lambda^2 H^{(2)}+$ ………….(2.1.4)

Where H^0 is the unperturbed Hamiltonian and is large compared with $H^{(1)}$ (i.e.) the energy associated with $H^{(0)}$ is large when compared with the energy associated with $H^{(1)}$.

Further it is also assumed that it is possible to expand eigen function ψ_n, and eigen value E_n of the total Hamiltonian of equation (2.1.2) in terms of λ as .

$E_n=E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+$---------------(2.1.5)

$\psi_n=\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+$ -----------(2.1.6)

in which the quantities $E_n^{(1)}$, $E_n^{(2)}$ …. and $\psi_n^{(1)}$, $\psi_n^{(2)}$ …is to be found.

Equations (2.1.4), (2.1.5) and (2.1.6) and now substituted in eq.(2.1.3), yielding.

$[H^{(0)}+\lambda H^{(1)}]\ [\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\text{-----}] = [E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}\text{----}]\ [\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\ldots\ldots]$

Which in turn gives

$H^{(0)}\psi_n^{(0)}+\lambda(H^0\psi_n^{(1)}+H^{(0)}\psi_n^{(0)}) + \lambda^2(H^{(0)}\psi_n^{(2)}+H^{(1)}\psi_n^{(1)})$ +--------

$=E_n^{(0)}\psi_n^{(0)}+\lambda(E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)})\lambda^2(E_n^{(1)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(1)}+E_n^{(2)}\psi_n^{(0)})+$------(2.1.7)

The above equation is satisfied for all powers of λ, only if the equal powers of λ on either side are equal. On comparing equal powers of λ^0,λ^1, λ^2. -----we get.

For λ^0, $H^0\psi_n^{(0)}=E_n^{(0)}\psi n0$ --(2.1.8)

For λ^1, $H^0\psi_n^{(1)}+H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)}+E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)}$ ---------…(2.1.9)

For λ^2, $H^{(0)}\psi_m^{(2)}+H^{(1)}\psi_m^{(1)} = E_m^{(1)}\psi_m^{(1)}+E_m^{(2)}\psi_m^{(0)}$ --------.-(2.1.10)

Equations(2.1.8),(2.1.9),(2.1.10) corresponds to unperturbed, first order perturbation and second order perturbation equation respectively, we can also obtain higher order terms to get more and more accurate corrections to exact solution. Using the equation (2.1.9) and (2.1.10) we calculate the 1st order and 2nd order energy values and eigen functions respectively.

First Order correction to the energy value $E_n^{(1)}$

Taking the eq.(2.1.9) we now obtain the first order corrections to the energy value $E_n^{(1)}$.

(i.e) $H^0\psi_n^{(1)}+H^{(1)}\psi_n^{(0)}=E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)}$ ------------(2.1.9).

Using the expansion theorem, the perturbed eigen function $\psi_n^{(1)}$ can be expanded interms of the unperturbed eigen function as

$$\psi_n^{(1)} = \sum_{n=0}^{\infty} \alpha_m \psi_m^{(0)} \quad \text{--------------(2.1.11)}$$

Substituting this equation (2.1.11) in eq.(2.1.9), we determine the first order correction, we have.

$$\sum_m \alpha_m H^0 \psi_m^{(0)} + H^{(1)}\psi_n^{(0)} = \sum_m \alpha_m E_n^{(0)} \psi_m^{(0)} + E_m^{(1)}\psi_n^{(0)} \quad \text{---------------(2.1.12)}$$

From the unperturbed system for mth level, we know

$$H^{(0)}\psi_n^{(0)} = E_m^{(0)}\psi_m^{(0)} \quad \text{-------------------(2.1.13)}$$

so that (2.1.12) now rewritten as.

$$\sum_m \alpha_m E_m^{(0)}\psi_m^{(0)} + H^1\psi_n^{(0)} - \sum_m \alpha_m E_n^{(0)}\psi_m^{(0)} = E_n^{(1)}\psi_n^{(0)}$$

(OR)

$$\sum_m \alpha_m \left(E_n^{(0)} - E_n^{(0)}\right)\psi_m^{(0)} + H^1\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \text{----------(2.1.14)}$$

On multiplying both sides with $\psi_n^{(0)^*}$ from left side and integrating over the space integral, we get

$$\int \sum_m \alpha_m \left(E_m^{(0)} - E_n^{(0)}\right)\psi_n^{(0)^*}\psi_m^{(0)} d\tau + \int \psi_n^{(0)^*} H^1 \psi_n^{(0)} d\tau = E_n^{(0)} \int \psi_n^{(0)^*}\psi_n^{(0)} d\tau \quad \text{--------(2.1.15)}$$

Making use of the orthonormal condition of the wave function

$$\left.\begin{aligned} &\text{(i.e.)} \quad \int \psi_n^{(0)^*} \psi_n^{(0)} d\tau = \delta_{ij} \\ &\text{where} \quad \delta_{ij} = 0 \text{ if } i \neq j \\ &\qquad\qquad = 1 \text{ if } i \neq j \end{aligned}\right\} \text{---------(2.1.16)}$$

The equation (2..1.15) below:

$$\int \psi_n^{(0)} H^{(1)} \psi_n^{(0)} d\tau = E_n^{(1)}$$

$$\text{OR} \quad E_n^{(1)} = \int \psi_n^{(0)^*} H^1 \psi_n^{(0)} d\tau = H_{nn}^{(1)} \quad \text{-----------(2.1.17)}$$

$$= \left\langle \psi_n^{(0)} \mid H^1 \mid \psi_n^{(0)} \right\rangle = H_{nn}^{(1)} \quad \text{-----------(2.1.17a)}$$

which is first order perturbation of the energy value.

First order correction for wave function $\psi_n^{(1)}$

For obtaining the first order wave function $\psi_n^{(1)}$, we once again consider the eq.(2.1.9) and multiplying on both sides with $\psi_m^{(0)*}$ from left side and then integrate over the space integral, we get the situation as

$$\int \sum_m \alpha_m \left[E_n^{(0)} - E_n^{(0)}\right] \psi_n^{(0)^*} \psi_m^{(0)} d\tau + \int \psi_m^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau$$

$$= \int E_n^{(1)} \psi_m^{(0)^*} \psi_n^{(0)} d\tau \quad \text{----------(2.1.18)}$$

Using the condition as per eq. (2.1.16), we have

$$\alpha_m \left[E_m^{(0)} - E_n^{(0)}\right] + \int \psi_m^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau = 0$$

$$\text{(i.e.)} \quad \alpha_m = \frac{-\int \psi_m^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau}{E_m^{(0)} - E_n^{(1)}}, m \neq n$$

$$= - \frac{\left\langle \psi_m^{(0)} \mid H^1 \mid \psi_n^{0} \right\rangle}{E_m^{(0)} - E_n^{(0)}} = \frac{H_{nm}^{(1)}}{E_m^{(0)} - E_n^{(0)}} \quad \text{------(2.1.19)}$$

so that $\psi_n^{(1)} = -\sum_{m=0}^{\theta 1} \left[\frac{\int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau}{E_m^{(0)} - E_m^{(0)}} \right] \psi_m^{(0)}$ -------(2.1.19a)

Now after the first order corrections to energy value and eigen function, we get.

$$E_n = E_n^{(0)} + \lambda E_n^{(1)}$$

$$= E_n^{(0)} + \lambda \int \psi_n^{(0)} H^{(1)} \psi_n^{(0)^*} d\tau = E_n^{(0)} + \lambda H_{nn}^{(1)} \quad \text{-----(2.1.20)}$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)}$$

$$= \psi_n^{(0)} - \lambda \sum_{m=0}^{\alpha 1} \left[\frac{\int \psi_n^{(0)} H^{(1)} \psi_n^{(0)} d\tau}{E_n^{(0)} - E_n^{(0)}} \right] \psi_n^{(0)}$$

(Σ^1 is written omitting m=n)

$$= \psi_n^{(0)} - \lambda \sum_{m=0}^{\alpha_1} \left(\frac{H_{nn}^{(1)}}{E_m^0 - E_n^0} \right) \psi_m^{(0)} \quad \text{------------------(2.1.21)}$$

Second order correction for energy value $E_n^{(2)}$

We consider the eq. (2.1.10) for evaluation a^2 $En^{(2)}$. Again the function $\psi_n^{(2)}$ is expressed as a linear combination of known function $\psi_m^{(0)}$, as

$$\psi_n^{(2)} = \sum_m \beta_m \psi_m^{(0)} \quad \text{----------------------(2.1.22)}$$

On substituting eqs. (2.1.22) and (2.1.11) in eq.(2.1.10), we get

$$\sum_m \beta_m H^{(0)} \psi_m^{(0)} + \sum_m \alpha_m H^{(1)} \psi_m^{(0)} = \sum_m \beta_m E_m^{(0)} \psi_m^{(0)} + \sum_m \beta_m E_n^{(1)} \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)} \quad \text{---------(2.1.23)}$$

on using eq.(2.1.13), we have

$$\sum_m \beta_m \left(E_m^{(0)} - E_n^{(0)} \right) \psi_m^{(0)} = \sum_m \alpha_m E_n^{(1)} \psi_m^{(0)} - \sum_m \alpha_m H^{(1)} \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$$

$$= \sum_m \alpha_m \left(E_n^{(1)} - H^{(1)} \right) \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)} \quad \text{--------(2.1.24)}$$

Now multiplying both sides of eq. (2.1.24) with $\psi_n^{(0)*}$ from left side, and integrating over the space integrals, we get.

$$\int \sum \beta_m \left(E_n^{(0)} - E_n^{(0)} \right) \psi_n^{(0)^*} \psi_m^{(0)} d\tau = \int \sum_m \alpha_m \psi_m^{(0)^*} \left(E_n^{(1)} - H^{(1)} \right) \psi_m^{(0)} d\tau + E_n^{(2)} \int \psi_n^{(0)^*} \psi_n^{(0)} d\tau \text{ -------(2.1.25)}$$

Applying condition (1.1.16) to eq. (2.1.25) we get.

$$E_m^{(2)} = \sum_m \alpha_m \int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau$$

$$= \sum_m \alpha_m \left\langle \psi_n^{(0)} \mid H^{(1)} \mid \psi_n^{(0)} \right\rangle = \sum_m (\alpha_m H_{nn}^{(1)} \text{ -------------(2.1.26)}$$

Substituting the value of α_m from eq. (2.1.19), we have

$$E_n^{(2)} = -\sum_m^{1} \frac{\int \psi_m^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau . \int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau}{E_n^{(0)} - E_n^{(0)}}$$

or $$E_n^{(2)} = -\sum_m^{1} \frac{H_{nn}^{(1)} . H_n^{(1)}}{E_n^{(0)} - E_n^{(0)}} \text{ ----------------(2.1.27)}$$

Second order correction to eigen function $\psi_n^{(2)}$

For obtaining $\underline{\psi_n}^{(2)}$, multiply eq.(2.1.24) with $\psi_n^{(0)*}$ on both sides from left; and integrating over the space integral, we get.

$$\sum_m \beta_m \int \left(E_m^{(0)} - E_n^{(0)} \right) \psi_m^{(0)^*} \psi_m^{(0)} d\tau$$

$$= \quad \alpha_m \sum_m \int \psi_m^{(0)^*} \left(E_n^{(1)} - H_n^1 \right) \int \psi_m^{(0)} d\tau + E_n^{(2)} \int \psi_m^{(0)^*} \psi_n^{(0)} d\tau. \text{ ---------(2.1.28)}$$

on using condition (2.1.16) again here also, the above equation is reduced to .

$$\beta_m \left[E_m^{(0)} - E_n^{(0)} \right] = \sum_m \alpha_m \left[E_n^{(1)} - \int \psi_m^{(0)^*} \psi_m^{(0)} d\tau \right]$$

or $$\beta_m = \sum_m \frac{\alpha_m}{E_m^{(0)} - E_n^{(0)}} \left[E_n^{(1)} - \int \psi_m^{(0)^*} H^{(1)} \psi_m^{(0)} d\tau \right] \text{---------(2.1.29)}$$

and $$\psi_n^{(2)} = -\sum_m \frac{\int \psi_m^{(0)} H^{(1)} \psi_n^{(0)}}{E_m^{(0)} - E_n^{(0)}} \left[\frac{E_n^{(1)} - \int \psi_m^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau}{E_m^{(0)} - E_n^{(0)}} \right] \psi_n^{(0)} \text{--------(2.1.30)}$$

(Σ^1 is used to omit m=n)

In order to get the energy values and eigen functions, the values of $E_n^{(1)}$, $E_n^{(2)}$ and $\psi_n^{(1)}$,$\psi_n^{(2)}$ are substituted from the equation (2.1.17), (2.1.27) and (2.1.19a), (2.1.30) in the following equation.

$$E_n^{(0)} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} \lambda^2 \psi_n^{(2)}$$

Using the above theoretical considerations, the corresponding 1st order and 2nd corrections to the perturbed system can be calculated.

Proceeding in the above manner, we can evaluate higher order corrections for the perturbed systems to more and more accuracy.

2.1.3 Application of the time dependent perturbation on theory for Non-degenerate system

In this we take up the following examples and evaluate the perturbed energy and eigen function.

(i) The perturbed Harmonic oscillator.

(ii) The Normal Helium atom.

i The Perturbed Harmonic Oscillator

Let us consider the wave equation for the perturbed Harmonic oscillator in one dimensions as.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{x^2}\left[E - \frac{1}{2}\frac{k\lambda^2}{x^2} - \frac{a\lambda^3}{v} - \frac{b\lambda^4}{v} \right]\psi = 0 \qquad \text{-------------(2.1.31)}$$

This equation reduces to Harmonic oscillator wave equation if the constants a and b are zero. Assuming a and b are small, we treat these terms as perturbation.

(i.e.) $H^{(1)} = ax^3 + bx^4$ …………(2.1.32)

Let us calculate the first order correction to the energy $En^{(1)}$ given by eq.(2.1.17)

(i.e.). $E_n^{(1)} = \int_{\alpha} \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau$

$$\int_{-\alpha}^{\alpha} \psi_n^{(0)^*} ax_3 \psi_m^0 d\tau + \int_{-\alpha}^{\alpha} \psi_n^0 bx^4 \psi_n^{(0)} d\tau \text{ -----(2.1.33)}$$

Since the first integral on the right side is an odd function as x^3 is odd and $\psi_n^{(0)^*}\psi_n^{(0)}$ is even function, over a symmetrical limits whose value is zero. As such the value of the first integral is zero (i.e.) first order perturbation due to ax^3 is zero.

Hence $E_n^{(1)} = b\int_{-\alpha}^{\alpha} \psi_n^{(0)^*} x^4 \psi_n^{(0)} d\lambda$ ………(2.1.34)

From the knowledge of the linear Harmonic oscillator, whose wave function is given by .

$$\psi_n^{(0)^*}(x) = N_n H_n(\xi)\exp\left[-\xi^2/2\right] \text{ ……..(.2.1.35)}$$

Where . $\xi = \alpha x \,\&\, \alpha = \left(\frac{mk}{x^2}\right)^{1/4} andh^2 = m\omega^2$

Substituting (2.2.5) in eq. (2.2.4) we get.

$$E_n^{(1)} = b.\int_{-\alpha}^{\alpha} N_n^2 H_n^2(\xi) e^{-\xi^2}.\left(\frac{\xi^4}{\alpha^4}\right)\left(.\frac{d\xi}{\alpha}\right)$$

$$= b.\frac{N_n^2}{\alpha^5}\int_{\alpha}^{p} H_n^2(\xi)\, e^{-\xi^2} .\xi^4.d\xi \text{ …….(2.1.36)}$$

For evaluating this integral, consider the following recurrence relations from Hermite polynomials.

$$\xi H_n(\xi) = \frac{1}{2}H_n + 1(\xi) + nH_n - 1(\xi) \text{ ………………(2.1.37)}$$

or $\xi^2 H_n(\xi) = \frac{1}{2}\xi H_n(+1(\xi) + n\xi H_n - 1(\xi)$ ………….(2.1.38)

Replaying n=n+1 and n=n-1 in eq.(2.1.38), we have

$$\xi H_n + 1(\xi) = \frac{1}{2} H_n + 2(\xi) + (n+1) H_n(\xi) \quad \text{…………..(2.1.39)}$$

$$\xi H_n - 1(\xi) = \frac{1}{2}\xi H_n - 1(\xi) + (n-1)\xi H_n - 2(\xi) \text{ ………(2.1.40)}$$

Now Substituting eqs. (2.1.39) and (.2.1.40) in eq. (2.1.38), we get.

$$\xi^2 H_n(\xi) = \frac{1}{2} H_{n+2}(\xi) + (n+\frac{1}{2}) H_n(\xi) + n(n-1) H_{n-2}(\xi) \text{ ……2.1.41.}$$

Squaring and substituting in eq. (2.1.36), we have

$$E_n^{(1)} = b.\frac{N_n^2}{\alpha^5}\int_{\alpha^5}^{\alpha} e^{-\xi^2}\left[\frac{1}{4}H_{n+2}(\xi) + (n+\frac{1}{2}) + n(n-1)H_{n-2}(\xi)\right]^2 d\xi \quad \text{……(2.1.42)}$$

From Hermite polynomials, we know that

$$\int_{-\alpha}^{\alpha} e^{-\xi^2} H_n(\xi) H_m(\xi) d\xi = 0 \text{ if m≠m}$$

$$= 2^\wedge n!\sqrt{\pi} \quad \text{if m=n……..….(2.1.42)}$$

Using those result in eq.(2.1.42), it becomes

$$E_n^{(1)} = b.\frac{N_n^2}{\alpha^5}\sqrt{\pi\left\{\frac{1}{16}\right.}\left(n+2)!2^{n+2} + (n+\frac{1}{2})^2 n!2^n (n-1)^2 2^{n-2}(n-2)!\right)$$

$$=\left[\frac{\alpha}{\Pi^{\frac{1}{2}}\, 2^n n!}\right]\frac{1}{\alpha^5}\sqrt{\pi\left\{\frac{1}{16}\right.}(n+2)\,{}^{n+2}2 + (n+\frac{1}{2})(n!)2^n + n^2(n-1)^2 2^{n-2}(n-2)\,|\}$$

Where we used the normalized function of Harmonic oscillator.

N_n value as $N_n = \left[\dfrac{\alpha}{\pi^{\frac{1}{2}} 2^n n!} \right]$

On simplification, we get

$$E_n^{(1)} = b.\frac{3}{4\alpha^4}(2n^2 + 2n + 1)$$

Now the total energy to first order becomes.

$$E_n = E_n^{(0)} + E_n^{(1)} = (n + \frac{1}{2})\hbar\omega_c + \frac{3b}{4}\frac{\lambda^2\hbar^2}{mK}(2n^2 + 2n + 1)$$

ii The Normal Helium atom:

Helium atom consists of a nucleus of charge Ze at the origin and two electrons with radius vectors r_1 and r_2 as shown in Fig. (2.1.1)

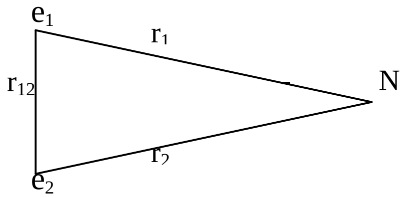

Fig. 2.1.1

Neglecting the motion of the nucleus, the Hamiltonian of the system is written as.

$$H = \left[-\frac{\lambda *^2 \nabla_1^2}{2m}\nabla_1^2 - \frac{ze^2}{r_1} \right] + \left[\frac{-\lambda *^2}{2m}\nabla_2^2 - \frac{ze^2}{r_2} \right] + \frac{e^2}{r_{12}} \text{ ....(2.1.43)}$$

in which ∇_1 and ∇_2 represent the coordinates of electrons 1 and 2 respectively.

Now, the wave equation for the two electrons is written as

$$\nabla_1^2\psi + \nabla_2^2\psi + \frac{2m}{\hbar^2}\left[E + \frac{ze^2}{r_1} + \frac{ze^2}{r_2} - \frac{e^2}{r_{12}} \right]\psi = 0 \quad \text{.....(2.1.44)}$$

The term $\dfrac{e^2}{r_{12}}$ is considered as the perturbed term, since omitting this term, the above equation can be exactly solved. Hence, the perturbed Hamiltonian is written as.

$$H^{(1)} = \frac{e^2}{r_{12}} \text{ ....(2.1.45)}$$

Separately writing the unperturbed wave equation into two equation by substituting.

$$\psi^0(x_1y_1z_1, x_2y_2z_2) = \upsilon_1^0(x_1y_1z_1)u_2^0(x_2y_2z_2) \text{ ....(2.1.46)}$$

In polar coordinates r_1, θ_1,ϕ_1, and r_2,θ_2, ϕ_2 to the normal state, the wave function is:

$$\psi^{(0)}_{100,100} = \psi^0_{100}(r_1\theta_1\phi_1)\psi^{(0)}_{100}(r_2\theta_2\phi_2) \text{ ......(2.1..47)}$$

$$= u_1^0(r_1\theta_1\phi_1)u_2^{(0)}(r_2\theta_2\phi_2)$$

and the corresponding energy value is:

$$E^{(0)}_{100,100} = E_1^{(0)} + E_2^{(0)} = -2Z^2E_{++} \quad \text{.....(2.1. 48)}$$

Where E_H is the energy corresponding to one electron = $\frac{me^4}{2\hbar^2} = 13.6eu$

The first order perturbed energy function $E^{(1)}$ is the average value of the perturbation function $H^{(1)}$ over the unperturbed state of the system. Hence, First order correction to the ground state energy is

$$E^{(1)} = \int \psi_n^{(0)^*} H^{(1)} \psi_n^{(0)} d\tau = \int \frac{e^2}{r_{12}} \left[\psi^{(0)}_{100,100}\right]^2 d\tau \text{ ....(2.1.49)}$$

$$= \int\int u_1^{(0)^*} u_2^{(0)^*} \frac{e^2}{r_{12}} u_1^{(0)} u_2^{(0)} d\tau_1 d\tau_2$$

We know that

$$u_1^{(0)} = \psi^{(0)}_{100} = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-(p/2)} \text{ ....(2.1.50)}$$

in which $\rho_1 = \frac{2Zr_1}{a_0}$ and radius $r_0 = \frac{\hbar^2}{4\pi^2 me^2}$

so that $\psi^{(0)}_{100,100} = \frac{Z^3}{\pi a_0^3} e^{-a_1/2} p^{-p_2/2}$ ......(2.1.51) and space integral dτ is

$$d\tau = d\tau_1 d\tau_2 = r_1^2 dr_1 Sin\theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 Sin\theta_2 d\theta_2 d\phi_2$$

on substituting (2.1.51) in energy equation (2.1.50), we get

$$E^{(1)} = \frac{Z^6 e^2}{\pi^2 a_0^6} \int\int \frac{1}{r_{12}} \exp\left[-\frac{2Z}{a_0}(r_1 + r_2)\right] d\tau_1 d\tau_2 \ldots\ldots(2.1.52)$$

Evaluation of the integral in eq.(2.1.52.) may be done by expanding $\frac{1}{r_{12}}$ in terms of legendre polynomials and hence the value of the integral leads to a value of $\frac{5ZE_H}{4}$ for the first order correction to the ground state.

The energy corrected to first order is then given by :

$$E = -2Z^2 E_H + \frac{5}{4} Z.E_H = -\left[2Z^2 - \frac{5}{4}Z\right] E_H$$

It may be noted that $E^{(1)}$ is about 31% of $E^{(0)}$, since

$$\frac{E^{(1)}}{E_0} = \frac{5ZE_{H/4}}{2Z^2 E_H} = \frac{5}{8Z}$$

The correction is subtractive which is understandable since the effect of the electron-electron contraction is to reduce the electron nucleus attraction. Then the result holds good for two electron atoms like Li^+, B_e^{++}, B^{3+} etc., ….with Z= 3,4,5 …….

Summary of the Lesson

Perturbation theory is an extremely important tool for describing real quantum systems, as it turns out to be very difficult to find exact solutions to the Schrodinger equation for Hamiltonians of even moderate complexity, most of the Hamiltonians to which we know exact solutions, such as the hydrogen atom, the quantum harmonic oscillator and the particle in a box, are too idealized to adequately describe most systems. Using perturbation theory, we can use the known solutions of these simple Hamiltonians to generate solutions for a wide range of more complicated systems.

Self-assessment questions

1) Calculate the second order energy for the above example.

2) The unperturbed wave function of a particle trapped on an infinite potential well of bottom a $\psi_n^{(0)} = (\frac{2}{a})^{1/2}.Sin\frac{a\pi x}{a}$

If the system is perturbed by raising the floor of the well by a constant amount V_0, calculate first order and second order corrections to the energy of the nth state.

3) Calculate the first order and second order energy correction in the case of the plane rotator under the influence of the electric field E^1, described by the wave equation .

$$\frac{d^2\psi}{d\phi^2} + \frac{2I}{\hbar^2}\left(E + \mu E^1 \cos\phi\right)\psi = 0$$

Where I is the moment of inertia and μ, the electric moment.

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UNIT – 2

LESSON -VII The time Independent perturbation theory – Degenerate case

Objective of the Lesson

In the discussion of perturbation theory for non-degenerate states of a system, we assumed that a given eigen value is associated with a single eigen function representing a single state of the systems. If a given eigen value is associated with several functions, which represent a multiplicity of state of equal (same) energy, then we say that this eigen state is degenerate.

2.2.1Theory

An energy level is called α-fold degenerate when these exist α linearly independent wave functions such as ψ_{k1}, ψ_{k2}……$\psi_{k\alpha}$ satisfying the wave equation.

Clearly, we can explain this if we have α eigen function $\psi_{k1}^{(0)}, \psi_{k2}^{(0)}\psi_{k3}^{(0)}........\psi_{k\alpha}^{(0)}$ corresponding to the eigen state $E_k^{(0)}$. Such that there is no relation of the form.

$$C_1\psi_{k1}^{(0)} + C_2\psi_{k2}^{(0)} - 1 - - - - - - + C_\alpha\psi_{k\alpha}^{(0)} = 0 \text{ ……(2.2.1)}$$

connecting them, then we say that the α eigen functions are linearly independent and this eigen state $E_k^{(0)}$ is α fold degenerate.

We have shown earlier that eigen functions belonging to different eigen values are orthogonal, however eigen functions belonging to the same eigen value need not be orthogonal.

Let, in the perturbed state, the Schrodinger wave equation be given by

$$H\psi = E\psi \text{ ……… ….(2.2.2)}$$

Where H is the perturbed Hamiltonian, E the perturbed energy and ψ the perturbed wave function.

Now, the perturbed Hamiltonian can be expressed interms of unperturbed Hamiltonian $H^{(0)}$ as.

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^2 \ \ldots\ldots\ldots\ldots\ldots(2.2.3)$$

Let us assume $\psi_{k1}^{(0)}, \psi_{k2}^{(0)} \ldots\ldots \psi_{k\alpha}^{(0)}$ are not orthogonal. We have,

$$H^0 \psi_{k1}^{(0)} = E_k^{(0)} \psi_{k1}^{(0)},\ H^0 \psi_{k2}^{(0)} = E_k^{(0)} \psi_{k2}^{(0)} \ldots\ldots H^0 \psi_{k\alpha}^{(0)} = E_k^{(0)} \psi_{k\alpha}^{(0)}$$

Consider the linear combination X_k^0

$$C_1 \psi_{k1}^{(0)} + C_2 \psi_{k2}^{(0)} \ldots\ldots\ldots C_\alpha \psi_{k\alpha}^{(0)} = X_k^{(0)} \ldots\ldots \ \ldots\ldots\ldots(2.\ 2.4)$$

so that we have

$$H^0 X_k^{(0)} = C_1 E_k^{(0)} \psi_{k1}^{(0)} + C^2 E_k^{(0)} \psi_{k2}^{(0)} + \ldots\ldots + C_\alpha E_{k2}^{(0)} \psi_{k\alpha}^{(0)} \ldots\ldots \qquad (2.2.5)$$

$$= E_k^0 X_k^0$$

which proves that the linear combination X_k^0 is also an eigen function corresponding to the same degenerate energy value.

We can choose the constants in eq.(2.2.4) in an infinite number of ways, we can construct infinite number of such linear combinations, all of them being eigen function of the same eigen value. There is nothing unique about any set of eigen functions for a degenerate level.

For instance, we can select the following α linear combination:

$$\left.\begin{aligned} X_{k1}^{(0)} &= C_{11} \psi_{k1}^{(0)} + C_{12} \psi_{k2}^{(0)} + \ldots\ldots\ldots + C_{1\alpha} \psi_{k\alpha}^{(0)} \\ X_{k2}^{(0)} &= C_{21} \psi_{k1}^{(0)} + C_{22} \psi_{k2}^{(0)} + \ldots\ldots\ldots + C_{2\alpha} \psi_{k\alpha}^{(0)} \\ X_{k\alpha}^{(0)} &= C_{\alpha 1} \psi_{k1}^{(0)} + C_{\alpha 2} \psi_{k2}^{(0)} + \ldots\ldots\ldots + C_{\alpha\alpha} \psi_{k\alpha}^{(0)} \end{aligned}\right\} \quad \ldots\ldots..2.2.6.$$

which may be represented as :

$$X_{kl}^{(0)} = \sum_{l=1}^{\alpha} C_{ll^1} \psi_{kl^1}^{(0)} \quad (l=1,2,3,\ldots\ldots\alpha)\ \ldots\ldots..2.2.7.$$

These combinations are entirely equivalent to the original set $\psi_{k1}^{(0)}, \psi_{k2}^{(0)} ...... \psi_{k\alpha}^{(0)}$. The transformation expressed by eq. (2.2.7) is known as linear transformation with constant coefficients. With this background about degenerate states, we now discuss the perturbation for such states.

The wave equation for unperturbed system is:

$$H^{0}\psi^{(0)} = E^{(0)}\psi^{(0)} \quad \text{……………………2.2.8.}$$

There are severed eigen states for this unperturbed system, each of them corresponding to several degenerate eigen function as

Energy value	eigen functions.
$E_0^{(0)}$	$\psi_{01}^{(0)}, \psi_{02}^{(0)}, \psi_{03}^{(0)} .... \psi_{0\alpha}^{(0)}$
$E_1^{(0)}$	$\psi_{01}^{(0)}, \psi_{12}^{(0)}, ... \psi_{0\alpha}^{(0)}$
$E_k^{(0)}$	$\psi_{k1}^{(0)}, \psi_{k2}^{(0)}, ... \psi_{0\alpha}^{(0)}$

We can assume the linear combination of eq.(2.2.7), provided the function ψ_{kl} is:

$$\psi_{kl} = \psi_{kl} + \lambda\psi_{kl}^{(1)} + \lambda^{2}\psi_{kl}^{(2)} \quad \text{…………. (2.2.9)}$$

and $$E_{kl} = E_{k}^{(0)} + \lambda E_{kl}^{(1)} + \lambda^{2} E_{kl}^{(2)} \quad \text{…………….(2.2.10)}$$

Now substitute the values of H, ψ_{kl}, E_{kl} from equation (2.2.3), (2.2.9) and (2.2.10) the perturbed equation given by

$$H\psi_{kl} - E_{kl}\psi_{kl} = 0 \quad \text{………………(2.2.11)}$$

We have

$$\left(H^{0} + \lambda H^{(1)} + \lambda^{2} H^{(2)} + ...\right)\left(X_{kl}^{(0)} + \lambda\psi_{kl}^{(1)} + \lambda^{2}\psi_{kl}^{(2)} + ...\right)$$

$$- \left(E_{k}^{0} + \lambda E_{kl}^{(1)} + \lambda^{2} E_{kl}^{(2)} + ...\right)\left(X_{kl}^{(0)} + \lambda\psi_{kl}^{(1)} + \lambda^{2}\psi_{kl}^{(2)} + ...\right) = 0$$

Rewriting the above.

$$\left(H^{0} X_{kl}^{(0)} - E_{k}^{(0)} X_{kl}^{(0)}\right) + \lambda\left(H^{0}\psi_{kl}^{(1)} + H^{(1)}\psi_{kl}^{(0)} - E_{k}^{0}\psi_{kl}^{(1)} - E_{kl}^{(1)} X_{kl}^{(0)}\right) + ... = 0 \quad \text{…….(2.2.12)}$$

We now take up the first order perturbation equation, which can be obtained by equating coefficient of λ equal to zero.

(i.e.) $H^{0}\psi_{kl}^{(1)} + H^{1}\psi_{kl}^{(0)} - E_{k}^{(0)}\psi_{kl}^{(0)} - E_{kl}^{(1)}X_{kl}^{(0)} = 0$ ……………..(2.2.13)

Let us expand $\psi_{kl}^{(1)}$ as.

$$\psi_{kl}^{(1)} = \sum_{k^1 l^1} C_{klk^1l^1}\psi_{k^1l^1}^{(0)} \quad \text{………………….(.2.2.14.)}$$

On substituting equation (2.2.14) and 2.2.7 in equation (2.2.13)

We get

$$\sum C_{klk^1l^1} H^{(0)}\psi_{k^1l^1}^{(0)} + \sum_{l=1}^{\alpha} C_{kl} H^{(1)}\psi_{kl^1}^{(0)} - \sum_{k^1l^1} C_{klk^1l^1} E_{k}^{(0)}\psi_{k^1l^1}^{(0)} - \sum_{l'=1}^{\alpha} .C_{ll^1} E_{kl}^{(1)}\psi_{kl^1}^{(0)} = 0$$

Since $H^{(0)}\psi_{k^1l^1}^{(0)} = E_{k^1}^{(0)}\psi_{k^1l^1}^{(0)}$ we have after recommendation.

$$\sum_{k^1l^1} C_{klk^1l^1}\left(E_{k^1}^{(0)} - E_{k}^{(0)}\right)\psi_{k^1l^1}^{(0)} = \sum_{l^1=1}^{\alpha} C_{ll^1}\left(E_{kl}^{(1)} - H^{(1)}\right)\psi_{k^1l^1}^{(1)} \quad \text{…………(2.2.15)}$$

Multiplying both sides with $\psi_{kj}^{(0)^*}$ from left, and integrating over configuration space

$$\sum_{k^1l^1} C_{klk^1l^1}\left(E_{k^1}^{(0)} - E_{k}^{0}\right)\int\psi_{kjl}^{(0)^*}\psi_{k^1l^1}^{(0)}d\tau$$

$$= \sum_{l'=1}^{\alpha} C_{ll^1}\left[E_{kl}^{(1)}\int\psi_{kj}^{(0)^*}\psi_{kl^1}^{(1)}d\tau - \int\psi_{kj}^{(0)^*}H^{(1)}\psi_{kl^1}^{(1)}d\tau\right] \quad \text{…………..(2.2.16)}$$

when k¹≠k, $\int\psi_{kj}^{(0)}\psi_{k^1l^1}^{(0)}d\tau = 0$ and when k=k¹, $E_{k'}^{(0)} - E_{k'}^{(0)} = 0$ L.H.S. reduces to zero.

So that eq.2.2.17.

We use the notation

$$H_{\alpha l'}^{(1)} = \int\psi_{kl}^{(0)}H^{(1)}\psi_{kl}^{(1)}d\tau \quad \text{…………..(2.2.18)}$$

and since $\psi_{kl}^{(0)}, \psi_{k2}^{(0)} ......\psi_{k\alpha}^{(0)}$ are non-orthogonal.

we introduce the symbol $\Delta_{jl^1} = \int\psi_{kj}^{(0)}\psi_{kl^1}^{(0)}d\tau$ ……….(2.2.19)

Using the above symbols, eq. 2.2.17 becomes

$$\sum_{l'=1}^{\alpha} C_{ll^1}(E_{kl}^{1}\Delta_{jl^1} - H_{jl^1}^{(1)}) = 0$$

or $$\sum_{l'=1}^{\alpha} C_{ll^1}(H_{jl^1}^{(1)} - E_{kl}^{(1)}\Delta_{jl^1}) = 0 \ldots\ldots\ldots\ldots(2.2.20)$$

As there are α eigen functions $\psi_{k1}^{(1)}, \psi_{k2}^{(0)}, \ldots\ldots \psi_{k\alpha}^{(0)}$ we can similarly get α equations like eq.(2.2.20) for j=0,1,2,3…..α Eq.(2.2.20) represents a system of α homogeneous linear simultaneous equation in α unknown quantities

In the expanded from, these α equations are.

$$(H_{11}^{1} - E_{kl}^{(1)}\Delta_{11})C_{11} + (H_{12}^{(1)} - E_{kl}^{(1)}\Delta_{12})C_{12} + \ldots\ldots + (H_{1\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{1\alpha})C_{1\alpha} = 0$$

$$(H_{21}^{1} - E_{kl}^{(1)}\Delta 21)C_{21} + (H_{22}^{(1)} - E_{kl}^{(1)}\Delta 22)C 22 + \ldots\ldots + (H_{2\alpha}^{(1)} - E_{1l}^{(1)}\Delta_{2\alpha})C_{2\alpha} = 0 \quad \ldots\ldots.(2.2.21)$$

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$$(H_{\alpha 1}^{1} - E_{kl}^{(1)}\Delta_{\alpha 1})C_{\alpha 1} + (H_{\alpha 2}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha 2})C_{\alpha 2} + \ldots\ldots + (H_{\alpha\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha\alpha})C_{\alpha\alpha} = 0$$

To understand how this set of equations is solved, a knowledge of determinations and their use in solving such equations is necessary, if such a set of homogeneous linear equations is to have non-zero solutions is that the determinant of the coefficients of the unknown quantities vanish.

(i.e)
$$\begin{vmatrix} H_{11}^{(1)} - E_{kl}^{(1)}\Delta_{11} & H_{12}^{(1)} - E_{kl}^{(1)}\Delta_{12} \ldots\ldots\ldots\ldots H_{\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{1\alpha} \\ H_{21}^{(1)} - E_{kl}^{(1)}\Delta_{12} & H_{22}^{(1)} - E_{kl}^{(1)}\Delta_{22} \ldots\ldots\ldots\ldots H_{2\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{2\alpha} \\ - & \text{- -} \\ - & \text{- - - - - - - - - - - - - - - - - - - -} \\ - & \text{- -} \\ & \\ H_{\alpha 1}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha 1} & H_{\alpha 2}^{(1)} - E_{kl}^{(1)}\Delta_{2\alpha} \ldots\ldots\ldots H_{\alpha\alpha}^{(1)} - E_{kl}^{(1)}\Delta_{\alpha\alpha} \end{vmatrix} = 0 \quad (2.2.22)$$

Using the condition $\Delta_{jl}^{1}=0$ if $j\neq l^{1}$

$= 1$ if $j=\Delta_{jl}^{'}$.

We have

$$\begin{vmatrix} (H_{11}^{1}-E_{kl}^{(1)}) & H_{12}^{(1)}.............H_{1\alpha}^{(1)} \\ H_{21}^{(1)} \quad (H_{22}^{(1)}-E_{kl}^{(1)}) & ....\,H_{2\alpha}^{(1)} \\ \text{- -} & \\ \text{- -} & \\ H_{\alpha 1}^{(1)} \quad H_{2\alpha}^{(1)} & ....\,H_{\alpha\alpha}^{(1)}-E_{kl}^{(1)} \end{vmatrix} = 0 \quad \text{………(2.2.23)}$$

equation (2.2.22) and (2.2.23) are known as secular equation.

If the secular equation is in diagonal form that is all the elements except on the principal diagonal are zero, then the initially assumed eigen functions $\psi_{k1}^{(0)},\psi_{k2}^{(0)},.......\psi_{k\alpha}^{(0)}$ are themselves the correct zeroth order wave functions.

The secular equation in which all the elements on the principal diagonal is in the form.

$$\begin{vmatrix} H_{11}^{(1)}-E_{kl}^{(1)} & 0 & 0 & \text{……………..}0 \\ 0 & H_{22}^{(1)}-E_{kl}^{(2)} & 0 & \text{--- --------}\ 0 \\ \text{- - - - - - - - - - - - - -} & \text{- - - - - - - - - - - - - -} & & \\ \text{- - - - - - - - - - - - - -} & \text{- - - - - - - - - - - - - - -} & & \\ 0 & 0 & 0\text{- - - - - - -} & H_{\alpha\alpha}^{(1)}-E_{kl}^{(1)} \end{vmatrix} = 0 \quad \text{…….(2.2.24)}$$

then its expansion is

$$(H_{11}^{(1)}-E_{kl}^{(1)})(H_{22}^{(1)}-E_{kl}^{(1)})--------(H_{\alpha\alpha}^{(1)}-E_{kl}^{(1)}) = 0$$

The roots of the equation are:

$$E_{kl}^{(1)} = H_{11}^{(1)}, H_{22}^{(1)}, ------ H_{\alpha\alpha}^{(1)}$$

In such a case, all the coefficients C_{l1}, C_{l2}……..$C_{l\alpha}$ turn out to the zero.

Equation (2.2.23) may be written in another useful from by making use of the substitution .

$$H_{ij} = H_{ij}^{(0)} + \lambda H_{ij}^{(1)} \quad \text{or} \quad H_{ij}^{(1)} = \frac{H_{ij} - H_{ij}^{(0)}}{\lambda}$$

$$\text{and} \quad E_{kl} - E_{k}^{(0)} + \lambda E_{kl}^{(1)} \quad \text{or} \quad E_{kl}^{(1)} = \frac{E_{kl} - E_{k}^{0}}{\lambda}$$

After taking αt 1/λ and using.

$H_{jl}^{(0)}$ =0 if j≠l

= $E_{k}^{(0)}$ if j=l.

With the above eq.(2.2.23) becomes

$$\begin{vmatrix} H_{11}-E_{kl} & H_{12} & \text{---------------------} & H_{1\alpha} \\ H_{21} & H_{22}-E_{kl} & \text{------------------} & H_{2\alpha} \\ \text{----------} & \text{----------} & \text{----------} & \text{----------} \\ \text{----------} & \text{----------} & \text{----------} & \text{----------} \\ H_{\alpha 1} & H_{\alpha 2} & \text{-----------------} & H_{\alpha\alpha}-E_{kl} \end{vmatrix} = 0 \qquad \text{…..(2.2.25)}$$

Observing the equations (2.2.22) and (2.2.23), we note that if a perturbation has non-vanishing matrix elements H_{ij} among a set of degenerate states, then it will change the wave function in the zeroth order. If the set of wave functions is non-degenerate on the other hand. The perturbation effect the wave functions only in the first and second orders.

2.2.2 Stark effect of Hydrogen atom

When an atom is placed in a uniform electric field, the energy levels are shifted. The shifting of energy levels produce a splitting of spectral line, called stark effect which was first observed in 1913 by stark in hydrogen atom.

Let us consider the first order change in energy levels of a hydrogen atom due to an external electric field of strength, E, along the positive Z-axis which is polar axis whose coordinates are Z= rCosθ.

For the hydrogen atom, the unperturbed Hamiltonian is given as

$$H^{(0)} = \frac{-\lambda^2}{2\mu}\nabla^2 - \frac{e^2}{r} \qquad \text{………………(2.2.26)}$$

Where μ is the reduced mass.

Now considering the perturbation $H^{(1)}$ is taken as

$$H^{(1)} = +eEz = +eErCos\theta \qquad \text{…………(2.2.27)}$$

in which e is electric charge and the external electric field E.

In case of hydrogen atom, potential energy and wave function are spherically symmetric. Now, the parity of the spherical harmonics depends on the azimuthal quantum number $\frac{1}{l}$ as $(-1)^l$, which gives odd parity, if $\frac{1}{l}$ is odd and even parity when l is even. Further, even if parities were different, matrix elements connecting states with different m values also vanish, making the interaction impotent to split m-degeneracy.

For the ground state of the hydrogen atom(n=1,l=0,m=0), the wave function is spherically symmetric and has the same form for all orientation, there is no degeneracy.

The ground state wave function for hydrogen atom is

$$\psi_{100} = R_{10}(r)Y_{00}(\theta,\phi)$$

$$= R_{10}(r)\frac{1}{\sqrt{4\pi}} \qquad \text{………………..(2.2.28)}$$

The perturbation $H^{(1)}$ has the odd parity according the eq. (2.2.29)

$$H^{(1)}_{100,100} = \int \psi_{100} H^{(1)} \psi_{100} \, d\tau = 0$$

In order to understand the above, we have

$$H^{(1)} = +eErCos\theta$$

The first order perturbation energy in the ground state of Hydrogen atom is.

$$H^{(1)}_{100,100} = +eE\int\int\int \psi_{100}(+rCos\theta)\psi_{100} r^2 Sin\theta d\theta dr d\phi$$

where $\psi_{100}=R_{10}\, Y_{00}\, (\theta,\phi)$

and $Y_{00}(\theta,\phi)=N_{00}P_0^0(Cos\theta)$ $\Phi_0(\phi)=\dfrac{1}{\sqrt{4\pi}}$

$$\therefore \phi_0(\phi) = \frac{1}{\sqrt{2\pi}} \qquad p_0^0(Cos\theta) = .1$$

$$N_{00}=\frac{1}{\sqrt{2}}$$

$$R_{10}(r) = \left[\frac{2^2}{a_0}\right]^{1/2} .\exp(\frac{-r}{a_0})$$

so that $\psi_{100}=\left[\dfrac{2^2}{a_0}\right]^{1/2} ..\exp(\dfrac{-r}{a_0}).\dfrac{1}{\sqrt{4\pi}}$

Now $\lambda H^{(1)}_{100,100} = +eE\int_0^{\alpha}\int_0^{2\pi}\int_0^{\pi} rCos\theta \dfrac{1}{\pi a_0^3}.e^{\frac{-2r}{a_0}} .r^2 Sin\theta dr d\theta d\theta = 0$ …….2.2.30

Thus we observe that there is no first order stark effect to the ground state of the hydrogen atom.

The first excited state (n=R) of hydrogen atom is four-fold degenerate since it has the (l,m) values (0,0), (1,0),(1,1) and (1,-1). Let the electric field E is applied along the positive Z-axis which interacts with the electric dipole moment giving the perturbing Hamiltonian, $H^{(1)}=eEZ=erECos\theta$.

with the help of the quantum number (n l m), the four-fold degenerates states are specified as

$\psi(nlm) : \psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$

As the degeneracy is four-fold. We have to evaluate sixteen matrix elements of $H^{(1)}$ in the perturbation theory for degenerate states.

Clearly, we write the above four wave function as .

$$\psi_{200} = R_{20}(r)Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}} R_{20}(r) \text{ ....(2.2.31)}$$

$$\psi_{210} = R_{21}(r)Y_{10}(\theta,\phi) = \frac{3}{\sqrt{4\pi}} R_{21}(r)Cos\theta \text{ ....(2.2.32.)}$$

$$\psi_{211} = R_{21}Y_{11} = \sqrt{\frac{3}{8\pi}} R_{21}(r)Sin\theta e^{i\phi} \text{ ....(2.2.32)}$$

$$\psi_{2,1,-1} = R_{21}Y_{1,-1} = \sqrt{\frac{3}{8\Pi}} Sin\theta \, e^{-i\phi} R_{21}(r) \quad \text{...........(2.2.33)}$$

In these ψ_{200} has even parity and ψ_{210}, ψ_{211}, and $\psi_{2.1.-1}$ have odd parity.

Writing down the secular equation with the sixteen matrix elements, we have.

$$\begin{vmatrix} H^{(1)}_{200,200} - E & H^{(1)}_{200,211} & H^{(1)}_{200,211} & H^{(1)}_{200,21,-1} \\ H^{(1)}_{211,200} & H^{(1)}_{211,211} - E & H^{(1)}_{211,210} & H^{(1)}_{211,21,-1} \\ H^{(1)}_{210,200} & H^{(1)}_{210,211} & H^{(1)}_{210,211} - E & H^{(1)}_{210,21,-1} \\ H_{21,-1,200} & H^{(1)}_{21,-1,211} & H^{(1)}_{21,-1,210} & H^{(1)}_{21,-1,21,-1} - E^{(1)} \end{vmatrix} \text{ .....2.2.34}$$

Since ψ_{200} and ψ_{200} have even parity. He element of the secular determinant.

$$H^{(1)}_{200,200} = \int_{-\alpha}^{\alpha} \psi_{200} H^{(1)} \psi_{200} d\tau = 0 \quad \ldots\ldots\ldots\ldots..2.2.35$$

Similar to the equation (2.2.4)

In a similar way, $H^{(1)}_{211,211}, H^{(1)}_{210,210}, H^{(1)}_{21,-1,21,-1}$ are Zero

That means the four diagonal elements of matrix are Zero since they correspond to same parity.

Now the off-diagonal elements between states of different in values (i.e.)

$$H^{(1)}_{211,210}; H^{(1)}_{211,21,-1}; H^{(1)}_{210,211}; H^{(1)}_{210,21,-1}; H^{(1)}_{21,-1,211}; H^{(1)}_{21,-1,210}; H^{(1)}_{200,211}; H^{(1)}_{211,200}; H^{(1)}_{200,21,-1}; and H_{21,-1,200}$$

are also Zero since.

$$\int_0^{2\Pi} \exp\left[i\left(m^1 - m\right)\theta\right] d\phi = 0 \text{ if } m^1 \neq m \quad \ldots\ldots\ldots..2.2.36$$

Hence, out of the sixteen matrix elements, the only two matrix elements remains non-Zero are $H^{(1)}_{200,210} and H^{1}_{210,200}$ These two are again symmetrical, it is enough if we valuate one element out of the two.

Let us consider.

$$H^{(1)}_{200,210} = \int \psi^{*}_{200} H^{(1)} \psi_{210} d\tau \ \ldots\ldots\ldots..2.2.37$$

For which $\psi_{200} = \dfrac{1}{\sqrt{4\pi}} R_{20} / r)$

The evaluation of $R^{(r)}_{20}$ is taken up from the radial part of the hydrogen atom wave function.

$$R_{nl}(r) - \left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{\ (n+l)!\ \}^3}\right]^{\frac{1}{2}} .\exp\left(\frac{-Zr}{na_0}\right).\left(\frac{2Zrl}{na_0}\right).\left\langle \frac{2l+1}{n+l}\left(\frac{2zr}{na_0}\right)\right.$$

Which in turn gives

$$R_{20}(r) = \left(\frac{1}{2a_0}\right)^{3/2} .\left(2\frac{-r}{\left(2 - \frac{r}{a0}\right.}\right) \exp\left(\frac{-r}{2a_0}\right)$$

so that

$$\psi_{200} = \frac{1}{\sqrt{4\pi}}(\frac{1}{200})^{3/2}(2\frac{-r}{a_0}).\exp(\frac{-r}{2a_0}) \quad \ldots\ldots\ldots\ldots(2.2.38)$$

In a similar way

$$\psi_{210} = \sqrt{\frac{3}{4\pi}}Cos\theta R_{21}(r)$$

$$= \sqrt{\frac{3}{4\pi}}Cos\theta(\frac{1}{Ra_0})^{3/2}.\frac{r}{a_0\sqrt{3}}.\exp(\frac{-r}{2a_0}) \quad \ldots\ldots\ldots\ldots(2.2.39)$$

Where a_0 is the radius of the first Bohr orbit

Substituting the values of (2.2.38) and 2.2.39in eq.(2.2.37) gives.

$$H^{(1)}_{200,210} = +\frac{eE}{\sqrt{4\pi}}.\sqrt{\frac{3}{4\pi}}\left\{\left[\int_0^{\alpha}(\frac{1}{2a_0})^{3/2}.(2-\frac{r}{a_0})\exp(\frac{-r}{2a_0})(\frac{1}{2a_0})^{3/2}\frac{r}{a_0\sqrt{3}}\right]\right\}$$

$$\exp(\frac{-r}{2a_0}).r^3dr\,][\int_0^{\pi}Cos^2\theta Sin\,\theta d\theta\,][\int_0^{2\pi}d\phi\,]\} \quad \ldots\ldots\ldots(2.2.40)$$

Now

$$\int_0^{\pi}Cos^2\theta Sin\,\theta d\theta = -\int_0^{\pi}Cos^2\theta d(Cos\,\theta) = -\frac{Cos^3\theta}{3} = -[\frac{-1}{3}-\frac{1}{3}) = \frac{2}{3}$$

$$\int_0^{2\pi}d\phi = 2\pi$$

$$\int_0^{\alpha}\left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)^{3/2}.\frac{r}{a_0\sqrt{3}}\overset{\frac{-r}{2a_0}}{e}.r^3dr.$$

$$=\left(\frac{1}{2a_0}\right)^3.\frac{1}{a_0\sqrt{3}}\left[\int_0^{\alpha}(2-x)\overset{-x}{e}.a_0^4x^4a_0dx.\right. \qquad \text{using } x = \frac{r}{a_0}$$

$$= \frac{a_0}{8\sqrt{3}}\int_0^{\alpha}(2-x)\overset{-x}{e}x^4dx$$

$$= \frac{a_0}{8\sqrt{3}}\left[2\int_0^{\alpha} x^4 \overset{-x}{e} dx - \int_0^{\alpha} x^5 \overset{-x}{e} dx \ \right]$$

$$= \frac{a_0}{8\sqrt{3}}[48 - 120\ ] = \frac{-a_0}{8\sqrt{3}} 42 = -3\sqrt{3a_0}$$

$$\therefore H^{(1)}_{200,210} = \frac{eF}{\sqrt{4\pi}}\sqrt{\frac{3}{4\pi}}.\frac{2}{3}.2\pi.(-3\sqrt{3a_0}$$

$= -3a_0 eF$, Now, the secular equation becomes

$$\begin{array}{c|cccc|c}
\text{(nlm)} & 200 & 210 & 211 & 21,-1 & \\
200 & -E & -3a_0eE & -0 & 0 & \\
210 & -3a_0eE & -E^{(1)} & 0 & 0 & =0 \\
211 & 0 & 0 & -E^{(1)} & 0 & \\
21,1 & 0 & 0 & 0 & -E^{(1)} &
\end{array}$$

It can be observed that the states ψ_{200},ψ_{210} are effected by the electric field and the sates ψ_{211}, ψ_{21-1} remain unchanged.

The eigen states corresponding to the eigen value 3eEa$_0$ is $(\psi_{200}-\psi_{210})/\sqrt{2}$ and the eigen state for –3eEa$_0$ is $(\psi_{200}+\psi_{210})/\sqrt{2}$. The energy along with the eigen states of the n=2 state of hydrogen atom in an electric field E along the Z-direction is illustrated in Fig.2.1.

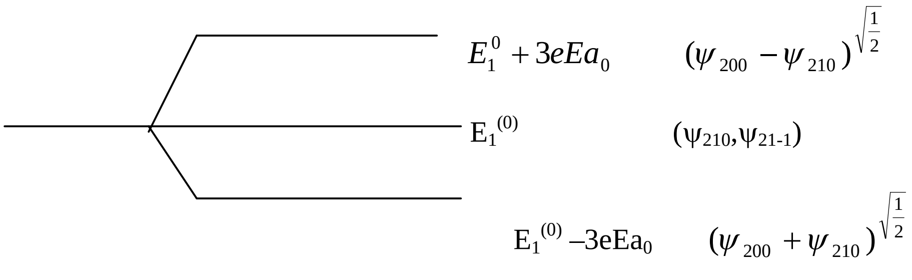

Fig. 2.2.1 Energies and wave functions of the first excited state of hydrogen atom in an electric field E.

This means that the hydrogen atom in the first excited state behaves as though it has a permanent dipole moment of magnitude $3a_0eE$ with three different orientations – one state parallel to the external electric field, one state anti-parallel to the field and two states with Zero component along the field. The states ψ_{211} and ψ_{21-1} do not posses dipole moments and therefore do not have a first order interaction with the field. Since the ground state of all atoms and nuclei are very likely to be non-degenerate, it is expected that an atom or nucleus in the ground state do not possess a permanent electric dipole moment. This means, atoms and nuclei in the ground state can possess electric charge, electric quadrupole moment, magnetic dipole moment etc., but not magnetic pole, electric dipole moment, magnetic quadrupole moment etc.,

Self Assessment Questions

1. Give the theory of time-independent perturbation theory for degenerate case.
2. Why do we say that the hydrogen atom in the first excited state possesses a permanent dipole-moment?
3. Why the hydrogen atom in the ground state does not show a first-order stark effect?

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UNIT – II

LESSON –VIII - The Variation method and W.K.B method

Objective of the lesson

Under some circumstances, perturbation theory is an invalid approach to take. This happens when the system we wish to describe cannot be described by a small perturbation imposed on simple system .in quantum electrodynamics, for instance, the interaction of quarks with the gluon field cannot be treated perturbatively at low energy because the interaction energy becomes too large. When faced with such systems, one usually turns into other approximation schemes, such as the variation methods and W.K.B approximation.

In the variation method, one has to make some guess of the wave function, they apply the variation principle to improve the guess of the wave function and obtain the upper bound for the ground state energy. Here we do not try to find a correction to already known unperturbed eigen value and eigenfunction, but determine the total eigen values and eigen functions as close to the experimental values as possible through a variation calculation.

2.3.1 The Variation method

(a) the variation principle and theory.

(b) application to ground state of helium atom.

The variation principle

The essential idea of the method is to evaluate the expectation value $\langle H \rangle$ of the Hamiltonian operator H of the system with respect to a trial wave function . In order to explain the principle involved to evaluate the energy of the ground state , let us consider the wave equation as

$$H\psi = E\psi \quad \ldots\ldots\ldots(2.3.1)$$

Where the Hamiltonian operator H = $-\frac{\hbar^2}{2m}\nabla^2 + V(r)$ and E is the energy value.

Multiplying eq.(2.3.1) with and integrating over all variables

$$\int \psi^* H\psi d\tau = \int \psi^* E\psi d\tau = E\int \psi^* \psi d\tau$$

$$E = \frac{\int \psi^* H\psi d\tau}{\int \psi^* \psi d\tau} \quad \ldots\ldots\ldots\ldots(2.3.2)$$

if φ is normalized wave function

$$E = \int \psi^* H\psi d\tau .....(2.3.3)$$

the equations give the expectation value of the energy of the system in the state represented by the wave function ψ .

The approximate wave function ψ can be obtained by variation principle. In this approach, we guess a wave function and calculate the energy value .The energy of the system is correct , if the trial wave function is correct. In accordance with principle of variation, if the true energy is E_0 and the correct wave function ψ_0, then any other acceptable wave function ψi ,indicates which trial wave functions is close to the true wave function to give the best energy value. For a proof of the theorem , express the trial wave function ψ as a linear combination of the true (but unknown) wave functions $\phi_1, \phi_2, \phi_3 \ldots\ldots$ of H_0

$$\psi = \alpha_1\phi_1 + \alpha_2\phi_2 + \alpha_3\phi_3 + \ldots\ldots.\alpha_n\phi_n \quad \ldots\ldots\ldots(2.3.4)$$

where α_1 , α_2 , α_3 , ……… α_n are the arbitrary parameters that can be varied to minimum in the energy .for our convenience, let us take

$\Psi=\alpha_1\phi_1+\alpha_2\phi_2$……….(2.3.5)

substitute this in equation (2.3.2), we get

$$E=\frac{\int(\alpha_1\phi_1^{*}+\alpha_2\phi_2^{*})H(\alpha_1\phi_1+\alpha_2\phi_2)d\tau}{\int(\alpha_1\phi_1^{*}+\alpha_2\phi_2^{*})(\alpha_1\phi_1+\alpha_2\phi_2)d\tau}$$

(i.e) $$E[\alpha_1^2\int\phi_1^{*}\phi_1 d\tau+2\alpha_2\alpha_2\int\phi_1^{*}\phi_2 d\tau+\alpha_2^2\int\phi_2^{*}\phi_2 d\tau]$$

$$=\alpha_1^2\int\phi_1^{*}H\phi_2 d\tau+2\alpha_2\alpha_2\int\phi_2^{*}H\phi_2 d\tau+\alpha_2^2\int\phi_2^{*}H\phi_2 d\tau..............(2.3.6)$$

as we require the minimum value of E, it is necessary to minimize the energy E

with respect to the parameter α_1 and α_2

differentiating with respect to α_1 , we get.

$$E[2\alpha_1\int\phi_1^{*}\phi_1\,d\tau+2\alpha_2\int\phi_1^{*}\phi_2\,d\tau]+\frac{\partial E}{\partial\alpha_1}[\alpha_1{}^2\int\phi_1^{*}\phi_1\,d\tau+2\alpha_1\alpha_2\int\phi_1^{*}\phi_2\,d\tau+$$
$$\alpha_2{}^2\int\phi_1^{*}\phi_2\,d\tau]=2\alpha_1\int\phi_1^{*}H\phi_1\,d\tau+2\alpha_2\int\phi_1^{*}H\phi_2\,d\tau]...........(2.3.7)$$

in a similar way, differentiating with respect to α_2 , we get

$$E[2\alpha_1\int\phi_1^{*}\phi_2 d\tau+2\alpha_2\int\phi_2{}^{*}\phi_2\,d\tau]+\frac{\partial E}{\partial\alpha_2}[\alpha_1{}^2\int\phi_1^{*}\phi_1\,d\tau+2\alpha_1\alpha_2\int\phi_1^{*}\phi_2\,d\tau+$$
$$\alpha_2{}^2\int\phi_2^{*}\phi_2\,d\tau]=2\alpha_1\int\phi_1^{*}H\phi_2\,d\tau+2\alpha_2\int\phi_2^{*}H\phi_2\,d\tau]...........(2.3.8)$$

in order to minimize E with respect to α_1 , and α_2 , then

$$(\frac{\partial E}{\partial\alpha_1})_{\alpha_2}=(\frac{\partial E}{\partial\alpha_2})_{\alpha_2}=0...................(2.3.9)$$

and using the symbols

$$H_{ij}=\int\phi_i^{*}H\phi_j d\tau \qquad ………………(2.3.10)$$

$$\Delta_{ij}=\int\phi_i^{*}\phi_j d\tau$$

applying the equation (2.3.9) and (2.3.10)to(2.3.7) we get

$$(H_{11} - E\Delta_{11})\alpha_1 + (H_{12} - E\Delta_{12})\alpha_2 = 0 \ldots\ldots\ldots\ldots\ldots(2.3.11)$$

similarly, from the equation(2.3.8), we get after minor rearrangements for H_{12}=$H_{21}$and Δ_{12}= Δ_{12} for convenience and symmetry.

$$(H_{21} - E\Delta_{21})\alpha_1 + (H_{22} - E\Delta_{22})\alpha_2 = 0 \ldots\ldots\ldots\ldots\ldots(2.3.12)$$

equation(2.3.11)and(2.3.12) together are called secular equations.

In our case , we consider only the first two terms of the variation function ψ, we can generalize to other term also.

Equation 2.3.11 and 2. 3.12 can be solved for ad provided the determinant for trivial solution is

$$\begin{vmatrix} H_{11} - E\Delta_{11} & H_{12} - E\Delta_{12} \\ H_{21} - E\Delta_{21} & H_{22} - E\Delta_{22} \end{vmatrix} = 0 \qquad \ldots\ldots\ldots\ldots\ldots(2.3.13)$$

in a more general way, for n independent functions the secular equation in the form of determinant is

$$\begin{vmatrix} H_{11} - E\Delta_{11} & H_{12} - E\Delta_{12} \ldots\ldots\ldots\ldots H_{1n} - E\Delta_{1n} \,.. \\ H_{21} - E\Delta_{21} & H_{22} - E\Delta_{22} \ldots\ldots\ldots\ldots H_{2n} - E\Delta_{2n} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. & \\ H_{n1} - E\Delta_{n1} & H_{n2} - E\Delta_{n2} \ldots\ldots\ldots\ldots H_{nn} - E\Delta_{nn} \end{vmatrix} = 0$$

2.3.2 Application of Variation Method

Application to the ground (normal) state of the Helium atom

As an example, we take up to obtain the energy of Helium atom in the ground state.

Helium atoms consist of electrons of charge ‘-e’, and nucleus ‘+Ze’.

The total potential is

$$V=V_1+V_2+V_3 \ldots\ldots\ldots\ldots\ldots (2.3.14)$$

Where the potential energies are given as :

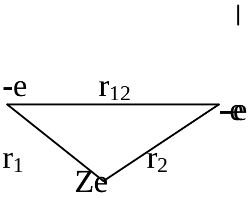

Fig:2.3.1 Helium atom

$$V_1 = \frac{-Ze^2}{r_1}, \frac{-Ze^2}{r_2}, \frac{e^2}{r_{12}} \qquad (2.3.15)$$

Neglecting the nuclear motion, the Hamiltonian is represented as

$$H = \frac{-\hbar^2}{8\pi^2 m}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}} \ldots\ldots.(2.3.16)$$

In atomic units, representing the Bohr radius $a_0 = \frac{h^2}{4\pi^2 me^2}$

The Hamiltonian becomes.

$$H = -\frac{1}{2}\frac{e^2}{a_0}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Ze^2}{a_0 R_1} - \frac{Ze^2}{a_0 R_2} + \frac{Ze^2}{a_0 R_{12}} \ldots\ldots..(2.3.17)$$

Here e^2/a_0 is the atomic unit of energy.

In atomic units H takes the form

$$H = -\frac{1}{2}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}} \ldots\ldots\ldots.(2.3.18)$$

For the case of Helium, suppose one of the electrons is labeled 1, in the ground states, and the other labeled 2 is in the exited state 2.The ground state electron experiences the full attractive force of charge ‘+2e’ .

The wave function is represented as

$$\Psi_1^{(0)} = \frac{1}{\sqrt{\pi}} Z^{\frac{3}{2}} e^{-ZR_2} \,(a.u.)............(2.3.19)$$

Even though the electron 2 does not experience attractive force from nuclear, in choosing the trial wave function for electron 2 is taken as

$$\Psi_2^{(0)} = \frac{1}{\sqrt{\pi}} \mathrm{Z}^{\frac{3}{2}} \mathrm{e}^{-\mathrm{ZR}_2} \,(\mathrm{a.u.})...........(2.3.20)$$

These considerations show that good trial wave function must be of the form.

$$\phi = \Psi_1^{(0)}\Psi_2^{(0)} = \frac{1}{\pi}\left(Z^1\right)^3 e^{-Z^1(R_1+R_2)}........(2.3.21)$$

Where Z^1 is between 1 and 2.

Since $\Psi_1^{(0)}$, $\Psi_2^{(0)}$ are normalized wave functions for hydrogen like atoms, Φ must be a normalized wave function.

The expression for H given in eq.(2.3.18) is now modified by adding and subtracting ($Z'/R_1 + Z'/R_2$)becomes

$$\mathrm{H} = \left[-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{\mathrm{Z}^1}{\mathrm{R}_1} - \frac{\mathrm{Z}^1}{\mathrm{R}_2}\right] - \frac{\mathrm{Z}-\mathrm{Z}^1}{\mathrm{R}_1} - \frac{\mathrm{Z}-\mathrm{Z}^1}{\mathrm{R}_2} + \frac{1}{\mathrm{R}_{12}}$$

$$= \mathrm{H}_0^1 - \left(\mathrm{Z}-\mathrm{Z}^1\right)\left[`\frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2}\right] + \frac{1}{\mathrm{R}_{12}}...........(2.3.22)$$

$$\text{Where, } \mathrm{H}_0^1 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{\mathrm{Z}^1}{\mathrm{R}_1} - \frac{\mathrm{Z}^1}{\mathrm{R}_2}$$

Since Φ is assumed a normalized function, the variational energy E_Φ is given as

$$E_\phi = \int \phi^* H\phi d\tau................(2.3.23)$$

Wehave,

$$H\phi = H_0^1\phi - \left(Z - Z^1\right)\left[`\frac{1}{R_1} + \frac{1}{R_2}\right]\phi + \frac{1}{R_{12}}\phi \qquad ....(2.3.24)$$

Let

$$H_0^1\phi = E_0^1\phi$$

$$(i.e), \left[-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z^1}{R_1} - \frac{Z^1}{R_2} \right]\phi = E_0^1\phi \qquad \text{.................(2.3.25)}$$

Which is similar to two individual hydrogen-like atom wave function; whose energy is

$$E_0^1\phi = -\left(Z^1\right)^2 a.u$$

Now eq 2.3.25 becomes

$$H\phi = -\left(Z^1\right)^2\phi - \left(Z - Z^1\right)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\phi + \frac{1}{R_{12}}\phi \text{........(2.3.26)}$$

Now the variational energy E_Φ of eq (2.3.23) becomes.

$$E_\phi = \int \phi^* \left[-\left(Z^1\right)\phi - \left(Z - Z^1\right)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\phi + \frac{1}{R_{12}}\phi \right] d\tau$$

$$= -\left(Z^1\right)^2 \int \phi^*\phi d\tau - \left(Z - Z^1\right)\int \phi^* \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\phi d\tau + \int \phi^* \frac{1}{R_{12}}\phi d\tau \qquad \text{.....(2.3.27)}$$

Since Φ is normalized.

$$\int \phi\phi * d\tau = 1 \qquad \text{......(2.3.28)}$$

And we write other integrals as.

$$I_1 = \int \frac{\left[-\left(Z^1\right)^3 e^{-Z^1(R_1+R_2)}\right]^*}{\pi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\frac{\left(Z^1\right)^3}{\pi} e^{-Z^1(R_1+R_2)} d\tau_1 d\tau_2$$

$$= -\frac{\left(Z^1\right)^6}{\pi^2}\left[\int \frac{e^{-2Z^1(R_1+R_2)}}{R_1} d\tau_1 d\tau_2 + \int \frac{e^{-2Z^1(R_1+R_2)}}{R_2} d\tau_1 d\tau_2 + \right] .....(2.3.29)$$

The first of the integral in the integral I, is

$$\mathrm{I} = \int \frac{e^{-2Z^1(R_1)}}{R_1} d\tau_1 \int e^{-2Z^1(R_2)} d\tau_2$$

$$= \int \frac{e^{-2Z^1(R_1)}}{R_1} R_1^2 dR_1 d\theta_1 \sin\theta_1 d\theta_1 \int e^{-2Z^1(R_2)} R_1^2 dR_2 \sin\theta_2 d\theta_2 d\theta_2$$

Using the knowledge of gamma functions and other simple integrals.

$$\mathrm{I} = \quad 16\pi^2 \int \frac{e^{-2Z^1R_1}}{} R_1^2 dR_{11} \int e^{-2Z^1R_2} R_1^2 dR_2 \ldots\ldots(2.3.30)$$

Similarly, the second integral in I, becomes.

$$I_1^{11} = \frac{\pi^2}{\left(Z^1\right)^5} .....(2.3.31)$$

Inserting these values of integral in eq2.3.29

$$I_1 = \frac{\left(Z^1\right)^6}{\pi^2}\frac{2\pi^2}{\left(Z^1\right)^5} = 2Z^1 ....2.3.32$$

Now the remaining integral in eq.2.3.27 is

$$I_2 = \int \phi^* \frac{1}{R_{12}} \phi d\tau$$

$$= \frac{\left(Z^1\right)^6}{\pi^2} \int \frac{e^{-2Z^1 R_1} e^{-2Z^1 R_2}}{R_{12}} d\tau_1 d\tau_2 .....2.3.33$$

The above integral can be evaluated using the knowledge of Legender polynomial and electrodynamics which yields the value.

$$I_2 = \frac{\left(Z^1\right)^6}{\pi^2} \frac{5}{8} \frac{\pi}{\left(Z^1\right)^5} = \frac{5}{8} Z^1 ......2.3.34$$

Using the results of 2.3.32 and 2.3.34 in eq.2.3.27 We get

$$E_\phi = -\left(Z^1\right)^2 - \left(Z - Z^1\right).2Z^1 + \frac{5}{8} Z^1$$

$$= \left(Z^1\right)^2 - 2ZZ^1 + \frac{5}{8} Z^1 ..(a.u.)....2.3.35)$$

$$I = 16\pi^2{}_1 \int e^{-2Z^1(R_1)} R_1 dR_1 \int e^{-2Z^1(R_2)} R_2^2 dR_2$$

$$= 16\pi^2 \left[\frac{1}{4\left(Z^1\right)^2} \frac{1}{4\left(Z^1\right)^3} \right] = \frac{\pi^2}{\left(Z^1\right)^5} ....2.3.30$$

to minimise E_Φ with respect to variational parameter Z^1, we set $dE/dZ^1=0$.

This gives

$$\frac{dE}{dZ^1} = 2Z^1 - 2Z + \frac{5}{8} = 0$$

$$Where, Z^1 = Z - 5/16.........(.2.3.36)$$

Thus Z^1 is taken as the effective nuclear charge of helium. The factor 5/16 is called the screening factor.

Substituting the Z^1 in the energy equation 2.3.35

$$E\phi = (Z^1)^2 - 2Z^1 \left(Z^1 + \frac{5}{16}\right) + \frac{5}{8} Z^1 \quad .a.u.$$

$$= -(Z^1)^2 \qquad a.u. \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.3.37)$$

$$=2 (Z^1)^2 E_{1s}(H) \qquad [\therefore E_1 or E_{1s}(H) = -1/2]$$ which is ground state energy of hydrogen atom in the 1s orbital

$$=2(Z-5/16)^2 E1s\ (Ъ)$$

$$=2 \left(\frac{27}{16}\right)^2 E_{1s}H \qquad (\therefore Z = 2 \text{ for Helium atom})$$

$$=2 \left(\frac{27}{16}\right)^2 (-13.60 \text{ eV}) \qquad (\therefore E_1 = -13.60 \text{ eV})$$

$$= -77.45 \text{ eV}$$

Which is the approximate ground state energy of helium atom. Further, the energy of the ground state He^+ ion is $4E_{1s}$ (H) = -54.40 eV.

Hence the ionization potential of helium is (-54.40) – (-77.45) = 23 eV.

The experimental value is 24.58 eV.

By introducing more parameters in the trial function, the accuracy may be improved further.

2.3.3 The WKB Method

(a) Validity of the Method

(b) Principle of the Method

(c) Connection formula for penetration of a barrier.

Introduction

Wentzel-Kramers-Brillouin (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. Problems of one dimension and also of three dimensions reducible in one dimension (radial) are solved by this method.

A slowly changing potential means the variation of potential energy V(r) slightly over several wavelengths (De Broglie waves) of the particles

The De Broglie wavelength associated with a particle moving with energy E in a region of potential V is

$$\lambda = \frac{h}{p} = \frac{\hbar}{[2m(E-V)]^{\frac{1}{2}}} \qquad \text{………(2.3.38)}$$

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

m^2v^2= 2 m (E-V)

p = mv = $\sqrt{[2m(E-V)]}$

The propagation constant

k = $\frac{2\pi}{\lambda}$ =(2m/$\hbar$) [E-V(x)]$^{1/2}$

$$P = \hbar\, k \Rightarrow \frac{p}{\hbar} = \frac{2\pi}{\lambda} \qquad \text{…………(2.3.39)}$$

Mathematically slowly varying potential can be expressed by the conditions

$$\left|\frac{1}{\hbar^2}\frac{dk}{d\lambda}\right| << 1$$

substituting value of k from (2.3.39), we get

$$\frac{\hbar m\left|\frac{\partial V}{\partial x}\right|}{\left[2m(E-V)\right]^{3/2}} << 1 \text{ or } \quad \frac{\lambda \frac{\partial V}{\partial x}}{\left[4\pi(E-V)\right]} << 1 \qquad \text{…………..(2.3.40)}$$

This equation gives the validity of W.K.B approximation.

Principle of the method

W.K.B. method consists of in introducing an expression in the powers of . Thus Schrodinger equation (at least in some regions of space) is reduced in its classical limit. However, the method has wider range of applicability than the classical approximation, because this procedure can be carried out even in regions of space where classical interpretation is meaningless (region E < V is inaccessible to classical particle)

Let ψ (x) be the wave function satisfying Schrodinger's equation.

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{2m}{\hbar^2}\left[E-V(x)\right]\varphi=0 \qquad \text{………(2.3.41)}$$

Let the solution of eqn. (2.3.41) be of the form

$$\varphi = Ce^{i\phi(x)/\hbar} \qquad \text{…………(2.3.42)}$$

Where C is constant, ϕ (x) is yet, an undetermined function of x, we have

$$\frac{\partial\varphi}{\partial x} = Ce^{i\phi(x)/\hbar}.\frac{\partial\phi}{\partial x}$$

$$\frac{\partial^2\varphi}{\partial x^2}= \frac{C}{\hbar}e^{i\phi(x)/\hbar}.\left(\frac{\partial\phi}{\partial x}\right)^2 + \frac{C}{\hbar}e^{i\phi(x)/\hbar}.\frac{\partial^2\phi}{\partial x^2} \qquad \text{…………..(2.3.43)}$$

now substituting $\frac{\partial\phi}{\partial x} = \phi'$ and $\frac{\partial\phi'}{\partial x} = \phi''$ equation (2.3.43) takes the form

$$\frac{\partial^2\varphi}{\partial x^2}=\frac{C}{\hbar^2}e^{i\phi(x)/\hbar}.(\phi')^2 + C\frac{i}{\hbar}e^{i\phi(x)/\hbar}.\phi'' \qquad \text{………..(2.3.44)}$$

Substituting values of ϕ and $\frac{\partial^2 \varphi}{\partial x^2}$ from(2.3.42) and (2.3.44) in (2.3.41), we get

$$-\frac{C}{\hbar^2} e^{i\phi(x)/\hbar} . (\phi')^2 + C\frac{i}{\hbar} e^{i\phi(x)/\hbar} . \phi'' + \frac{2m}{\hbar^2}\left[E - V(x)\right] Ce^{i\phi(x)/\hbar} = 0$$

or $\frac{C}{\hbar^2} e^{i\phi(x)/\hbar} \left[-\phi'^2 + i\hbar\phi'' + 2m(E - V)\right] = 0$

As $\psi = Ce^{i\phi(x)/\hbar} \neq 0$,therefore above equation gives

$i\hbar\phi'' - \phi'^2 + 2m(E - V) = 0$ ……….(2.3.45)

To get an approximate solution of (4.8), we apply W.K.B. method and hence expand

ϕ(x) in powers of $\hbar$ i.e.,

$$\phi(x) = \phi_0(x) + \hbar\phi_1(x) + \frac{\hbar^2}{2}\phi_2^{'}(x) + - - - - \qquad (2.3.46)$$

where the subscripts ϕ's are independent of $\hbar$. Let us assume that on account of the smallness of $\hbar$, the first two terms in equation (2.3.46) give a sufficiently good approximation to ϕ.

Differentiating equation (2.3.43), we get

$$\left.\begin{aligned} \phi'(x) &= \phi_0^{'}(x) + \hbar\phi_1^{'}(x) + \frac{\hbar^2}{2}\phi'_2(x) + - - - - - - \\ \phi''(x) &= \phi_0^{''} + \hbar\phi''^{'}_1(x) + \frac{\hbar^2}{2}\phi'_2(x) + - - - - - - \end{aligned}\right\} \qquad (2.3.47)$$

Substituting values of ϕ' and ϕ'' from (2.3.47) in equation (2.3.45), we get

$$i\hbar\ [\phi_0^{''} + \hbar\phi''^{'}_1(x) + \frac{\hbar^2}{2}\phi'_2(x) + - -] - [\phi_0^{'}(x) + \hbar\phi_1^{'}(x) + \frac{\hbar^2}{2}\phi'_2(x) + - -]^2 + 2m(E - V) = 0 \ldots.(2.3.48)$$

collecting coefficients of various powers of $\hbar$, we see that up to second order in

$\hbar$, we see the result is

$$[2m(E - V) - \phi'^2_0] + \hbar\left[i\phi''_0 - 2\phi'_0\,\phi_2^{'}\right] + \hbar^2\left[i\phi_1\right] + \hbar^2[i\phi_1'' - \phi'^2_1 - \phi'_0\,\phi''_2] = 0 \ \ldots.(2.3.49)$$

in order to that equation (2.3.49) may hold identically in $\hbar$, the coefficients of each power of $\hbar$ must vanish separately. This requirement leads to the following leads series of equations.

$$\left.\begin{aligned} &2m(E-V)-\phi'^2_0=0 \quad \text{(a)} \\ &i\phi''_0-2\phi'_0\,\phi_2^{'}=0 \quad \text{(b)} \\ &i\phi_1''-\phi'^2_1-\phi'_0\,\phi''_2=0 \quad \text{(c)} \end{aligned}\right\} \quad \ldots\ldots \quad 2.3.50$$

and so on..

These equations may be solved successively. That is the first equation ,ϕ_0 in terms of (E-V),the second equation defines ϕ_{1},the third defines ϕ_2 in terms of ϕ_1 and ϕ_0 etc..

From equation (2.3.50a), we obtain,

$$\phi'_0=\pm\sqrt{2m(E-V)} \quad \ldots\ldots\ldots(2.3.51)$$

integration of above eq. gives,

$$\phi_0=\pm\int_{x_0}^{x}\sqrt{2m(E-V)}dx \qquad \ldots\ldots..(2.3.52)$$

where x_0 is an arbitrary fixed value of x.

From equation(2.3.50b) we obtain

$$\phi_1=\frac{i\phi_0^{''}}{2\phi_0^{'}}$$

integration of above equation yields

$$\phi_1=\frac{i}{2}\log\phi_0^{'}+C_1 \qquad \ldots\ldots\ldots\ldots(2.3.53)$$

where C_1 is a constant integration. This result is inconvenient if $\phi_0^{'}$ is negative. Therefore keeping in mind the log of negative of function differs only by an imaginary constant from the logarithm of absolute value of the function. We replace eqn.2.3.53 by

$$\phi_1 = \frac{i}{2}\log\left|\phi_0^{'}\right| + C_2 \qquad \text{…………(2.3.54)}$$

Where C_2 is an arbitrary constant.

Similarly

$$\phi_2 = \frac{1}{2}\frac{m\left(\frac{\partial V}{\partial x}\right)}{\left[2m(E-V)\right]^{\frac{3}{2}}} - \frac{1}{4}\int_{x_0}^{x}\frac{m^2\left(\frac{\partial V}{\partial x}\right)}{\left[2m(E-V)\right]^{\frac{3}{2}}}dx \qquad \text{………..(2.3.55)}$$

From equation 2.3.54 we see that ϕ_2 is represented as logarithm of $\left|\phi_0{}'\right|$,therefore it is not, in general, small compared with ϕ_2. Consequently ϕ_2 and ϕ_2 both must be retained. On the other hand from eqn.(2.3.55) we see that ϕ_2 will be small whenever dv/dx is small and(E-V) is not too close to zero. Further it can be seen easily that the smallness of the higher approximations (ϕ_2 ,ϕ_2 ….etc) requires the smallness of all derivatives of V. Thus the W.K.B. approximation will be suitable in cases where V is a sufficiently smooth and slowly varying function of position.

Thus the approximate W.K.B. solution of eqn. (2.3.45) may be expressed in the form

$$\phi = \phi_0\left(x + \frac{1}{2}i\hbar\log\left|\phi_0^{'}\right|\right) \qquad \text{……..(2.3.56)}$$

assuming constant C_2 is absorbed in $\phi_0(x)$

Substituting value of $\phi(x)$ from (2.3.6) in equation (2.3.42) and rearranging the result, we finally obtain the approximate solution ϕ_{app} of equation (2.3.44) in the form

$$\psi_{app} = C\left[2m(E-V)\right]^{-\frac{1}{4}}\left[A\exp\left(\frac{i}{\hbar}\right)\int_{x_0}^{x}\left(\sqrt{2m(E-V)}\right)dx\right] \qquad \text{………..(2.3.57)}$$

Where C remains arbitrary. The two solutions contained in (2.3.57) and differing in sign of the exponent are linearly independent, and hence the approximate general solution, according to W.K.B. approximation is

$$\psi_{app} = C[2m(E-V)]^{-\frac{1}{4}}\left[\left(A\exp\left(\frac{i}{\hbar}\right)\int_{x_0}^{x}\left(\sqrt{2m(E-V)}\right)dx\right)+\left(B\exp\left(\frac{-i}{\hbar}\right)\int_{x_0}^{x}\left(\sqrt{2m(E-V)}\right)dx\right)\right] \text{…..} \quad (2.3.58)$$

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.

$e^{\frac{ipx}{\hbar}}$ and $e^{\frac{-ipx}{\hbar}}$

The alternative from of equation (2.3.58) may be expressed as

$$\psi_{app} = C[2m(E-V)]^{-\frac{1}{4}}\cos\int_{x_0}^{x}\left(\sqrt{2m(E-V)}\right)dx+\phi$$

Where C and ϕ are arbitrary constants.

The approximate solutions (2.3.57) and (2.3.58) of the Schrodinger equation are usually called W.K.B. ψ - functions.

Connection Formulas for penetration of a barrier

W.K.B. method is applicable to the problems only where the potential function does not change too rapidly, because in the regions approximation considered do not apply. In the problems where the potential function vary slowly in some regions, so that W.K.B. method is inapplicable; we find the solution in the regions of inapplicability of W.K.B. method by some other methods and carry it to the regions where W.K.B. method is applicable. In order to connect these two solutions: we need for the connection formulas.

To treat the problem of barrier penetration where W.K.B approximation is valid, we must find how to connect solutions in the region where V>E with those where

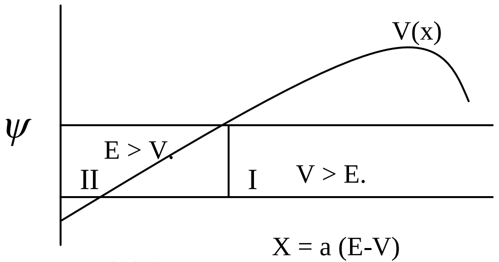

Fig 2.3.2

Consider the potential barrier shown in Fig. 2.3.2 Suppose the energy of particle is such that E = V at point x = a..

Classically, the particle should slow down to zero velocity at this point and then turn back. Quantum mechanically we know that the wave penetrates some distance further into the barrier. Obviously we cannot use the W.K.B. approximation in the region near x=a because when E=V, the condition for its applicability breaks down.

Thus if we start with a given solution at some distance to the right of x = a (in I region) say,

$$\varphi \sim \frac{1}{\sqrt{p_1}} \exp \int_a^x \frac{P_1 dx}{\hbar} \qquad (2.3.59)$$

where $P_1 = \sqrt{2m(V-E)}$

From W.K.B. approximation method, we know that a sufficient distance to left of x =a (in region II), the approximate solution will be

$$\varphi \sim \frac{A}{\sqrt{p_1}} \exp\left(i\int_a^x \frac{P_1 dx}{\hbar} \right) + \frac{B}{\sqrt{p_2}} \exp\left(-i\int_a^x \frac{P_2 dx}{\hbar} \right) \quad \text{……..(2.3.60)}$$

φ where $P_2 = \sqrt{2m(E-V)}$ and A and B are unknown constants . The values of A and B can not be found By W.K.B. method alone, because they are determined by the nature of the solution in the region of inapplicability of W.K.B. method. To obtain the values of A and B we need an exact solution near x = a ; but it is too complex problem to be solved. If the W.K.B. method is applicable at small enough region x = a; then the potential function can be represented approximately by a straight line with in region, with slope equal to that of potential curve at the classical turning point x = a. as E = V, we can write,

$$V - E = C\,(x-a),$$

Where C is a constant equal to $\left(\frac{\partial V}{\partial x} \right)_{x=a}$. Thus in the region x = a , the Schrodinger equation reduces approximately to

$$\frac{\partial^2\varphi}{\partial x^2}-\frac{2m}{\hbar^2}C(x-a)\varphi=0 \qquad \text{……..(2.3.61)}$$

This difficult equation can be solved by Bessel’s function The solution of the equation (2.3.61) is carried far enough from x = a, so that W.K.B. approximation becomes applicable. In this way, we may determine the constants A and B. Here we shall simply results without going through the complex procedure.

Case (A) Barrier to the right

Let V>E, to the right of x = a and P_1 = $\sqrt{2m(V-E)}$; P_2 = $\sqrt{2m(E-V)}$

Let us consider that far to the right of x= a, the W.K.B. approximate solution, which is exponential, Viz.,

$$\varphi_1\approx\frac{B}{\sqrt{p1}}\exp\left(-i\int_a^x\frac{P_1dx}{\hbar}\right) \qquad \text{………(2.3.61)}$$

for to the left to x= a , the connection formula states this solution approaches,

$$\varphi_2\approx\frac{B}{\sqrt{p_2}}\cos\left(-i\int_a^x\frac{P_2dx}{\hbar}-\frac{\pi}{4}\right) \qquad \text{………..(2.3.62)}$$

Thus the connection formula may be expressed as

$$\frac{1}{\sqrt{p1}}\exp\left(-i\int_a^x\frac{P_1dx}{\hbar}\right)=\frac{2}{\sqrt{p_2}}\cos\left(-i\int_a^x\frac{P_2dx}{\hbar}-\frac{\pi}{4}\right) \qquad \text{…….(2.3.63)}$$

similarly, if the approximate solution is an increasing exponential to the right of x= a, the following connection hold.

$$\frac{1}{\sqrt{p_1}}\sin\left(-i\int_a^x\frac{P_2dx}{\hbar}-\frac{\pi}{4}\right)=\frac{1}{\sqrt{p_2}}\exp\left(i\int_a^x\frac{P_2dx}{\hbar}\right) \qquad \text{……..(2.3.64)}$$

Case (B) Barrier to the left

For the solution which decays exponentially to the left of x=a, we obtain the connection formula.

$$\frac{1}{\sqrt{p_2}}\exp\left(-i\int_a^x \frac{P_2 dx}{\hbar}\right) = \frac{2}{\sqrt{p_2}}\cos\left(i\int_a^x \frac{P_2 dx}{\hbar} - \frac{\pi}{4}\right) \quad \text{……….(2.3.65)}$$

If the solution increases exponentially to the left, we obtain the following connection formula.

$$\frac{1}{\sqrt{p_1}}\sin\left(-i\int_a^x \frac{P_2 dx}{\hbar} - \frac{\pi}{4}\right) = \frac{1}{\sqrt{p_2}}\exp\left(i\int_a^x \frac{P_2 dx}{\hbar}\right)$$

Conclusion and summary

It may be noted that the connection formulas enable us only to obtain the relation between the solutions in a region at some distance to the right of the turning point x=a, with those in a region some distance to the left. In order to obtain the form of the wave function in the intermediate region, we have should consider the exact solution, which involves Bessel functions of order $\frac{1}{3}$.

For applying W.K.B. approximation, the following requirements must be satisfied.

1. On either side of the turning point, there exist regions when the potential functions changes slowly so that W.K.B. approximation is applicable.
2. In the region near the turning point x=a where W.K.B. method becomes inapplicable, the kinetic energy can be represented approximately by a straight line (E-V) = C(x-a). In order other words the potential should not undergo a large fractional change in slope within this region. Inside the barrier W.K.B. approximation begins to hold after.

$$\int_0^x \sqrt{2m(E-V)}dx/\hbar$$

becomes appreciably greater than unity.

In this lesson, we develop another approximate method, which gives a direct solution of Schrodinger equation. This method, which is usually referred to as W.K.B. method is applicable to potentials which are such that the Schrodinger equation is separable to one dimensional equation,

further, the potential should be slowly varying we obtain the W.K.B. solution of the one dimensional schrodinger equation. Those solutions are used to describe the quantization condition which determiner the energy values corresponding to bound state problem.

Conclusion We have shown that the quantization condition is closely related to the Bohr-Sommerfield quantization condition of the old quantum theory.

Self assessment questions

1 Apply the W.K.B. method to evaluate the energy eigen value corresponding to the

Harmonic oscillator potential. $\left[V(\lambda)=\frac{1}{2}m\omega^2\lambda^2\right]$

2 Show that the W.K.B. energy levels corresponding to the free fall of a particle in

earth's gravitational field is given by $E_n=\frac{1}{2}\left[9\left(n+\frac{3}{4}\right)^2\pi^2mg^2\hbar^2\right]^{1/3}$

3 Use the variation method to estimate the ground state energy of a particle in the

potation. V=∞ $\lambda < 0$

V=K∞ $\lambda > 0$

Choose $\lambda e^{-\alpha\lambda}$ as the trial wave function.

4. A particle of mass m is bound by a potential $V(r)=-V_0e^{-r/a}$ where $\hbar^2/_m V_0a^2=0.75$

Use variation method with the trial wave function $e^{-\alpha r/a}$ to get a good limit on the

lowest energy eigen values.

5. Calculate the transmission probability of a particle through a potential well with the

Help of W.K.B. method.

6. Evaluate the energy values of a) normal state of hydrogen, b) normal state of helium using variation method.

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UNIT – 2

LESSON – IX - Time-dependent perturbation theory

Objective of the Lesson

Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation v(.t.) applied to a time independent Hamiltonian H^0. The eigen functions and eigen state of this perturbed Hamiltonian is also time-dependent.

We are interested in the following quantities:

(i) Time-dependent expected value of some observable, with a specified initial state.

(ii) The time-dependent amplitudes of those quantum states that are energy eigen kets in the unperturbed systems.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigen state, which is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas where a time-dependent electric field is applied.

2.4.1. The method of variation of constants

Consider the time-dependent schrodinger wave equation of an unperturbed system.

$$H^{(0)}\psi_n^{(0)} = -\frac{\hbar}{2i}\frac{\partial \psi_n^{(0)}}{\partial t} \quad \text{……………………….(2.4.1)}$$

If the unperturbed system is conservative, then the Hamiltonian $H^{(0)}$ depends only on the space variable r but not on time t. Now, for such a case, the total wave function $\psi_n^0(r,t)$ including time is

$$\psi_n^{(0)}(r,t) = \psi_n^{(0)}(r).e[\ ^{\frac{-2\pi i E_n^{(0)} dt}{\hbar}}\ ]$$

$$=\psi_n^{(0)} e^{-\frac{iE_n^{(0)}t}{\hbar}}$$ ……………………(2.4. 2.)

Where $E_n^{(0)}$ is the energy of the stationary states and $\psi_n^{(0)}(r)$ are eigen functions of the time-independent wave equation.

$$H^{(0)}\psi_n^{(0)}(r)=E_n^{(0)}\psi_n^{(0)}(r)$$ …………(2.4. 3).

The general solution of eq. (2.4.1) is a linear combination of solutions representing different stationary states.

(i.e.) $\psi^{(0)}(r,t)=\sum_n a_n\psi_n^{(0)}(r,t)$ …………………(2.4. 4.)

If $\psi_n^{(0)}(r)$ is normalized like the functions $\psi_n^{(0)}(r,t)$ forming an orthonormal set, then for each n value, $|a_n|^2$ represents the probability of the system in that particular stationary state. The sum of the squares of the mixing Coefficients a_n is represented as.

$\sum|a_n|^2=1$ ………………………(.2..4. 5.)

since $\int\psi^*\psi d\tau=\sum_n a_n{}^*a_n=\sum_n|a_n|^2=1$

Further $|a_n|^2=1$, $a_n=1$, when the unperturbed system is in the stationary state $\psi_n^{(0)}(r,t)$, then all the coefficients $a_k(k\neq n)$ in eq. (2.4..4) are zero.

Now, consider the wave equation of a perturbed system.

$$H(r,t)\psi(r,t)=-\frac{*}{i}\frac{\partial}{\partial t}[\psi(r,t)]$$ ………..(2.4. 6.)

As the Hamiltonian depends on space variables r as well as on time t, the energy cannot be conserved and there can be no stationary states. For solving eq.(2.4.6) by perturbation theory, let us take the Hamiltonian $H^{(r,t)}$ as sum of two terms, the time-independent Hamiltonian $H^0(r)$ of the unperturbed system and a small perturbation $H^1(r,t)$ which depends on space variables r and time t.

Now, the perturbed wave equation is.

$$\left(H^{(0)}+H^{(1)}\right)\psi=-\frac{\hbar}{2\pi i}\frac{\partial\psi}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.4.\ 7)$$

Whose general solution is of the form.

$$\psi(x_1,x_2\ldots\ldots\ldots,t)=\sum a_n(t)\psi_n^{(0)}(x_1,x2\ldots\ldots t)\ldots\ldots(2.4.\ 8)$$

The Coefficients $a_n(t)$ being functions of time t.

Substituting eq. (2.4.8) in eq. (2.4.6) gives

$$\sum a_n(t)H^0\psi_n^{(0)}+\sum a_n(+)H^{(1)}\psi_n^{(0)}$$

$$=-\frac{\hbar}{2\pi i}\sum\psi_n^{(0)}\frac{\partial a_n(t)}{\partial t}-\frac{\hbar}{2\pi i}\sum a_n(t)\frac{\partial\psi_n^{(0)}}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.4.\ 9)$$

Again $H^0\psi_n^{(0)}=-\frac{\hbar}{2\pi i}\frac{\partial\psi_n^{(0)}}{\partial t}$

Hence, we get from (2.4..8)

$$\sum a_n(t)H^{(1)}\psi_n^{(0)}=-\frac{\hbar}{2\pi i}\sum\psi_n^{(0)}\frac{\partial a_n(t)}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots(2.4.\ 10)$$

multiply eq.(2.4.10) by $\psi_m^{(0)^*}$ and integrating over the configuration space. We have

$$\sum_n\int a_n(t)\psi_m^{(0)^*}H^{(1)}\psi_n^{(0)}d\tau=-\frac{\hbar}{2\pi i}.\sum_n.\int\frac{\partial a_n(t)}{\partial t}\psi_m^{(0)^*}\psi_n^{(0)}d\tau$$

$$\therefore\frac{\partial a_m(t)}{\partial t}=a_m(t)=-\frac{2\pi i}{h}\sum_n a_n(t)\int\psi_m^{(0)^*}H^{(1)}\psi_n^{(0)}d\tau \quad \ldots\ldots\ldots\ldots 2..4.11.$$

with m=0,1,2,3,…………..

Thus we obtained a set of first-order differential equations involving the functions $a_m(t)$. At the time t=0 a measurement of energy will lead to a particular value corresponding to one of the stationary states of an unperturbed system because it is only for stationary states that the energy has a definite value. Let this be denoted as $E_l^{(0)}$.

This means at time t=0, the wave equation is represented by $\psi_l^{(0)}$ but not by eq. (2.4. 4)

Hence, at time t=0,

$$\left.\begin{array}{ll} a_l(0)=1, & n=l=m. \\ a_n(0)=0, & n\neq l. \end{array}\right\} \quad \text{……(2.4. 12. .)}$$

or $a_n(0)=\delta_{mn}$

Therefore, we can find solution of eq.(2.4. 11) numerically but physically it cannot be done, as there are infinite equations.

If $H^{(1)}(r,t)$ is small, the rate of change of the Coefficients $\frac{da}{dt}$ is small in the time interval t=0 to t in which it acts and the relation (2.4. 12) is valid throughout this interval. We now solve the equation (2.4.11) by neglecting all terms except with n=l, retaining $a_l^1(t)$ on the right hand side, we have.

$$\frac{da_l(t)}{dt}=-\frac{2\pi i}{\hbar}a_l(t)H_{ll}^{(1)}\text{…………………(2.4. 13)}$$

Where $H_{ll}^{(1)}=\int\psi_l^{(0)^*}H^{(1)}\psi_l^{(0)}d\tau$

Rewriting equation 2.4.13 as

$$\frac{da_l(t)}{a_l(t)}=-\frac{2\pi i}{\hbar}.H_{ll}^{(1)}dt$$

Integrating

$$\int_0^t\frac{da_l(t)}{dt}=-\frac{2\pi i}{\hbar}\int_0^t H_{ll}^{(0)}dt$$

(i.e.) $\log[a_l(t)]=-\frac{2\pi i}{\hbar}H_{ll}^{(1)}t$

or $a_n(t) = \exp\left[-\frac{2\pi i}{\hbar} H_{ll}^{(1)} t\right]$ ……………….(2.4.14).

From eq.(4.1.14), we can understand how the Coefficient a_l changes during the time when the perturbation is acting, during the time, the wave function is

$$a_n(t)\psi_l^{(0)} = \exp\left[-\frac{2\pi i}{\hbar} H_{ll}^{(1)} t\right]\psi_l^{(0)} \quad \text{(from eq. 2.4.8)}$$

$$= \psi_l^{(0)} \exp\left[-\frac{2\pi i}{h}\left(E_l^{(0)} + H_{ll}^{(1)}\right)+\right] \quad \text{(using eq. 2.4.2)} \quad ……(2.4.15)$$

Now, our aim is to consider the remaining set of equation in (2.4. 11) and find the behaviour of the Coefficients $a_m(t)$ with $m \neq l$.

Using the initial value of $a_l(0)=1$, on the R.H.S. of eq.2.4. 11. and neglecting all other a_n's we obtain.

$$\frac{da_m(t)}{dt} = -\frac{2\pi i}{h}\int \psi_m^{(0)^*} H^{(1)} \psi_l^{(0)} d\tau$$

$$= -\frac{2\pi i}{h}\int \psi_m^{(0)^*} \exp\left[+\frac{2\pi i}{h} E_m^{(0)} t\right] H^{(1)} \psi_l^{(0)} \exp\left[-\frac{2\pi i}{h} E_l^{(0)} t\right] d\tau$$

$$\therefore \frac{da_m(t)}{dt} = -\frac{2\pi i}{h} H_{ml}^{(1)} \exp\left[-\frac{2\pi i}{h}\left(E_l^{(0)} - E_m^{(0)}\right)t\right] \quad ………(2.4.\ 16)$$

With $H_{ml}^{(1)} = \int \psi_m^{(0)^*} H^{(1)} \psi_l^{(0)} d\tau$

Let the field act during the time interval t=0 to t in which perturbation $H^{(1)}$ remains constant and it is zero before and after the field applied.

Now, we integrate eq.(2.4. 16) during the interval t from 0 to t.

We have

$$a_m(t) = -\frac{2\pi i}{h}\int_0^t H_{ml}^{(0)} e^{-\frac{2\pi i}{h}}\left(E_l^{(0)} = E_m^{(0)}\right) + dt \quad \text{for } m \neq l.$$

$$= -\frac{2\pi i}{h} H^{(1)}_{ml} \left[\frac{e^{\frac{-2\pi i}{h}\left(E_l^{(0)} - E_m^{(0)} t\right)t}}{-\frac{2\pi i\left(E_l^{(0)} - E_m^{(0)}\right)}{h}} \right]^t$$

$$= H^{(1)}_{ml} \left[\frac{e^{\frac{-2\pi i\left(E_l^{(0)} - E_m^{(0)}\right)t}{h}}}{E_l^{(0)} - E_m^{(0)}} \right]$$

$$= -\frac{H^{(1)}{}_{ml}}{h} \frac{e^{i\omega_{ml} t} - 1}{\omega_{ml}} \quad \text{where } \omega_{ml} = \frac{E_m^{(0)} - E_l^{(0)}}{\hbar}$$

$$\therefore a_m(t) = -\frac{1}{\hbar} H^{(1)}_{ml} \left[\frac{e^{i\omega_{ml} t} - 1}{\omega_{ml}} \right] \quad \text{………………(2.4.17.)}$$

Which is the first order perturbation theory.

Now, we calculate the probability of the particle in the mth state in the following procedure:

$$\text{Probability} = \quad a^*_m(t) a_m(t) = / a_m(t) /^2 \quad \text{……………(2.4. 18.)}$$

$$= \frac{1}{\omega^2{}_{ml}} \left(e^{i\omega_{ml} t} - 1\right)\left(e^{-i\omega_{ml} t} - 1\right) X \, \frac{1}{\hbar^2} | H^{(1)}_{ml} |^2$$

$$\therefore | a_m(t) |^2 = \frac{4}{\omega^2{}_{ml}} \frac{| H^{(1)}_{ml} |^2}{\hbar^2} . Sin^2\left(\omega_{ml} t / 2\right) \quad \text{……………(.2.4. 19)}$$

Let us plot y against x=ω_{ml} as shown in Fig. 2.4.1. It can be observed that the most important contributions to the transition probability come from those final states with energy E_m which are very close to and centered around the initial state of energy E_l. The full width of the curve at half maximum $\frac{\Delta E}{2\pi} \sim \frac{\pi}{\tau}$ (2.4.20)

$$y = \frac{Sin^2(\omega_{mlt} / 2)}{\omega^2{}_{ml}}$$

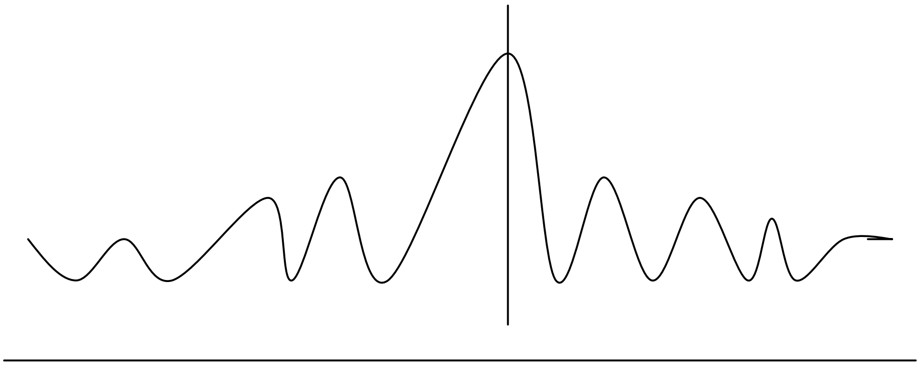

Fig. 2.4.1

If we interpret ΔE as the uncertain by in energy and Δt(τ) is the certainty in time 't', the equation (2.4.20) then implies that

ΔE Δt ~ 2πħ

This can be explained more clearly as below: for maximum value of Y we get.

$$\frac{Sin^2\left(\omega_{ml}\ t/2\right)}{\omega^2 ml} = \frac{1}{\omega^2 ml}\left[\left(\frac{\omega_{ml}t}{2}\right)-\left(\frac{\omega_{ml}t}{2}\right)^3\frac{1}{3!}+\left(\frac{\omega_{ml}t}{2}\right)^5\frac{1}{5!}-+-------\right]^2$$

$$= \frac{1}{(\omega_{ml})^2}.\left(\frac{\omega_{ml}t}{2}\right)^2$$ neglecting higher powers of t.

$$= \frac{t^2}{4}$$

The highest peak value is $\frac{t^2}{4}$, which can be easily observed from the Fig. (2.4.1).

The peak values we get, when Y is zero.

(ie.) $\frac{Sin^2\left(\omega_{ml}\ t/2\right)}{\omega^2 ml} = 0$

(ie.) $\omega_{ml} = \pm\frac{2\pi n}{t}$ where n=0, 1,2,3,---------

This means the height of the peak values is proportional to t^2 and its width decreases inversely as t. Since the area under the curve is proportional to t, the probability of time during the system in one or another states is proportional to t, which implies the probability per unit time.

Transition to the Continuum

We have so far considered transition between states and m and l. We shall now consider transitions from a discrete state m to a continuum of states around E_l, where the densities of state are ρ(m). When the final states are densely packed forming a continuum, we can replace the summation by an integral. In order to obtain the explicit expression for transition probability, let us assume that the system is enclosed in a cubical box. The stationary states of the system are discrete, but separated in energy by an interval, which is inversely proportional to the volume of the box.

If we consider a box of infinite size, the levels with in the energy interval increases and merge into a continuum.

Now the transition probability for mth state is given as.

$$T = |a_m(t)|^2 = |H_{ml}^{(1)}|^2 \frac{4.Sin^2(\omega_{ml}t/2)}{\hbar^2\omega^2{}_{ml}}$$

In this, the probability is largest for the states whose unperturbed energy $E_m^{(0)}$ is close to $E_l^{(0)}$. As the levels are closer, they form a cluster around $E_m^{(0)} - E_l^{(0)}$ and all the levels in the cluster nearly represent the same physical properties. Summing all levels in the cluster and we get the total transition.

Probability (i.e.) $\sum|a_m(t)|^2$

(i.e.) $\sum|a_m(t)|^2 = \int|a_m(t)|\rho(m)dE$

Where ρ(m) is the density of final states and ρ(m)dE is the number of such states in the range dE.

Instead of considering transition to a particular state, we may consider transition to group of states of nearly equal energies. The probability of transition per unit time is now obtained, by considering the central peak of $\frac{4Sin^2(\omega_{ml}t/2)}{\omega^2{}_{ml}}$ as the domain of integration in the interval (-∞,∞)

$$\therefore P(t) = \frac{1}{\hbar^2} |H_{ml}^{(1)}|^2 \ \rho(m) \int_{-\infty}^{\infty} \frac{4.Sin^2(\omega_{ml}t/2)}{\omega^2{}_{ml}} dE$$

$$\because E = \hbar\omega, dE = \hbar d\omega$$

$$\text{p(t)}=\frac{1}{\hbar} |H_{ml}^{(1)}|^2 \ \rho_m \int_{-\infty}^{-\infty} \frac{4Sin^2(\omega_{ml}t/2)}{\omega^2{}_{ml}} d\omega$$

on integration, we get.

$$\text{P(t)}=\frac{1}{\hbar} |H_{ml}^{(1)}|^2 \ \rho(m).2\pi t$$

Transition per unit time is

$$\text{T} = \frac{2\pi}{\hbar} |H_{ml}^{(1)}|^2 \ \rho(m)$$

Which has wide application in quantum mechanics.

This is known as **Fermi's Golden Rule**. It may be concluded that the transition probability per unit time$^{(i)}$

i) is proportional to $|H_{ml}^{(1)}|^2$.

ii) Is proportional to ρ(m) density states.

iii) Is non-zero only between continuum states of the equal energy.

Einstein transition probabilities

Spontaneous emission, absorption and induced emission of radiation were satisfactorily given by Direc. In this we discuss the Einstein Coefficients of emission and absorption of radiation.

The transition taking place from a non-degenerate stationary state of energy E_k to another degenerate stationary state $E_l(E_k>E_l)$ causing an emission or absorption of radiation of frequency, is given, according to Bohr's frequency rules, as

$$\vartheta_{kl} = \frac{E_k - E_l}{\hbar} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.4.20)$$

The probability that a system in the lower energy state absorb a quantum of radiation energy and goes to the higher state in unit time is.

$$B_{l->k}\,\rho(\vartheta_{kl})$$

$B_{n\to m}$ is known as Einstein's Coefficient of absorption . Let N_l atoms are present in a state at any instant of time then number of transition per second is

$$N_l\,B_{l\to k}\,p(\vartheta_{kl})$$

The probability of emission consists of two parts (i.e.) one part independent of the radiation density and the other proportional to the density.

Since the transition from the upper state to lower state energy causes emission of radiation of energy is.

$$A_{k\to l} + B_{k\to l}\,p(\vartheta_{lk})$$

in which $A_{k->l}$ is the Einstein Coefficient of spontaneous emission $B_{K->l}$ is the Einstein Coefficient of induced emission.

Now, let the number of atoms in this state is denoted by N_k then the number of reverse transition is.

$$N_k\left[A_{k->l} + B_{k\to l}\,p(\vartheta_{kl}\right]$$

The emission and absorption must be equal at the thermal equilibrium.

$$N_l\,B_{l->k}p(\vartheta_{kl}) = N_k\left[A_{k->l} + B_{k->l}\,p(\vartheta_{kl})\right]$$

or $$\frac{N_l}{N_k} = \frac{A_{k->l} + B_{k->l}\,\rho(\vartheta_{kl})}{B_{l->k}\,\rho(\vartheta_{kl})} \qquad (2.4.21)$$

From quantum statistical mechanics.

$$\frac{N_l}{N_k} = -(E_l - E_k)\,|\,KT = e^{h\vartheta kl|KT} \qquad (\ 2.4.22)$$

Equating (2.4.21) and (2.4.22), we get

$$e^{h\vartheta kl|KT} = \frac{[A_{k->l} + B_{k->l}\, p(\vartheta_{kl})]}{B_{l->k}\, p(\vartheta_{Kl})}$$

or $B_{l->k}\, p(\vartheta_{Kl}) e^{\hbar^2}\ Kl\,/\,KT - B_{K->l}\, p(\vartheta_{kl}) = A_{K->l}$

or $\rho(\vartheta_{kl}) = \dfrac{A_{k->l}}{B_{l->k} e^{\hbar\vartheta kl|Kt} - B_{K->l}}$

The radiation energy, according to Planck's law, is

$$\rho(v) = \frac{8\prod h\vartheta^3}{C^3} \cdot \frac{1}{[ex(-h\vartheta\,/\,Kt) - 1]}$$

Hence Einstein Coefficients are related by

$B_{n->m} = B_{m->n}$

and $A_{l\to k} = \dfrac{8\pi h\vartheta_{kl}^3}{C^3} ....B_{l\to k}$

Adiabatic Approximation

In the adiabatic case, we expect on physical grounds that solutions of the Schrodinger equation can be approximated by means of stationary eigenfunctions of the instantaneous Hamiltonian, so that a particular eigenfunction at one time goes over continuously into corresponding eigenfunction at a later time.

If the equation

$$H(t)\phi_n(t) = E_n(t)\phi_n(t)$$

can be solved at any time we assume that a system that is discrete non-degenerate state $\psi_m^{(0)}$ with energy $E_m^{(0)}$ at t=(0) is likely to be in the state $\phi_n^{(t)}$ with energy $E_n^{(t)}$ at time t, provided that H(t) varies very slowly with time.

The wave function ψ obeys the time-dependent schrodinger equation.

$$i\hbar\frac{\partial\psi}{\partial t} = H(t)\psi$$

$$\psi = \sum_l a_l(t)\phi_l(t)\exp\left[\frac{1}{i\hbar}\int_0^t E_l(t^{'})dt^{'}\right]$$

Then $\sum_l l\hbar[a_l\phi_l + a_1\phi_l]\left[\exp\frac{1}{l\hbar}\int_0^t E_l(t^{'})dt^{'}\right] = 0$

Multiplying by ϕ_ψ we has

$$\sum_l [\partial_l < \phi_n | \phi_l > + a_l < \phi_n | \phi_l >]\exp\left[\frac{1}{l\hbar}\int_0^t E_l(t^{'}) - E_n(t^{'})dt^{'}\right] = 0$$

or $\partial_n = -\sum a_t < \phi_n | \phi_l > \exp\left[\frac{1}{l\hbar}\int_0^t E_l(t^{'}) - E_n^{\left(1^{'}\right)}dt^{'}\right]$

To evaluate $<\phi_n|\phi_l>$, we have

$$\frac{\partial H}{\partial t}\phi_l + H\phi_l = E_{l\phi l} + E_{l\phi l}$$

or $\left\langle \phi_n | \frac{\partial H}{\partial t} | \phi_l \right\rangle + E_n\langle \phi_n | \phi_l \rangle = E_l\langle \phi_n | \phi_l \rangle = E_l\langle \phi_n | \phi_l \rangle$

or $\langle \phi_n | \phi_l \rangle = \dfrac{\left\langle \phi_n | \frac{\partial H}{\partial t} | \phi_l \right\rangle}{E_l - E_n}$

To find $<\phi_n|\phi_n>$, on differentiating $<\phi_n|\phi_n>=1$ w.r.t. time.

A Charged Particle in an Electromagnetic Field

In order to apply the time-dependent perturbation theory to the charged particle, the effect of electric and magnetic fields on the particle must be investigated.

The electromagnetic force on a particle of charge e, and mass m moving with velocity v in an electromagnetic field characterised by electric field E and magnetic field B (or scalar potential ϕ and vector potential A) is

$$F = cE + e\frac{vxB}{c}$$

c being speed of electromagnetic waves.

$<\phi_n|\phi_n>+<\phi_n|\phi_n>=0$

$<\phi_n|\phi_n>=i\alpha(t)$, $\alpha \rightarrow$ real.

For new eigen function $\phi_n^{'} = \phi_n e^{tr(.)}$.

We have $<\phi_n^{'}|\phi_n>=I(\alpha+\gamma)$.

Choosing γ suitably, we can make this vanish. Hence

$$\partial_n = \sum_l{}^{'} \frac{a_l}{\hbar_{\omega_{nn}}} \left\langle \phi_n \,|\, \frac{\partial H}{\partial t} \,|\, \phi_l \right\rangle \exp\left[i\int_0^t \omega_{nl}(l^{'})dt^{'} \right]$$

Let the System be initially at state m and the time variation is small: thus

$$\partial_n \approx \frac{1}{\hbar_{\omega_{nn}}} \left\langle \phi_n \,|\, \frac{\partial \omega}{\partial t} \,|\, \phi_m \right\rangle e^{i\omega_{mn} t} \;; n \neq m$$

$$\partial_n(t) \approx \frac{1}{\hbar_{\omega_{nn}}} \left\langle \phi_n \,|\, \frac{\partial \omega}{\partial t} \,|\, \phi_m \right\rangle e^{i\omega_{mn} t} - l.$$

With the above approximation this equation shows that the probability amplitude for a state other than the initial states oscillates in time and show no steady increase over long periods of time even though H changes by a finite amount.

Sudden Approximation

The sudden approximation consists of the change in Hamiltonian discontinuous on different times.

Suppose that $H=H_0$ for $t < 0$

and $H=H_1$ for $t > 0$

Then $H_0 u_n = E_n^0 \vartheta_n$ for $t < 0$

$H_0 u_n = E_n \vartheta_n$ for $t > 0$

$$\psi = \sum_e a_n u_n e^{-iE_n} \, {}^{1}\!/_{\hbar}$$

and
$$\psi = \sum_e a_t u_t e^{-iE_n} \, {}^{1}\!/_{\hbar}$$

Equating the two solutions at t(0)=0.

$$b_t = \sum_e a_n < u_e \,|\, u_n >$$

The sudden approximation consists in using above equation when the change in the Hamiltonian occupies a very short finite interval of time t_0. Suppose that

$H=H_0$ for $t < 0$,

$H=H_1$ for $t > 0$

and $H=H_1$ for $0 < t < t_0$.

The intermediate Hamiltonian H_l which is taken constant in time, has a complete set of energy eigen functions:

$H_l W_k = E_k W_k$

The exact solution can be expanded in terms of the u's with constant coefficients.

$$\psi = \sum_k C_k W_k \exp\left(-iE_k \, {}^{t}\!/_{\hbar}\right), \mathit{for} \, 0 < t < t_0$$

Application of the continuity condition at t=0 gives

$$C_k = \sum_n a_n < W_k | W_n >= \sum_n a_{n<k|n>}$$

and at t=t_0 gives

$$b_t = \sum_k C_k \langle \mu | k \rangle \exp\{-i(E_k - E_\mu) t_\alpha / \hbar\}$$

$$= \sum_n a_n \langle \mu | k \rangle \exp\{-i(E_k - E_t) t_{0/\hbar}\} < k | n >$$

When t_0=0, the exponential is equal to unity and b_e is given by (1).

The sudden approximation will be best only when t_2 is small. So on expansion exponential term in above equation.

$$a_\beta \approx \Sigma a_n \sum_n \langle \mu | k \rangle \left[1 - \frac{it_0}{\hbar}(E_k - E_t)\right] \langle k | n \rangle$$

or $$a_t \approx \sum a_n \left\langle \mu | \left[\frac{it_0}{\hbar}(H_l - H_l)\right] | n \right\rangle$$

Thus error in sudden approximation is proportional to t_0 for small t_0. If H_1 depends upon time, then $\int_0^{0} H_1 dt$ can be taken in place of $H_1 t_0$.

If H_1=H_0 then

$$b_t = \partial_{km} \frac{it_0}{\hbar} \langle k | H_i - H_0 | m \rangle$$

This can be used even when (h-H_0) is not small as compared to H_0 taking t_0 small.

Self Assessment Questions

1. Outline the theory of time-dependent perturbation theory.
2. State and probe Fermi-Goden rule for the rate of transitions induced by a constant Perturbation.
3. Calculate the transition probability per unit time and per unit of radiation. Evaluate the Einstein's Coefficients for spontaneous emission.
4. Write notes on (i) Adiabatic approximation. (ii) Sudden approximation.

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UNIT – 3

LESSON -X - Algebra of Angular Momentum

Objective of the Lesson

In this lesson, the quantum mechanical definition of the angular momentum., its operator form is given in the beginning. The components of angular momentum and the commutation relations between

$[L_i, r_i]$, $[L_i, p_i]$, $[L_i, L_j]$ have been worked out.

3.1.1 Introduction

Angular momentum (which is described as an operator) plays a much importance role in quantum mechanics than in classical mechanics (where it is described as a dynamical variable). This is probably due to greater importance of periodic motions in quantum mechanics. A periodic motion can be understood as a motion in a closed orbit, which involves angular momentum. The existence of the intrinsic angular momentum (spin angular momentum) could also be another reason and another most importance reason is that the angular momentum is quantized which is not the case with the linear momentum.

Whenever a conservation law holds good for a physical quantum system, the Hamiltonian of the system is invariant under the corresponding group of transformations. The converse of this statement is not true as even if the system has a Hamiltonian, which is invariant under a group of transformations, there may nor be a corresponding conservation law. Wigner showed that all symmetry transformations of quantum mechanical states can be chosen so as to correspond to either unitary orantiunitary operators. It is unitary transformations, it has other consequences which may be tested by the experiments.

The present chapter is devoted to symmetries with respect to rotations , which is reflected in the angular momentum vector operator (not an ordinary vector as in classical mechanics) has been defined by the commutation rules for its components, the orbital angular momentum and spin angular momentum of particle have been constructed , their eigen values and eigen functions have been obtained and the connection between rotations and angular momentum has been established.

This entire unit is divided in to five parts: i) Deals with the preliminaries of the angular momentum, commutator algebra etc.; ii) The eigen value problem of orbital angular momentum is described in detail; iii) In this the spin angular momentum, the pauli spin matrices and their properties have been discussed; .iv) In this lesson the emphasize is given to the eigen value problem of total angular momentum J. v) The last part of the unit consist of the addition of angular momenta associated with different physical systems and related numerical problems

3.1.2Angular Momentum operator

Central forces are derivable from a potential that depends only on the distance r of the moving particle from a fixed point, usually the coordinate origin. The Hamiltonian operator is

$$H = \frac{P^2}{2m} + V(r) = \frac{\hbar^2}{2m}\nabla^2 + V(r)$$

Since central forces produce no torque about the origin, the orbital angular momentum

L = **r** x **p**

Is conserved. In classical mechanics this is the statement of Keplar’s second law.

According to the correspondence principle, we must expect angular momentum to play an equally essential role in quantum mechanics. The operator that represents angular momentum in the coordinate representation is obtained from L = r x p by replacing **p** by ($\hbar$/i) ∇ :

L= **r** x ($\hbar$/i) ∇

Where **r** = $x\hat{i} + y\hat{j} + z\hat{k}$

and p, the linear momentum operator = $p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$ =

$$\text{Hence } L = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= i(yp_z - zp_y) + j(zp_x - xp_z) + k(xp_y - yp_x)$$

The three components of operator L, can therefore be written as,

$$L_x = (yp_z - zp_y)$$

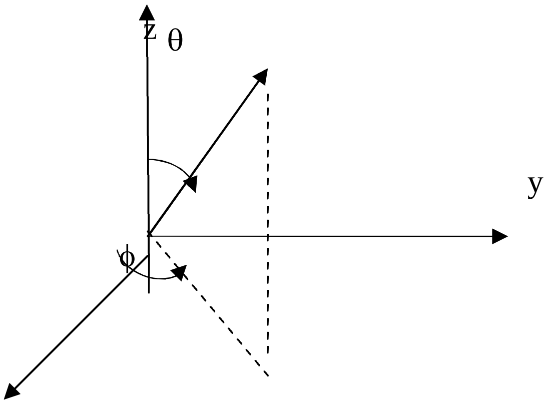
$$= -i\hbar\left(y\frac{\partial}{\partial x} - z\frac{\partial}{\partial y} \right)$$

$$L_y = (zp_x - xp_z)$$

$$= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)$$

$$L_z = (xp_y - yp_x)$$

$$= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$



$x = r\sin\theta \cos\phi$;

$y = r\sin\theta \sin\phi$;

$z = r\cos\theta$

Fig. 3.1.1 the axes along which three components of the angular momentum are resolved

3.1.2 The three components of orbital angular momentum in spherical polar coordinates

$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)$

$L_y = -i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$

$L_z = -i\hbar\frac{\partial}{\partial\phi}$

And $L^2 = L_x^2 + L_y^2 + L_z^2$

On substituting the values of L_x , L_y and L_z

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

3.1.3 Commutation algebra of the angular momentum operator

a) with position operators

(i) $[L_x, x] = [(yp_z - zp_y), x] = 0;$

$[L_x, y] = [(yp_z - zp_y), y]$

$= [yp_z, y] - [zp_y, y] = i\hbar z$

and

$[L_x, z] = -i\hbar y$

Similarly

ii) $[L_y, x] = [(zp_x - xp_z), x]$

$= z(p_x, x) = -i\hbar z; \quad [L_y, y] = 0$

and

$[L_y, z] = i\hbar x$

iii) $[L_z, x] = i\hbar y;$

$[L_z, y] = -i\hbar x;$

$[L_z, z]=0$

in these equations the value of the Heisenberg commutator

$[r_i, p_j] = 0$ if $i \neq j$

$= i\hbar$ if $i = j$

has been used

b) with linear momentum operators

i) $[L_x, P_x] = 0;$

$[L_x, P_y] = [(yp_z - zp_y), p_y]$

$= (yp_z, p_y) - (zp_y, p_y)$

$= [y, p_y]\, p_z$

$= i\hbar p_x$

and $[L_x, p_z] = [yp_z, p_z] - [zp_y, p_z]$

$= -i\hbar p_y$

ii) $[L_y, P_x] = -i\hbar p_z;$

$[L_y, P_y] = 0$

and $[L_y, p_z] = i\hbar p_x,$

iii) $[L_z, P_x] = i\hbar p_y,$

$[L_z, P_y] = -i\hbar p_x$

and $[L_z, P_z] = 0;$

c) with angular momentum operators

i) $[L_x, L_y] = [(yp_z - zp_y), (zp_x - xp_z)]$

$= (yp_z, zp_x) - (zp_y, xp_z)$

$= y(p_z,z)\, p_y - x(z,p_z)\, p_y$

$= -i\hbar y p_x + i\hbar x p_y$

$= i\hbar(x p_y - y p_x)$

$= i\hbar L_z$

Similarly

$[L_y, L_z] = i\hbar L_x$

and $[L_z, L_x] = i\hbar L_y$

combining the three relations we have

$$\Rightarrow \boxed{L \times L = i\hbar L}$$

$$= \begin{vmatrix} i & j & k \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix}$$

$= i[L_y,L_z] + j[L_z,L_x] + k[L_x,L_y] = i\hbar L$

(d) $[L^2, L_i] = [L^2_x + L^2_y + L^2_z, L_x]$

$= [L^2_x, L_x] + [L^2_y, L_y] + [L^2_z, L_z]$

$= [L_y L_y, L_x] + [L_z L_z, L_x]$ (Since $[L^2_x, Lx] = 0$)

$= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$

$= L_y[i\hbar L_z] + (-i\hbar L_z L_y) + L_z(i\hbar L_y) + i\hbar L_y L_z$

$= 0$

Thus the components of the angular momentum operator do not commute among themselves through they commute with the square of the angular momentum operator. As will be shown, the commutation relations, $[L_i, L_j] = i\hbar \in_{ijk} L_k$., determine the quantal properties of the angular momentum . That is the eigen values and the eigen vectors of the angular momentum operator are completely determined by above commutator and the general properties of the Hilbert space. Therefore, the commutation relations themselves are taken for the definition of the angular momentum operator in quantum mechanics.

3.1.4 The angular momentum operator commutes with Hamiltonian operator(H)

H = K.E+ P.E

= T+V

$$T = \frac{P^2}{2m} = \frac{L^2}{2mr^2}$$

$$L^2 = r^2 p^2 + \hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right)$$

Hence $T = \frac{L^2}{2mr^2} - \frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right)$

Or [L, T] = 0 since $[L^2, L] = 0$

And [L, V] = 0

Hence [L, T+V] = [L, H] = 0

Thus the operator L commutes with H. For this reason the operator L is also known as constant of motion

Summary of the lesson

The angular momentum definition and its three components are given in detail. The three components of angular momenta are also described in spherical polar coordinates. The commutation relations of angular momentum with the position operators, with the components of the linear momentum are worked out. The values of the commutator between angular momenta components in pairs have also been obtained and it is also shown that the commutator $[L^2, L_i]=0$ for any value of i.

Key terminology

Angular momentum, Components of the angular momentum, commutation relations,

Self Assessment questions

1. Define the angular momentum operator
2. Write the three components of the angular momentum operator in Cartesian and spherical polar coordinates
3. Obtain the commutation relations
    a) the components of the angular momentum. and position coordinates
    b) components of the angular momentum and the components of linear momentum
    c) between the components of the angular momentum in pairs

4. Show that LXL = iђL

5. Prove that the operator L^2 commutes with any component of the angular momentum operator

6. Show that the orbital angular momentum operator is a constant of motion.

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UNIT – 3

LESSON – XI - Eigen Value Problem Of Orbital Angular Momentum

Objective of the lesson

In this lesson the eigen value problem of the operators L_z and L^2 are discussed. The problem consist of writing the two operators in spherical polar coordinates, their eigen functions and evaluation of their eigen values

3.2.1 Problem of L_z

Consider

$L_z = xp_y - yp_x$

$$= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \text{-----------(3.2.1)}$$

$$\frac{\partial}{\partial y} = \frac{\partial}{\partial r}.\frac{\partial r}{\partial y} + \frac{\partial}{\partial \theta}.\frac{\partial \theta}{\partial y} + \frac{\partial}{\partial \phi}.\frac{\partial \phi}{\partial y} \text{-----------------(3.2.2)}$$

Similarly

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}.\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}.\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \phi}.\frac{\partial \phi}{\partial x} \text{--------------------(3.2.3)}$$

In spherical polar coordinates

$x = r \sin\theta \cos\phi$;

$y = r \sin\theta \sin\phi$;

$z = r \cos\theta$

$r = \sqrt{x^2 + y^2 + z^2}$;

$\tan\Phi = y/x$;

Tanθ = $\sqrt{x^2+y^2}$ /z

$$\frac{\partial r}{\partial y} = \frac{y}{r};$$

$$\frac{\partial \theta}{\partial y}.\sec^2\theta = \frac{2y}{2z\sqrt{x^2+y^2}}$$

Tan Φ = y/x

$$\frac{\partial \theta}{\partial y} = \frac{y}{z\sec^2\theta\sqrt{x^2+y^2}} \text{ -----(3.2.4)}$$

$$\frac{\partial \phi}{\partial y} = \frac{1}{x\sec^2\phi}$$

Similarly

$$\frac{\partial \theta}{\partial x} = \frac{x}{z\sec^2\theta.\sqrt{x^2+y^2}} \quad ; \quad \frac{\partial \phi}{\partial x} = \frac{-y}{x^2\sec^2\phi} \quad ; \quad \frac{\partial r}{\partial x} = \frac{x}{r} \text{ ;------------(3.2.5)}$$

Substituting (3.2.4) in (3.2.2), we get

$$x\frac{\partial}{\partial y} = \frac{\partial}{\partial r}.\frac{xy}{r} + \frac{xy}{z\sec^2\theta.\sqrt{x^2+y^2}.}.\frac{\partial}{\partial \theta} + \frac{x}{x\sec^2\phi}.\frac{\partial}{\partial \phi} \text{ ------------} \qquad (3.2.6)$$

and

$$y.\frac{\partial}{\partial x} = \frac{xy}{r}.\frac{\partial}{\partial r} + \frac{xy}{z\sec 2\theta\sqrt{x2+y2}}\frac{\partial}{\partial \theta} - \frac{y2}{x2\sec 2\phi}.\frac{\partial}{\partial \phi} \text{ -------} \qquad \text{-(3.2.7)}$$

then eqn (3.2.1) becomes

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= -i\hbar\left(\frac{1}{\sec^2\phi} + \frac{y^2}{x^2\sec^2\phi}\right)\frac{\partial}{\partial \phi}$$

$$= -i\hbar\left(1+\frac{y^2}{x^2}\right)\frac{1}{\sec^2\phi}.\frac{\partial}{\partial\phi}$$

$$= -i\hbar\frac{\partial}{\partial\phi} \qquad \left(\because \sec^2\phi = 1+\frac{y^2}{x^2}\right)$$

$$\therefore \quad L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$\therefore$

Eigen value and Eigen function of L_z

Let the operator L_z acts on the ϕ, gives the eigen value m.

$$L_z\Phi = m\Phi$$

$$-i\hbar\frac{\partial\Phi}{\partial\phi} = m\Phi \Rightarrow \frac{d\Phi}{\Phi} = \frac{i}{\hbar}\text{m}$$

$$\Phi = \Phi o\exp\left(\frac{i}{\hbar}m\phi\right)$$

Φ is the eigen function of L_z

In one complete rotation ϕ changes to (ϕ +2π) or n complete revolutions. It will be ($\phi + 2\pi n$). During this process, the wave function remains unchanged.

i.e., $\Phi\left(\phi + 2\pi n\right) = \Phi_0 \exp(\frac{im}{\hbar}\left(\phi + 2\pi n\right)$

From this $\frac{mn}{\hbar}$ is an integer, if n=1, $\frac{mn}{\hbar} = \frac{m}{\hbar}$ in one revolution; So on can take only inter times $\hbar$ values.

3.2.2 Problem of L^2

$L^2 = L^2_x + L^2_y + L^2_z$

Consider $L_x = y\,p_z - z\,p_y$

$$= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$L^2_x = -\hbar^2\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$L^2_x = -\hbar^2\left[y^2\frac{\partial^2}{\partial z^2} + z^2\frac{\partial^2}{\partial y^2} - 2yz\frac{\partial^2}{\partial y\partial z} - y\frac{\partial}{\partial y} - z\frac{\partial}{\partial z}\right]$$

Similarly

$$L^2{}_y = -\hbar^2\left[z^2\frac{\partial^2}{\partial x^2} + x^2\frac{\partial^2}{\partial z^2} - 2zx\frac{\partial^2}{\partial z\partial x} - x\frac{\partial}{\partial x} - z\frac{\partial}{\partial z}\right]$$

$$L^2_z = -\hbar^2\left[y^2\frac{\partial^2}{\partial x^2} + x^2\frac{\partial^2}{\partial y^2} - 2xy\frac{\partial^2}{\partial x\partial y} - y\frac{\partial}{\partial y} - x\frac{\partial}{\partial x}\right]$$

Then

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$= \left[\left(y^2+z^2\right)\frac{\partial^2}{\partial x^2} + \left(x^2+z^2\right)\frac{\partial^2}{\partial y^2} + \left(x^2+y^2\right)\frac{\partial^2}{\partial z^2} - 2x\frac{\partial}{\partial x} - 2y\frac{\partial}{\partial y} - 2z\frac{\partial}{\partial z} - 2xy\frac{\partial^2}{\partial x\partial y} - 2yz\frac{\partial^2}{\partial y\partial z} - 2zx\frac{\partial^2}{\partial z\partial x}\right]$$

$$= -\hbar^2\left[r^2\nabla^2 - r\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)\right]$$

$$= -\hbar^2\left[r^2\nabla^2 - r^2\frac{\partial^2}{\partial r^2} - 2r\frac{\partial}{\partial r}\right]$$

but the value of Laplacian operator ∇^2 in terms of spherical polar coordinates is given by

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

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

Hence, $$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Let $Y_l^m(\theta,\phi)$ is the eigen function for the operator L^2 then L^2 Y=c Y is the eigen value equation. Then

$$\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + c\,Y = 0$$

Let $Y^l_m(\theta,\phi) = \eta(\theta)\xi(\phi)$

is the solution of the above equation . By applying variable and separable method, the above equation can be divided in two separate equations

Multiplying with $\sin^2\theta$ on both sides, the above equation becomes ,

$$\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + c\sin^2\theta Y + \frac{\partial Y^2}{\partial\phi^2} = 0$$

Separating the two variables

$$\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + c\sin^2\theta Y = -\frac{\partial Y^2}{\partial\phi^2} = m^2(say)$$

$$\frac{\partial Y^2}{\partial\phi^2} + m^2\theta = 0$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + (c - \frac{m^2}{\sin^2\theta})Y = 0$$

then solution of the I of above two equations is

$$\xi(\theta) = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

The second is associated Legendre polynomial if C=ℓ (ℓ+1)

And hence its solution is

$$\eta(\theta)=\sqrt{\frac{(2l+1)(l-|m\ ||}{2(l+m)|}}P^{m}{}_{l}\left(\cos\theta\right)$$

Therefore eigen value equation for L^2 is

$$L^2\ Y_m^l\ \left(\theta,\phi\right)=\ell l(\ell+1)\hbar^2\ Y_m^l\ \left(\theta,\phi\right)\left(\theta,\phi\right)$$

The eigen value of the operator L^2 is ℓ (ℓ+1) and the eigen function for L^2 is

$$Y_m^l\ \left(\theta,\phi\right)=\sqrt{\frac{(2l+1)(l-|m\ |)}{4\pi(l+m)}}P_l^m\left(\cos\theta\right)\exp(im\phi)$$

thus from the above equation the eigen value equations for the two operators are represented by

$$L_z y_l^m=\frac{\hbar}{i}\frac{\partial Y_l^m}{\partial\phi}=m\hbar y_l^m$$

$$L^2 y_l^m=\frac{\hbar}{i}\frac{\partial Y_l^m}{\partial\phi}=l(l+1)\hbar^2 y_l^m$$

The first few spherical harmonics are listed below:

$$Y_0^0\ =\ \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0\ =\sqrt{\frac{3}{4\pi}}\cos\ \theta\ =\sqrt{\frac{3}{4\pi}}\frac{z}{r}$$

$$Y_1^{\pm1}=\mp\sqrt{\frac{3}{8\pi}}e^{\pm i\phi}\sin\theta=\mp\sqrt{\frac{3}{8\pi}}\frac{x\pm iy}{r}$$

$$Y_2^0=\mp\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)=\mp\sqrt{\frac{5}{16\pi}}\frac{2z^2-x^2-y^2}{r^2}$$

$$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \cos\theta \sin\theta = \mp\sqrt{\frac{15}{8\pi}}\,\frac{(x \pm iy)z}{r^2}$$

$$Y_2^{\pm 2} = \mp\sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} \sin^2\theta = \mp\sqrt{\frac{15}{32\pi}}\,\frac{(x \pm iy)^2}{r^2}$$

Under a coordinate reflection, or inversion, through the origin, which is realized by the transformation φ ⟶ φ+π φ ⟶ π -θ, the azimuthal wave function $e^{im\theta}$ is multiplied by $(-1)^m$, and $P_l^m(\cos\theta)$ by $(-1)^{l+m}$, hence , $Y_m^l(\theta,\phi)$ is multiplied by$(-1)^l$, when r is changed to –r.

The spherical harmonics are thus eigen functions of the parity operator Up which changes r in to –r.

$$\mathrm{Up}\,\psi(r) = \psi(-r)$$

$$\mathrm{Up}\,Y_l^m(\theta,\phi) = (-1)^l\, Y_l^m(\theta,\phi)$$

i.e., Y_l^m has definite parity in consonance with the parity of angular momentum quantum number ℓ.

The spherical harmonics form an orthonormal set since

$$\int_0^{2\pi}\int_0^{\pi} \mathrm{Y}^{\mathrm{l}}_{\mathrm{m}}(\theta,\phi)^*\, \mathrm{Y}^{\mathrm{l}^{\mathrm{i}}}_{\mathrm{m}^{1}}(\theta,\phi) \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi = \delta_{\ell\ell^1}\delta_{\mathrm{mm}^1}$$

We may now define two new operators:

$L_+ = L_x + iL_y$,

$L^- = L_x - iL_y$

Which can be written in terms of spherical polar coordinates as

$$L_+ = \hbar e^{i\theta}\left(\frac{\partial}{\partial\theta} + i\cot\theta\,\frac{\partial}{\partial\theta}\right)$$

$$L_- = -\hbar e^{-i\theta}\left(\frac{\partial}{\partial\theta} - i\cot\theta\,\frac{\partial}{\partial\theta}\right)$$

The eigen value equations for these two operators are

$$L_+\, Y_l^m(\theta,\phi) = \hbar\sqrt{(\ell-m)(\ell+m+1)}\,Y_l^{m+1}(\theta,\phi)$$

$$L^-\, Y_l^m(\theta,\phi) = \hbar\sqrt{(\ell-m)(\ell-m+1)}\,Y_l^{m-1}(\theta,\phi)$$

The operators L_+ and L^- are in fact raising and lowering operators for the magnetic quantum number.

Summary of the Lesson

The summary of the problem of the orbital angular momentum can be written as follows:

Quantity	Operator form	Eigen function	Eigen value
L_z	$-i\hbar\frac{\partial}{\partial\phi}$	$\xi(\theta)=\frac{1}{\sqrt{2\pi}}\exp(im\phi)$	$m\hbar$
L^2	$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$	$\eta(\theta)=\sqrt{\frac{(2l+1)(l-\lvert m\;\rvert\lvert)}{2(l+m)\lvert}}P^{m}{}_{l}(\cos\theta)$	$l(l+1)\hbar^2$

Further the two new angular momentum operators L_+ and L_- (which are identified as raising and lowering operators) are defined and their eigen value equations also given

Key terminology

The operators L^2, L_z, raising and lowering operators, orthogonality of spherical harmonics

Self assessment questions

Derive the eigen value and eigen function of the operator L_z

1. Derive the eigen value and eigen function of the operator L^2
2. Derive the expression for the kinetic energy in terms of the operator L^2
3. Define the operators and write down its eigen value equation

Reference books

1. Advanced Quantum Mechanics – B. S. Rajput (Pragati Prakasan, Meerut 1990)
2. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
3. Introduction to Quantum Mechanics – Mathews P T (Mc Graw Hill Book Co., New York).

4. Quantum Mechanics by V. K. Thankappan (Wiley Eastern. Ltd, New Delhi,1986

UNIT - 3

LESSON – XII - The Spin Angular Momentum

Objective of the lesson

In this lesson the intrinsic angular momentum or spin angular momentum of the particles is discussed. The components of the spin angular momentum along the three coordinate axes are defined in terms of Pauli's spin operator. The matrix form of the operators are derived and their properties are discussed in detail

3.3.1 The Spin Angular Momentum

Definition In 1920, it was found that orbital quantum properties are unable to explain some observed troubled features, which were observed in the spectra of alkali halides. The spectral lines of alkali like atoms appears doublets which could not be explained by the wave function which is a function of orbital angular momentum alone. The true explanation of the doublet structure of the terms of alkali halides is explained by introducing the concept of electron spin. Spin (S) is a vector quantity, with the dimensions of angular momentum. Stern and Gerlach experiment later verified its existence experimentally. The total angular momentum is a sum of orbital angular momentum and the spin of electron.

i.e. $\bar{J} = \bar{L} + \bar{S}$

The characteristic values of the component of the spin in any prescribed direction are $\frac{\hbar}{2} \& -\frac{\hbar}{2}$. The spin is measured in the units of $\hbar$ and the characteristic values are reformed to as 1/2 and –1/2 . Now we will see the interpretation of the theory of spin of the electron given by Pauli.

As we have said already, the spin of the electron is represented by the $\bar{S}$ and besides this let us introduce an operator σ (known as Pauli's spin operator) such that

$$\bar{S} = \frac{\hbar}{2}\sigma \text{ -------------(3.3.1)}$$

Spin of the electron is also angular momentum as mentioned before. Therefore, it should satisfy the angular momentum commutation relations.

$\bar{S}\ X\ \bar{S} = iS$ In the units of $\hbar$

$[S_x S_y - S_y S_x] = i\hbar S_z$-------------- (3.3.2)

Now introducing (1) and (2), we get

$$\left.\begin{aligned} \sigma_x\sigma_y - \sigma_y\sigma_x &= 2i\sigma_z \\ \sigma_y\sigma_z - \sigma_z\sigma_y &= 2i\sigma_x \\ \sigma_z\sigma_x - \sigma_x\sigma_z &= 2i\sigma_y \end{aligned}\right\} \text{---------------------(3.3.3)}$$

all in the units of $\hbar$

The eigen values of S^2 are S (S+1) = 1/2(1/2+1)= 1/4 --------------(3.3.4)

$$\therefore \; S^2 = \frac{\hbar^2}{2}\sigma^2 = \frac{1}{4}\left[\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right] \text{ --------------------(3.3.5)}$$

From the equations (4) and (5) the condition that gives the expectation value of 1/4 is

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$

The spin operators are anti commute in pairs

i.e. $\sigma_x\sigma_y + \sigma_y\sigma_x = 0$

Consider $2i\,[\sigma_x\sigma_y + \sigma_y\sigma_x] = \sigma_x[\sigma_z\sigma_x - \sigma_x\sigma_z] + [\sigma_z\sigma_z - \sigma_x\sigma_z]\sigma_x$

$$= \sigma_x\sigma_z\sigma_x - \sigma_x^2\sigma_z + \sigma_z\sigma_x^2 - \sigma_x\sigma_z\sigma_x \quad =0$$

$$\therefore [\sigma_x\sigma_y + \sigma_y\sigma_x] = 0$$

i.e. $[\sigma_x \ \sigma_y]_+ = 0$

Similarly $[\sigma_y \ \sigma_z]_+ = 0$

and $[\sigma_z \sigma_x]_+ = 0$

In view of this equation,

$$\sigma_x\sigma_y - \sigma_y\sigma_x = 2i\sigma_z$$

becomes

$$2i\sigma_x\sigma_y = 2i\sigma_z$$

$\therefore \sigma_x\sigma_y = i\sigma_z$;

$\sigma_y\sigma_z = i\sigma_x$

and $\sigma_z\sigma_x = i\sigma_y$

3.3.2 spin matrices $\sigma_x, \sigma_y, \sigma_z$

Let the operator σ_z be operated on the ket $|k\rangle$ giving the eigen value a

i.e. $\sigma_z|k\rangle = a|k\rangle$

$$\sigma_z^2|k\rangle = a^2|k\rangle$$

$\therefore$ a= ± 1

Therefore, there are two eigen values corresponding to in operator σ_z which are ± 1.

The matrix representation of these eigen values is a 2X2 matrix.

$$\therefore \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

σ_x :- Since σ_z is a 2 x 2 matrix , $\sigma_x and \sigma_y$ should also be 2 x 2 matrices since this has two anti commute.

Let $\sigma_x = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}$

Consider $\sigma_x \sigma_z + \sigma_z \sigma_x = 0$

$$\begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix} = 0$$

$$\Rightarrow \begin{pmatrix} a_1 & -a_2 \\ a_3 & -a_4 \end{pmatrix} + \begin{pmatrix} a_1 & a_2 \\ -a_3 & -a_4 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

i.e.

$$\Rightarrow \begin{pmatrix} 2a_1 & 0 \\ 0 & -2a_4 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \Rightarrow a_1 = a_4 = 0$$

$$\therefore \sigma_x = \begin{pmatrix} 0 & a_2 \\ a_3 & 0 \end{pmatrix}$$

and

$$\sigma^{+}_{x} = \begin{pmatrix} 0 & a_3^{:*} \\ a_2^{*} & 0 \end{pmatrix}$$

$$\Rightarrow \quad a_2 = a_3^{:*} \text{ and } a_3^{:} = a_2^{:*}$$

$$\therefore \sigma_x = \begin{pmatrix} 0 & a_2 \\ a_2^{*} & 0 \end{pmatrix}$$

$$\sigma_x^2 = \begin{pmatrix} 0 & a_2^{*} \\ a_2 & 0 \end{pmatrix}\begin{pmatrix} 0 & a_2^{*} \\ a_2 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} a_2 a_2^{*} & 0 \\ 0 & a_2^{*} a_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Rightarrow |a_2|^2 = 1$$

We may take $a_2 = \exp(i\alpha)$

$$\therefore \sigma_x = \begin{pmatrix} 0 & e^{i\alpha} \\ e^{i\alpha} & 0 \end{pmatrix}$$

$$Similarly \sigma_y = \begin{pmatrix} 0 & e^{i\beta} \\ e^{i\beta} & 0 \end{pmatrix}$$

$\sigma_x \sigma_z + \sigma_z \sigma_x = 0$

$$\begin{pmatrix} 0 & e^{i\alpha} \\ e^{-i\alpha} & 0 \end{pmatrix}\begin{pmatrix} 0 & e^{i\beta} \\ e^{-i\beta} & 0 \end{pmatrix} + \begin{pmatrix} 0 & e^{i\beta} \\ e^{-i\beta} & 0 \end{pmatrix}\begin{pmatrix} 0 & e^{i\alpha} \\ e^{-i\alpha} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \exp(i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) \end{pmatrix} + \begin{pmatrix} \exp(i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \exp(i(\alpha-\beta)) + \exp(-i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) + \exp(-i(\alpha-\beta)) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \cos(\alpha-\beta) & 0 \\ 0 & \cos(\alpha-\beta) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$(\alpha-\beta) = \frac{\pi}{2}$$

$$\beta = \alpha + \frac{\pi}{2}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

setting $\alpha = 0; \beta = \frac{-\pi}{2}$

These matrices are known as Pauli’s spin matrices.

$$\sigma_y = \begin{pmatrix} 0 & \exp(-i\frac{\pi}{2}) \\ \exp(i\frac{\pi}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & -i\sin\frac{\pi}{2} \\ i\sin\frac{\pi}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\therefore \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} and \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

3.3.3 Eigen functions for σ_z

let $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ is the eigen function of σ_z and a its eigen value. Then the eigen value equation of σ_z is

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = a\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \Rightarrow c_1 = ac_1$$

$$-c_2 = ac_2$$

$$or\, |c_1c_2| = a^2|c_1c_2| \Rightarrow a = \pm 1$$

$$if a = 1$$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

If a =1, c_1=1,c_2= 0

If a= -1, c_1= 0, c_2=1

The two wave functions are $\begin{pmatrix} 1 \\ 0 \end{pmatrix} and \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \text{ and } \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

α and β represent , what is called , pure states.. In an ensemble of spin $\frac{1}{2}$ particles, it is unlikely that all the particles are spin-up or all and spin down. It is more likely that some of the particles are spin-up and the others are spin –down. The spin-wave front, or spinor,χ corresponding to an ensemble is, therefore, a linear superposition of α and β:

$$\chi = c_1\alpha + c_2\beta = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$= \chi_+ + \chi_-,$$

where $|c_1|^2 + |c_2|^2 = 1$

The first one is known as spin up function denoted by the symbol (↑) and the second one is known as spin down function. denoted by the symbol (↓)

Spin multiplets

Consider the system consisting of two spins, the total value of spin s= 1 then the ways of arranging these three spins is given by

$$|\uparrow\uparrow\rangle ; \ \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle\right]; \ |\downarrow\downarrow\rangle$$

these are called triplet states. In this case the spins are parallel for s=0 the state is called singlet state, the spins are anti parallel and it is represented by

$$\frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle\right]$$

3.3.4 Properties of the Pauli's Spin Matrices

These matrices are 2x2 matrices

i) Hermitian matrices

i.e. $\sigma_x = \sigma_x^\dagger$; $\sigma_y = \sigma_y^\dagger$ $\sigma_z = \sigma_z^\dagger$

for example $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

and $\sigma\dagger_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$; hence $\sigma_y = \sigma_y{}^\dagger$

similarly we can prove $\sigma_y = \sigma_y^\dagger$ and $\sigma_z = \sigma_z^\dagger$

ii) Trace less matrices

That means the sum of the diagonal elements of all the three matrices is zero

$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sum a_{ii} = 0$ and similarly for σ_y and σ_z the trace is zero

iii) Anticommute in pairs

$\sigma_x\sigma_y + \sigma_y\sigma_x = 0$ and cyclic

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = 0$$

iv) **$\sigma_x \sigma_y = i \sigma_z$ and cyclic**

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and v**) $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$**

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Summary of the lesson

The three components of the spin operator are derived in the form of matrices known as Pauli's spin matrices. The properties of these spin matrices are discussed in depth. The wave function associated with the Z component of the spin angular momentum is also derived.

Self assessment - questions

1. Derive Pauli spin matrices.
2. State and prove the properties of the Pauli spin matrices.
3. Write down the eigen function of the operator σ_z

Reference books

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. Introduction to Quantum Mechanics – Mathews P T (Mc Graw Hill Book Co., New York).
3. Quantum Mechanics by V. K. Thankappan (Wiley Eastern. Ltd, New Delhi,1986
4. Quantum Mechanics – Gupta , Kumar , Sarma (Pragati Prakasanm, Meerut 1990

UNIT - 3

LESSON - XIII THE TOTAL ANGULAR MOMENTUM OPERATOR J

Objective of the lesson

This lesson is devoted to understand the algebra of total angular momentum operator J, which is defined as J = L ± S. It is further planned to derive the commutation relations of the three resolved components of J and the operator J^2.

3.4.1 Introduction

The total angular momentum is defined as J = L ± S and J_x, J_y, J_z are the components of J. In analogy with the orbital angular momentum operators, we have the relations,

$[J_x, J_y]=i\hbar J_z [J_y, J_z]=i\hbar J_x$

and $[J_z, J_x]= i\hbar J_y$-----------(3.4.1)

$J \times J= i J$---------------------(3.4.2)

And $[J^2,J]=0$-----------(3.4.3)

$J^2= J^2_x+ J^2_y + J^2_z$

Let us now consider the Eigen value problem of J_z and J^2.

Let $\lambda\hbar^2$ and $m\hbar$ are the eigen values of J^2 and J_z respectively. To find out the relation between λ and m, let us construct new the operators:

3.4.2 Definitions of J_+ and J_- operators

$$\left.\begin{aligned} J_+ &= J_x + iJ_y \\ \text{and} \quad J_- &= J_x - iJ_y \end{aligned}\right\} \text{----------------------(3.4.4)}$$

Then $[J^2, J_{\pm}] = [J^2, J_x \pm iJ_y]$

$= [J^2, J_x] \pm i\,[J^2, J_y]$

$\Rightarrow [J^2, J_{\pm}] = 0$ -------------(3.4.5)

$$\left.\begin{aligned} &\text{similarly, } J_z J_+ - J_+ J_z = \hbar J_{+(} \\ &J_- J_z - J_z J_- = \hbar J_- \end{aligned}\right\} \text{ --------- (3.4.6)}$$

From equation (3.4.4) $J_x = \dfrac{J_+ + J_-}{2}$

$$J_y = \frac{J_+ - J_-}{2i} = \frac{-i}{2}\left[J_+ - J_-\right]$$

$[J_z, J_+] = [J_z, J_x + iJ_y]$

$= [J_z, J_x] + i[J_{z.}, J_y]$

$= i\,\hbar\,[J_z + iJ_y]$

$= \hbar\, J_+$

Similarly $[J_z, J_-] = -\hbar\, J_-$

$\Rightarrow \left[J_z, J_{\pm}\right] = \pm J_{\pm}$ ----------------(3.4.7)

$[J_+, J_-] = [(J_x + iJ_y), (J_x + iJ_y)]$

$= [J_x, J_x] - i[[J_x, J_y] + i[J_y, J_x] + [J_y, J_y]$

$=-i[i\hbar J_z]+i[-i\hbar J_z]$

$[J_+, J_-] = 2\hbar J_z$ ----------------------(3.4.8)

or $\left[J_\pm, J_\mp\right] = \pm 2\hbar J_z$

similarly

Now, the eigen value equations of J_z and J_2 are

$$J_z\left|\lambda m\right\rangle = m\hbar\left|\lambda m\right\rangle - - - - - - - - - - - - (3.4.9)$$

$$J^2\left|\lambda m\right\rangle = \lambda\hbar^2\left|\lambda m\right\rangle - - - - - - - - - - - - - (3.4.10)$$

J^2 and J_z can have the simultaneous eigen function $\left|\lambda m\right\rangle$ since they commute.

To show $\lambda \geq m^2$

Consider the expectation value of (J^2-J^2_z)

i.e. $J^2 - J^2_z = J^2_x + J^2_y = 1/2[J_+J_- + J_-J_+] = 1/2[J_+J^\dagger_+ + J^\dagger_+J_+]$

Since, $J_+ J_+^\dagger \geq 0$

$J^2 - J^2_z$, has only non-negative expectation values.

$$i.e. \left\langle\lambda m\right| J^2 - J_z^2 \left|\lambda m\right\rangle \geq 0$$

$$\lambda - m^2 \geq 0$$

$$\lambda \geq m^2$$

$$m^2 \leq \lambda - - - - - - - - - - - - - (3.4.11)$$

$\Rightarrow$ m lies in between - $\sqrt{\lambda}$ and $\sqrt{\lambda}$

To show J₊ and J₋ are rising and lowering operators

Next we develop again a ladder procedure similar to the method employed for the harmonic oscillator. If we act on Eq. 3.4.7 with J_+ and J- and apply 3.4.9 and 3.4.10. We obtain the following equations

$[J_z, J_\pm] = \pm\hbar J_\pm \; J_zJ_\pm - J_\pm J_z = \pm\hbar J_\pm$

$J_zJ_\pm = J_\pm J_z + \hbar J_\pm = J_\pm(J_z \pm \hbar)$

$J_z J_\pm \left|\lambda m\right\rangle = J_\pm(J_z \pm \hbar)\left|\lambda m\right\rangle$

$= J_\pm(m\hbar \pm \hbar)\left|\lambda m\right\rangle$

$= (m+1)\hbar J_\pm\left|\lambda m\right\rangle$

$J_z\{J_+\left|\lambda m\right\rangle\} = (m+1)\hbar J_+\left|\lambda m\right\rangle$

$\Rightarrow J_+\left|\lambda m\right\rangle$ is an eigen function with eigen values $(\mathrm{m}+1)\hbar$.

$J_z\{J_-\left|\lambda m\right\rangle\} = (m-1)\hbar J_-\left|\lambda m\right\rangle$

$\Rightarrow J_-\left|\lambda m\right\rangle$

is an eigen function with eigen values (m-1) $\hbar$.

If the successive operations are performed like this we found J_+ is a raising operator and J_- is a lowering operator but the minimum value can never be less than -$\sqrt{\lambda}$*and* the maximum value can never be greater than +$\sqrt{\lambda}$ .Let m_1 and m_2 are the upper and lower limits of m. Then$J_+\left|\lambda m_1\right\rangle = 0$

and $J_-\left|\lambda m_2\right\rangle = 0$

$J_+J_- = (J_x - iJ_y)(J_x + iJ_y)$

$=J^2_x+J^2_y+I[J_x, J_y]$

$=J^2_x+J^2_y- \hbar J_z$

$$(J_2 - J_z^2 - J_z)\left|\lambda m_1\right\rangle = 0$$

$$\Rightarrow (\lambda - m_1^2 - m_1)\hbar^2\left|\lambda m_1\right\rangle = 0$$

$$\Rightarrow \lambda - m_1^2 - m_1 = 0$$

$$J_+J_-\left|\lambda m_2\right\rangle = \left|\lambda - m_2^2 - m_2\right\rangle\left|\lambda m_2\right\rangle = 0$$

$$\Rightarrow \lambda - m_2^2 - m_2 = 0$$

Hence,

$$\lambda - m_1^2 - m_1 = \lambda - m_2^2 - m_2$$

$$\Rightarrow (m_2^2 - m_1^2 - m_2 + m_1) = 0$$

$$\Rightarrow (m_1 + m_2)(m_2 - m_1) - (m_2 - m_1) = 0$$

$$(m_2 + m_1)(m_2 - m_1 - 1) = 0$$

$$\Rightarrow m_2 = -m_1 and m_2 = m_1 + 1.$$

The second possibility is ruled out since the lowest value m_2 can never be more than highest value $m_1$of m.

We therefore have $m_2 = -m_1$

$m_1 = - m_2 = j$ (say)

=>The eigen value of J_z lies between –j to +j.

Then

$$\lambda - m_1^2 - m_1 = 0$$

$$\Rightarrow \lambda = m_1(m_1 + 1) = j(j+1)$$

m= .-j, -j+1---------------j-1, j ……………………(3.4.11)

thus, for a given value of J , the eigen values of J_z are $m\hbar$ = J$\hbar$, (j-1) $\hbar$,(j-2)$\hbar$,--------,- (j-I) $\hbar$,-j $\hbar$,These are 2j+1 in number, and there are thus 2j+1 orthogonal eigen vectors for every value of j. Since 2j+1 can be any positive number, we see that for every dimension it is possible to construct a vector space that is closed under operations of the algebra of the three operators J_x, J_y, J_z that are constrained by the commutation relations .

Since the value of j, the maximum value of the projection of the angular momentum vector on the z-axis, fixes the length of the angular momentum vector uniquely, the latter is usually specified by its j value. Thus the statement: the angular momentum of the particle is 3/2, means that the

angular momentum vector is of length $\sqrt{\frac{3}{2}.\frac{5}{2}}\hbar$. This length can, however, never be observed directly

For a given value of j, there are (2j+1) linearly independent vectors $|jm\rangle$, corresponding to the (2j+1) different values of m given by (11), which are common eigen vectors J^2 and J_z . If

one of these vectors is given, the others can be generated from it by the repeated application of J_+ and J-.

let (2j+1) =M (say) an integer .

$$j = \frac{M-1}{2} = 0, \frac{1}{2}, \frac{2}{2}, \frac{3}{2} - - - - - - - -$$

$$= 0, \frac{1}{2}, 1, \frac{3}{2} - - - - - - - -$$

and $\lambda = j(j+1) = 0, \frac{3}{4}, 2, \frac{5}{4} - - - - -$

Now consider, the eigen value equations of J_+ and J_- operators ,

$$J_+ \left| \lambda m \right\rangle = c_+ (\lambda m)\hbar \left| \lambda m + 1 \right\rangle$$

$$J_- \left| \lambda m \right\rangle = c_+ (\lambda m)\hbar \left| \lambda m + 1 \right\rangle$$

$$\left\langle \lambda m \right| J_+ J_- \left| \lambda m \right\rangle = \left| c_+^2 \right| \hbar^2 \left\langle \lambda m + 1 \middle| \lambda m - 1 \right\rangle$$

$$\left\langle \lambda m \right| J^2 - J_z^2 - \hbar J_z \left| \lambda m \right\rangle$$

$$= (\lambda - m^2 - m)\hbar^2$$

$$\Rightarrow \left| c_+ \right|^2 = \lambda^2 - m^2 - m$$

$$= j(j+1) + m^2 - m$$

$$= j^2 + j + m^2 - m$$

$$= (j+m)(j-m) + (j-m)$$

$$\left| c_+ \right| = \sqrt{(j-m)(j+m+1)}\hbar$$

Similarly $\Rightarrow c_- = \sqrt{(j+m)(J-m+1)}\hbar$

$$\therefore J_+ \left| \lambda m \right\rangle = \sqrt{(j-m)(j+m+1}\hbar \left| \lambda m + ! \right\rangle$$

andJ $_- \left| \lambda m \right\rangle = \sqrt{(j-m)(j-m+1)}\hbar \left| \lambda m - 1 \right\rangle$

3.4.2 Matrices for J^2 and J_z

Matrix element $(J_+)_{m^1 m}$ = $\langle \lambda m^1 | J_+ | \lambda_j m \rangle = \sqrt{(j-m)(J+m+1)}\delta_{m^1 m+1}$

Consider j=1/2 then J^2 eigen values are j(j+1)$\hbar^2 = 3/4\hbar^2$

J_z eigen values = +1/2 and –1/2 (since (2j+1)=(2*1/2+1=2)

Therefore

$$J^2 = \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

similarly

$$J_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & \frac{-\hbar}{2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and

$$J_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$J_x = \frac{1}{2}(J_+ + J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J_y = \frac{i\hbar}{2}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$J_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Summary of the lesson

The total angular momentum operator J is defined. The commutation relations between the three components J and the operator J^2 are derived. The operators J_+ and J_- are also defined and their commutation for a given value of J , the eigen values of J_z are $m\hbar = J\hbar$, (j-1) $\hbar$,(j-2)$\hbar$,--------,- (j-I) $\hbar$,-j $\hbar$,These are 2j+1 in number, and there are thus 2j+1 orthogonal eigen vectors

for every value of j. Since 2j+1 can be any positive number, we see that for every dimension it is possible to construct a vector space that is closed under operations of the algebra of the three operators J_x , J_y, J_z which are constrained by the commutation relations n relations with operators J and J^2 are also derived.

The eigen value equations of the operators J_+ and J_- have been obtained. The matrix representation of operators J_x, J_y, J_z, J_+, J_-, J^2 has also been presented.

Key terminology

Total angular momentum operator J-The operators J_+ and J_-, the operator J^2-Eigen value equations of the operators J_+ and J_--The matrix representation of operators J_x, J_y, J_z, J_+, J_-, J^2

Self assessment questions

1. Define the operators J_+ and J_- and show that these two operators commute with the operator J^2
2. Obtain the commutation relations between the operators J_z and $J_\pm$
3. Obtain the eigen value equations for the operators J_+ and
4. Give the matrix representation of the operators J_x, J_y, J_z, J_+, J_-, J^2 by taking J=1/2

Reference Books

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3. Introduction to Quantum Mechanics – Mathews P T (Mc Graw Hill Book Co., New York).
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UNIT - 3

LESSON - XIV The Addition of Angular Momentum

Objective of the lesson

In this lesson the problems related to the addition of angular momenta associated with different systems have been discussed. The Clebsch -Gordon Coefficients also known as Wigner coefficients have been evaluated for different values of J. Wigner- Ecart Theorem which is most widely used in the evaluation of transition probabilities in the radiation emission problems has also been included

3.5.1The Addition of Angular Momentum

If two distinct physical systems or two distinct sets of dynamical variables of one system ,which are described in two different vector spaces, are merged ,the states of the composite system are , vectors in the direct product space of the two previously separate vector spaces. If J_1 and J_2 are the angular momentum of the two physical systems , Then

$J= J_1 + J_2$ is the total angular momentum of the entire system. J_{1x} , J_{1y}, J_{1z} are the components of J_1, J_{2x}, J_{2y}, J_{2z} components of J_2.

$$J_x = J_{1x} + J_{2x} \text{ and so on}$$

Each component of J_1 commutes with each component. The total component of J satisfies the angular momentum commutation relations:

$$[J_x,J_y]= i\hbar J_z \;;\quad [J_y, J_z] = i\hbar J_x \;;\quad [J_z, J_x]= i\hbar J_y \qquad (3.5.1)$$

Now, the problem of addition of two angular moment consists of obtaining the eigen values of J_z and J^2 and their eigen vectors in terms of the direct products of the eigen vectors of J_{1z} and J_1^2 and of J_{2z} and J^2_2 . The normalized simultaneous eigen vectors of the four operators J_1^2, J^2_2, J_{1z} , J_{2z} can be symbolized by the direct product kets.

$$|\, j_1 j_2 m_1 m_2 \rangle = |\, j_1 m_1 \rangle |\, j_2 m_2 \rangle \quad \text{------------------------} \quad (3.5.2)$$

These constitute a basis in the direct product space . These form a basis in the product space . From this basis , it is desire to construct a new basis with the eigen vectors of J_z and J^2 .

Corresponding to three angular momentum vectors J_1,J_2 ,J we have six hermitian operators . J^2_1, J^2_2, J_{1z} , J_{2z} ,J^2 and J_z out of these J^2_1 and J^2_2 commute with every component of J and J^2 also .

i.e. $[J_2, J^2_1] = [J_2, J^2_2] = [J^2, J^2_1] = [J^2, J^2_2] = 0$----------------------------(3.5.3)

But J^2 does not commute with J_{1z} and J_{2z} we therefore have two sets of simultaneous eigen functions .They are

1. J^2_1, J^2_2, J_{1z} , J_{2z}.
2. J^2_1, J^2_2, J^2 , J_z

3.5.2 Clebsch-Gordon coefficients

3. The basis vectors corresponding to first set of vectors, J^2_1, J^2_2, J_{1z} , J_{2z}.

is denoted by

$$|\, j_1 j_2 m_1 m_2 \rangle = |\, j_1 m_1 \rangle |\, j_2 m_2 \rangle \quad \text{---------------------}(3.5.4)$$

or briefly with $|\, m_1 m_2 \rangle$

4. and corresponding to the second set, J^2_1, J^2_2, J^2 , J_z

it is given by

$|\, j_1 j_2\, jm \rangle$ are briefly by $|\, jm \rangle$

We thus have

$$\left.\begin{aligned}
J_1^2 \mid j_1 j_2 m_1 m_2 \rangle &= j_1 (j_1 + 1)\hbar^2 \mid j_1 j_2 m_1 m_2 \rangle \\
J_{1z} \mid j_1 j_2 m_1 m_2 \rangle &= m_1 \hbar \mid j_1 j_2 m_1 m_2 \rangle \\
J_2^2 \mid j_1 j_2 m_1 m_2 \rangle &= j_2 (j_2 + 1)\hbar^2 \mid j_1 j_2 m_1 m_2 \rangle \\
J_{2z} \mid j_1 j_2 m_1 m_2 \rangle &= m_1 \hbar \mid j_1 j_2 m_1 m_2 \rangle
\end{aligned}\right\} \text{---------------(3.5.5)}$$

$$\left.\begin{aligned}
J^2 \mid j_1 j_2 jm \rangle &= j\ (j+1)\hbar^2 \mid j_1 j_2 jm \rangle \\
J_z \mid j_1 j_2 jm \rangle &= m\hbar \mid j_1 j_2 jm \rangle \\
J_1^2 \mid j_1 j_2 jm \rangle &= j_1 (j_1 + 1)\hbar^2 \mid j_1 j_2 jm \rangle \\
J_2^2 \mid j_1 j_2 jm \rangle &= j_2 (j_2 + 1)\hbar^2 \mid j_1 j_2 jm \rangle
\end{aligned}\right\} \text{-----------------(3.5.6)}$$

We shall now write the transformation equation between $\mid j_1 j_2 jm \rangle$ and $\mid j_1 j_2 m_1 m_2 \rangle$ as

$$\mid j_1 j_2 jm \rangle = \sum_{m_1 m_2} \mid j_1 j_2 m_1 m_2 \rangle \langle j_1 j_2 m_1 m_2 \mid j_1 j_2 jm \rangle \text{---------------(3.5.7)}$$

Here j$_1$, j$_2$ can be assumed to have fixed values and m$_1$,m$_2$ are variables.

In the above equation, the transformation coefficient

$$\langle j_1 j_2 m_1 m_2 \mid j_1 j_2 jm \rangle = C^{j_1 j_1 j}_{m_1 m_2 m} \quad \text{-----------(3.5.8)}$$

is also called **Clebsch-Gordon coefficient** or Wigner coefficient. The problem of addition of angular momentum now consists of founding the above coefficients. Occasionally the above coefficients can also written as

$$\langle j_1 j_2 m_1 m_2 \mid j_1 j_2 jm \rangle = \langle m_1 m_2 \mid jm \rangle$$

With j$_1$ and j$_2$ are the maximum values of m$_1$ and m$_2$.

Now let us apply the operator $j_z = j_{1z} + j_{2z}$ on the two kets, then we have

$$J_z | j_1 j_2 jm\rangle = m\hbar | j_1 j_2 jm\rangle \quad = \mathrm{m}\hbar \sum_{m_1 m_2} | j_1 j_2 m_1 m_2 \rangle\langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle$$

Similarly $\langle j_1 j_2 m_1 m_2 | (J_{1z} + J_{2z}) \rangle = (m_1 + m_2)\hbar | j_1 j_2 m_1 m_2 \rangle$

Or $\langle j_1 j_2 m_1 m_2 | j_z | j_1 j_2 jm\rangle = m\hbar \langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle$

And $\langle j_1 j_2 m_1 m_2 | J_{1z} + J_{2z} | j_1 j_2 jm\rangle = (m_1 + m_2)\hbar \langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle$

$\langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle = 0$ unless $m = m_1 + m_2$ -----(3.5.10)

Now apply J_- on $| jm\rangle$, we have $| m_1 m_2 \rangle J_- | jm\rangle = | m_1 m_2 \rangle J_{1-} + J_{2-} | jm\rangle$

i.e. $\sqrt{(j+m)(j-m+1)}\langle m_1 m_2 | jm-1\rangle = \sqrt{(j_1 - m_1)(j_1 + m_1 + 1)}\langle m_1 + 1 m_2 | jm\rangle +$

$$\sqrt{(j_2 - m_2)(j_2 + m_2 + 1)}\langle m_1 m_2 + 1 | jm\rangle$$

Similarly operating J_+ we get

$$\sqrt{(j-m)(j+m+1)}\langle m_1 m_2 | jm+1\rangle = \sqrt{(j_1 + m_1)(j_1 - m \ \ + 1)}\langle m_1 - 1 m_2 | jm\rangle +$$
$$\sqrt{(j_2 + m_2)(j_2 - m_2 + 1)}\langle m_1 m_2 - 1 | jm\rangle \text{---------------(3.5.12)}$$

Now in the first of the above two equations, if we let m=j, $m_1 = j_1$ then

$m_1 + 1 + m_2 = m \Rightarrow m_2 = j - j_1 - 1$

Then, the first equation given

$$\sqrt{2}j\langle j_1 (j - j_1 - 1) | j(j-1)\rangle \sqrt{(j_2 - j + j_1 - 1)(j_2 + j - j_1)}\langle j_1 j - j_1 | jj\rangle \text{ ----------(3.5.13)}$$

And let in the second equation m= j-1,$m_1 = j_1$; m_2+m1 –1=m =>$m_2 = j - j_1$

With this, we have,(from the second equation)

$$\sqrt{2}j\langle j_1 (j - j_1) | jj\rangle = \sqrt{(j_2 + j - j_1)(j_2 - j + j_1 + 1)}\langle j_1 j - j_1 - 1 | jj-1\rangle \sqrt{2}j\langle (j_1 - 1)(j - j_1) | jj-1\rangle \text{ ---- (3.5.14)}$$

These equations are known as recursion relations.

According to condition (3.5.13) $\langle j_1(j-j_1-1)|\, j(j-1)\rangle$ can be determined if $\langle j_1-1j-j_1\,|\,jj\rangle$ is known then $\langle j_1 j-j_1\,|\,jj\rangle$ can be determined of both of them are known. Continuing in this manner, for fixed values j_1,j_2,j we can determine all the C.G coefficients in terms of just one of them.

i.e. $\langle j_1 j-j_1\,|\,jj\rangle$ or $\langle j_1 j_2 j_1(j-j_1)|\, j_1 j_2 jj)\rangle$

The above coefficient is different from zero only if $-j_2 \le j-j_1 \le j_2$ i.e. the range of m_2

Or $j_1-j_2 \le j \le j_1+j_2$ (3.5.15)

The coefficients can equally be expressed as terms $\langle (j_1-j)\, j_2\,|\,jj\rangle$ or $\langle j_1-j_2\, j-j_2\, j_2\,|\, j_1 j_2 jj)\rangle$

With $-j_1 \le j-j_2 \le j_2$ or $j_2-j_1 \le j \le j_1+j_2$ -------(3.5.16)

From (!5)and (16) the three angular momentum quantum numbers must satisfy the condition.

$$|\ j_2-j_1\ | \le j \le |\ j_1+j_2\ | \text{---------------}(3.5.17)$$

$$\Rightarrow\ j = j_1+j_2,\, J_1+J_2-1 \text{--------------------} |j_1-j_2|$$

i.e. for the fixed values of j_1,j_2 the equation

$$|\, j_1 j_2 jm\rangle = \sum_{m_1 m_2} |\, j_1 j_2 m_1 m_2\rangle\langle j_1 j_2 m_1 m_2\,|\, j_1 j_2 jm\rangle$$

gives a new basis in the $(2j_1+1)(2j_2+1)$ dim space.

3.5.3 C.G coefficients $j_1=1$,$j_2=1/2$.

The total number of C.G coefficients are $(2j_1+1)(2j_2+1)=6$ .The C.G coefficient matrix is a 6X6 matrix. m_1 takes the values 1 0-1 and m_2 takes 1/2, -1/2 and m takes the values j_1+j_2 to $|j_1-j_2|$ i.e. 3/2, 1/2, -1/2, -3/2 j values corresponding to $j_1=1$, $j_2=1/2$.are given by

m	m_1	m_2	j
$j_1+j_2=3/2$	$j_1=1$	$j_2=1/2$	$m=3/2$
$j_1+j_2-1=1/2$	$j_1=1$	$j_2-1=-1/2$	$j_1+j_2=3/2$
	$j_1-1=1$	$j_2=½$	$j_1+j_2-1=1/2$
$j_1+j_2-2=-1/2$	$j_1-1=0$	$j_2-1=-1/2$	$j_1+j_2=3/2$
	$j_1-2=-1$	$j_2=½$	$j_1+j_2-1=1/2$
$j_1+j_2-3=-3/2$	$j_1-2=-1$	$j_2-1=-1/2$	$j_1+j_2=3/2$

j → 3/2	3/2	1/2	3/2	1/2	3/2
m → 3/2	1/2	1/2	1/2	1/2	3/2

$$\begin{array}{cc}
m_1 & m_2 \\
1 & 1/2 \\
1 & -1/2 \\
0 & 1/2 \\
0 & -1/2 \\
-1 & 1/2 \\
-1 & -1/2
\end{array}
\begin{pmatrix}
c_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & c_{22} & c_{23} & 0 & 0 & 0 \\
0 & c_{32} & c_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & c_{44} & c_{45} & 0 \\
0 & 0 & 0 & c_{54} & c_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}$$

Now consider

$$|\,jm\rangle \qquad\qquad\qquad |m_1m_2\rangle$$

$$\begin{pmatrix}
\left|\frac{3}{2}\,\frac{3}{2}\right\rangle \\
\left|\frac{3}{2}\,\frac{1}{2}\right\rangle \\
\left|\frac{1}{2}\,\frac{1}{2}\right\rangle \\
\left|\frac{3}{2}\,\frac{-1}{2}\right\rangle \\
\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle \\
\left|\frac{3}{2}\,\frac{-3}{2}\right\rangle
\end{pmatrix}
=
\begin{pmatrix}
c_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & c_{22} & c_{23} & 0 & 0 & 0 \\
0 & c_{32} & c_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & c_{44} & c_{45} & 0 \\
0 & 0 & 0 & c_{54} & c_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}
\begin{pmatrix}
\left|1\,\frac{1}{2}\right\rangle \\
\left|1\,\frac{-1}{2}\right\rangle \\
\left|0\,\frac{1}{2}\right\rangle \\
\left|0\,\frac{-1}{2}\right\rangle \\
\left|-1\,\frac{1}{2}\right\rangle \\
\left|-1\,\frac{-1}{2}\right\rangle
\end{pmatrix}$$

$$\left|\frac{3}{2}\frac{3}{2}\right\rangle = c_{11}\left|1\frac{1}{2}\right\rangle = c_{11}\left|\frac{3}{2}\right\rangle\left\langle\frac{3}{2}\right|1\frac{1}{2}\right\rangle$$

$$\Rightarrow c\left\langle\frac{3}{2}\frac{3}{2}\right|1\frac{1}{2}\right\rangle = \left|c_{11}\right|\left\langle 1\frac{1}{2}\right|1\frac{1}{2}\right\rangle$$

$$\left\langle\frac{3}{2}\frac{3}{2}\right| = \left\langle 1\frac{1}{2}\right| \Rightarrow c_{11}^{2} = 1 \Rightarrow c_{11} = 1$$

$$\Rightarrow\left|\frac{3}{2}\frac{3}{2}\right\rangle = c_{11}\left|1\frac{1}{2}\right\rangle$$

$$\left\langle 1\frac{1}{2}\right|\frac{3}{2}\frac{3}{2}\right\rangle = c_{11}\left\langle 1\frac{1}{2}\right|1\frac{1}{2}\right\rangle$$

$$c_{11} = 1 ----------(3.5.18)$$

Now to find the other coefficients let us apply J_- on $\left|\frac{3}{2}\frac{3}{2}\right\rangle$, then we have

$J_-\left|\frac{3}{2}\frac{3}{2}\right\rangle = (J_{1-}+J_{2-})\left|1\frac{1}{2}\right\rangle$

i.e. $\sqrt{(j+m)(j+m+1)}\left| jm-1\right\rangle = \sqrt{(j_1+m_1)(j_1-m_1+1}\left| m_1m_2\right\rangle + \sqrt{(j_2+m_2)(j_2-m_2+1)}\left| m_1m_2-1\right\rangle$

i.e. $\sqrt{3\left|\frac{3}{2}\frac{1}{2}\right\rangle} = \sqrt{(1+1)}\left|0\frac{1}{2}\right\rangle + \sqrt{1}\left|1\frac{-1}{2}\right\rangle$

$$\left|\frac{3}{2}\frac{1}{2}\right\rangle = \sqrt{\frac{2}{0}}\left|0\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|1\frac{-1}{2}\right\rangle \text{-------------(3.5.19)}$$

From the matrix, we have

$$\left|\frac{1}{2}\frac{1}{2}\right\rangle = c_{32}\left|1\frac{-1}{2}\right\rangle + c_{33}\left|0\frac{1}{2}\right\rangle$$

Multiplying the above two equations , we get

$$\left\langle 1\frac{-1}{2}\middle|\frac{3}{2}\frac{1}{2}\right\rangle = 0 = \sqrt{\frac{2}{3}}c^{*}_{33}\left\langle 0\frac{1}{2}\middle|0\frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}c^{*}_{32}\left\langle 1\frac{-1}{2}\middle|1\frac{-1}{2}\right\rangle$$

$$=\sqrt{\frac{2}{3}}c^{*}_{33}+\frac{1}{\sqrt{3}}c^{*}_{32}$$

$$\Rightarrow \frac{c^{*}_{33}}{c^{*}_{32}} = \frac{\frac{1}{\sqrt{3}}}{\frac{-\sqrt{2}}{-\sqrt{3}}} = \frac{c_{33}}{c_{32}}$$

because they are real coefficients.

Now consider equation (3.5.19) and apply J_- on both sides, we get

$$J_-\left|\frac{3}{2}\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left(J_{1-}+J_{2-}\right)\left|0\frac{1}{2}\right\rangle + \left(J_{1-}+J_{2-}\right)\frac{1}{\sqrt{3}}\left|1\frac{-1}{2}\right\rangle$$

L.H.S

$$\sqrt{2.2}\left|\frac{3}{2}\frac{-1}{2}\right\rangle$$

R.H.S(1) : $\sqrt{\frac{2}{3}}\sqrt{(1+0)\sqrt{1-0+1}}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\sqrt{1}\left|0\frac{-1}{2}\right\rangle$

$$=\sqrt{\frac{2}{3}}\sqrt{2}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

R.H.S(2): i.e $\left(J_{1-}+J_{2-}\right)\frac{1}{\sqrt{3}}\left|1\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}}\sqrt{2}\left|0\frac{-1}{2}\right\rangle + 0$

$$\therefore 2\left|\frac{3}{2}\frac{-1}{2}\right\rangle = \frac{2}{\sqrt{3}}\left|-1\frac{1}{2}\right\rangle + 2.\sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

$$\left|\frac{3}{2}\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

Again from the matrix

$$\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle = c_{54}\left|0\,\frac{-1}{2}\right\rangle + c_{55}\left|-1\,\frac{1}{2}\right\rangle$$

Multiplying the above two equations, we have

$$\left\langle\frac{1}{2}\,\frac{-1}{2}\middle|\frac{3}{2}\,\frac{-1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,c_{54}^{*}\left\langle 0\,\frac{-1}{2}\middle|0\,\frac{-1}{2}\right\rangle + \frac{1}{\sqrt{3}}\,c_{55}^{*}\left\langle -1\,\frac{1}{2}\middle|-1\,\frac{1}{2}\right\rangle$$

$$\Rightarrow \sqrt{\frac{2}{3}}\,c_{54}^{*} = -\frac{1}{\sqrt{3}}\,c_{55}^{*}$$

$$\frac{c_{54}^{*}}{c_{55}^{*}} = \frac{\frac{-1}{\sqrt{3}}}{\sqrt{\frac{2}{3}}} = \frac{c_{54}}{c_{55}}\,and$$

$C_{66}=1$,

With this the CG coefficient matrix for $J_1=1$ and $J_2 = 1/2$ are

$$\begin{pmatrix} \left|\frac{3}{2}\,\frac{3}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}\,\frac{1}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{-1}{2}\right\rangle \\ \left|\frac{1}{2}\,\frac{-1}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{-3}{2}\right\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0 \\ 0 & \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & -\sqrt{\frac{2}{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \left|1\,\frac{1}{2}\right\rangle \\ \left|1\,\frac{-1}{2}\right\rangle \\ \left|0\,\frac{1}{2}\right\rangle \\ \left|0\,\frac{-1}{2}\right\rangle \\ \left|-1\,\frac{1}{2}\right\rangle \\ \left|-1\,\frac{-1}{2}\right\rangle \end{pmatrix}$$

3.5.3 The Wigner- Eckart theorem

The Wigner- Eckart Theorem is in general used in calculating the transition probabilities of laser emission transitions. Before going to the proof of the theorem first let us get acquainted with some of the preliminaries used in the theorem

Euler angles

The operator J can be expressed as a unitary operator as a rotation at operator as

$$R_n(\theta) = \exp(-\frac{i(n.J)\theta}{\hbar})$$

$$\mathrm{R}\,(\alpha\beta\gamma) = R\ \ (\alpha)R_y(\chi)R_z(\gamma) = Exp(-\frac{i\alpha J_z}{\hbar})Exp\left(\frac{-i\beta J_y}{\hbar}\right)Exp\left(\frac{-i\gamma J_z}{\hbar}\right)$$

Rotation Matrix

Consider $\mathrm{R}\left\langle \alpha\beta\gamma \mid jm\right\rangle = \sum_{m^1} \left| jm^1\right\rangle\left\langle jm^1 \left|R(\alpha\beta\gamma)\right| jm\right\rangle$

$$\left\langle jm^1 \left|R(\alpha\beta\gamma)\right| jm\right\rangle = \left\langle jm^1 \right| \exp\left(\frac{-i\alpha J_z}{\hbar}\right)\exp\left(\frac{-i\beta J_y}{\hbar}\right)\exp\left(\frac{-i\gamma J_z}{\hbar}\right)\left\| jm\right\rangle$$

$$= \mathrm{Exp}\left(\frac{-im^1\alpha}{\hbar}\right)\left\langle jm^1 \right| \exp\left(\frac{-i\beta J_y}{\hbar}\right)\left\| jm\right\rangle \exp\left(\frac{-i\gamma m}{\hbar}\right)$$

$$= \mathrm{Exp}\left(\frac{-im^1\alpha}{\hbar}\right)d^{\,j}_{m^1m}\ \exp\left(\frac{-i\gamma m}{\hbar}\right) = D^{\,j}_{m^1m}(\alpha\beta\gamma)$$

Where $d^{\,j}_{m^1m} = \left\langle jm^1 \right| \exp\left(\frac{-i\beta J_y}{\hbar}\right)\left\| jm\right\rangle$

Therefore $R(\alpha\beta\gamma)\left| jm\right\rangle = \sum_{m^1=-j}^{j} D^{\,j}_{m^1m}(\alpha\beta\gamma)\left| jm^1\right\rangle$

$D^{\,j}_{m^1m}(\alpha\beta\gamma) = \exp(-im^1\alpha)d^{\,j^1}_{m^1m}\ \exp(-im\gamma)$ is called rotation matrix.

Some properties of the Rotation matrix

1. **Unitary**

$$\sum_{m^1} D^{J^*}_{m^1 m} D^{j}_{m^1 m^{11}} = \delta_{mm^{11}}$$

$$\sum_{m} D^{J}_{m^1 m} D^{j^*}_{m^1 m^{11}} = \delta_{m^1 m^{11}}$$

2.Symmetry

$$d^{j}_{m^1 m}(\beta) = (-1)^{m^1 m^{11}} d^{j}_{m^1 m^{11}}(-\beta)$$

$$= d^{j}_{mm^1}(-\beta) = (-1)^{2j}(\beta + 2\pi)$$

3.In the case of a system consists of two particles with angular momenta j_1 and j_2 , we have

$$|\, j_1 m_1 \rangle |\, j_2 m_2 \rangle = |\, j_1 j_2 m_1 m_2 \rangle = \sum_{j} C^{j_1 j_2 j}_{m_1 m_2 m} |\, jm \rangle$$

of the system is not rotated through ($\alpha\beta\gamma$) ,we have

$$R(\alpha\beta\gamma) |\, j_1 m_1 \rangle |\, j_2 m_2 \rangle = \sum_{m^1=-j}^{j} C^{j_1 j_2 j}_{m_1 m_2 m} R(\alpha\beta\gamma) |\, jm \rangle$$

$$\sum_{m_1^1 m_2^1} D^{j_1}_{m_1^1 m_1} D^{j_2}_{m_2^1 m_2} |\, j_1 m_1^1 \rangle |\, j_2 m_2^1 \rangle = \sum_{jm^1} C^{j_1 j_2 j}_{m_1 m_1 m} D^{j}_{m^1 m} |\, jm^1 \rangle$$

$$\sum_{m_1^1 m_2^1} D^{j_1}_{m_1^1 m_1} D^{j_2}_{m_2^1 m_2} \sum_{jm^1} C^{j_1 j_2 j}_{m_1^2 m_2^1 m^1} |\, jm^1 \rangle = \sum_{jm^1} C^{j_1 j_2 j}_{m_1 m_2 m} D^{j}_{m^1 m} |\, jm^1 \rangle$$

Equating the coefficients of $|\, jm^1 \rangle$ on both sides we have

$$D^{j}_{m^1 m} = \sum_{m_1^1 m_2^1} D^{j_1}_{m_1^1 m_1} D^{j_2}_{m_2^1 m_2} C^{j_1 j_2 j}_{m_1^1 m_2^1 m^1} C^{j_1 j_1 j}_{m_1 m_1 m}$$

i.e. $$D^{j}_{m^1 m} = \sum_{m_1^1 m_2^1} C^{j_1 j_2 j}_{m_1^1 m_2^1 m^1} C^{j_1 j_1 j}_{m_1 m_1 m} D^{j_1}_{m_1^1 m_1} D^{j_2}_{m_2^1 m_2}$$

$$D^{j_1}_{m_1^1 m_1} D^{j_2}_{m_2^1 m_2} = \sum_{j} C^{j_1 j_2 j}_{m_1^1 m_2^1 m^1} C^{j_1 j_1 j}_{m_1 m_1 m} D^{j_1}_{m^1 m} |\, jm^1 \rangle$$

with $m = m_1 + m_2$ and $m^1 = m^1_1 + m^1_2$

These equations are known as Clebsch-Gordon series .

4. $\int D^{j}_{m^1 m} d\Theta = 8\Pi^2$

where $d\Theta = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma = 8\pi^2$

5. $\int D^{j_1^*}_{m_1^1 m_1}(\Theta) D^{j_2}_{m_2^1 m_2}(\Theta) d(\Theta) = \dfrac{8\pi^2}{2j_1+1}$

$$\int D^{j_3^*}_{m_3^1 m_3}(\Theta) D^{j_2}_{m_2^1 m_2}(\Theta) D^{j_1}_{m_1^1 m_1} d(\Theta) = \frac{8\pi^2}{2j_1+1} C^{j_1 j_2 j_3}_{m_z^1 m_2^1 m_3^1} C^{j_1 j_2 j_3}_{m_1 m_2 m_3}$$

III. Spherical Tensor

The (2k+1) operators T^k_q for q= -k, -k…… k are said to form the components of a spherical tensor of rank k of they transform under rotations.

i.e. $$T^k_q(r) \to T^k_q(r_1) = \sum_{q^1} D^k_{q^1 q} T^k_{q^1}(r)$$

where r_1 and r are the positions of a point in the rotated and original systems.

Some properties of spherical tensor T^k_q

(a) The matrix element of T^k_q

$\langle \alpha^1 j^1 m^1 | T^k_q | \alpha j m \rangle$ vanishes unless k=m^1-m and $|j - j^1| \le q \le j + j^1$

jj' mm^1 are angular momentum quantum numbers $\alpha and \alpha^1$ represent the totality of all quantum numbers needed to specify eigen states of system completely.

2) commutation relations of T^k_q are

$[J_z T^k_q] = k\hbar T^k_q$

$[J_+ T^k_q] = \sqrt{(q-k)(q+k+1)}\hbar T^{k+1}_q$

$[J_- T^k_q] = \sqrt{(q+k)(q-k+1)}\hbar T^{k-1}_q$

3) $R(\alpha\beta\gamma) T^k_q = \sum D^k_{q^1 q} T^k_{q^1}(r)$

The statement of Wignar-Eckart theorem

$\left\langle j_2 m_2 \left| T_q^k \right| j_1 m_1 \right\rangle = C^{j_1 k j_2}_{m_1 q m_2} \dfrac{\left\langle j_2 \left\| T^k \right\| j_1 \right\rangle}{\sqrt{2 j_2 + 1}}$ where $\left\| T^k \right\|$ matrix element is called reduced matrix.

Proof

$$\left\langle j_2 m_2 \left| T_q^k \right| j_1 m_1 \right\rangle = \left\langle j_2 m_2 \left| R^{-1} R T_k^q R^{-1} R \right| j_1 m_1 \right\rangle = \sum_{m_1^1 m_2 q} \left\langle j_2 m_2 \left| T_{q^1}^k \right| j_1 m_1^1 \right\rangle D^{j_2^*}_{m_2^1 m_2} D^k_{q^1 q} D^{j_1}_{m_1^1 m_1}$$

Integrating on both sides, we have

$$\left\langle j_2 m_2 \left| T_q^k \right| j_1 m_1 \right\rangle = \frac{8\pi^2}{2 j_2 + 1} \sum_{m_1^1 q^1 m_2^1} C^{j_1 k j_2}_{m_1^1 q^1 m_2^1} C^{j_1 k j_2}_{m_1 q m_2} \left\langle j_2 m_2^1 \left| T_{q^1}^k \right| j_1 m_1^1 \right\rangle$$

$$\therefore \left\langle j_2 m_2 \left| T_q^k \right| j_1 m_1 \right\rangle = C^{j_1 k j_2}_{m_1 q m_2} \frac{1}{\sqrt{2 j_2 + 1}} \left\{ \sum_{m_1^1 q^1 m_2^1} \frac{1}{\sqrt{2 j_2 + 1}} C^{j_1 k j_2}_{m_1^1 q^1 m_2} \left\langle j_2 m_2^1 \left| T_{q^1}^k \right| j_1 m_1^1 \right\rangle \right\}$$

$$\left\langle j_2 m_2 \left| T_q^k \right| j_1 m_1 \right\rangle = C^{j_1 k j_2}_{m_1 q m_2} \frac{\left\langle j_2 \left\| T^k \right\| j_1 \right\rangle}{\sqrt{2 j_2 + 1}}$$

Summary of the lesson

The eigen value problem of the resultant operators J^2 and Jz has been discussed in depth. The values of the C.G coefficients have been determined for J_1=1 and J_2= 1/2 . The rotational operators and spherical symmetric tensor have been explained and using these quantities the Wigner- Ecart theorem has been proved.

Self assessment questions

1. Derive the recursion relations for the total angular momentum operator for a system of two particles
2. What are C. G. Coefficients. Evaluate the C.G. coefficients for J_1=1 and J_2= ½
3. State and Prove Wigner- Ecart theorem

Key terminology

Recursion relations- C. G. Coefficients- Spherical tensor- Wigner- Ecart theorem

Reference books

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UNIT - 4

LEESON - XV - Equations of motion in Schrodinger and in Heisenberg Pictures

OBJECTIVES OF THE LESSON

1. To learn the equations of motion in the Schrodinger and Heisenberg representations
2. To study the correspondence between these two representations.
3. Study on the similarity between Heisenberg equation of motion and corresponding classical equation.

4.1.1 Introduction

The dynamics of a system can be studied with the help of equation of motion. If the state of the system is known at a particular time, one can find the state at a previous/future time. As the state of physical system is described by a state vector in the vector space, the equation of motion could be equation for the state vector. A state vector or a dynamical variable as such is not observable. But the expectation value of the dynamical variable is an observable quantity. Therefore, the variation of expectation value of dynamical variable with time can be considered as an equation of motion.

The time dependence can be viewed as a change in the state vector or in the dynamical variable, or in both. When the state vector changes with time by keeping operator constant, then the resulting equation of motion represents the Schrodinger picture. In the Heisenberg picture, the operator changes with time while the state vector remains constant, however in the interaction picture, both the state vector and the operator change with time. Here, we discuss Schrodinger and Heisenberg pictures only.

4.1.2 Schrodinger Picture

In this picture the state vectors are time dependent kets and the operators are constant in time. So, the equation of motion is the equation for Ψ:

$$i\hbar\frac{\partial\left|\psi_s(t)\right\rangle}{\partial t} \quad = \quad H\left|\psi_s(t)\right\rangle \qquad (4.1.1)$$

The subscript s indicates Schrodinger picture. One can express the time dependence of $\Psi_s(\mathbf{r},t)$, in the Schrodinger picture, by unitary transformation

$\Psi_s(\mathbf{r},t) = U(t)\,\Psi_s(\mathbf{r})$ (4.1.2)

with the condition that U(0)=1, then one can write

$\Psi_s(\mathbf{r}) = \Psi_s(\mathbf{r},0)$. (4.1.3)

Now,

$$\left\langle\psi_s\middle|\psi_s\right\rangle = \left\langle U\psi_s\middle|U\psi_s\right\rangle = \left\langle\psi_s\middle|U^{\dagger}U\middle|\psi_s\right\rangle = \left\langle\psi_s\middle|\psi_s\right\rangle = 1 \text{ if } U^{\dagger}(t)U(t) = 1$$

which would imply that if $\Psi_s(\mathbf{r})$ is normalized, $\Psi_s(\mathbf{r}, t)$remains normalized at all time ,t, only when U(t) is unitary. From eqans (4.1.1) and (4.1.2), we have

$$\left[i\hbar\frac{\partial U(t)}{\partial t} - HU(t)\right]\psi_s(\overline{r}) = 0$$

The corresponding operator equation is

$$i\hbar\frac{\partial U(t)}{\partial t} = HU(t)$$

If H does not depend on time, t, then above equation has a solution of the form

$$U(t) = U(0)e^{-iHt/\hbar} = e^{-iHt/\hbar} \qquad (4.1.4)$$

Therefore from eqn (4.1.2), we obtain

$$\left|\psi(\bar{r},t)\right\rangle = e^{-iHt/\hbar}\left|\psi_s(\bar{r})\right\rangle \qquad (4.1.5)$$

From eqn (4.1.1) and eqn (4.1.5), the time rate of change of the matrix element of an observable A_s, with time is given by

$$\begin{aligned}\frac{d}{dt}\langle A_s\rangle &= \frac{d}{dt}\langle\psi_s|A_s|\psi_s\rangle \\ &= \left[\frac{d}{dt}\langle\psi_s|\right]A_S|\psi_s\rangle + \langle\psi_s|\frac{\partial A_S}{\partial t}|\psi_s\rangle + \langle\psi_s|A_S\left[\frac{d}{dt}|\psi_s\rangle\right] \\ &= \langle\psi_s|\frac{\partial A_S}{\partial t}|\psi_s\rangle + i\hbar\langle\psi_s|A_sH - HA_s|\psi_s\rangle \\ &= \langle\psi_s|\frac{\partial A_S}{\partial t}|\psi_s\rangle + i\hbar\langle\psi_s|[A_s,H]|\psi_s\rangle \qquad (4.1.6)\end{aligned}$$

If A_s does not depend explicitly on time, first term of the right side of eqn (4.1.6) reduces to zero. Then eqn (4.1.6) becomes

$$\frac{d}{dt}\langle A_s\rangle = \mathrm{i}\hbar\langle\psi_s|[A_s,H]|\psi_s\rangle \qquad (4.1.7)$$

Comparing this equation with the equation of motion for the dynamical variables A in classical mechanics, we see that the expectation values of operators obey the same equation of motion in quantum mechanics (Ehrenfest's theorem), provided we identify the commutatory bracket divided by iħ with the quantum mechanical Poisson Bracket.

4.1.3 The Heisenberg Picture

In this representation, the wave function $\psi_H(\mathbf{r})$ does not change with time while the operators change with time. The subscript H stands for Heisenberg picture. The time-independent state $\psi_H(\mathbf{r})$ is obtained from $\psi_s(\mathbf{r},t)$ by the unitary transformation (U(t)=exp(-iHt/ħ)) i.e.,

$$\psi_H(r) = U^{-1}(t)\psi_s(r,t) \qquad (4.1.8)$$

where $\psi_s(\mathbf{r},t)$ is the state vector in Schrodinger picture, and $\psi_H(r)$ is in the Heisenberg picture and is independent of time.

The operator in the Heisenberg picture can be written as

$$A_H(t) = U^{-1}(t) A_s U(t) = e^{iHt/\hbar} A_s e^{-iHt/\hbar}$$

Differentiating this equation with respect to time, we get

$$\begin{aligned}
\frac{d}{dt} A_H &= \frac{d}{dt}\left(e^{iHt/\hbar} A_s e^{-iHt/\hbar}\right) \\
&= \frac{i}{\hbar}\left(e^{iHt/\hbar} H A_s e^{-iHt/\hbar}\right) - \frac{i}{\hbar}\left(e^{iHt/\hbar} A_s H e^{-iHt/\hbar}\right) + U^{\dagger}\frac{\partial A_s}{\partial t} U \\
&= \frac{i}{\hbar}\left[HA_H - A_H H\right] + \frac{\partial A_H}{\partial t} \\
&= -\frac{i}{\hbar}\left[A_H, H\right] + \frac{\partial A_H}{\partial t} \\
&= \frac{1}{i\hbar}\left[A_H, H\right] + \frac{\partial A_H}{\partial t} \qquad (9)
\end{aligned}$$

The eqn (9) represents the variation of dynamical variables with time in the Heisenberg picture.

In the interaction Picture the state vector and operators can be represented as

$$\left|\Psi_I(t)\right\rangle = \exp(iH_{os}t/\hbar)\left|\psi_s(t)\right\rangle$$

$$A_I(t) = \exp(iH_{os}t/\hbar)\, A_s \exp(-iH_{os}t/\hbar)$$

So that the interaction and Heisenberg pictures are the same when $H' = 0$ (H' represents the explicit time dependence of Hamiltonian). In this case $H_{os} = H_{oI}$.

4.1.4 Correspondence between Schrodinger Picture and Heisenberg Pictures

In quantum mechanics, we have two fundamental entities, one is the state vector, representing state of a the physical system and the other is dynamical operator. We are interested in knowing the time development of these quantities i.e., their equations of motion. In Schrodinger picture, the state vector $\psi_s(t)$, depends on time while operator, say A_s, is time independent. Whereas, in Heisenberg representation the operator change with time while the state vector remains constant. As the physical process cannot depend on a particular choice of representation, there must exit some relation between them.

At t = 0, state vector and operator are to be identical in both representations, i.e.,

The Schrodinger state vector at time t, $\left|\psi_s(r,t)\right\rangle$ is related to $\left|\psi_s(r,0)\right\rangle$ by unitary operator as

$\left\langle\psi_s(r,t)\middle|\psi_s(r,t)\right\rangle = \left\langle\psi_s(r,0)\middle|\psi_s(r,0)\right\rangle$ due to conservation of probility.

$$\left|\psi_s(r,0)\right\rangle = \left|\psi_H(r)\right\rangle \qquad \textit{and} \qquad A_s = A_H(0).$$

$$\left|\psi_s(r,t)\right\rangle = U(t)\left|\psi(r,0)\right\rangle$$

$$= U(t)\left|\psi(r,0)\right\rangle \qquad (4.1.10)$$

Since $\left|\psi_H\right\rangle$ does not depend on time, the time differential of the above equation gives

$$i\hbar\frac{\partial\left|\psi_s(t)\right\rangle}{\partial t} = i\hbar\frac{\partial U}{\partial t}\left|\psi_H\right\rangle \qquad (4.1.11)$$

Further, $\left|\psi_s(t)\right\rangle$ satisfies the Schrodinger time dependent equation (eqn.1),

so the above equation can be written as

$$H_s\left|\psi_s(r,t)\right\rangle = i\hbar\frac{\partial U}{\partial t}\left|\psi_H(r)\right\rangle$$

$$or \qquad H_s U(t)\left|\psi_s(r,0)\right\rangle = i\hbar\frac{\partial U}{\partial t}\left|\psi_H(r)\right\rangle$$

$Since \quad \left|\psi_H(r)\right\rangle = \left|\psi_s(r,0)\right\rangle,$ *the above equation reduces to*

$$H_s U(t) \;=\; i\hbar\frac{\partial U(t)}{\partial t} \qquad (4.1.12)$$

The solution of eqn (12) is

U(t) = exp(-iH_st/ђ) (4.1.13)

Where H_s is assumed to be time-independent.

For conservative systems, the Hamiltonian gives the energy of the system. Therefore, in any representation H does not depend on time, so that $H_H = H_s = H$. Hence

Since the expectation value of an operator is the same, irrespective of its representation, so

$$\left|\psi_s(t)\right\rangle = e^{-iHt/\hbar}\left|\psi_H\right\rangle = U\left|\psi_H\right\rangle \qquad (4.114)$$

$$\langle \psi_H | A_H(t) | \psi_H \rangle = \langle \psi_s(t) | A_s | \psi_s(t) \rangle = \langle \psi_H U^\dagger | A_s | U \psi_H \rangle$$

Therefore,

$$A_H(t) = U^\dagger A_s U \qquad (4.1.15)$$

This gives us the relation between any Heisenberg and Schrodinger operators, defining observables.

We will now show that the eigenvalues of operators, being the results of physical measurements, must be same in both the representations.

Let the state vector in Schrodinger representation be

$$|\psi_s\rangle = \sum c_i |u_i^s\rangle \qquad (4.1.16)$$

where $|u_i^s\rangle$ *are eigenstates* $(i = 1, 2, 3, ...)$ *on which* A_s *is measured*

to yield eigenvalues λ_i, *i.e.,*

$$A_s |u_i^s\rangle = \lambda_i |u_i^s\rangle$$

Multiplying both sides by $U^\dagger$ with $U U^\dagger = 1$, the above equation becomes

$$U^\dagger A_s U U^\dagger |u_i^s\rangle = \lambda U^\dagger |u_i^s\rangle$$

$$\text{where} \quad U^\dagger A_s U = A_H \qquad \text{and} \qquad |u_i^s\rangle = U |u_i^H\rangle$$

$$\text{or} \qquad A_H |u_i^H\rangle = \lambda_i |u_i^H\rangle_i \qquad (4.1.17)$$

Eqn (17) shows that λ_i's are also the eigenvalues of the operator A_H. Hence the eigenvalues of the operators are the same in Schrodinger and Heisenberg representations.

Now, let us show that the probabilities of finding the system in corresponding eigenstates are same in both representations. For that, consider the eqn (4.1.16),

$$\left|\psi_s\right\rangle = \sum_i c_i \left|u_i^s\right\rangle$$

Multiplying both sides by $U^\dagger$, we obtain

$$U^\dagger \left|\psi_s\right\rangle = \sum_i c_i U^\dagger \left|u_i^s\right\rangle$$

or

$$\left|\psi_H\right\rangle = \sum_i c_i \left|u_i^H\right\rangle \qquad (4.1.18)$$

In eqn (16), c_i 's give the probabilities of finding the system in the i^{th} eigenstate and the same c_i 's occur as coefficients in eqn (18) also. Therefore, the probabilities of finding the system in the corresponding eigenstates are same in both representations, i.e.,

$$\left|c_i\right|^2 = \left|\left\langle u_i^s \middle| \psi_s\right\rangle\right|^2 = \left|\left\langle u_i^H \middle| \psi_H\right\rangle\right|^2$$

Since two pictures are equivalent, in principle, we can do our calculations using either one of them. However, for a general operator equations of motions in Heisenberg picture is difficult to solve for most systems (there are exceptions) and therefore, we use the Schrodinger picture in which we deal with the more familiar linear differential equations.

Summarising with the help of metaphor, we can say that the Schrodinger picture rotates the dance floor with the dancers remaining still, while the Heisenberg picture leaves the dance floor alone and lets the dancers rotate.

SUMMARY OF THE LESSON

The equations of motion in Schrodinger and Heisenberg pictures are discussed. The correspondences between these two pictures are explained in detail

KEY TERMINOLOGY

Schrodinger Picture, Heisenberg Picture, Dynamical variable, Unitary operator, Poisson bracket, Commutator.

SELF ASSESSMENT QUESTIONS

1. State and explain the equations of motion in the Schrodinger and Heisenberg pictures.
2. Show that the probabilities of finding the system in the corresponding eigenstates are same in Schrodinger and Heisenberg representations.
3. What is unitary transformation ? Show that the operator equations remain unchanged in a unitary transformation.

REFERENCE BOOKS

1. Quantum Mechanics by S.N. Biswas (Books and Allied (P) Ltd), India, 1998.
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3. Quantum Mechanics by G.Aruldhas (Prentice-Hall of India Private Ltd), N.Delhi, 2002.
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UNIT - 4

LESSON - XVI Heisenberg equation: Correspondence with Classical equation and Application to Harmonic Oscillator

OBJECTIVES OF THE LESSON:

1. To learn the correspondence between Heisenberg equation with Classical Mechanics.
2. To study the Application of Heisenberg equation to the Harmonic oscillator.

4.2.1 correspondence between Heisenberg equation with Classical Mechanics.

In order to get the similarity between Heisenberg equation of motion and corresponding classical equation, we review briefly the structure of classical hamiltonian theory. Let the hamiltonian is a function of coordinates and momenta, i.e., H = H (q_1, q_2, . . .; p_1, p_2, . . .), and writing a relation between hamiltonian and

$$H(q_1, q_2, ...; p_1, p_2, ...; t) \; = \; \sum p_i \, \dot{q}_i - L$$

Lagrangian as

The variation of Hamiltonian, H, lead to the Hamilton's equations of motion

$$\dot{q} = \frac{\partial H}{\partial p_i} \qquad and \qquad \dot{p} = -\frac{\partial H}{\partial q_i} \qquad\qquad i = 1, 2, 3, ...$$

The time dependence of any function of the coordinates, momenta, and the time, calculated along a moving phase point, is

$$\frac{d}{dt} F\left(q_i, p_i, t\right) \; = \; \frac{\partial F}{\partial t} + \sum \left(\frac{\partial F}{\partial q_i} \dot{q}_i \; + \; \frac{\partial F}{\partial p_i} \, \dot{p}_i \right)$$

$$= \frac{\partial F}{\partial t} + \sum \left(\frac{\partial F}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \, \frac{\partial F}{\partial p_i} \right)$$

Here the Hamilton's equations have been used to get the above equation. The Poisson bracket {A, B} of any two functions of the coordinates and momenta is defined as

$$\{A, B\} = \sum\left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} + \frac{\partial B}{\partial q_i}\frac{\partial A}{\partial p_i}\right)$$

In terms of Poisson bracket, the equation of motion for the function F of the dynamical variables becomes

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\}$$

The resemblance between the above equation and Heisenberg equation, suggests that quantum analogs of the classical equations of motion can be found by substituting the commutator bracket divided by i ħ for the Poisson bracket,

$$\{A, B\} = \frac{1}{i\hbar}[A, B]$$

and working with the Heisenberg picture.

4.2.2 Application of Heisenberg equation to Harmonic Oscillator

In the Heisenberg representation the time dependence is assigned to operators leaving the state vector time independent. The Heisenberg equation of motion for an operator is given by

$$i\hbar\, dA/dt = [A, H]$$

where A is an operator. He has used this equation of motion to Harmonic oscillator.

Let us consider a linear harmonic oscillator having the Hamiltonian

$$H = p^2/(2m) + (1/2)\, k\, x^2$$

$$= p^2/(2m) + (1/2)\, m\omega^2 x^2 \qquad (4.2.1)$$

where p and x are time dependent operators with infinite Hermitian matrices satisfying the commutation relation

$$\left[x, p_x\right] = i\hbar$$

The equation of motion for the operator x in the Heisenberg picture is

$$i\hbar \frac{dx}{dt} = [x, H]$$

$$= \frac{1}{2m}\left[x, p^2\right] + \frac{1}{2}m\omega^2\left[x, x^2\right]$$

$$= \frac{1}{2m}\left(p[x, p] + [x, p]\,p\right)$$

$$= \frac{i\hbar p}{m}$$

or $\dot{x} = \frac{p}{m}$ (4.2.2)

In the similar way we can write that

$$\dot{p} = -m\omega^2 x \tag{4.2.3}$$

Differentiating eqn (4.2.2) with respect to t and combining it with eqn (4.2.3), we have

$$\ddot{x} + \omega^2 x = 0 \tag{4.2.4}$$

This equation can be written in the matrix form as

$$\left(\ddot{x}\right)_{kn} + \omega^2 x_{kn} = 0 \tag{4.2.5}$$

The solution of this equation is

$$x_{kn}(t) = x_{kn}\left(0\right)\exp(i\omega_{kn}t) \tag{4.2.6}$$

where $\omega_{kn} = (E_k - E_n)/\hbar$

Differentiating the eqn (4.2.6) twice with respect to time, we get

$$\left(\ddot{x}\right) = -w_{kn}^{2}\, x_{kn}\left(0\right)\exp\left(i w_{kn} t\right) = -w_{kn}^{2}\, x_{kn} \qquad (4.2.7)$$

Substituting eqn (4.2.7) in eqn (4.2.5), we obtain

$$\left(\omega_{kn}^{2} - \omega^{2}\right) x_{kn}(t) = 0 \quad \text{or} \quad \left(\omega_{kn}^{2} - \omega^{2}\right) x_{kn}\left(0\right) = 0 \qquad (4.2.8)$$

It is convenient to derive the relations for the matrix elements, which are independent of time. Generalization is not different as similar relations hold for matrices that depend on time. In view of eqn (4.2.8), all matrix elements $x_{kn}(0)$ vanish except those for which the transition frequency $\omega_{kn} = \pm\, \omega$. Therefore

$$x_{kn}\left(0\right) = 0 \quad \text{if} \quad \omega_{kn} \neq \pm\omega \; ;$$

$$and \quad x_{kn}\left(0\right) \neq 0 \quad \text{if} \quad \omega_{kn} = \pm\omega$$

That is, for a given value of k only two x_{kn} elements are non-vanishing and those are n=k+1 and n=k-1:

$$x_{k,k-1} \text{ corresponds to } \omega_{k,k-1} = \frac{E_k - E_{k-1}}{\hbar} = +\omega \qquad (4.2.9)$$

and

$$x_{k,k+1} \text{ corresponds to } \omega_{k,k+1} = \frac{E_k - E_{k+1}}{\hbar} = -\omega \qquad (4.2.10)$$

The structure of x matrix would then be

$$\left(x\right) = \begin{bmatrix} 0 & x_{01} & 0 & 0 & . & . \\ x_{10} & 0 & x_{12} & 0 & . & . \\ 0 & x_{21} & 0 & x_{23} & . & . \\ 0 & 0 & x_{32} & 0 & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix}$$

Similar way the elements of the *p* matrix can be obtained as

$$p_{kn}(0) = im\omega_{kn} x_{kn}(0)$$

In view of eqns (4.2.9) and (4.2.10), the non-vanishing elements of the *p* matrix are

$p_{k,k-1} = im\omega x_{k,k-1}$ and $p_{k,k+1} = -im\omega x_{k,k+1}$ (4.2.11)

The structure of *p* matrix is

$$p(x) = im\omega \begin{bmatrix} 0 & -x_{01} & 0 & 0 & . & . \\ x_{10} & 0 & -x_{12} & 0 & . & . \\ 0 & x_{21} & 0 & -x_{23} & . & . \\ 0 & 0 & x_{32} & 0 & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix}$$

The Heisenberg equation of motion of an operator allows us to get the structure of the *x* and *p* matrices. To get the elements of the *x* and *p* matrices, we have to use the fundamental equation of Heisenberg method. The diagonal (k,k) elements of the fundamental commutation relation is

$$\left(xp\right)_{kn} - \left(px\right)_{kn} = i\hbar$$

Substituting the matrices for *x* and *p* and using matrix multiplication procedures, we get

$$2im\omega \begin{bmatrix} x_{01}x_{10} & 0 & 0 & 0 & . & . \\ 0 & -x_{01}x_{10} + x_{12}x_{21} & 0 & 0 & & \\ 0 & 0 & -x_{12}x_{21} + x_{23}x_{32} & 0 & . & . \\ 0 & 0 & 0 & -x_{23}x_{32} + x_{34}x_{43} & . & \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix} = i\hbar\delta_{kn}$$

where δ_{kn} is the unit matrix. Equating the elements on both sides, we have

$$
\begin{aligned}
x_{01}x_{10} &= \frac{\hbar}{2m\omega} \\
x_{12}x_{21} &= \frac{2\hbar}{2m\omega} \\
.. &= .. \\
.. &= .. \\
x_{k,k+1}x_{k+1,k} &= \frac{(k+1)\hbar}{2m\omega} \\
.. & \quad .. \\
.. & \quad ..
\end{aligned}
$$

Solving this system of equations, Since x is Hermitian, we can write

$$\left|x_{k,k+1}\right|^2 = \frac{(k+1)\hbar}{2m\omega} \qquad or \qquad x_{k,k+1} = \left(\frac{(k+1)\hbar}{2m\omega}\right)^{1/2} \qquad (4.2.12)$$

and

$$x_{k-1,k} = \left(\frac{k\hbar}{2m\omega}\right)^{1/2} \qquad (4.2.13)$$

From eqns. (4.2.11), (4.2.12), and (4.2.13),   we have

$$
\begin{aligned}
p_{k,k+1}p_{k+1,k} &= \left(-im\omega x_{k,k+1}\right)\left(im\omega x_{k+1,k}\right) \\
&= \frac{m\omega(k+1)\hbar}{2}
\end{aligned}
$$

or

$$p_{k,k+1} = \left(\frac{m\omega(k+1)\hbar}{2}\right)^{1/2}$$

and

$$p_{k,k-1} = \left(\frac{m\omega k\hbar}{2}\right)^{1/2}$$

Now

$$(x^2)_{nn} = (xx)_{nn} = \Sigma\, x_{ni}\, x_{in} = x_{n,n+1}\, x_{n+1,n} + x_{n,n-1}\, x_{n-1,n}$$

$$= (n+1)\,\hbar / (2m\,\omega) + n\hbar / (2m\,\omega)$$

$$= (2n+1)\,\hbar / (2m\,\omega)$$

and

$$(p^2)_{nn} = m\,\omega\,(n+1)\,\hbar / 2 + m\,\omega\, n\,\hbar / 2 = m\,\omega\,(2n+1)\,\hbar / 2$$

Then the Hamiltonian matrix is

$$H_{nn} = (1/2m)\, m\,\omega\,(2n+1)\,\hbar / 2 + m\,\omega^2\,(2n+1)\,\hbar / (4\,m\,\omega)$$

$$= (2n+1)\hbar\,\omega / 2$$

The eigenvalues E_n of the Hamiltonian are given by

$$E_n = (\, n + ½)\,\hbar\,\omega, \qquad n = 0,1,2,3,\ldots \qquad (4.2.14)$$

This is the same as the usual way one can obtain.

Now, one can write the explicit form of the matrices for x(0) and p(0) based on the above equations as

$$x(0) = \left(\frac{\hbar}{2mw}\right)^{1/2} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0\ \ldots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0\ \ldots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0\ \ldots \\ .\,.\,.\ \ldots & & \ldots & & .\,.\,. \end{pmatrix}$$

and

$$p(0) = \left(\frac{mw\hbar}{2}\right)^{1/2} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & 0\ \ldots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & 0\ \ldots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0\ \ldots \\ .\,.\,.\ \ldots & & \ldots & .\,.\,. & \ldots.. \end{pmatrix}$$

We could obtain the energy quantization of the harmonic oscillator results from the application of Heisenberg equation of motion.

Summary of the lesson

The Heisenberg representation in the quantum mechanics is a powerful tool in explaining physical phenomena. A similarity between Heisenberg equation of motion and corresponding classical equation has been shown. That is the quantum analogs of the classical equations of motion can be found by substituting the commutator bracket divided by $i\hbar$ for the Poisson bracket and working with the Heisenberg picture. An application of the Heisenberg picture is also discussed. Making use of the Heisenberg equation of motion the eigenvalues of the harmonic oscillator were evaluated.

Key Terminology: Heisenberg picture, commutator bracket, harmonic oscillator, eigenvalues.

Self Assessment Questions

1. Obtain a correspondence between Heisenberg equation of motion and classical equation of Motion.
2. Derive eigenvalues of the harmonic oscillator using Heisenberg equation of motion.

Reference Books

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2. Quantum Mechanics by G. Aruldhas (Prentice-Hall of India Private Ltd., 2002).
3. Quantum Mechanics by S.N. Biswas (Books and Allied (P) Ltd., 1998).

UNIT - 4

LESSON – XVI RELATIVISTIC QUANTUM MECHANICS-I : KLEIN-GORDON EQUATION

OBJECTIVES OF THE LESSON

1. To study the need of relativistic quantum mechanics
2. To learn the Klein-Gordon equation and its solutions
3. To know the difficulties with the Klein-Gordon equation
4. To study an application to Klein - Gordon equation

RELATIVISTIC QUANTUM MECHANICS

4.3.1 Introduction

The quantum mechanics studied so far is based on a non- relativistic Hamiltonian and does not satisfy the requirements of special theory of relativity. In the non-relativistic Schrodinger wave equation, the time is in the first order and space is in the second order derivatives. This contradicts the space-time symmetry of relativity. In this chapter we deal with the motion of particles those with velocities close to that of light. One of the characteristic feature of relativistic wave equations is these equations are invariant under Lorentz transformation. In the following, two relativistic equations are considered i.e., particle with spin zero equation due to Klein-Gordon and the spin 1/2 particle due to Dirac.

4.3.2 Klein -Gordon Relativistic Equation

Schrodinger equation for a free particle of mass m is based on the non-relativistic relation, $E = p^2/2m$, between the energy and momentum of a free particle and the corresponding relativistic relation is given by

$$E^2 = c^2 p^2 + m^2 c^4 \qquad (4.3.1)$$

Replacing E and p by their operators

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad \text{and} \quad p \rightarrow -i\hbar\nabla$$

in the eqn (4.3.1) and multiplying with the wave function Ψ(**r**,t) on both sides of the equation gives

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = -\hbar^2 c^2 \nabla^2 \psi + m^2 c^4 \psi$$

or

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \nabla^2\psi + \left(\frac{mc^2}{\hbar}\right)^2 \psi = 0 \qquad (4.3.2)$$

This equation is also known as Schrodinger relativistic equation. Rearranging the terms, we get

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi(r,t) = \frac{m^2c^2}{\hbar^2}\psi(r,t)$$

or

$$\Box\psi(r,t) = \frac{m^2 c^2}{\hbar^2}\,\psi(r,t) \qquad (4.3.3)$$

where ڨ is a D' Alembertian operator. The above equation is known as Klein-Gordon equation.

4.3.3 Plane wave solution

Taking the plane wave solutions of the Klein-Gordon equation as

Ψ(**r**,t) = exp[i(**p.r** - Et) / ħ]

and substituting in the Klein-Gordon equation would yield

$E = \pm\ (p^2 c^2 + m^2 c^4)^{½}$

This means that there exist solutions of negative energy. Klein and Gordon were not able to give a proper explanation to the negative energy states.

4.3.4 Application of Klein-Gordon Equation to the Hydrogen atom

The Klein-Gordon equation for a free particle is give by

$$\left(i\hbar\frac{\partial}{\partial t}\right)^2\psi\left(r,t\right)=-\hbar^2c^2\nabla\left(r,t\right)+m^2c^4\psi\left(r,t\right) \qquad (4.3.4)$$

For charged particle in the coulomb field of potential *V*(r) can be obtained by *E* -*V*(r) , where the potential for the electron is given by

$$V(r)=-\frac{ze^2}{r} \qquad (4.3.5)$$

Therefore, the equation of motion of the electron under the influence of coulomb filed is given by

$$-\hbar^2c^2\nabla^2\psi(r,t)-\left(i\hbar\frac{\partial}{\partial t}+\frac{ze^2}{r}\right)^2\psi(r,t)+m^2c^4\psi(r,t)=0$$

$$\text{or}\quad \nabla^2\psi(r,t)+\frac{1}{\hbar^2c^2}\left(i\hbar\frac{\partial}{\partial t}+\frac{ze^2}{r}\right)^2\psi(r,t)+\frac{m^2c^4}{\hbar^2c^2}\psi(r,t)=0 \qquad (4.3.6)$$

Since the potential is independent of time, eqn (4.3.3) can be separated with respect to variables r and t with the solution of the form

$$\psi\,(r,t)=\psi\,(r)e^{-iEt/\hbar} \qquad (4.3.7)$$

Substituting eqn (4.3.7) in eqn (4.3.6) and rearranging the terms, we get

$$\nabla^2\psi(\overline{r})+\frac{1}{\hbar^2c^2}\left(E+\frac{ze^2}{r}\right)^2\psi(r)-\frac{m^2c^4}{\hbar^2c^2}\psi(r)=0 \qquad (4.3.8)$$

Since the potential is spherically symmetric, we can obtain the solutions, which are separated into radial and angular parts

$$\psi(r,\Theta,\Phi) = R(r)Y_{lm}(\Theta,\Phi) \qquad (4.3.9)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\hbar^2c^2}\left\{\left(E+\frac{ze^2}{r}\right)^2-m^2c^4-\frac{l(l+1)}{r^2}\right\}R=0 \qquad (4.3.10)$$

On substitution of eqn (4.3.9) in eqn (4.3.8) and making use of separation variables method, we can write the radial parts of wave equation as

Rewriting eqn (4.3.10), with substitution $\rho=\alpha r$ becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left(\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)-\gamma^2}{\rho^2}\right)R=0 \qquad (4.3.11)$$

where $\gamma=\dfrac{ze^2}{c\hbar}$; $\lambda=\dfrac{2E\gamma}{\hbar c\alpha}$ and $\alpha^2=\dfrac{4\left(m^2c^4-E^2\right)}{\hbar^2c^2}$ (4.3.12)

Eqn (4.3.11) is similar to nonrelativistic hydrogen atom theory, except for the factor $l(l+1)-\gamma^2$ in place of $l(l+1)$. By writing

$$s(s+1)=l(l+1)-\gamma^2 \qquad (4.3.13)$$

eqn (4.3.11) takes convenient form

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left(\frac{\lambda}{\rho}-\frac{1}{4}-\frac{s(s+1)}{\rho^2}\right)R=0 \qquad (4.3.14)$$

Well behaved solution of eqn (4.3.14) exist only if

$$\lambda=n'+s+1 \qquad n'=0,1,2,\ldots \qquad (4.3.15)$$

and *s* to be non-negative to make R(r) finite at the origin. The value of *s* can be obtained from eqn (4.3.13) as

$$s = \frac{-1 \pm (1 + 4l^2 + 4l - 4\gamma^2)^{1/2}}{2} = -\frac{1}{2} \pm \left[\left(l + 1/2\right)^2 - \gamma^2\right]^{1/2} \qquad (4.3.16)$$

Substituting the positive *s* value from eqn (4.3.16) and λ value from eqn (4.3.12) in eqn (4.3.15), we get

$$\frac{E\gamma}{(m^2c^4 - E^2)^{1/2}} = n' + \frac{1}{2}\left[\left(l + 1/2\right)^2 - \gamma^2\right]^{1/2} \qquad (4.3.17)$$

$$\approx n' + \frac{1}{2} + \left(l + 1/2\right)\left[1 - \frac{\gamma^2}{2\left(l + 1/2\right)^2}\right]$$

$$= n' + \frac{1}{2} + l + \frac{1}{2} - \frac{\gamma^2}{2\left(l + 1/2\right)}$$

$$= n' + l + 1 - \frac{\gamma^2}{2\left(l + 1/2\right)}$$

$$= n' - \frac{\gamma^2}{2\left(l + 1/2\right)} \qquad \left(\because n = n' + l + 1\right)$$

$$= A^{1/2} \qquad \left(\text{taking } A^{1/2} = n' - \frac{\gamma^2}{2\left(l + 1/2\right)}\right)$$

Taking squares on both sides, we get

$$\frac{E^2\gamma^2}{m^2c^2 - E^2} = A^2$$

or

$$E = mc^2\left(1 + \frac{\gamma^2}{A}\right)^{-1/2}$$

$$\approx\ mc^2\left(1-\frac{\gamma^2}{2A}+\frac{3\gamma^4}{8A^2}\right)\ =\ mc^2\left(1-\frac{\gamma^2\,A^{-1}}{2}+\frac{3\gamma^4\,A^{-2}}{8}\right)$$

Expanding A^{-1} and A^{-2} in terms of binomial series and retaining terms up to γ^4, we obtain

$$E\approx mc^2\left\{1-\frac{\gamma^2}{2n^2}\left(1+\frac{2\gamma^2}{2n\left(l+\frac{1}{2}\right)}\right)+\frac{3\gamma^4}{8n^4}\right\}$$

$$=mc^2\left[1-\frac{\gamma^2}{2n^2}-\frac{\gamma^4}{2n^4}\left(\frac{n}{\left(l+\frac{1}{2}\right)}-\frac{3}{4}\right)\right] \qquad (4.3.18)$$

The first term of this equation is the rest energy and the second term $-mc^2\gamma/2n^2$ gives the Balmer levels of the hydrogen atom. The third term is the relativistic correction, which removes the orbital degeneracy and gives a fine structure to each of *l* levels.

Is it all well with the Klein-Gordon equation?

We expect that probability density P($\mathbf{r}$,t) and probability current density S($\mathbf{r}$,t) to satisfy a continuity equation of the form

$$\frac{\partial P(r,t)}{\partial t}+\nabla.S(r,t)\ =\ 0.$$

To obtain such an equation, we multiply Klein-Gordon equation on the left by ψ^* , and its complex conjugate equation by ψ and then subtracting one from the other, we get

$$\psi^* \frac{\partial^2\psi}{\partial t^2} - \psi \frac{\partial^2\psi^*}{\partial t^2} = c^2 (\psi * \nabla^2\psi - \psi\nabla^2\psi^2)$$

or

$$\frac{\partial}{\partial t}\left(\psi^* \frac{\partial\psi}{\partial t} - \psi \frac{\partial\psi^*}{\partial t}\right) = c^2\nabla.(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

This is continuity equation with

$$P(r,t) = \frac{i\hbar}{2mc^2}\left(\psi^* \frac{\partial\psi}{\partial t} - \psi \frac{\partial\psi^*}{\partial t}\right) \qquad (4.3.19)$$

$$S(r,t) = -\frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

The expression for S(**r**, t) coincides exactly with corresponding non-relativistic case. However, the expression for P(**r**, t) is completely different from the one in the non-relativistic case. If ψ is real, P(**r**, t) vanishes. When ψ is complex, eqn (19) can be written as

$$\begin{aligned} P(r,t) &= \left[\psi^* i\hbar \frac{\partial\psi}{\partial t} + \psi\left(-i\hbar\frac{\partial}{\partial t}\right)\psi^*\right]\frac{1}{2mc^2} \\ &= \frac{1}{2mc^2}\left[\psi^* E\psi + \psi E\psi^2\right] \\ &= \frac{E}{mc^2}|\psi|^2 \end{aligned}$$

It follows from this equation that P(**r**, t) is positive when *E* is positive and negative when *E* is negative. In other words, the probability density takes both positive and negative values. Hence P(**r**, t) given by eqn (19) can not be regarded as position probability density. This problem was resolved by Pauli and Weisskopf by interpreting eP(**r**, t) as the charge density and eS(**r**, t) as the corresponding current density. Since charges can take negative and positive values, this theory is useful only a system of particles having both signs of charges.

Summary

Since non-relativistic Schrodinger equation did not satisfy the requirements of special theory of relativity, Klein-Gordon made an attempt to modify the non-relativistic Schrodinger equation. Though they were successful to a limited extent but could not explain the result of negative probability density, which they encountered. In addition they were unable to explain the negative energy solutions. But Klein-Gordon could explain the fine structure of each *l* levels in the hydrogen atom spectra.

Key Terminology

Relativistic quantum mechanics, Klein-Gordon equation, hydrogen atom, probability charge density, probability current density.

Self Assessment Questions

1. Explain necessity of relativistic quantum mechanics ?
2. Derive Klein-Gordon equation
3. Elucidate the difficulties with the Klein-Gordon equation.
4. Obtain the expression for energy of a charged particle in a coulomb potential using Klein-Gordon equation and explain the significance of the result.

Reference Books

1. Quantum Mechanics by L. I. Schiff (McGraw-Hill Kogakusha, Ltd, 1968).
2. Quantum Mechanics by G. Aruldhas (Prentice-Hall of India, 2002).
3. Quantum Mechanics by S. Lokanathan and A. Ghatak

UNIT - 4

LESSON - XVIII RELATIVISTIC QUANTUM MECHANICS-II : DIRAC EQUATION

OBJECTIVES OF THE LESSON

1. To study the Dirac equation
2. To learn the Dirac matrices
3. To study the plane wave solutions of the Dirac equation
4. To understand the results of Dirac equation

4.4.1 Dirac equation

In the previous lesson we have seen that the solution of the relativistic Klein-Gordon equation gives the probability density as a negative instead of a positive definite. To prevent such an occurrence of negative probability, which is unrealistic, the relativistic equation must be modified. Therefore, Dirac modified the hamiltonian operator in order to ensure that the hamiltonian or energy should be linear in the momentum without affecting the relativistic symmetry between energy and momentum. In addition Klein-Gordon could not explain the negative energy states. Whereas, Dirac gave the explanation for the origin of negative states.

The Dirac proposed that Hamiltonian describing the motion of particle, let us say the electron could be written as

$$H = c\alpha . p + \beta m c^2 \qquad (1)$$

Where H is linear in p; β and the coefficients α_x, α_y, α_z are to be determined.

With substitution of the hamiltonian from eqn (1) in the time dependent Schrodinger equation of motion

$$i\hbar \frac{\partial}{\partial t}\psi(\underline{r},t) = H\psi(\underline{r},t)$$

transforms to

$$i\hbar \frac{\partial \psi}{\partial t} = -i\hbar c\bar{\alpha}.\nabla + \beta m c^2 \qquad (2)$$

`

This is the Dirac equation of motion for a free particle.

Let us understand the four quantities α_x, α_y, α_z and β defined in equation (1). We know that the space and time derivatives are to appear only in p and E, and not in α and β, since eqn (5) is to be linear in all these derivatives. Therefore, α and β have to be independent of p and E and commute with them. Nevertheless, α_x, α_y, α_z and β may not be mere scalar numbers. If they were, the square of the energy (Hamiltonian) operator (eqn 4) would contain terms proportional to p_x, p_y, p_z, mc^2 etc. But the relativistic expression (eqn 1) contains no such term. Hence, the commutative relations to α_x, α_y, α_z and β were determined by requiring that H^2 should reduce to the expression $E^2 = p^2 c^2 + m^2 c^4$. Writing H^2 as HH to facilitate observance of the non-commuting factors while multiplying, we have

$$c^2(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta mc)(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta mc) = c^2(p^2 + m^2c^2)$$

$$or$$

$$\alpha_x{}^2 p_x{}^2 + \alpha_x\alpha_y p_x p_y + \alpha_x\alpha_z p_z p_x + \alpha_x\beta p_x mc + \alpha_y\alpha_x p_x p_y + \alpha_y{}^2 p_y{}^2 +$$
$$\alpha_y\alpha_z p_y p_z + \alpha_y\beta p_y mc + \alpha_z\alpha_x p_z p_x + \alpha_z\alpha_y p_y p_z + \alpha_z{}^2 p_z{}^2 + \alpha_z\beta p_z mc +$$
$$mc\beta\alpha_x p_x + mc\beta\alpha_y p_y + mc\beta\alpha_z p_z + \beta^2 m^2c^2 = p_x{}^2 + p_y{}^2 + p_z{}^2 + m^2c^2$$

Comparing the coefficients of p_x^2, p_y^2, p_z^2 and m^2c^2, we obtain

$$\alpha_x{}^2 = \alpha_y{}^2 = \alpha_z{}^2 = \beta^2 = 1 \qquad (3)$$

Since the products like p_xp_y, p_yp_z, p_zp_x and p_x, p_y, p_z do not appear on the right side so the coefficients on the left hand side must vanish, which determines the relation between α_x, α_y, α_z and β, i.e.,

The four quantities α_x, α_y, α_z, β are said to anti commute in pairs and square of each is unity.

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0$$
$$\alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0 \qquad (4)$$

4.4.2 Dirac Matrices

As the Dirac Hamiltonian is Hermitian therefore the α_x, α_y, α_z and β must be Hermitian. One of the constraints on the **α**'s and β is that these are non-commuting entities. The simplest non-commuting entities, which are independent of space-time variables and differential operators are matrices. Therefore, α_x, α_y, α_z and β are taken to be matrices and these matrices have to obey the eqns (3 & 4). Since the squares of all four matrices are unity, so the eigenvalues are +1 and -1.

We can write

$$\alpha_x = \alpha_x \beta^2 = \alpha_x \beta\beta = -\beta\alpha_x \beta$$

taking the trace (= sum diagonal elements = sum of the eigenvalues) of the matrices on the both sides, we have

$$tr(\alpha_x) = -tr(\beta\alpha_x\beta) = -tr(\alpha_x\beta^2) = -tr(\alpha_x) \qquad (i)$$

(In the third step the cyclic property of trace of matrices i.e., *tr*(ABC)=*tr*(BCA), is used)

It is evident from (i) that $tr(\alpha_x)=0$ which mean that α_x must have the same number of +1 eigenvalues and -1 eigenvalues. The same is true for the other matrices. This restricts the dimension of the matrices and has to be even number. The simplest possibility is n = 2. There are already three anti-commuting 2x2 matrices known as the Pauli's matrices, which are given by

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \quad \sigma_x = \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}; \quad \sigma_x = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The squares of the each of these matrices are also unity. But these are ruled out because we need four and fourth one can not be formed with these three matrices.

With the dimension n = 4, one can find four anti-commuting matrices. Arbitrarily, b matrix is taken to be diagonal with two +1 eigenvalues and two -1 eigenvalues. Then one can find the other three 4x4 matrices anti-commuting with β and satisfying other conditions specified by equations (3 & 4). These are

$$\beta=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix}=\begin{bmatrix}I&O\\O&I\end{bmatrix};\quad \alpha_x=\begin{bmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{bmatrix}=\begin{bmatrix}O&\sigma_x\\\sigma_x&O\end{bmatrix}$$

$$\alpha_y=\begin{bmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{bmatrix}=\begin{bmatrix}O&\sigma_y\\\sigma_y&O\end{bmatrix};\quad \alpha_z=\begin{bmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{bmatrix}=\begin{bmatrix}O&\sigma_z\\\sigma_z&O\end{bmatrix} \qquad (6)$$

Obviously these matrices are Hermitian since $\alpha_{x,}$ α_y and α_z are Hermitian and these are the Dirac matrices. We can also abbreviate these matrices as

$$\beta=\begin{bmatrix}I&O\\O&-I\end{bmatrix} \quad \text{and} \quad \alpha=\begin{bmatrix}O&\sigma\\\sigma&O\end{bmatrix} \qquad (7)$$

4.4.3 Plane Wave Solutions

Consider the Dirac equation

$$i\hbar\frac{\partial}{\partial t}\psi(r,t)=-i\hbar c\alpha\nabla\psi(r,t)+\beta mc^2\psi(r,t) \qquad (8$$

where α_x, $\alpha_{y,}$ α_z and β are constant matrices. Now we try with plane wave solutions of above equation of the form

$$\psi(r,t)=U(p)e^{i(p.r-Et)/\hbar} \qquad (9)$$

Substituting eqn (2) in eqn (1) gives

$$EU(p)=(c\alpha.p+\beta mc^2)U(p) \qquad (10)$$

Since components of **α** are 4 x 4 matrices, so that ψ and U should also be 4-component objects on which these matrices can operate. Writing the four-column vector of U as partitioned into two components such as

$$U = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = \begin{pmatrix} v \\ w \end{pmatrix} \qquad (11)$$

$$\text{where } v = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}; \qquad w = \begin{bmatrix} u_3 \\ u_4 \end{bmatrix}$$

Then the substitution of equations of two component forms of **α**'s and β and *U* in the eqn (3), we get

$$E\begin{bmatrix} v \\ w \end{bmatrix} = c\begin{bmatrix} 0 & \sigma p \\ \sigma p & 0 \end{bmatrix} + mc^2\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} v \\ w \end{bmatrix} \qquad (12)$$

After multiplication of matrices on the right hand side and rearranging the terms, we have

$$(E - mc^2)w = c(\sigma.p)v \qquad (13)$$

$$(E + mc^2)w = c(\sigma p)v \qquad (14)$$

Multiplying eqn (13) with (E+mc^2) and replacing (E+mc^2) by c.(**σ.p**)v from eqn (14), we get

$$\begin{aligned} (E^2 - m^2c^4)v &= c(\sigma.p).c(\sigma.p)v \\ &= c^2(\sigma.p)^2 v \\ &= c^2p^2v \end{aligned}$$

or

$$(E^2 - c^2p^2 - m^2c^4)v = 0$$

For non-trivial solution, $v \neq 0$. Hence

$$= E^{\pm}$$

$$\text{or} \quad E = \pm(c^2p^2 + m^2c^4) \qquad (15)$$

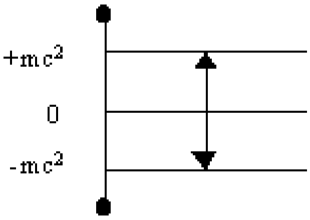
$$E^2 - c^2p^2 - m^2c^4 = 0$$

The same result would follow if we eliminate *v* rather than *w* from eqns (13) and (14). From eqn(15) one expect that a free particle consists of two branches of energy: one corresponding to E_+ and other to E_-.

4.4.4 Negative Energy States

We found that there are two solutions for the energy from previous topic and they are

$$\begin{aligned} E &= \pm\left(c^2 p^2 + m^2 c^4\right)^{1/2} \\ &= E_\pm \end{aligned}$$



When p = 0, the solutions for the energy are $E_+ = mc^2$ and $E_- = - mc^2$. So the energy spectrum of a free electron has two branches corresponding to E_+ and E_-: one starting at mc^2 and extending to $+\infty$ as $|p| \to \infty$ and other starting at mc^2 and extending to $-\infty$ as $\infty|p| \to -\infty$ (see Fig). The two branches are separated by a forbidden gap of width 2 mc^2. It is very difficult to imagine negative energy states because even a weak electromagnetic field or a small other perturbation could cause an electron which is in a state of positive energy to undergo a quantum transition to a state of energy $E \to -\infty$, resulting in the release of an infinite amount of energy. No such thing takes place in reality. To overcome this serious problem, Dirac postulated that all the negative energy states are ordinary occupied by electrons. This sea of negative energy electrons would have no physically observable effects. Since electrons obey Pauli exclusion principle, these occupied states can not accommodate any more electrons. Thus transitions to negative energy states are prevented. Further, it is assumed that, when electron occupying the negative energy state receives energy, it goes to positive energy state and create an empty space and is designated as 'hole' in the negative energy sea. The minimum energy required to jump electron from negative energy state to positive energy is $2mc^2$. The empty space created in the negative energy states behaves as if it is a particle of positive charge. This explanation was accepted when positron was discovered in cosmic rays by Chadwik.

4.4.5 Position Probability Density

The other relativistic equation must yield the probability density ρ(r, t) must be positive. This can be shown by considering Dirac equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi = -i\hbar c\alpha.\nabla\psi + \beta mc^2\psi \qquad (16)$$

and it's conjugate

$$-i\hbar\frac{\partial\psi^{\dagger}}{\partial t} = i\hbar c\nabla\psi^{\dagger}.\alpha + mc^2\psi^{\dagger}\beta \qquad (17)$$

The Hermitian property of α and β and the rule that the order of factors in any matrix product reversed on Hermitian conjugation are used while writing eqn (2). Multiplying eqn (1) from left by $\psi^{\dagger}$ and eqn (2) by ψ on right and subtracting one from other, we obtain

$$i\hbar\left(\psi^{\dagger}\frac{\partial\psi}{\partial t} + \frac{\partial\psi^{\dagger}}{\partial t}\psi\right) = -i\hbar c(\psi^{\dagger}\alpha.\nabla\psi + \nabla\psi^{\dagger}\alpha\psi)$$

$$or$$

$$\frac{\partial}{\partial t}(\psi^{\dagger}\psi) + \nabla.(c\psi^{\dagger}\alpha\psi) = 0 \qquad (18)$$

This is a continuity equation, with *P*(**r**, t)=$\psi^{\dagger}$ ψ and *S(***r**,t)=c$\psi^{\dagger}$ αψ.

Here, the quantities P(**r**, t), S(**r**,t) can be interpreted as probability density and probability current densities. The expression for P has same form as the non-relativistic one and is positive definite and the interpretational difficulties experienced with the Klein-Gordon equation do not arise here.

4.4.6 Electron in an Electromagnetic Field

Replacing **p** by **p** - e**A**/c and E by E - eφ in the Dirac equation, we get the Dirac equation for an electron in the electromagnetic field, i.e.,

$$i\hbar\frac{\partial\psi}{\partial t} = c\alpha.(p - eA/c)\psi + \beta mc^2\psi + e\phi\psi \qquad (19)$$

where **A** and φ are the vector and scalar potentials of the electromagnetic field and let these are time independent. There exist stationary state solutions

$$\psi\left(r,t\right)=u\left(r\right)e^{-iEt/\hbar} \qquad (20)$$

Substituting these solutions eqn (1), we obtain

$$E\,u(\mathbf{r}) = c\,\boldsymbol{\alpha}.(\mathbf{p} - e\,\mathbf{A}/c)\,u(\mathbf{r}) + \beta\, m c^2\, u(\mathbf{r}) + e\,\varphi\, u(\mathbf{r}) \qquad (21)$$

Taking

$$u = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = \begin{pmatrix} v \\ w \end{pmatrix} \; ; \quad where \quad v = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \; and \;\; w = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix}$$

and substituting for u, **α** and β in the modified Dirac eqn (21) and then rearranging the terms, we can write two equations for 2-component quantities *v*, *w* as

$$c\,\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)\,w = (E - e\,\varphi - m c^2)\,v \qquad (22)$$

$$c\,\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)\,v = (E - e\,\varphi + m c^2)\,w \qquad (23)$$

Since we are interested in the positive energy solutions, choose

$$E = m c^2 + \varepsilon \qquad (24)$$

We can write eqn (23) with eqn(24) as

$$c\,\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)\,v = (2 m c^2 + \varepsilon - e\,\varphi)\,w \qquad (25)$$

For small values of ε and φ , we can write the above equation as

$$w \approx 1/(2 m c)\,\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)\,v \qquad (26)$$

Substituting this equation in eqn (23), we obtain

$$1/(2m)\,[\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)]^2\, v = (\varepsilon - e\,\varphi)\,v \qquad (27)$$

Using the vector identity $(\boldsymbol{\sigma}.\mathbf{B})\,(\boldsymbol{\sigma}.\mathbf{C}) = \mathbf{B}.\mathbf{C} + i\,\boldsymbol{\sigma}.(\mathbf{B} \times \mathbf{C})$

We have $[\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c)]^2 = (\mathbf{p} - e\mathbf{A}/c)^2 + i\,\boldsymbol{\sigma}.(\mathbf{p} - e\mathbf{A}/c) \times (\mathbf{p} - e\mathbf{A}/c)$

Since **p** and **A** are an operators, the vector product in the last term does not vanish. In deed we have

$$(\mathbf{p} - e\mathbf{A}/c) \times (\mathbf{p} - e\mathbf{A}/c) = -e/c\,(\mathbf{A} \times \mathbf{p} + \mathbf{p} \times \mathbf{A}$$

$$= ie\hbar/c\ \nabla \times A = ie\hbar/c\ H$$

Thus the eqn. (27) gives

$$\{ 1/2m\,(\mathbf{p} - e\mathbf{A}/c)^2 - e\,\hbar/2mc\ \boldsymbol{\sigma} \cdot \mathbf{H} + e\,\varphi \}\, v = \varepsilon\, v \qquad (28)$$

This is known as the Pauli's equation for the electronwith spin 1/2.. This is very similar to non-relativistic Schrodinger equation with one extra term. This term suggests that the electron, in a magnetic field, acquires an extra energy, that is $\boldsymbol{\mu} \cdot \mathbf{H} = - e\,\hbar/2mc\ \boldsymbol{\sigma} \cdot \mathbf{H}$, so that it behaves as if it has a magnetic moment $\boldsymbol{\mu}$ associated with its spin:

$$\boldsymbol{\mu} = e\,\hbar/2mc\ \boldsymbol{\sigma}$$

$$= \mu_B\, \boldsymbol{\sigma} \qquad (29)$$

where μ_B is the Bohr magneton. Thus, the Dirac equation predicts that for a spin 1/2 particle will have the magnetic moment.

SUMMARY OF THE LESSON

To overcome the problems of Klein-Gordon equation, Dirac modified the hamiltonian operator in order to ensure that the hamiltonian or energy should be linear in the momentum without affecting the relativistic symmetry between energy and momentum. The solution of the Dirac equation reveals the existence of the negative energy states. The explanation of the negative energy states led to ' hole ' concept. The existence of the hole was confirmed when Chadwik discovered the positron. Dirac could show that the probability charge density is a positive definite. When an electron motion is considered in the electromagnetic field, the solution predicts the existence of spin 1/2 for the electron.

KEY TERMINOLOGY

Relativistic mechanics, Dirac equation, Dirac matrices, Negative energy states, electromagnetic field, probability density, hole.

SELF ASSESSMENT QUESTIONS

1. Obtain Dirac equation.
2. Determine the Dirac matrices and discuss their properties.
3. Elucidate the negative energy states due to solution of Dirac equation.
4. Show that charge probability density is positive definite using Dirac equation.

REFERENCE BOOKS

1. Quantum Mechanics by L.I. Schiff (McGraw-Hill Kogakusha, Ltd.), 1968.
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