M.Sc. Final Year
Physics, MP-05

QUANTUM MECHANICS

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
MADHYA PRADESH BHOJ (OPEN) UNIVERSITY - BHOPAL

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SYLLABI-BOOK MAPPING TABLE

Quantum Mechanics

Syllabi	Mapping in Book
UNIT - I: **Time-Independent Perturbation Theory & Variational Methods** Ehrenfest theorem. Expansion of wave function in eigen fuctions, orthogonality, normality and closure property of eigenfunctions. Dirac Delta function. Time-independent perturbation theory for non-degenerate case upto second order and its application to (i) Ground state of Helium and (ii) Degenerate time-independent perturbation theory and its application to Zeeman effect, with and without electron spin in hydrogen like atom. Variational method and its application to ground state of Helium atom.	**Unit-1:** Time – Independent Perturbation Theory and Variational Method **(Pages 3-40)**
UNIT - II: **Approximation Methods & Time-Dependent Perturbation Theory** Born-Oppenheimer approximation of LCAO, Heitler-London theory of hydrogen molecule. WKB approximation and its application to alpha decay. Time dependent perturbation theory. Transition probabilities. Fermi-Golden rule, Emission and Absorption of radiation, Einstein's A and B coefficients. Exchange degeneracy of indistinguishable particles. Wave function for many electron system, Pauli's exclusion principle.	**Unit-2:** Approximation Methods and Time-dependent Perturbation Theory **(Pages 41-81)**
UNIT - III: **Angular Momentum and Spin** Eigenvalues and eigenvectors of angular momentum, characteristic algebraic relation, spectrum of J^2, J_z, eigenvectors of J^2 & J_z. Orbital angular momentum and the spherical harmonics. The spectrum of L^2 and L_z, definitions and construction of spherical harmonics. Angular momentum and rotation operator, rotational invariance and conservation of angular momentum, rotational degeneracy. **Spin:** electron spin, spin 1 /2 and Pauli matrices, observable and wave functions of spin 1 .2 particle, spin of fields, vedorfields and particles and spin 1, spin- independent interactions of atoms, Spin-independent nucleon-nucleon interactions. Addition of angular momenta, eigenvectors of total angular momentum Clebsch-Gordon coefficients. Application to two nucleon systems.	**Unit-3:** Angular Momentum and Spin **(Pages 83-125)**
UNIT - IV: **Scattering Theory** Introduction, definition of cross-section, stationary wave of scattering, representation of the scattering phenomenon by a bundle of wave packets, scattering of a wave packet by a potential, calculation of cross-section, laboratory system and centre of mass-system. Scattering by a central potential, partial wave analysis and phase shift method. Impact parameters, relation between phase shift and logarithmic derivatives. Behaviour of phase shifts at low energies scattering by a hard sphere.	**Unit-4:** Scattering Theory **(Pages 127-184)**

Scattering resonances, scattering by a deep square well, study of a scattering resonance, metastable states. Observation of the lifetime metastable states.

Integral representations of phase-shifts, dependence upon the potential, sign of the phase-shifts, Born approximation, effective range theory, the Bethe formula.

UNIT - V:

Relativistic Quantum Mechanics

Classical relativistic dynamics and the Lorentz group. The Klein-Gordon equation. Dirac equation, covariant form of Dirac equation. Properties of Dirac matrices. The free electron-plane waves, central potentials, free spherical waves. The hydrogen atoms.

Large and small components, the Pauli theory as the non-relativistic limit of the Dirac theory applications. Hyperfine position theory. Difficulties with the hole theory.

Identical Particles: Similar particles and symmetrical representation, permutation operators. Algebra of permutation operators, identical particles and symmetrization postulate. Bosons and Bose-einstein statistics, Fermions and Fermi Dirac statistics, Exclusion principle.

Unit-5: Relativistic Quantum Mechanics
(Pages 185-242)

CONTENTS

INTRODUCTION

NOTES

Quantum Mechanics (QM), also known as quantum physics, quantum theory, the wave mechanical model, matrix mechanics or quantum field theory, is a fundamental theory in physics which describes nature at the smallest scales of energy levels of atoms and subatomic particles. Principally, the quantum mechanics differs from classical physics in that energy, momentum, angular momentum and other quantities of a bound system are restricted to discrete values (quantization); objects have characteristics of both particles and waves (wave-particle duality); and there are limits to the precision with which quantities can be measured, uncertainty principle.

The foundations of quantum mechanics were established during the first half of the 20th century by Max Planck, Niels Bohr, Werner Heisenberg, Louis de Broglie, Arthur Compton, Albert Einstein, Erwin Schrödinger, Paul Dirac, David Hilbert, and others. The modern theory is formulated in various specially developed mathematical formalisms. In one of them, a mathematical function, the wave function, provides information about the probability amplitude of position, momentum, and other physical properties of a particle. The Schrödinger equation, applied to the free particle, predicts that the centre of a wave packet will move through space at a constant velocity.

This book, *Quantum Mechanics* is divided into five units that follow the self-instruction mode with each unit beginning with an Introduction to the unit, followed by an outline of the Objectives. The detailed content is then presented in a simple but structured manner interspersed with Check Your Progress Questions to test the student's understanding of the topic. A Summary along with a list of Key Terms and a set of Self-Assessment Questions and Exercises is also provided at the end of each unit for recapitulation.

UNIT 1 TIME – INDEPENDENT PERTURBATION THEORY AND VARIATIONAL METHOD

NOTES

Structure

1.0 INTRODUCTION

The Ehrenfest theorem is a special case of a more general relation between the expectation of any quantum mechanical operator and the expectation of the commutator of that operator with the Hamiltonian of the system. Wave function expansion, a very abstractly method, is the fundamental importance in physics. This calculation, transferred to the process of the molecule's decomposition, it is identical to an approach where the ground state wave function Ψ (G) is obtained by expanding the rotational Eigen functions.

The Dirac delta function is the name given to a mathematical structure, i.e., intended to represent an idealized point object, such as a point mass or point charge. The condition for two eigen functions to be orthogonal is that their inner product is zero.

Time-independent perturbation theory is one of two categories of perturbation theory, the other being time-dependent perturbation. Time-independent Perturbation theory is a mathematical tool for treating quantum systems whose Hamiltonian involves small static perturbing terms which do not induce transitions to other quantum states.

The spin quantum number has only two possible values of +1/2 or -1/2. If a beam of hydrogen atoms in their ground state ($n = 1$, $\ell = 0$, $m_\ell = 0$) or 1s is sent through a region with a spatially varying magnetic field, then the beam splits into two beams.

NOTES

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigen state or ground state, and some excited states. This allows calculating approximate wave functions, such as molecular orbitals. The basis for this method is the variational principle.

In this unit, you will study about the Ehrenfest theorem, expansion of wave function in eigen function, orthogonality, normality and closure properties of eigen function, Dirac delta function, time-independent Perturbation theory, with and without electron spin in hydrogen like atom, variational method and it's applications to ground state of helium atom.

1.1 OBJECTIVES

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

- Explain the Ehrenfest theorem
- Discuss the expansion of wave function in eigen function
- State the Dirac delta function
- Interpret the orthogonality, normality and closure properties of eigen function
- Describe the time-independent Perturbation theory for degenerate and non-degenerate cases
- Elaborate on the variational method and its applications to ground state of helium atom

1.2 EHRENFEST THEOREM

P. Ehrenfest in 1927 stated, in regard to the correspondence between the motion of a classical particle and the motion of a wave packet representing the particle, the following theorem.

The averages or the expectation values of the quantum mechanical variables satisfy the same equations of motion as the corresponding classical variables in the corresponding classical description. Specifically the theorem states that,

$$\frac{d}{dt}\langle x\rangle = \frac{l}{m}\langle p_x\rangle$$

$$\frac{d}{dt}\langle p_x\rangle = \left\langle -\frac{dV(x)}{dx}\right\rangle$$

provided that the wavefunction $\psi(x, t)$ with respect to which averages are computed satisfies the time-dependent Schrödinger equation,

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

or

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

Proof of Ehrenfest's Theorem

Consider a particle of mass m moving along the x-axis under the action of a force-field described by the potential energy $V(x)$ for the particle. If $\psi(x, t)$ be the wave function describing the state of the particle at the instant t we have the expectation value of the coordinate x of the particle in the state given by,

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x, t)\, x\psi(x, t)dx$$

The time derivative of $\langle x \rangle$ is,

$$\frac{d\langle x \rangle}{dt} = \frac{\partial}{\partial t}\int_{-\infty}^{+\infty} \psi^*(x, t)\, x\psi(x, t)dx \qquad \text{...(1.1)}$$

The Schrödinger equation satisfied by $\psi(x, t)$ is,

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x, t) \qquad \text{...(1.2)}$$

The above gives,

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{-i}{\hbar}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x, t) \qquad \text{...(1.3)}$$

Taking complex conjugate of Equation (1.3), we get,

$$\frac{\partial \psi^*(x, t)}{\partial t} = \frac{-i}{\hbar}\left[\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x, t) \qquad \text{...(1.4)}$$

Equation (1.1) gives,

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{\partial \psi^*(x, t)}{\partial t}\, x\psi(x, t)\, dx + \int_{-\infty}^{+\infty} \psi^*(x, t) x\, \frac{\partial \psi^{+\infty}\,(x, t)}{\partial t}\, dx$$

Using Equations (1.3) and (1.4) in the above, we get,

$$\frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \frac{i}{\hbar}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x, t)\, x\psi\,(x, t)dx$$

$$+ \int_{-\infty}^{+\infty} \psi^*(x, t)\, x\left(\frac{-i}{\hbar}\right)\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x, t)dx$$

Simplifying, we get,

$$\frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left[x\psi^*(x, t)\frac{\partial^2 \psi(x, t)}{\partial x^2} - x\psi(x, t)\frac{\partial^2 \psi^*(x, t)}{\partial x^2}\right]dx \qquad \text{...(1.5)}$$

Let,

$$I = \int_{-\infty}^{+\infty} x\psi(x, t)\frac{\partial^2 \psi^*(x, t)}{\partial x^2}\, dx$$

Integrating by parts, we get,

$$I = \left\{ x\psi(x,t)\frac{\partial\psi^*(x,t)}{\partial x} \right\}_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\partial\psi^*(x,t)}{\partial x^{-\infty}} \frac{\partial}{\partial x}[x\psi(x,t)]dx \qquad ...(1.6)$$

For a localized wave packet we have the boundary conditions,

$$\left.\begin{aligned} \psi(x,t) &\to 0 \qquad \text{as} \quad x \to \pm\infty \\ \frac{\partial\psi(x,t)}{\partial x} \text{ and } \frac{\partial\psi^*(x,t)}{\partial x} &\to 0 \quad \text{as} \quad x \to \pm\infty \end{aligned}\right\} \qquad ...(1.7)$$

Use of conditions given by Equation (1.7) in Equation (1.6), we obtain,

$$I = -\int_{-\infty}^{+\infty} \frac{\partial}{\partial x}[x\psi(x,t)]\frac{\partial\psi^*(x,t)}{\partial x}$$

Integrating once again by parts, we get

$$I = -\int_{-\infty}^{+\infty} \left\{ \frac{\partial}{\partial x}[x\psi(x,t)]\,\psi^*(x,t) \right\}_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial^2}{\partial x^2}[x\psi(x,t)]dx$$

Using condition given by Equation (1.7), the above becomes,

$$\begin{aligned} I &= \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial^2}{\partial x^2}[x\psi(x,t)]dx \\ &= \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial}{\partial x}\left[\psi(x,t) + x\frac{\partial\psi(x,t)}{\partial x}\right]dx \\ &= \int_{-\infty}^{+\infty} \psi^*(x,t)\left[\frac{\partial\psi(x,t)}{\partial x} + x\frac{\partial^2\psi(x,t)}{\partial x^2} + \frac{\partial\psi(x,t)}{\partial x}\right]dx \end{aligned}$$

or

$$I = \int_{-\infty}^{+\infty} \psi^*(x,t)\left[2\frac{\partial\psi(x,t)}{\partial x} + x\frac{\partial^2\psi(x,t)}{\partial x^2}\right]dx \qquad ...(1.8)$$

Using Equation (1.8) in Equation (1.5) we obtain,

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left[x\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2} - 2\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x} - \psi^*(x,t)x\frac{\partial^2\psi(x,t)}{\partial x^2}\right]dx$$

or

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty} -2\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}dx$$

or

$$\frac{d\langle x\rangle}{dt} = \frac{1}{m}\int_{-\infty}^{+\infty} \psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t)dx$$

or

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p_x\rangle}{m}, \quad \text{since } \langle p_x\rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\,\hat{p}_x\,\psi(x,t)dx$$

or

$$\langle p_x\rangle = m\frac{d\langle x\rangle}{dt} \qquad ...(1.9)$$

In the limiting case if the wave packet reduces to a point, i.e., the particle becomes *completely localized*, we get,

$$\langle x \rangle = x \text{ and } \langle p_x \rangle = p_x \qquad ...(1.10)$$

so that Equation (1.6) reduces to the classical definition,

$$p_x = m\frac{dx}{dt} \qquad ...(1.11)$$

We have the expectation value of p_x in the state described by the wavefunction $\psi(x, t)$ given by,

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t)dx$$

Taking time derivative of the above we obtain,

$$\frac{d\langle p_x \rangle}{dt} = \frac{\partial}{\partial t}\int_{-\infty}^{+\infty} \psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t)dx$$

or

$$\frac{d\langle p_x \rangle}{dt} = -i\hbar\int_{-\infty}^{+\infty} \frac{\partial\psi^*(x,t)}{\partial t}\frac{\partial\psi(x,t)}{\partial x}dx$$

$$-i\hbar\int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial}{\partial x}\left(\frac{\partial\psi(x,t)}{\partial t}\right)dx$$

Substituting for $\frac{\partial\psi^*(x,t)}{\partial t}$ and $\frac{\partial\psi(x,t)}{\partial t}$ from Equations (1.4) and (1.3) in the above we obtain,

$$\frac{d.\langle p_x \rangle}{dt} = -i\hbar\int_{-\infty}^{+\infty} \frac{i}{\hbar}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}dx$$

$$-i\hbar\int_{-\infty}^{+\infty} \psi^*(x,t)\left(\frac{-i}{\hbar}\right)\frac{\partial}{\partial x}\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t)\,dx$$

$$= \frac{-\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}dx$$

$$+\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial}{\partial x}\left[\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t)\,dx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\frac{\partial^2\psi^*(x,t)}{\partial x^2}\frac{\partial\psi(x,t)}{\partial x}dx + \int_{-\infty}^{+\infty} V(x)\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}dx$$

$$+\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \psi^*(x,t)\frac{\partial}{\partial x}\left(\frac{\partial^2\psi(x,t)}{\partial x^2}\right)dx - \int_{-\infty}^{+\infty}\psi^*(x,t)\frac{\partial}{\partial x}[V(x)\psi(x,t)]\,dx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[\psi^*(x,t)\frac{\partial}{\partial x}\left(\frac{\partial^2\psi(x,t)}{\partial x^2}\right) - \frac{\partial^2\psi^*(x,t)}{\partial x^2}\frac{\partial\psi(x,t)}{\partial x^2}\right]dx$$

$$+\int_{-\infty}^{+\infty}\left[V(x)\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x} - \psi^*(x,t)\frac{\partial}{\partial x}\,[V(x)\psi\,(x,t)]\,dx\right.$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[\frac{\partial}{\partial x}\left(\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2}\right) - \frac{\partial\psi^*(x,t)}{\partial x}\frac{\partial^2\psi(x,t)}{\partial x^2} - \frac{\partial^2\psi^*(x,t)}{\partial x^2}\frac{\partial^2\psi(x,t)}{\partial x^2}\right]dx$$

$$+\int_{-\infty}^{+\infty}\psi^*(x,t)\left[\frac{-\partial V(x)}{\partial x}\right]\psi(x,t)dx$$

$$= \frac{-\hbar^2}{2m}\int_{-\infty}^{+\infty}\left[\frac{\partial}{\partial x}\left(\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2}\right)-\frac{\partial}{\partial x}\left[\frac{\partial\psi^*(x,t)}{\partial x}\frac{\partial\psi(x,t)}{\partial x}\right]dx\right. + \left\langle\frac{-\partial V}{\partial x}\right\rangle$$

Using the condition given by Equation (1.7) in the above we find the first term in the above equation to vanish to yield,

$$\frac{d\langle p_x\rangle}{dt} = \left\langle\frac{-\partial V(x)}{\partial x}\right\rangle$$

The force F_x corresponding to the potential energy function $V(x)$ is,

$$F_x = \frac{-\partial V}{\partial x}$$

The above two equations give,

$$\frac{d\langle p_x\rangle}{dt} = \langle F_x\rangle \qquad ...(1.12)$$

In the limiting case of the wave packet reducing to a point, i.e., the particle being completely localized we get,

$$\langle p_x\rangle = p_x \quad \text{and} \quad \langle F_x\rangle = F_x$$

and Equation (1.12) in that case takes the form,

$$F_x = \frac{dp_x}{dt}$$

Which is Newton's second law of motion.

1.3 EXPANSION OF WAVE FUNCTION IN EIGEN FUNCTION

The wave equation given by Equation (1.13) can be solved using the method of separation of variables.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial^2\phi^2}+\frac{2T_0}{h^2}E\psi$$

$$= 0 \qquad ... (1.13)$$

We can write Equation 1.12 $\psi(\theta, \phi) = \Theta(\theta)\,\Phi(\phi)$ ...(1.14)

where Θ and Φ are respectively functions of θ alone and ϕ alone.

Using Equation (1.14) in Equation (1.13) we obtain

$$\Phi\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\Theta\frac{1}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{2I_0E}{\hbar^2}\Theta\Phi = 0$$

Dividing the above throughout by $\frac{\Theta\Phi}{\sin^2\theta}$, we get

$$\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2I_0E}{\hbar^2}\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \qquad ...(1.15)$$

The left hand side of Equation (1.15) depends only on θ while the right hand side depends only on θ. Hence for the Equation (1.15) to be valid, each side of it must separately be equal to a constant. For convenience we set

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \ (m = \text{constant})$$

Or $$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \qquad ...(1.16)$$

Let us call it Φ equation.

We also have

$$\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2I_0E}{\hbar^2}\sin^2\theta = m^2$$

Dividing the above by $\frac{\sin^2\theta}{\Theta}$ we obtain

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2I_0E}{\hbar^2}\Theta = \frac{m^2}{\sin^2\theta}\Theta$$

or

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\frac{2I_0E}{\hbar^2} - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad ...(1.17)$$

Let us call it Θ equation.

Solution of the Φ Equation

The most general solution of Equation (1.16) is given by

$$\Phi = Ae^{\pm im\phi} \qquad ...(1.18)$$

where A is an arbitrary constant, and can be evaluated using the requirement of the normalization of Φ

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

Using Equation (1.18) in the above we obtain

$$|A|^2 \int_0^{2\pi} d\phi = 1$$

Or

$$|A|^2\, 2\pi = 1$$

Or

$$|A|^2 = \frac{1}{2\pi}$$

Or

$$A = \frac{1}{\sqrt{2\pi}} \qquad ...(1.19)$$

For Φ to be a factor in the total wavefunction of the rotator, the single valuedness of Φ demands

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Using Equation (5.65) in the above we get

$$Ae^{\pm im\phi} = Ae^{\pm im(\phi+2\pi)}$$

or

$$e^{\pm im\phi} = e^{\pm im\phi}\, e^{\pm 2\pi mi}$$

or

$$e^{\pm 2\pi mi} = 1$$

or

$$\cos 2\pi m \pm i \sin 2\pi m = 1$$

NOTES

The above demands m to be zero or an integer positive as well as negative, i.e.,

$$m = 0, \pm 1, \pm 2,... \qquad ...(1.20)$$

Using the results given in Equations (1.19) and (1.20), we obtain from Equation (1.19)

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad ...(1.21)$$

The integer m can be identified as the *magnetic quantum number*.

Note: The Lagrangian function L for the rigid rotator is by definition given by

$$L = T - V.$$

Or $L = E\,(\because V = 0 \text{ and } E = T)$

Using the expression for the total energy E so we get

$$L = \frac{1}{2} I\,(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

We observe that ϕ does not appear explicitly in the Lagrangian function and hance ϕ is a cyclic or ignorable coordinate.

Solution of the Θ Equation

Putting $\lambda = \frac{2I_0E}{\hbar^2}$ ...(1.22)

the Θ equation which is given by Equation (1.17) becomes

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad ...(1.23)$$

Let us introduce a new variable ξ as

$$\xi = \cos\theta \qquad ...(1.24)$$

Now

$$\frac{d\Theta}{d\theta} = \frac{d\Theta}{d\xi}\frac{d\xi}{d\theta} = -\sin\theta\frac{d\Theta}{d\xi} \quad \text{(using Equation 1.24)}$$

or

$$\frac{d}{d\theta} = -\sin\theta\frac{d}{d\xi} \qquad ...(1.25)$$

Using Equations (1.24) and (1.25) in Equation (1.23) we get

$$-\frac{d}{d\xi}\left[-(1-\xi)^2\frac{d\Theta}{d\xi}\right] + \left[\lambda - \frac{m^2}{1-\xi^2}\right]\Theta = 0$$

or

$$(1-\xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi\frac{d\Theta}{d\xi} + \left[\lambda - \frac{m^2}{1-\xi^2}\right]\Theta = 0 \qquad ...(1.26)$$

For mathematical convenience let us substitute

NOTES

$$\Theta = (1-\xi^2)^{\frac{m}{2}} X(\xi) \qquad ...(1.27)$$

where $X(\xi)$ is a function of only ξ.

Substituting for $\frac{d\Theta}{d\xi}$ and $\frac{d^2\Theta}{d\xi^2}$ as obtained from Equation (1.27) in Equation (1.26) and simplifying we obtain

$$(1-\xi^2)\frac{d^2X}{d\xi^2} - 2(m+1)\xi\frac{dX}{d\xi} + [\lambda - m(m+1)]X = 0 \qquad ...(1.28)$$

Equation (1.28) can be solved using power series method. For this we express the function X as a power series in ξ as

$$X = \sum_{n=0}^{\infty} a_n \xi^n, \quad n = 0, 1, 2,... \qquad ...(1.29)$$

The above gives

$$\frac{dX}{d\xi} = \sum_{n=0}^{\infty} n\, a_n \xi^{n-1} \qquad ...(1.30)$$

and

$$\frac{d^2X}{d\xi^2} = \sum_{n=2}^{\infty} n(n-1)\xi^{n-2} \qquad ...(1.31)$$

Substitution of Equations (1.29), (1.30) and (1.31) in Equation (1.31) yields

$$\sum_{n=2}^{\infty} n(n-1)\, a_n \xi^{n-2} - \sum_{n=2}^{\infty} n(n-1) a_n \xi^n - 2(m+1)\sum_{n=1}^{\infty} n\, a_n \xi^n$$

$$+ [\lambda - m(m+1)]\sum_{n=0}^{\infty} a_n \xi^n = 0 \qquad ...(1.32)$$

For Equation (1.32) to be valid for all possible values of ξ, the coefficients of the individual powers of ξ must separately vanish.

Thus we obtain, in general, for the coefficient of ξ^n

$$(n+1)(n+2)a_{n+2} - n(n-1)a_n - 2(m+1)na_n + [\lambda - m(m+1)]\, a_n = 0$$

or

$$a_{n+2} = \frac{n(n-1) + 2n(m+1) + m(m+1) - \lambda}{(n+1)(n+2)}\, a_n$$

or

$$\frac{a_{n+2}}{a_n} = \frac{n(n-1) + 2n(m+1) + m(m+1) - \lambda}{(n+1)(n+2)} \qquad ...(1.33)$$

Equation (1.32) is referred to as the *Recursion formula* for the coefficients of the series for $X(\xi)$. In order that the polynomial X represents a satisfactory part of the total wavefunction of the rotator, the series for X must break off (terminate) after a finite number of terms (otherwise it diverges). Considering that polynomial breaks off after the nth term we get,

$$a_{n+2} = 0$$

and hence Equation (1.33) gives

$$n(n-1) + 2n\,(m+1) + m(m+1) - \lambda = 0$$

or
$$\lambda = (n+m)\,(n+m+1) \qquad \text{...(1.34)}$$

In Equation (1.34) $m = 0, 1, 2, \ldots$ and $n = 0, 1, 2, \ldots$, Hence we may write $n + m = l$ is an integer including 0 ...(1.35)

We can thus write Equation (1.34) as
$$\lambda = l(l+1) \qquad \text{...(1.36)}$$

Using the above values of λ, Equation (1.26) becomes

$$(1-\xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi\frac{d\Theta}{d\xi} + \left[l(l+1) - \frac{m^2}{1-\xi^2}\right]\Theta = 0 \qquad \text{...(1.37)}$$

It is well known that the associated Legendre function $p_l^{|m|}(\xi)$ of degree l and order $|m|$ where $l = 0, 1, 2, \ldots$ and $m = 0, 1, 2, \ldots, l$ is defined in terms of Legendre polynomial $P_l(\xi)$ as

$$P_l^{|m|}(\xi) = (1-\xi^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{d\xi^{|m|}}P_l(\xi) \qquad \text{...(1.38)}$$

$P_l(\xi)$ satisfies the Legendre differential equation

$$\frac{d}{d\xi}\left[(1-\xi^2)\frac{dP_l(\xi)}{d\xi}\right] + l(l+1)\,P_l(\xi) = 0 \qquad \text{...(1.39)}$$

Differentiating Equation (1.39) $|m|$ times with respect to ξ and using Equation (1.38) we obtain,

$$(1-\xi^2)\frac{d^2P_l^{|m|}}{d\xi^2} - 2\xi\frac{dP_l^{|m|}(\xi)}{d\xi} + \left\{l(l+1) - \frac{m^2}{1-\xi^2}\right\}P_l^{|m|}(\xi) = 0 \qquad \text{...(1.40)}$$

Comparing Equations (1.38) and (1.42) we identify

$$\Theta(\theta) = P_l^{|m|}(\xi) = P_l^{|m|}(\cos\theta) \qquad \text{...(1.40)}$$

Thus we can express the general solution of the Θ equation as,
$$\Theta(\theta) = B\,P_l^{|m|}\,(\cos\theta) \qquad \text{...(1.42)}$$

In the above the constant B is determined by requiring $\Theta(\theta)$ to be normalized, i.e.,

$$\int_0^{\pi}\Theta^*(\theta)\Theta(\theta)\sin\theta\,d\theta = 1$$

Using Equation (1.42) in the above we obtain,

$$B^2\int_{-1}^{+1}\{P_l^{|m|}(\cos\theta)\}^*\{P_l^{|m|}(\cos\theta)\}\,d(\cos\theta) = 1$$

or

$$B^2\,\frac{2(l+|m|)!}{2l+l(l-|m|)!} = 1$$

The above gives

$$B = \sqrt{\frac{2l + l(l - |m|)!}{2(l + |m|)!}} \qquad \text{...(1.43)}$$

Thus the general solution of the Θ equation given by Equation (1.43) becomes

$$\Theta(\theta) = \sqrt{\frac{2l + l(l - |m|)!}{2(l + |m|)!}}\, P_l^{|m|}(\cos\theta) \qquad \text{...(1.44)}$$

In view of Equation (1.21) and Equation (1.44) we can now write the wavefunction ψ for the rigid rotator with free axis as

$$\psi_{l,|m|} = \Theta(\theta)\Phi(\theta) = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{2l + l(l - |m|)!}{2(l + |m|)!}}\, P_l^{|m|}(\cos\theta)e^{im\phi} \qquad \text{...(1.45)}$$

Set of values of l and $|m|$ give the different energy **eigenfunctions** for the rotator.

The corresponding energy **eigenvalues** are obtained from

$$\lambda = l(l + 1) \qquad \text{...(1.46)}$$

or

$$\frac{2I_0E_l}{\hbar^2} = l(l + 1) \qquad \text{...(1.47)}$$

or

$$E_l = \frac{\hbar^2}{2I_0}[l(l + 1)] \qquad \text{...(1.48)}$$

1.3.1 Orthogonality, Normality and Closure Properties of Eigen Function

Orthogonality Eigen Function

The condition for two eigen functions to be ***orthogonal*** is that their inner product is zero. In **Dirac notation** this would mean:

$$\langle \psi_n | \psi_m \rangle = 0, \qquad m \neq n, \qquad (1.49)$$

And in wave function notation for Equation (1.49) will be becomes is following equation:

$$\langle \psi_{n|\psi m\rangle} = \int_{-\infty}^{\infty} \psi_{n(x)}{}^{*\psi}{}_{m(x)dx=0,} \qquad m\neq n \qquad \text{...(1.50)}$$

You can from here verify that the eigenstates of the infinite square well Hamiltonian corresponding to different values of n (the ψ_n) are orthogonal.

You could also infer this from the fact that since $\hat{H}$ is Hermitian its eigen functions corresponding to different eigenvalues are necessarily orthogonal. Since each energy eigen function of the 1D-infinite square well has a different energy value they must be pairwise orthogonal.

Orthogonality Theorem: Eigen functions of a Hermitian operator are orthogonal if they have different eigenvalues. Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof: ψ and φ are two eigen functions of the operator $\hat{A}$ with real eigen values a1 and a_2, respectively. Since the eigenvalues are real, $a^*_1=a_1$ and $a^*_2=a_2$.

$$\hat{A}\psi = a_1\psi \tag{1.51}$$

$$\hat{A}^*\psi^* = a_2\psi^* \tag{1.52}$$

Multiply the first equation by φ∗ and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^* \psi \, d\tau \tag{1.53}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a_2 \int \psi \psi^* \, d\tau \tag{1.54}$$

Subtract the two equations in Equation (1.54) to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^* \psi^* \, d\tau = (a_1 - a_2) \int \psi^* \psi \, d\tau \tag{1.55}$$

The left-hand side of Equation (1.55) is zero because Â is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^* \psi \, d\tau \tag{1.56}$$

If a_1 and a_2 in Equation (1.56) are not equal, then the integral must be zero. This result proves that non-degenerate eigen functions of the same operator are orthogonal.

Normality of Eigen Function

Principles of ***Quantum Mechanics*** by R. Shankar, he describes finding the eigen values and eigen functions of the operator ***K*= −*i*D = −*i* d/dx**. For context, he does this:

$$K|k\rangle = K|k\rangle \tag{1.57}$$

Following to standard procedure

$$\langle x|K|k\rangle = k\langle x|k\rangle$$

$$\int \langle x|K|x'\rangle \langle x'|k\rangle \, dx' = k\psi_k(x)$$

$$-i\frac{d}{dx}\psi_k(x) = k\psi_k(x)$$

Where by definition $\psi_k(x) = \langle x|k\rangle$. This is equation could have been written directly had we made the immediate substitution ***K*= −*i* d/d*x*** in the

X basis. The solution of the above equation simply form are following:

$$\psi_k(x) = Ae^{ikx} \qquad (1.58)$$

Where ***A***, is the overall scale, is a free parameter unspecified by eigen value problem. So the eigen value ***K*** is a fully solved: any real number of ***K*** is an eigen value and the corresponding eigen value is given by Ae^{ikx}**.** A usual the freedom in scale will be used to normalised the solution. We choose to ***A*** to be $(1/2\pi)^{-1/2}$ so that

$$|k\rangle \leftrightarrow \frac{1}{(2\pi)^{1/2}}\, e^{ikx}$$

And

$$\langle k|k'\rangle = \int_{-\infty}^{\infty} \langle k|x\rangle\langle x|k'\rangle\, dx = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i(k-k')x}\, dx = \delta(k-k') \qquad (1.59)$$

Equation 1.60 is also are equal to Fourier transform,

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i(k-k')x} dx = \delta(k-k'). \qquad (1.60)$$

The eigen functions of an operator are orthogonal functions. We will as well assume that they are normalized. Consider two eigen functions u_n, u_m of an operator ***A*** and the inner product defined by $\langle f|g\rangle = \int d^3x\, f^*(x)g(x)$**.** Then we have

$$\int d^3x\; u_m^*(\mathbf{x})u_n(\mathbf{x}) = \delta_{nm}$$

Closure of Eigen Function

The coefficients of expansion given by following Equation (1.61) can be found using the *orthonormality relation:*

$$\langle\psi_n|\psi_m\rangle = \mathbf{d}_{mn} \qquad (1.61)$$

Taking the scalar product of both sides of (1.60) with eigen function ψ_m we ge

$$\langle\psi_m|\Psi\rangle = \sum_n c_n\langle\psi_m|\psi_n\rangle = \sum_n c_n\delta_{mn} \qquad (1.62)$$
$$= c_m$$

Considering the case of one particle system, we write explicitly

$$\Psi(\vec{r},t)=\sum_n\left[\int\psi_n^*(\vec{r}')\Psi(\vec{r}',t)\,d\vec{r}'\right]\psi_n(\vec{r})$$

$$=\int\left[\sum_n\psi_n^*(\vec{r}')\psi_n(\vec{r})\right]\Psi(\vec{r}',t)\,d\vec{r}'$$

And therefore

$$\sum_n\psi_n^*(\vec{r}')\psi_n(\vec{r})=\delta(\vec{r}-\vec{r}')$$

This is the **closure relation** of eigen function.

1.4 DIRAC-DELTA FUNCTION

Consider a function $\delta(x)$ which is zero everywhere except at $x = 0$ and tends to ∞ in such a manner that $\int_{-\infty}^{\infty}\delta(x)\,dx = 1$ ...(1.63)

with $\delta(t) = 0$ if $t \neq 0$ ...(1.64)

$= \infty$ if $t = 0$

This is known as *Dirac-delta function* and used in mathematical physics wherever functions exist with non-zero values in very short interval, *e.g.*, an impulsive force acting for a short while is defined as $\delta(x - \xi)$ by $\lim\limits_{a\to 0} Ce^{-(x-\xi)2/a}$,

where the constant $C(a)$ is chosen such that $\int_{-\infty}^{\infty}\delta(x-\xi)\,dx = 1$

and hence using the mean value theorem of integral calculus, we have

$$\int_{-\infty}^{\infty} f(x)\,\delta(x-\xi)\,dx = f(\xi).$$

Let us again consider a function

$$\delta_a(x) = \frac{1}{2a},\ -a < x < a$$

$$= 0,\ |x| > a \qquad ...(1.65)$$

Then, $$\int_{-\infty}^{\infty}\delta_a(x)\,dx = \int_{-\infty}^{-a}\delta_a(x)\,dx+\int_{-a}^{a}\delta_a(x)\,dx+\int_{a}^{\infty}\delta_a(x)\,dx$$

$$= 0+\int_{-a}^{a}\frac{1}{2a}\,dx+0=\frac{1}{2a}\{a-(-a)\}$$

$$= 1 \qquad ...(1.66)$$

In case $f(x)$ in integrable in the interval $(-a, a)$, then from mean value theorem,

$$\int_{-\infty}^{\infty} f(x)\,\delta_a(x)\,dx = \frac{1}{2a}\int_{-a}^{a} f(x)\,dx \quad f(\theta\, a);\ |\theta| \leq 1$$

Let us now define $\delta(x) = \lim\limits_{a\to\infty}\delta_a(x)$

As such (1.65) and (1.66) yield

$$\delta(x) = 0, \text{ when } x \neq 0 \qquad ...(1.67)$$

and

$$\int_{-\infty}^{\infty} \delta(x)\,dx = 1 \qquad ...(1.68)$$

which define Dirac-delta function.

Further, since we have

$$\int_{a}^{\infty} f(x)\,\delta_a(x)\,dx = \frac{1}{2a}\int_{-\infty}^{a} f(x)\,dx = f(\theta\, a),\ |\theta\,| \leq 1$$

$$\therefore \quad \int_{-\infty}^{\infty} f(x)\,\delta(x)\,dx = f(0). \qquad ...(1.69)$$

which by change of variable, reduces to

$$\int_{-\infty}^{\infty} f(x)\,\delta(x-a)\,dx = f(a) \qquad ...(1.70)$$

or symbolically, $f(x)\,\delta(x - a) = f(a)\,\delta(x - a)$ ...(1.71)

In case $f(x) = x$, Equation (1.71) yields, $x\delta x = 0$ ...(1.72)

In a similar manner we can show

$$\delta(-x) = \delta x \qquad ...(1.73)$$

$$\delta(ax) = \frac{1}{a}\delta(x),\ a > 0 \qquad ...(1.74)$$

$$\delta(\alpha^2 - x^2) = \frac{1}{2a}\{\delta(x-a)+\delta(x+a)\},\ a > 0 \qquad ...(1.75)$$

Now assuming that $\delta'(x)$ *i.e.*, differential of $\delta(x)$ exists and regarding $\delta(x)$ and $\delta'(x)$ both as ordinary functions in the rule for integrating by parts, we have

$$\int_{-\infty}^{\infty} f(x)\,\delta'(x)\,dx = \left[f(x)\,\delta(x)\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f'(x\,\delta(x)\,dx$$

$$= 0 - f'\,(0) \qquad \text{[by Equation (1.76)]}$$

$$= -f'\,(0) \qquad ...(1.77)$$

If $\delta^{(n)}$ be the nth derivative of $\delta(x)$, then similarly we find on repeating this process n times,

$$\int_{-\infty}^{\infty} f(x)\,\delta^{(n)}\,(x)\,dx = (-1)^n f^{(n)}(0) \qquad ...(1.78)$$

COROLLARY: Heaviside unit function or (unit step function).

We define Heaviside unit function $H(x)$ as

$$H(x) = 1 \text{ for } x \geq 0 \qquad ...(1.79)$$

$$= 0 \text{ for } x < 0$$

For $a > 0$, we can write this result as

$$H(x - a) = 1 \text{ for } x \geq a \qquad ...(1.80)$$

$$= 0 \text{ for } x < a$$

It is evident that

$$\delta(x) = H'(x) \qquad ...(1.81)$$

NOTES

Illustrations

1. *To show that* $\int_{-\infty}^{\infty} \delta(x-y)\, \delta(y-a)\, dy = \delta(x-a)$

We have,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x)\, \delta(x-y)\, \delta(y-a)\, dy\, dx = \int_{-\infty}^{\infty} \delta(y-a) \left\{\int_{-\infty}^{\infty} f(x)\, \delta(x-y)\, dx\right\} dy$$

$$= \int_{-\infty}^{\infty} \delta(y-a) \cdot f(y)\, dy$$

$$= \int_{-\infty}^{\infty} f(x)\, \delta(x-a)\, dx$$

(on replacing y by x)
which follows that

$$\int_{-\infty}^{\infty} \delta(x-y)\, \delta(y-a)\, dy = \delta(x-a)$$

2. *To show that*

$$\int_{0}^{\infty} \cos(x, y) \cos(xy')\, dx = \frac{1}{2} \pi \delta(x-y')$$

where $y > 0$, $y' > 0$ and $\delta(y-y')$ is the Dirac-delta function.

Noting that $\frac{\cos 2\pi nx}{\pi x} \to \infty$ as $x \to 0$ and $\frac{\cos 2\pi nx}{\pi x} \to 0$ as $x \neq 0$, but it is sufficiently large. This follows that cosine function tends to become a Dirac-delta function if divided by πx, so that taking $xy = Y - X$ and $xy' = Y' - X$, we have

$$\cos xy = \cos(Y-X) = \delta(Y-X) \text{ (say)}$$

and

$$\cos xy' = \cos(X-Y') = \delta(X-Y') \text{ (say)}$$

In view of Illustration 1,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(y)\, \delta(Y-X)\, \delta(X-Y')\, dY\, dX = \pi x \int_{-\infty}^{\infty} f(Y)\, \delta(Y-Y')\, dY$$

as $\delta(Y-Y')$ is a function of cosine.

$$\therefore \int_{-\infty}^{\infty} \cos xy \cos xy' dx = \pi x \cdot \delta(Y-Y')$$

$$\Rightarrow 2\int_{0}^{\infty} \cos xy \cos xy' dx = \pi x \cdot \delta(xy - xy') \text{ as } Y - Y' = xy - xy'$$

$$\Rightarrow \int_{0}^{\infty} \cos xy \cos xy' dx = \frac{\pi x}{2} \cdot \frac{1}{x} \delta(y-y')$$

$$\delta(ax) = \frac{1}{a} \delta(x), a > 0$$

$$= \frac{\pi}{2} \delta(y-y').$$

Check Your Progress

1. State the Ehrenfest theorem.
2. Give the definition of Lagrangian function L for rigid rotator.
3. What do you understand by Recursion formula for coefficients?
4. State the orthogonality theorem.
5. Define the Dirac delta function.
6. Heaviside unit function is a corollary of what function?

1.5 TIME-INDEPENDENT PERTURBATION THEORY

NOTES

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a 'small' term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated. This is only approximate because the sum of a Coulomb potential with a linear potential is unstable (has no true bound states) although the tunneling time (decay rate) is very long.

The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say a, is very small. Typically, the results are expressed in terms of finite power series in a that seem to converge to the exact values when summed to higher order. After a certain order n ~ 1/a however, the results become increasingly worse since the series are usually divergent (being asymptotic series). There exist ways to convert them into convergent series, which can be evaluated for large expansion parameters, most efficiently by the variational method.

Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence. The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In this paper Schrödinger referred to earlier work of Lord Rayleigh, who investigated harmonic vibrations of a string perturbed by small in-homogeneities. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.

First Order Corrections

Consider an unperturbed Hamiltonian, H0, which is also assumed to have no time dependence. It has known energy levels and eigenstates, arising from the time independent Schrödinger equation of the form:

$$H_0 \left|n^{(0)}\right\rangle = E_n^{(0)} \left|n^{(0)}\right\rangle, \qquad n = 1, 2, 3, \cdots$$

For simplicity, assume that the energies are discrete. The (0) superscripts denote that these quantities are associated with the unperturbed system. Note the use of bra–ket notation.

We now introduce a perturbation to the Hamiltonian. Let V be a Hamiltonian representing a weak physical disturbance, such as a potential energy produced by an external field. Thus, V is formally a Hermitian operator. Let λ be a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation). The perturbed Hamiltonian is represented as,

$$H = H_0 + \lambda V$$

The energy levels and eigenstates of the perturbed Hamiltonian are again given by the Schrödinger equation:

$$(H_0 + \lambda V)\,|n\rangle = E_n|n\rangle$$

The objective is to express E_n and $|n\rangle$ in terms of the energy levels and eigenstates of the old Hamiltonian. If the perturbation is sufficiently weak, we can write them as a (Maclaurin) power series in λ:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \cdots$$

Where,

$$E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}\bigg|_{\lambda=0}$$
$$\left|n^{(k)}\right\rangle = \frac{1}{k!}\frac{d^k |n\rangle}{d\lambda^k}\bigg|_{\lambda=0}$$

When $k = 0$, these reduce to the unperturbed values, which are the **first term** in each series. Since the perturbation is weak, the energy levels and eigenstates should not deviate too much from their unperturbed values, and the terms should rapidly become smaller as we go to higher order.

Substituting the power series expansion into the Schrödinger equation, we obtain,

$$(H_0 + \lambda V)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \cdots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \cdots\right)$$

Expanding this equation and comparing coefficients of each power of λ results in an infinite series of simultaneous equations. The zeroth-order equation is simply the Schrödinger equation for the unperturbed system. The first order equation is,

$$H_0\left|n^{(1)}\right\rangle + V\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(1)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle$$

Operating through by $\langle n^{(0)}|$,, the first term on the left-hand side cancels the first term on the right-hand side as per the unperturbed Hamiltonian is Hermitian. This leads to the first order energy shift:

$$E_n^{(1)} = \left\langle n^{(0)}\right| V \left|n^{(0)}\right\rangle$$

This is simply the expectation value of the perturbation Hamiltonian while the system is in the unperturbed state.

The Stark Effect for $n = 2$ Hydrogen

The Stark effect for the $n = 2$ states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of E_0. That is $H_0\phi_{2\ell m} = E_0\phi_{2\ell m}$.

The degenerate states are $\phi200$, $\phi211$, $\phi210$ and $\phi21(-1)$.

The perturbation due to an electric field in the z direction is $H_1 = +e\mathcal{E}z$.

So the first order degenerate state perturbation theory equation is,

$$\sum_i \alpha_i \left\langle \phi^{(j)} \left| H_0 + e\mathcal{E}z \right| \phi^{(i)} \right\rangle = (E_0 + E^{(1)})\alpha_j.$$

This is essentially a 4 x 4 matrix eigenvalue equation. There are 4 eigenvalues $(E_0 + E^{(1)})$, distinguished by the index n .

Because of the exact degeneracy $(H_0\phi^{(j)} = E_0\phi^{(j)})$, the H_0 and E_0 can be eliminated from the equation.

$$\begin{aligned}
\sum_i \alpha_i (E_0\delta_{ij} + \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle) &= (E_0 + E^{(1)})\alpha_j \\
E_0\alpha_j + \sum_i \alpha_i \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle &= E_0\alpha_j + E^{(1)}\alpha_j \\
\sum_i \alpha_i \left\langle \phi^{(j)} \left| e\mathcal{E}z \right| \phi^{(i)} \right\rangle &= E^{(1)}\alpha_j
\end{aligned}$$

This is just the eigenvalue equation for H_1 which we can write in (pseudo) matrix form as follows,

$$\begin{pmatrix} \\ H_1 \\ \\ \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

Now, in fact, most of the matrix elements of H_1 are zero. We can define that because $[L_z, z] = 0$, hence all the matrix elements between states of unequal m are zero. Another way of saying this is that the operator z does not 'change' m . Here is a little proof.

$$\langle Y_{lm} \left| [L_z, z] \right| Y_{l'm'} \rangle = 0 = (m - m') \langle Y_{lm} \left| z \right| Y_{l'm'} \rangle$$

This implies that $\langle Y_{lm}\,|z|\,Y_{l'm'}\rangle = 0$ unless $m = m'$.

Let us define the one remaining nonzero (real) matrix element to be γ.

$$\gamma = e\mathcal{E}\,\langle \phi_{200}\,|z|\,\phi_{210}\rangle$$

The equation that is labelled with the basis states to define the order is.

$$\begin{array}{c} \phi_{200} \\ \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{array} \begin{pmatrix} 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

We can see by inspection that the eigenfunctions of this operator are ϕ211, ϕ21–1, and $\frac{1}{\sqrt{2}}\left(\phi_{200} \pm \phi_{210}\right)$ with eigenvalues (of H_1) of 0, 0, and $\pm\gamma$.

What remains is to compute γ. Recall $Y_{00} = \frac{1}{\sqrt{4\pi}}$ and $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$.

$$\begin{aligned}
\gamma &= e\mathcal{E}\int (2a_0)^{-3/2}\, 2\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00}\, z\, (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{10} d^3r \\
&= 2e\mathcal{E}\,(2a_0)^{-3} \frac{1}{\sqrt{3}} \int r^3 d^3r \left(1 - \frac{r}{2a_0}\right)\left(\frac{r}{a_0}\right) e^{-r/a_0} \int \frac{1}{\sqrt{4\pi}} \cos\theta Y_{10} d\Omega \\
&= 2eE(2)^{-3} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \int_0^\infty \left(\frac{r^4}{a_0^4} - \frac{r^5}{2a_0^5}\right) e^{-r/a_0} dr \\
&= \frac{a_0 e\mathcal{E}}{12}\left[\int_0^\infty x^4 e^{-x} dx - \frac{1}{2}\int_0^\infty x^5 e^{-x} dx\right] \\
&= \frac{a_0 e\mathcal{E}}{12}\left[4\cdot 3\cdot 2\cdot 1 - \frac{5\cdot 4\cdot 3\cdot 2\cdot 1}{2}\right] \\
&= \frac{a_0 e\mathcal{E}}{12}(-36) \\
&= -3e\mathcal{E}a_0 \qquad \Rightarrow \qquad E^{(1)} = \mp 3e\mathcal{E}a_0
\end{aligned}$$

This is first order in the electric field, as we would expect in first order (degenerate) perturbation theory.

If the states are not exactly degenerate, we have to leave in the diagonal terms of H_0. Assume that the energies of the two (mixed) states are $E_0 \pm \Delta$, where Δ comes from some other perturbation, like the hydrogen fine structure. The ϕ211 and ϕ21 (–1) are still not mixed by the electric field.

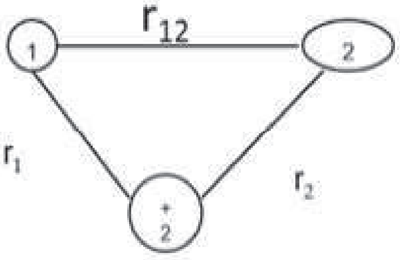
$$\begin{pmatrix} E_0 - \Delta & \gamma \\ \gamma & E_0 + \Delta \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

$$E = E_0 \pm \sqrt{\gamma^2 + \Delta^2}$$

This is correct in both limits, $\Delta \gg \gamma$, and $\gamma \gg \Delta$. It is also correct when the two corrections are of the same order.

1.5.1 Application of Perturbation to Theory Ground State of Helium Atom

Helium atom is a three particle system (2 electrons and one nucleus) for which the Schrödinger equation cannot be solved exactly. Therefore, we use here perturbation theory in first order to solve helium atom Schrödinger equation.



The helium atom has two electrons with co-ordinates $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$ with respect to nucleus which carries +2e charge (Z = 2). The Schrödinger equation for helium atom is given as

$$\hat{H} = -\frac{h^2}{8\pi^2 m_e}\left(\nabla_{e1}^2 + \nabla_{e2}^2\right) - \frac{h^2}{8\pi^2 m_n}\nabla_n^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

...(1.82)

Where $\boldsymbol{m_e}$ is the mass of electron, $\boldsymbol{m_n}$ is the mass of the nucleus; “$^{2}_{\text{5Ø[Ü}}$ is the Laplacian operator with respect to the position of the nucleus and “$^{2}_{e}$ is the Laplacian operator with respect to the electronic coordinates of the two respective electrons present in the system. To simplify this 3 body problem, nucleus is considered fixed at the origin as $\boldsymbol{m_n >> m_e}$, which reduces the Schrödinger equation for helium atom

$$\boldsymbol{\$ = -h^2/\ 8\pi^2\ m_e\ (\Delta^2_{e1} + \Delta^2_{e2}) - 2e^2/4\pi^2\varepsilon_0 r_1 - 2e^2/4\pi^2\varepsilon_0 r_2 + e^2/4\pi^2\varepsilon_0 r_{12}}$$

...(1.83)

The last term in the Hamiltonian expression ($e^2/4\pi^2\varepsilon_0 r_{12}$) is the inter-electronic repulsion term which causes difficulty in solving the **Schrödinger equation** (1.83). If we neglect this electron-electron repulsion term, then the Hamiltonian becomes a two body problem.

$$\boldsymbol{\$ = -h^2/\ 8\pi^2\ m_e\ (\Delta^2_{e1} + \Delta^2_{e2}) - 1/4\pi^2\varepsilon_0\ [2e^2/r_1 - 2e^2/r_2]} \qquad (1.84)$$

Rearranging equation (1.84) gives

$$\hat{H} = \left(-\frac{h^2}{8\pi^2 m_e}\left(\nabla_{e1}^2\right) - \frac{2e^2}{4\pi\varepsilon_0 r1}\right) + \left(-\frac{h^2}{8\pi^2 m_e}\left(\nabla_{e2}^2\right) - \frac{2e^2}{4\pi\varepsilon_0 r2}\right)$$

... (1.85)

That means, if we consider nucleus at origin and ignore inter-electronic repulsion, we get helium atom Hamiltonian as a sum of two hydrogen like Hamiltonian (or one electron Hamiltonian). Or, one can say that the ground state Hamiltonian of helium atom becomes equal to sum of two helium ion (He^+) terms, i.e., one electron Hamiltonian.

$$\hat{H}_o = \left(-\frac{h^2}{8\pi^2 m_e}\left(\nabla^2_{e1}\right) - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right) + \left(-\frac{h^2}{8\pi^2 m_e}\left(\nabla^2_{e2}\right) - \frac{2e^2}{4\pi\varepsilon_0 r2}\right) \quad \text{... (1.86)}$$

NOTES

The zero order ground state wave function for helium atom then can be taken as a product of individual electron wave function, i.e., wave function of two He^+ ions not interacting with each other (approximated as hydrogen like one electron wave function).

$$\Psi_o(r_1, r_2) = \psi_1(r_1).\psi_2(r_2)$$

Where one electron hydrogen like wave function is given by

$$\Psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o} \quad \text{...(1.87)}$$

With $\mathbf{a_o}$ representing the Bohr's radius and Z the charge on the nucleus. And ground state helium atom energy (sum of one electron hydrogen atom like energy) is given by Equation (1.88)

$$\mathbf{E_0 = -\ 2\pi^2\ m_e Z^2\ e^4/\ n^2h^2\ (4\pi\varepsilon_0)^2 -\ 2\pi^2\ m_e Z^2\ e^4/\ n^2h^2\ (4\pi\varepsilon_0)^2} \quad \text{... (1.71)}$$

1.5.2 Degenerate Time Independent Perturbation Theory

Degeneracy: Degeneracy occurs when more than one possible state of a system corresponds to the exact same energy. If take a measurement of the energy of one of these degenerate states, and then took a measurement of the energy of another of the degenerate states, both being fundamentally and physically different states, and we get the same result. The two states would appear identical. Degeneracy stems from symmetries inherent to a systems geometry. Distortion of the symmetry that allows multiple states to have the same energy spreads the energies of the different states apart, and they become measurably distinguishable.

Consider a Hamiltonian of the form:

$$\$ = \$_0 + \$'$$

Where $\$$ is the total Hamiltonian, $\$_0$ is the unperturbated Hamiltonian, and $\$'$ is the relatively small contribution due to the perturbation.

We now suppose that $\$_0$ has degenerate eigenstates, and in so doing depart from non-degenerate perturbation theory. Suppose for example that the ground state of

$\$_0$ has q degenerate states (q-fold degeneracy). If a perturbation potential is applied that destroys the symmetry permitting this degeneracy, the ground state $E_n^{(0)}$ will separate into q distinct energy levels.

One of the primary goals of Degenerate Perturbation Theory is to allow us to calculate these new energies, which have become distinguishable due to the effects of the perturbation. As in the non-degenerate case, we start out by expanding the first order wave functions of $\$$ in terms of the eigenstates of $\$_0$.

$$\varphi_n^{(1)} = \sum_i c_{ni}\varphi_{ni}$$

Solving for the coefficients $\{c_{ni}\}$ gives the expression:

$$c_{ni} = \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}}$$

But consider the denominator of c_{ni} when $E_n^{(0)} = E_i^{(0)}$ (our degeneracy condition) .it is zero. This causes c_{ni} to blow up to infinity due to the degeneracy of H_0. In fact c_{ni} blows up for any $(n, i < q)$ because all q of those eigen energies are equal.

$$E_1^{(0)} = E_2^{(0)} = \ldots = E_q^{(0)}$$

1.5.3 Application of Perturbation Theory to Zeeman Effect

The ***Zeeman effect*** is a phenomenon by which the energy eigen states of an atomic or molecular system are modified in the presence of a static, external, magnetic field. This phenomenon was first observed experimentally by P. Zeeman. Let us use perturbation theory to study the Zeeman effect.

Consider a hydrogen-like atom placed in a uniform *z*-directed magnetic field, **B**. The change in energy of the outermost electron is:

$$H_B = -\boldsymbol{\mu}\cdot\mathbf{B},$$

Where,

$$= -\frac{e}{2\,m_e}\,(\mathbf{L} + 2\,\mathbf{S})$$

Its magnetic moment, including both the spin and orbital contributions.

$$H_B = \frac{e\,B}{2\,m_e}\,(L_z + 2\,S_z).$$

Suppose that the energy-shifts induced by the magnetic field are much smaller than those induced by spin-orbit interaction. In this situation, we can treat H_B as a small perturbation acting on the eigenstates of $H_0 + H_{LS}$. Of course, these states are the simultaneous eigenstates of J^2 and J_z. Let us consider one of these states, labelled by the quantum numbers j and m_j, where $j = l \pm 1/2$. From standard perturbation theory, the first-order energy-shift in the presence of a magnetic field is,

$$\Delta E_{nlm_j\pm} = \langle l \pm 1/2, m_j|\, H_B\, |l \pm 1/2, m_j\rangle.$$

Because

$$L_z + 2\,S_z = J_z + S_z,$$

NOTES

We find that

$$\Delta E_{nlm_j\pm} = \frac{e\,B}{2\,m_e}\,(m_j\,\hbar + \langle l \pm 1/2, m_j|\,S_z\,|l \pm 1/2, m_j\rangle)\,.$$

$$= \pm\sqrt{\frac{l \pm m_j +}{2\,l +}} \quad + \sqrt{\frac{l \mp m_j + 1/2}{2\,l + 1}}\,|m_j + 1/2, -1/2\rangle.$$

It follows that

$$\langle l \pm 1/2, m_j|\,S = \frac{\hbar}{2\,(2\,l+1)}\,[(l \pm m_j + 1/2) - = \pm\frac{m_j\,\hbar}{2\,l+1}.2)]$$

Thus, we obtain the so-called ***Landé formula*** for the energy-shift induced by a weak magnetic field:

$$\Delta E_{nlm_j\pm} = \mu_B\,B\,m_j\left(1 \pm \frac{1}{2\,l+1}\right),$$

Where

$$\mu_B = \frac{e\,\hbar}{2\,m_e} = 5.788 \times 10^{-5}\,\mathrm{eV\,T}^{-1}$$

is called the ***Bohr magnetron.*** Incidentally, for the special case in which l =0, the plus sign applies. Note, finally, that the eigenstates of $\boldsymbol{H_0 + H_{LS}}$ are not eigenstates of $\boldsymbol{H_B}$. However, $\boldsymbol{H_B}$ only couples eigenstates with different values of ***j***. It follows that such eigenstates are non-degenerate (because the eigenvalues of $\boldsymbol{H_{LS}}$ are different for states with different values of ***j.*** Hence, there is no danger of singular terms arising in the ***perturbation expansion*** to second order.

1.5.4 Application With and Without Electron Spin in Hydrogen Like Atom

In ***atomic physics***, the inherent angular momentum of a particular particle is parametrized by *spin quantum number*. The spin quantum number is the fourth number. The rest three are a principal quantum number, azimuthal quantum number, and magnetic quantum number. The spin quantum number explains the unique quantum state of an electron. This is denote as'*s*'.

The Spins play a remarkable role in quantum mechanics in computing the characteristics of elementary units like electrons. The direction of spin of the particle regulates several things like the spin quantum number, angular momentum, the degree of freedom, etc. Let us learn more about the electron spin in this segment.

The electron spin is one of the three inherent properties of the electrons; the others are mass and charge of the electron. The electron spin is described as the spinning of the electron around its axis.

It is expressed as**:** $||S|| = \sqrt{\boxed{s\ (s+1)h}}$

Where,

s is equivalent to a quantized spin vector

The spin vector is expressed as ||s||

The spin quantum number (*s*) is associated with the spin angular momentum and *h* is the Planck's constant.

The spin quantum number can be expressed as: *s* = 1/2

Any non-negative integer can be *n*. The permitted values of the spins are 0, 1/2, 1, 3/2, 2, etc. The intrinsic angular momentum of electron is signified by quantum number **½.**The total angular momentum s is expressed by:

$$s = \sqrt{\boxed{s\ (s+1)h}}\ s = n\ (n+1)h$$

$$s = \sqrt{\boxed{12\ (12+1)h}}\ s = 12(12+1)h$$

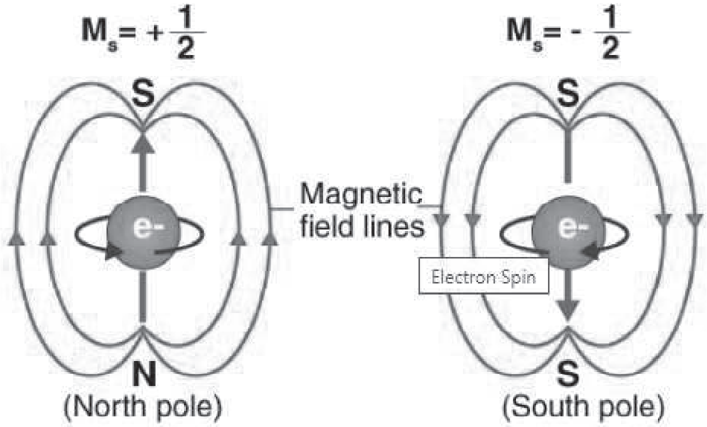
$$S = \sqrt{\boxed{34^{-}\ h}}$$

Where,

The reduced Planck's constant is '

' = h/2π.

Electron Spin Theory: The electron spin theory describes the electron as a quantum particle instead of the simple sphere as in the classical theory. The theory says that the electron spin direction and its influence on certain properties like the magnetic properties of the atom.



The electron can spin in two directions:

- Spin up

- Spin down

The spin up and spin down direction are corresponding to the spinning in the +z or –z direction. These spins (spin up and spin down) are the particles that have spin s equal to 1/2, i.e., for electrons. In the quantum theory, the electron is thought of like the minute magnetic bar, and its spin points the north pole of the minute bar. If two proximate electrons have a similar spin direction, the magnetic field formed by them strengthens each other and therefore a strong magnetic field is gained. If the proximate electrons have an opposite spin direction, the magnetic field formed by them cancels each other and no magnetic field is existent.

With Electron Spin in Hydrogen Atom

The spin of the electron adds a last quantum number, the projection of the electron's ***spin angular momentum*** along the ***z***-axis, which can take on two values. Therefore, any eigenstate of the electron in the '**Hydrogen Atom'** is described fully by four quantum numbers. According to the usual rules of quantum mechanics, the actual state of the electron may be any superposition of these states. This explains also why the choice of ***z***-axis for the directional quantization of the angular momentum vector is immaterial: an orbital of given ***l*** and ***m'*** obtained for another preferred axis ***z'*** can always be represented as a suitable superposition of the various states of different ***m*** (but same ***l***) that have been obtained for ***z***.

Mathematical Summary of Eigenstates of Hydrogen Atom: In 1928, Paul Dirac found an equation that was fully compatible with special relativity, and (as a consequence) made the wave function a 4-component 'Dirac Spinor' including 'Up' and 'Down' spin components, with both positive and 'Negative' energy (or matter and antimatter). The solution to this equation gave the following results, more accurate than the Schrödinger solution.

Energy Levels: The energy levels of hydrogen, including fine structure (excluding Lamb shift and hyperfine structure), are given by the ***Sommerfeld fine structure*** expression:

$$\begin{aligned} E_{jn} &= -\mu c^2 \left[1 - \left(1 + \left[\frac{\alpha}{n - j - \frac{1}{2} + \sqrt{\left(j+\frac{1}{2}\right)^2 - \alpha^2}}\right]^2\right)^{-1/2}\right] \\ &\approx -\frac{\mu c^2 \alpha^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right], \end{aligned}$$

Where α is the fine-structure constant and ***j*** is the total angular momentum quantum number, which is equal to $\left|\ell \pm \frac{1}{2}\right|$ depending on the orientation of the electron spin relative to the orbital angular momentum.This formula represents a small correction to the energy obtained by Bohr and Schrödinger equation. The factor in square brackets in the last expression is nearly one; the extra term arises from relativistic effects. It is worth noting that this expression was first obtained by

A. Sommerfeld in 1916 based on the relativistic version of the old Bohr theory. Sommerfeld has however used different notation for the quantum numbers. Consider a H_2 atom, which has the simplest atomic configuration with a single electron revolving round the nucleus. The total energy of such an electron is given by $-\frac{me^4}{8\varepsilon_0 h^2 n^2}$, where m and e are mass and charge of the electron respectively, ε_0 is the permittivity of free-space, h is the Planck's constant and n is known as principal quantum number. Thus, the total energy for such an electron solely depends on n. We know that for a given value of n, we get other three quantum numbers whose values depend on n in the following manner:

l (orbital quantum number) = 0, 1, 2, 3, ..., $(n-1)$

m_1 (magnetic orbital quantum number) = –1, (–1 + 1), (–1 + 2), ..., –2, –1, 0, 1, 2, ..., (1–1), 1

m_s (magnetic spin quantum number) = $-\frac{1}{2}, +\frac{1}{2}$ (for each value of m_1)

All n, l and m_l are integers or zero (but $n \neq 0$).

A specific energy level corresponds to a specific value of n. For different integral values of n, we get different discrete energy levels. On the other hand, each discrete set of the four quantum numbers, *i.e.* $\{n, l, m_1, m_s\}$, designates each energy state. Let's have an example to make these concepts clear.

Consider $n = 2$ energy level.

n-value	*l-value*	*m_l-value*	*m_s-value*	*Energy states*	*No. of energy states*
2	0	0	$-\frac{1}{2}, \frac{1}{2}$	$\left(2,0,0,-\frac{1}{2}\right)$	2
				$\left(2,0,0,+\frac{1}{2}\right)$	
2	1	–1	$-\frac{1}{2}, \frac{1}{2}$	$\left(2,1,-1,-\frac{1}{2}\right)$	6
				$\left(2,1,-1,+\frac{1}{2}\right)$	
		0	$-\frac{1}{2}, \frac{1}{2}$	$\left(2,1,0,-\frac{1}{2}\right)$	
				$\left(2,1,0,\frac{1}{2}\right)$	
		+1	$-\frac{1}{2}, \frac{1}{2}$	$\left(2,1,+1,-\frac{1}{2}\right)$	
				$\left(2,1,+1,\frac{1}{2}\right)$	

For $n = 2$, $l = 0, 1$.

For $l = 0$, $m_1 = 0$ and $m_s = -\frac{1}{2}, +\frac{1}{2}$

For $l = 1$, $m_1 = -1, 0, +1$ and $m_s = -\frac{1}{2}, +\frac{1}{2}$ for each value of m_1.

Thus for $n = 2$ energy level, we get eight distinct energy states, But all these eight energy states have the same value of the total energy because, the total energy, as already stated, depends only on the principal quantum number. Such type of distinct energy states having the same total energy are known as *degenerate states* and it is said that the energy level $n = 2$ is *8-fold degenerate*. Similarly, we can show that $n = 3$ energy level is 18-fold degenerate. Note that this type of degenerate states are direct consequence of the symmetry of the respective system.

Without Electron Spin in Hydrogen Atom

Each atomic orbital is associated with an angular momentum ***L***. It is a vector operator, and the eigenvalues of its square $\mathbf{L}^2$ **a”** $\mathbf{L}_x^2 + \mathbf{L}_y^2 + \mathbf{L}_z^2$ are given by:

$$\hat{L}^2 Y_{\ell m} = \hbar^2 \ell(\ell+1) Y_{\ell m}$$

The projection of this vector onto an arbitrary direction is quantized. If the arbitrary direction is called ***z***, the quantization is given by:

$$\hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m},$$

Note that $\boldsymbol{L^2}$ and $\boldsymbol{L_z}$ commute and have a common eigenstate, which is in accordance with ***Heisenberg’s uncertainty principle***. Since $\boldsymbol{L_x}$ and $\boldsymbol{L_y}$ do not commute with $\boldsymbol{L_z}$, it is not possible to find a state that is an eigenstate of all three components simultaneously. Hence the values of the ***x*** and ***y*** components are not sharp, but are given by a probability function of finite width. The fact that the ***x*** and ***y*** components are not well-determined, implies that the direction of the angular momentum vector is not well determined either, although its component along the ***z***-axis is sharp. These relations do not give the total angular momentum of the electron. For that, electron spin must be included. This quantization of angular momentum closely parallels that proposed by Niels Bohr in 1913, with no knowledge of wave functions.

1.6 VARIATIONAL METHOD AND ITS APPLICATION TO GROUND STATE OF HELIUM ATOM

The variational method is the key approximate method/technique typically used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian, i.e., one which makes the perturbation small but is still solvable. On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.

The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator.

These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions, such as molecular orbitals. The basis for this method is the variational principle. The method consists of choosing a ‘trial wavefunction’ depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an upper bound to the ground state energy. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.

Basically the ‘Trial Wavefunction’ for the problem consists of some adjustable parameters called termed as the ‘variational parameters’. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.

Suppose we are given a Hilbert space and a Hermitian operator over it called the Hamiltonian, *H*. Ignoring complications about continuous spectra, consider the discrete spectrum of *H* and the corresponding eigenspaces of each eigenvalue »:

$$\langle \psi_{\lambda_1} \mid \psi_{\lambda_2} \rangle = \delta_{\lambda_1 \lambda_2}$$

Where $\delta_{i,j}$ is the Kronecker delta,

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j, \\ 1 & \text{if } i = j. \end{cases}$$

And the Hamiltonian is related to » through the typical eigenvalue relation,

$$\hat{H} \left| \psi_\lambda \right\rangle = \lambda \left| \psi_\lambda \right\rangle$$

Physical states are normalized, meaning that their norm is equal to 1. Once again ignoring complications involved with a continuous spectrum of *H*, suppose it is bounded from below and that its greatest lower bound is E_0. Suppose also that we know the corresponding state |Èé’. The expectation value of *H* is then,

$$\begin{aligned} \langle \psi \mid H \mid \psi \rangle &= \sum_{\lambda_1, \lambda_2 \in \mathrm{Spec}(H)} \langle \psi | \psi_{\lambda_1} \rangle \langle \psi_{\lambda_1} | H | \psi_{\lambda_2} \rangle \langle \psi_{\lambda_2} | \psi \rangle \\ &= \sum_{\lambda \in \mathrm{Spec}(H)} \lambda \left| \langle \psi_\lambda \mid \psi \rangle \right|^2 \geq \sum_{\lambda \in \mathrm{Spec}(H)} E_0 \left| \langle \psi_\lambda \mid \psi \rangle \right|^2 = E_0 \end{aligned}$$

Evidently, in order to vary over all possible states with norm 1 trying to minimize the expectation value of H, the lowest value would be E_0 and the corresponding state would be an eigenstate of E_0. Varying over the entire Hilbert space is usually too complicated for physical calculations, and a subspace of the entire Hilbert space is chosen, parametrized by some (real) differentiable parameters $\pm_i$ ($i = 1, 2, ..., N$). The choice of the subspace is called the ansatz. Some choices of ansatzes lead to better approximations than others, therefore the choice of ansatz is important.

Assume that there is some overlap between the ansatz and the ground state (otherwise, it is a bad ansatz). We still wish to normalize the ansatz, so we have the constraints,

$$\langle\psi(\alpha) \mid \psi(\alpha)\rangle = 1$$

And to minimize,

$$\varepsilon(\alpha) = \langle\psi(\alpha)|H|\psi(\alpha)\rangle$$

If ψ (α) is expressed as a linear combination of other functions (α_i being the coefficients), as in the Ritz method, there is only one minimum and the problem is straightforward.

Although generally limited to calculations of the ground state energy, this method can be applied in certain cases to calculations of excited states as well. If the ground state wavefunction is known, either by the method of variation or by direct calculation, a subset of the Hilbert space can be chosen which is orthogonal to the ground state wavefunction.

$$|\psi\rangle = |\psi_{\text{test}}\rangle - \langle\psi_{\text{gr}} \mid \psi_{\text{test}}\rangle\,|\psi_{\text{gr}}\rangle$$

The resulting minimum is usually not as accurate as for the ground state, as any difference between the true ground state and ψ_{gr} results in a lower excited energy. This defect is worsened with each higher excited state.

In another formulation,

$$E_{\text{ground}} \leq \langle\phi|H|\phi\rangle$$

This holds for any trial Æ since, by definition, the ground state wavefunction has the lowest energy, and any trial wavefunction will have energy greater than or equal to it.

Proof: φ can be expanded as a linear combination of the actual eigenfunctions of the Hamiltonian (which we assume to be normalized and orthogonal):

$$\phi = \sum_n c_n \psi_n$$

Then, to find the expectation value of the Hamiltonian,

$$\begin{aligned}&\langle\phi|H|\phi\rangle\\&=\left\langle\sum_n c_n\psi_n|H|\sum_m c_m\psi_m\right\rangle\\&=\sum_n\sum_m\langle c_n^*\psi_n|E_m|c_m\psi_m\rangle\\&=\sum_n\sum_m c_n^*c_mE_m\,\langle\psi_n\mid\psi_m\rangle\\&=\sum_n|c_n|^2E_n.\end{aligned}$$

Now, the ground state energy is the lowest energy possible, i.e., $E_n \geq E_g$. Therefore, if the guessed wave function Æ is normalized:

$$\langle\phi|H|\phi\rangle \geq E_g\sum_n|c_n|^2 = E_g$$

For a Hamiltonian *H* that describes the studied system and any normalizable function ψ with arguments appropriate for the unknown wave function of the system, we define the functional,

$$\varepsilon[\Psi] = \frac{\left\langle\Psi|\hat{H}|\Psi\right\rangle}{\langle\Psi\mid\Psi\rangle}$$

The variational principle states that,

- $\varepsilon \geq E_0$, where E_0 is the lowest energy eigenstate (ground state) of the Hamiltonian.
- $\varepsilon = E_0$ if and only if ψ is exactly equal to the wave function of the ground state of the studied system.

The variational principle formulated above is the basis of the variational method used in quantum mechanics and quantum chemistry to find approximations to the ground state.

Another feature in variational principles in quantum mechanics is that since ψ and ψ^+ can be varied separately (a fact arising due to the complex nature of the wave function), the quantities can be varied in principle just one at a time.

Helium Atom Ground State

The helium atom consists of two electrons with mass ***m*** and electric charge **–e**, around an essentially fixed nucleus of mass *M* >> *m* and charge +2e. The Hamiltonian for it, neglecting the fine structure, is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right)$$

where $\hbar$ is the reduced Planck constant, ε_0 is the vacuum permittivity, r_i (for $i = 1, 2$) is the distance of the ith electron from the nucleus, and $|\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the two electrons.

NOTES

If the term $V_{ee} = e^2/(4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|)$, representing the repulsion between the two electrons, were excluded, the Hamiltonian would become the sum of two hydrogen-like atom Hamiltonians with nuclear charge $+2e$. The ground state energy would then be $8E_1 = -109$ eV, where E_1 is the Rydberg constant, and its ground state wavefunction would be the product of two wavefunctions for the ground state of hydrogen-like atoms:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

Where a_0 is the Bohr radius and $Z = 2$, Helium's nuclear charge. The expectation value of the total Hamiltonian H (including the term V_{ee}) in the state described by ψ_0 will be an upper bound for its ground state energy. $<V_{ee}>$ is $-5E_1/2 = 34$ eV, so $<H>$ is $8E_1 - 5E_1/2 = -75$ eV.

A tighter upper bound can be found by using a better trial wavefunction with 'tunable' parameters. Each electron can be thought to see the nuclear charge partially 'shielded' by the other electron, so we can use a trial wavefunction equal with an 'effective' nuclear charge $Z < 2$: The expectation value of H in this state is:

$$\langle H \rangle = \left[-2Z^2 + \frac{27}{4} Z \right] E_1$$

This is minimal for $Z = 27/16$ implying shielding reduces the effective charge to ~1.69. Substituting this value of Z into the expression for H yields $729E_1/128 = -77.5$ eV, within 2% of the experimental value, -78.975 eV.

Deuteron Ground State

Deuterium or hydrogen-2, symbol D or ^{2}H, also known as heavy hydrogen, is one of two stable isotopes of hydrogen (the other being protium, or hydrogen-1). The nucleus of deuterium, called a deuteron, contains one proton and one neutron, whereas the far more common protium has no neutron in the nucleus. Deuterium has a natural abundance in Earth's oceans of about one atom in 6420 of hydrogen. Thus deuterium accounts for approximately 0.02% (or, on a mass basis, 0.03%) of all the naturally occurring hydrogen in the oceans, while protium accounts for more than 99.98%.

The deuteron has spin +1 'triplet state' and is thus a boson. The NMR frequency of deuterium is significantly different from common light hydrogen. Infrared spectroscopy also easily differentiates many deuterated compounds, due to the large difference in IR absorption frequency seen in the vibration of a chemical bond containing deuterium, versus light hydrogen. The two stable isotopes of hydrogen can also be distinguished by using mass spectrometry.

The triplet deuteron nucleon is barely bound at $E_B = 2.23$ MeV, and none of the higher energy states are bound. The singlet deuteron is a virtual state, with a negative binding energy of ~60 keV. There is no such stable particle, but this virtual particle transiently exists during neutron-proton inelastic scattering, accounting for the unusually large neutron scattering cross-section of the proton.

Variation method – ground state of helium atom – ground state of Deuteron.

Check Your Progress

7. What is perturbation theory? When is it applied?
8. State the time independent perturbation theory.
9. Define the stark effect.
10. State the electron spin theory.
11. Define variational principle.
12. What does variational principle state?

1.7 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The averages or the expectation values of the quantum mechanical variables satisfy the same equations of motion as the corresponding classical variables in the corresponding classical description. Specifically the theorem states that,

$$\frac{d}{dt}\langle x\rangle = \frac{l}{m}\langle p_x\rangle$$

$$\frac{d}{dt}\langle p_x\rangle = \left\langle -\frac{dV(x)}{dx}\right\rangle$$

2. The Lagrangian function L for the rigid rotator is by definition given by $L = T - V$.

   Or $L = E$ $(\because V = 0 \text{ and } E = T)$
3. Eigen functions of a Hermitian operator are orthogonal if they have different eigenvalues. Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.
4. The *Recursion formula* for the coefficients of the series for $X(\xi)$. In order that the polynomial X represents a satisfactory part of the total wavefunction of the rotator, the series for X must break off (terminate) after a finite number of terms (otherwise it diverges).
5. Consider a function $\delta(x)$ which is zero everywhere except at $x = 0$ and tends to ∞ in such a manner that $\int_{-\infty}^{\infty} \delta(x)\, dx = 1$

$$\text{with} \quad \delta(t) = 0 \text{ if } t \neq 0$$
$$= \infty \text{ if } t = 0$$

This is known as *Dirac-delta function.*

6. Heaviside unit function is a corollary of Dirac delta function.
7. In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a 'small' term to the mathematical description of the exactly solvable problem. For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect) can be calculated.
8. Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.
9. The Stark effect for the $n = 2$ states of hydrogen requires the use of degenerate state perturbation theory since there are four states with (nearly) the same energies. In the first calculation, we will not consider the hydrogen fine structure and assume that the four states are exactly degenerate, each with unperturbed energy of E_0. That is $H_0\phi_{2\ell m} = E_0\phi_{2\ell m}$.

   The degenerate states are $\phi200$, $\phi211$, $\phi210$ and $\phi21(-1)$.
10. The electron spin theory describes the electron as a quantum particle instead of the simple sphere as in the classical theory. The theory says that the electron spin direction and its influence on certain properties like the magnetic properties of the atom.
11. The variational principle is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions. Any physical law which can be expressed as a variational principle describes a self-adjoint operator. These expressions are also called Hermitian. Such an expression describes an invariant under a Hermitian transformation.
12. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground state energy.

1.8 SUMMARY

- Consider a particle of mass m moving along the x-axis under the action of a force-field described by the potential energy $V(x)$ for the particle.
- We observe that ϕ does not appear explicitly in the Lagrangian function and hance ϕ is a cyclic or ignorable coordinate.
- The *Recursion formula* for the coefficients of the series for $X(\xi)$. In order that the polynomial X represents a satisfactory part of the total wavefunction of the rotator, the series for X must break off (terminate) after a finite number of terms (otherwise it diverges).
- The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say a, is very small. Typically, the results are expressed in terms of finite power series in a that seem to converge to the exact values when summed to higher order.
- There exist ways to convert them into convergent series, which can be evaluated for large expansion parameters, most efficiently by the variational method.
- Time independent perturbation theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.
- The time independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics.
- Consider an unperturbed Hamiltonian, H0, which is also assumed to have no time dependence. It has known energy levels and eigenstates, arising from the time independent Schrödinger equation.
- If the states are not exactly degenerate, we have to leave in the diagonal terms of H_0. Assume that the energies of the two (mixed) states are $E_0 \pm \Delta$, where Δ comes from some other perturbation, like the hydrogen fine structure. The ϕ211 and ϕ21 (–1) are still not mixed by the electric field.
- A specific energy level corresponds to a specific value of n. For different integral values of n, we get different discrete energy levels. On the other hand, each discrete set of the four quantum numbers, *i.e.* $\{n, l, m_1, m_s\}$, designates each energy state. Let’s have an example to make these concepts clear.
- Such type of distinct energy states having the same total energy are known as *degenerate states* and it is said that the energy level $n = 2$ is *8-fold*

degenerate. Similarly, we can show that $n = 3$ energy level is 18-fold degenerate.

- The variational method is the key approximate method/technique typically used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian, i.e., one which makes the perturbation small but is still solvable.
- Basically the 'Trial Wavefunction' for the problem consists of some adjustable parameters called termed as the 'variational parameters'. These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.
- Physical states are normalized, meaning that their norm is equal to 1. Once again ignoring complications involved with a continuous spectrum of H, suppose it is bounded from below and that its greatest lower bound is E_0.
- Although generally limited to calculations of the ground state energy, this method can be applied in certain cases to calculations of excited states as well. If the ground state wavefunction is known, either by the method of variation or by direct calculation, a subset of the Hilbert space can be chosen which is orthogonal to the ground state wavefunction.
- The resulting minimum is usually not as accurate as for the ground state, as any difference between the true ground state and ψ_{gr} results in a lower excited energy. This defect is worsened with each higher excited state.
- The helium atom consists of two electrons with mass ***m*** and electric charge **–e**, around an essentially fixed nucleus of mass $M >> m$ and charge +2e.
- Deuterium or hydrogen-2, symbol D or ^{2}H, also known as heavy hydrogen, is one of two stable isotopes of hydrogen (the other being protium, or hydrogen-1). The nucleus of deuterium, called a deuteron, contains one proton and one neutron, whereas the far more common protium has no neutron in the nucleus.

1.9 KEY TERMS

- **Perturbation theory:** It is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one.

- **Time independent perturbation:** The theory is one of two categories of perturbation theory, the other being time dependent perturbation. In time independent perturbation theory the perturbation Hamiltonian is static, i.e., possesses no time dependence.
- **Electron spin theory:** The electron spin theory describes the electron as a quantum particle instead of the simple sphere as in the classical theory. The theory says that the electron spin direction and its influence on certain properties like the magnetic properties of the atom.
- **Variational principle:** It is a scientific principle used within the calculus of variations, which develops general methods for finding functions which extremize the value of quantities that depend upon those functions.
- **Hermitian:** Any physical law which can be expressed as a variational principle describes a self-adjoint operator are also called Hermitian.
- **Variational parameters:** The trial wavefunction for the problem consists of some adjustable parameters called termed as the variational parameters.

1.10 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What dose Ehrenfest theorem state?
2. Give the orthogonality property of eigen function.
3. What do you understand by Dirac delta function?
4. Give the application of Perturbation theory related to helium atom.
5. What is Zeeman effect?
6. What is perturbation theory of first order?
7. Define the stark effect in hydrogen atom.

Long-Answer Questions

1. Discribe the expansion of wave function in eigen function.
2. Analyse the orthogonality, normality and closure properties of eigen function.
3. Discuss the significance of perturbation theory in quantum mechanics.
4. Discuss in detail about the time-independent Perturbation theory by giving its applications to ground state of helium and Zeeman effect.
5. Discuss the time independent perturbation theory by giving appropriate examples.
6. Discuss the variational method by giving appropriate examples.
7. Explain the equations involved in expressing and evaluating the ground state.
8. Discuss the ground state of helium atom and deuteron.

1.11 FURTHER READING

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UNIT 2 APPROXIMATION METHODS AND TIME-DEPENDENT PERTURBATION THEORY

Structure

2.0 INTRODUCTION

In quantum chemistry and molecular physics, the Born-Oppenheimer (BO) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the wave functions of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The Heitler-London (HL) theory for H2 is the simplest example of Valence Bond (VB) theory applied to the covalent part of the wave function for H2.

The WKB approximation or WKB (Wentzel-Kramers-Brillouin) method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wave function is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.

In quantum physics, Fermi's golden rule is a formula that describes the transition rate (the probability of a transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation.

Absorption is when electrons in a substance take up energy from electromagnetic radiation or types of light. Emission is when a substance gives off electromagnetic radiation. The electromagnetic radiation in both cases has some type of energy with a specific wavelength.

The Einstein A coefficients are related to the rate of spontaneous emission of light, and the Einstein B coefficients are related to the absorption and stimulated emission of light.

Exchange degeneracy in physical systems consisting of several particles describes the process in which the system changes the state by exchanging space between two particles, which is degenerate with the original state, i.e., has the same energy.

In quantum mechanics, the physical state of an electron is described by a wave function. According to the standard probability interpretation, the wave function of an electron is probability amplitude, and its modulus square gives the probability density of finding the electron in a certain position in space. The Pauli exclusion principle is the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously.

In this unit, you will study about the Born-Oppenheimer (BO) approximation OF LCAO, Heitler-London (HL) theory for hydrogen atom, WKB approximation and its applications to alpha decay, transition probability and Fermi's golden rule, absorption and emission of radiation, Einstein A and B coefficients, exchange degeneracy for indistinguishable particle, wave function for many electron systems, Pauli exclusion principle.

2.1 OBJECTIVES

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

- Analyse the Born-Oppenheimer (BO) approximation OF LCAO
- Describe the Heitler-London (HL) theory for hydrogen atom
- State the WKB approximation and its applications to alpha decay
- Elaborate on the transition probability and Fermi's golden rule
- Explain in detail about the absorption and emission of radiation
- Discuss the Einstein’s A and B coefficients
- Describe the wave function for many electron systems
- State the Pauli exclusion principle

2.2 BORN-OPPENHEIMER APPROXIMATION OF LCAO

NOTES

In quantum chemistry and molecular physics, the Born–Oppenheimer (BO) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the wave functions of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927, in the early period of quantum mechanics.

The approximation is widely used in quantum chemistry to speed up the computation of molecular wave functions and other properties for large molecules. There are cases where the assumption of separable motion no longer holds, which make the approximation lose validity (it is said to 'Break Down'), but is then often used as a starting point for more refined methods.

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms, for example $E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{nuclear\ spin}$. These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies $E_{electronic}$ consist of kinetic energies, inter electronic repulsions, inter nuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

1. When nuclei of two atoms come close to each other, there election cloud interact and result in the formation of molecular orbitals.
2. Each molecular orbital can be described by a wave function ψ^2, known as molecular orbital wave function ψ^2 represent the probability density or election density.
3. Each ψ^2 is associated with a definite set of quantum numbers which describes the shape and energy of the molecular orbital.
4. Each ψ is associated with a discrete value of energy.
5. The total energy of the molecule is the sum of the energies of the occupied molecular orbitals.
6. Elections tend to fill in molecular orbitals in similar way as they do in atomic orbitals by obeying Afbau's principle, Pauli's exclusion principle and Hund's rule.
7. Each election in a molecular orbital belong to all the nuclei present in the molecule.
8. Each election in as molecular orbital is either having clockwise $\left(+\frac{1}{2}\right)$ or anticlock wise $\left(-\frac{1}{2}\right)$ spin.

Formation of Molecular orbitals in H_2 molecule by LCAO method/ Formation of bonding and anti bonding molecular orbitals by LCAO method

According to linear combination of atomic orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals. Suppose that the wave functions of two atomic orbitals on two atoms A and B of AB type molecule (hetero-diatomic molecule) are represented as ψ_A and ψ_B respectively. There are two different ways in which ψ_A and ψ_B can combine linearly with each other. These two different ways are discussed below:

(a) **Additive overlap (also called positive overlap of ++ overlap) and formation of bonding molecular orbital**: In this type of linear combination, the positive lobe (i.e., the lobe having + sign) of ψ_A overlaps with the positive love of ψ_B and a molecular orbital is formed. This molecular orbital has lower energy than each of the two isolated atomic orbital wave functions viz. ψ_A and ψ_B (decrease in energy) and hence the formation of this molecular orbital produces attraction between the two nuclei of A and B atoms. This attraction results in the establishment of a stable chemical bond between A and B. Since this molecular orbital leads to the formation of a stable bond, it is called bonding molecular orbital which is represented as ψ^b.

(b) **Subtractive overlap (also called negative or + - overlap) and formation of anti-bonding molecular orbital:** In this type of linear combination the positive lobe of ψ_A overlaps with the negative lobe (i.e., the lobe having-sign) of ψ_B and a molecular orbital is formed. This molecular orbital has higher energy than each of the two atomic orbital wave functions (ψ_A and ψ_B) (increase in energy) and hence the formation of this molecular orbital produces repulsion between the two nuclei of A and B. This repulsion opposes the formation of any bond between the nuclei. Since this molecular orbital opposes the formation of any bond between the nuclei, it is called anti-bonding molecular orbital which is represented as ψ^*.

Here, it should be understood clearly than + and – sings of the lobes are only geometric signs of the atomic orbital wave function and should not be confused with positive (+) and negative (-) charges.

Above discussion shows that the formation of bonding molecular orbital wave function $\left(\psi^b\right)$ and anti-bonding molecular orbital wave function $\left(\psi^*\right)$ by the linear combination of two atomic orbital wave functions viz., ψ_A and ψ_B can be represented by the following equations:

$$\psi^b = +\psi_A + \psi_B \ (++\ \text{overlap}) \qquad \ldots(2.1)$$

$$\psi^* = +\psi_A - \psi_B \ (+-\ \text{overlap}) \qquad \ldots(2.2)$$

When we show the contributions made by ψ_A and ψ_B in ψ^b and ψ^*

molecular orbitals, Equations (2.1) and (2.2) are written as:

$$\psi^{b} = \frac{1}{\sqrt{2}}\left(\psi_{A} + \psi_{B}\right) \qquad \text{….(2.3)}$$

$$\psi^{*} = \frac{1}{\sqrt{2}}\left(\psi_{A} - \psi_{B}\right) \qquad \text{….(2.4)}$$

Obviously the sum of the squares of the coefficients of atomic orbital wave functions ψ_A and ψ_B appearing in the bonding molecular orbital wave function is equal to unity $\left[\left(\frac{1}{\sqrt{2}}\right)^{2} + \left(\frac{1}{\sqrt{2}}\right)^{2}\right]$.

Similarly this sum for anti-bonding molecular orbital is also equal to unity.

The relative order of the energy of ψ_A, ψ_B, ψ^b and ψ^* can be shown pictorially in Figure 2.1.

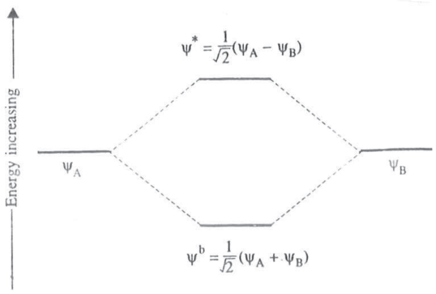

Fig. 2.1 *Relative Order of the Energy of* ψ_A, ψ_B, ψ^b *and* ψ^*.

Probability Density Variation with Internuclear Distance in H_2 Molecule

Consider two H-atoms H_A and H_B combine to form H_2 molecule let the wave function of these atoms may be represented by ψ_{H_A} and ψ_{H_B}. The positive overlap of ψ_{H_A} and ψ_{H_B} will give bonding molecular orbital $\psi^{b}_{H_2}$ and the negative overlap of ψ_{H_A} and ψ_{H_B} will produce anti-bonding molecular orbital, $\psi^{*}_{H_2}$ thus

$$\psi^{b}_{H_2} = \psi_{H_A} + \psi_{H_B} \qquad \text{….(2.5)}$$

$$\psi^{*}_{H_2} = \psi_{H_A} - \psi_{H_B} \qquad \text{….(2.6)}$$

On squaring equation (2.5), we get:

$$\left(\psi^{b}_{H_2}\right)^{2} = \psi^{2}_{H_A} + \psi^{2}_{H_B} + 2\psi_{H_A}\psi_{H_B} \qquad \text{….(2.7)}$$

In equation (2.7) $\left(\psi^{*}_{H_2}\right)^{2}$ denotes electron probability density or electron charge density in the bonding molecular orbital $\left(\psi^{b}_{H2}\right)$ while $\psi^{2}_{H_A}$ and $\psi^{2}_{H_B}$ indicate the electron charge density in the isolated (i.e., uncombined) atomic orbitals viz. ψ_{H_A} and ψ_{H_B}. From equation (2.7), it is clear that $\left(\psi^{b}_{H_2}\right)^{2}$ is greater than $\left(\psi^{2}_{H_A} + \psi^{2}_{H_B}\right)$ by an amount equal to $2\psi_{H_A}\psi_{H_B}$. This means that the electron charge density in the bonding molecular orbital $\left(\psi^{b}_{H2}\right)$ is greater by $2\psi_{H_A}\psi_{H_B}$ than the sum of the electron charge densities of the isolated atomic orbitals, ψ_{H_A} and ψ_{H_B}. The excess or increase in electron charge density $\left(\psi 2\psi_{H_A}\psi_{H_B}\right)$ occurs in the region lying in between the two positively charged nuclei. The increase in electron charge density between the two positive nuclei shields (i.e., screens) the two nuclei from mutual repulsion, i.e., due to the increase in electron charge density, the two nuclei are attracted towards each other. Thus the formation of bonding molecular orbital produces attraction between the two nuclei and hence leads to the establishment of a stable chemical bond. The attraction between the nuclei (i.e., the formation of a stable bond) leads to a decrease in the energy of the bonding molecular orbital in the event of its being occupied by electrons. In other words, the bonding molecular orbital has lower energy than each of the isolated atomic orbitals from which this molecular orbital is derived.

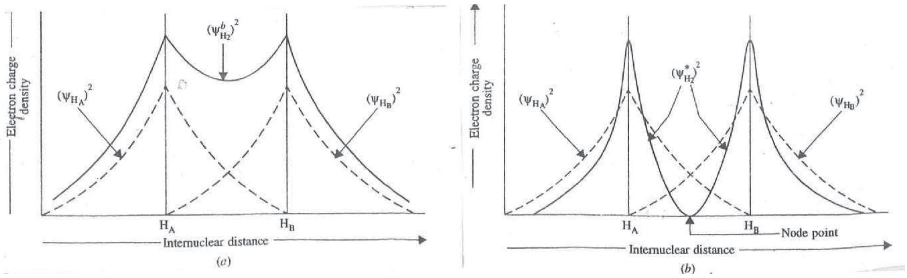

Fig. 2.2 *Inter Nuclear Distance and Electron Density Graph in H_2 Molecule*

At this stage it should be easy to understand since $\psi^{b}_{H_2}$ leads to the formation of a state bond, it is called bonding molecular orbital.

On squaring equation (2.6), we get:

$$\left(\psi^{*}_{H_2}\right)^2 = \psi^2_{H_A} + \psi^2_{H_B} - 2\psi_{H_A}\psi_{H_B} \qquad \text{.... (2.8)}$$

In this equation $\left(\psi^{*}_{H_2}\right)^2$ represents the electron charge density in the anti-bonding molecular orbital $\left(\psi^{*}_{H_2}\right)$. As is evident from Equation (2.8), $\left(\psi^{*}_{H_2}\right)^2$ is smaller than $\left(\psi^2_{H_A} + \psi^2_{H_B}\right)$ by an amount equal to $2\psi_{H_A}\psi_{H_B}$. This means that electron charge density $\left(\psi^{*}_{H_2}\right)^2$ the anti-bonding molecular orbital $\left(\psi^{*}_{H_2}\right)$ is smaller by $2\psi_{H_A}\psi_{H_B}$ than the sum of the electron charge densities of the uncombined atomic orbitals, ψ_{H_A} and ψ_{H_B}. The decrease in the electron charge density $\left(= 2\psi_{H_A}\psi_{H_B}\right)$ occurs in the region lying in between the two positively charged nuclei. The decrease in electron charge density between the nuclei means that there is no shielding of the nuclei, i.e., due to the decrease in electron charge density between the nuclei, these are repelled from each other. Thus the formation of anti-bonding molecular orbital produces repulsion between the two nuclei and hence opposes the formation of any bond between the nuclei. The repulsion between the nuclei leads to an increase in the energy of the anti-bonding molecular orbital in the event of its being occupied by electrons. In other words, the anti-bonding molecular orbital has higher energy than each of isolated atomic orbitals from which this molecular orbital is derived (Refer Figure 2.2). Since $\psi^*_{H_2}$ molecular orbital opposes the formation of any bond, it is called anti-bonding molecular orbital.

2.3 HEITLER-LONDON THEORY OF HYDROGEN MOLECULE

Walter Heitlor and Fritz London proposed the theory called Heitler-London theory in 1927 and it talks about exchange of electron in orbital of H_2 molecule and it was the first quantum-mechanical system which explains chemical bonding hydrogen molecule. Understand the Heitler-London theory; first we need to know about hydrogen molecule bonding as well as interaction between their electron and nuclei.

The Hydrogen Molecule

When two atoms brought together and form a covalent bond then their combine energy will be lower than the sum of individual hydrogen atom it shows that when two hydrogen atoms form a bonding then their dynamical system changed

A hydrogen molecule H_2 has a simplest electron bond pair, and it has a covalent bond. The hydrogen molecule is a four-particle system, two electron and two nucleons.

We have drowned hydrogen molecule in coordinate's term as shown in Figure (2.3):

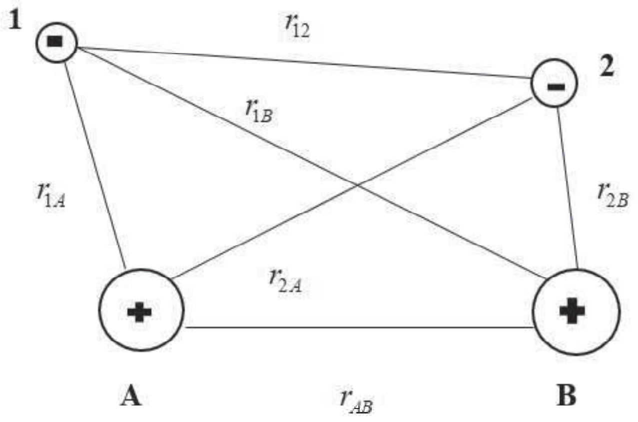

Fig. 2.3 *Hydrogen Molecule in Term of Coordinates*

The Hamiltonian four-particle Hydrogen molecule system is given by

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{r_{AB}}$$

Since the masses of nuclei are much greater than compare with electron

NOTES

i.e., mass of Proton = 1836 AMU

and mass of electron = 1 AMU.

Therefore, kinetic energy of nucleon will be negligibly small compared to those electrons.

Using Born-Oppenheimer approximation, we can write Schrödinger wave equation for electron as

$$\hat{H}_{elec.}\psi(r_1, r_2, R) = E_{elec.}(R)\psi(r_1, r_2, R)$$

Where, Hamiltonian is

$$\hat{H}_{elec.} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{r_{AB}}.$$

The separation r_{AB} i.e., the separation between nucleus occurs as parameter. Suppose r_{AB} as R. so that

$$\hat{H}_{elec.} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{R}$$

The internuclear separation R occurs as parameter in the Schrödinger equation therefore, in concept, Schrödinger equation must be solved for every value of R. The solution of Schrödinger equation for the hydrogen molecule is shown in the following figure:

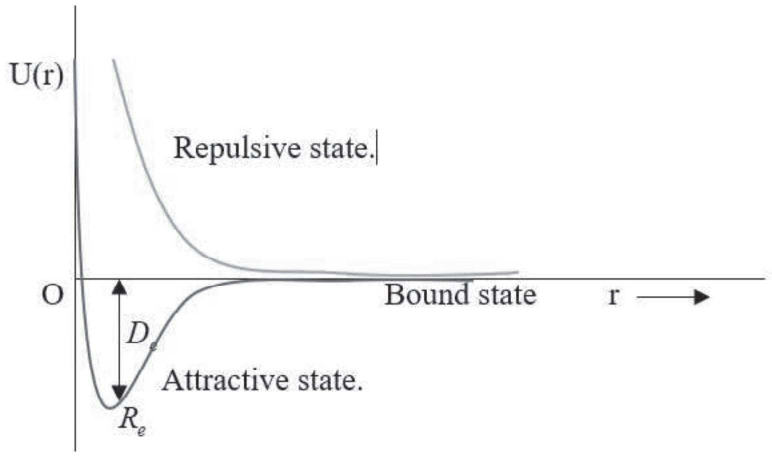

Fig. 2.4. *Potential Energy Curve for Diatomic Molecule*

For the bound state, the energy minima occur at $R = R_e$, that is called equilibrium inter-nuclear distance. The potential depth at internuclear distance R_e, that is D_e, called binding energy or dissociation energy. For the hydrogen molecule H_2, the value of dissociation energy $D_e = 4.52$ eV and the value of internuclear equilibrium distance $R_e = 0.074\ nm$.

When there is a heavier nucleus then the massive nuclei will move slowly in comparison to the electron. Therefore, if we see from nuclei point of view, that the electron will adjust its position instantaneously to any changes in the internuclear distance.

Therefore, now we can conclude that the electronic energy will behave as potential energy for the motion of nuclei in the Schrödinger equation.

Thus,

$$\left[-\frac{1}{2M_A}\nabla_A^2-\frac{1}{2}\nabla_B^2+V(r)\right]\psi(r_A,r_B)=E(r)\psi(r_A,r_B)$$

Where, $V(r)=E_{electronic}(r)$, $\psi(r_A,r_B)$ is the wavefunction of nucleus, M_A is mass of nucleus of hydrogen atom A and M_B is the mass of the nuclease of hydrogen atom B.

The hydrogen molecule is a homogeneous molecule, and it must me neutral therefore, we can take a condition when the nuclei of hydrogen atom are far apart and then the attraction between two hydrogen atoms will be negligibly. Therefore, the system can be taken as two approximate hydrogen atom independent system, shown in following figure.

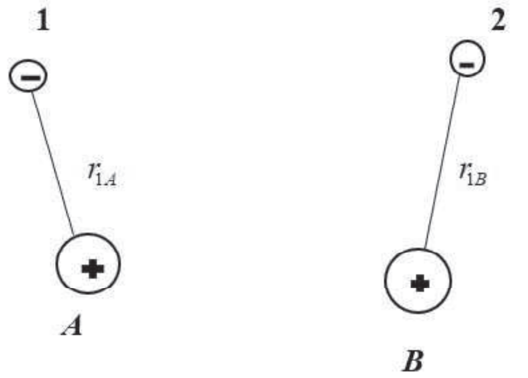

Fig.2.5 *Atom at a Far Apart-Attractive Potential will be Negligible and it behave like Two Independent Electron-Nuclei System*

The potential energy of the hydrogen atom A would be proportional to $-\frac{e^2}{r_{1A}}$ and the potential energy of atom B is proportional to $-\frac{e^2}{r_{1B}}$. Therefore, the total potential energy of hydrogen molecule system is.

$$V(r_1,r_2)=-\frac{e^2}{r_{1A}}-\frac{e^2}{r_{1B}}.$$

The wave function of ground state of hydrogen atom would be product of wave function of s-orbital of hydrogen atom A and wave function of s-orbital of hydrogen atom B. If wave function for the ground state energy of atom A is $1s_A(r_1)$ and the wave function for ground state energy of atom B is $1s_B(r_2)$. Therefore, the total wave function is given by

$$\psi(r_1,r_2)=1s_A(r_1)\cdot 1s_B(r_2)$$

Substitute this wave function in Schrodinger wave equation and it would give the same behavior as attractive potential state but not the same behavior. The wave function $\psi(r_1, r_2) = 1s_A(r_1) \cdot 1s_B(r_2)$ behavior is shown in figure with dotted blue line.

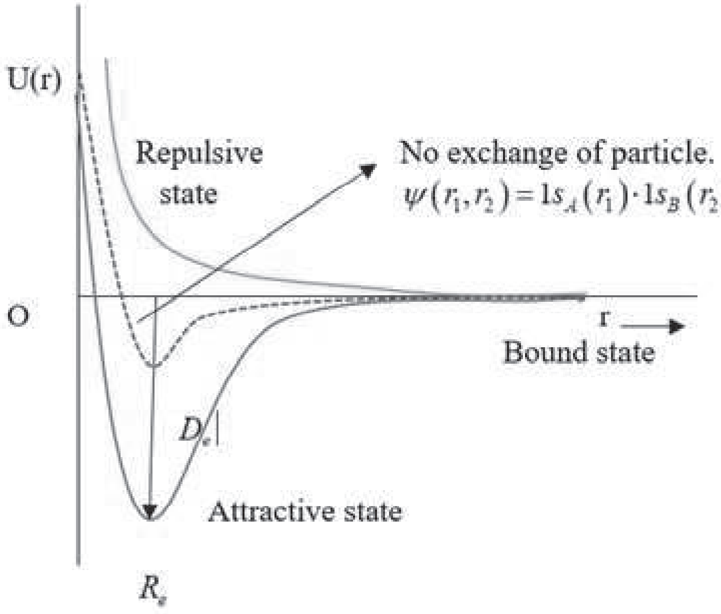

Fig.2.6 *Behaviour of Diatomic Molecule Wavefunction without Exchange of Electrons*

2.3.1 Heitler-London Theory Treatment for Hydrogen Molecule

The quantum-mechanical treatment for hydrogen atom was first given by Hietlor-London theory in the 1927. Heitlor-London theory came into picture after one year of Schrodinger equation. It shows how to use Schrodinger equation to explain the interactions between atom and particle quantum mechanically. According to Heitlor-London theory, since the hydrogen molecule is of combination of two hydrogen atoms A and B, the wave function of its electronic state will be approximately.

$$\psi(r_1, r_2) = 1s_A(r_1) \cdot 1s_B(r_2)$$

And the treatment of hydrogen molecule H_2 by Heitlor-London theory allow nuclei A and B to share the electrons 1 and 2, i.e., the electron exchange between nuclei A and B. Now, we should consider both $1s_A(r_1) \cdot 1s_B(r_2)$ and $1s_A(r_2) \cdot 1s_B(r_1)$. Therefore, wave function will become.

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}\left[1s_A(r_1) \cdot 1s_B(r_2) + 1s_A(r_2) \cdot 1s_B(r_1)\right]$$

Where, the factor $\frac{1}{\sqrt{2}}$ is normalization constant.

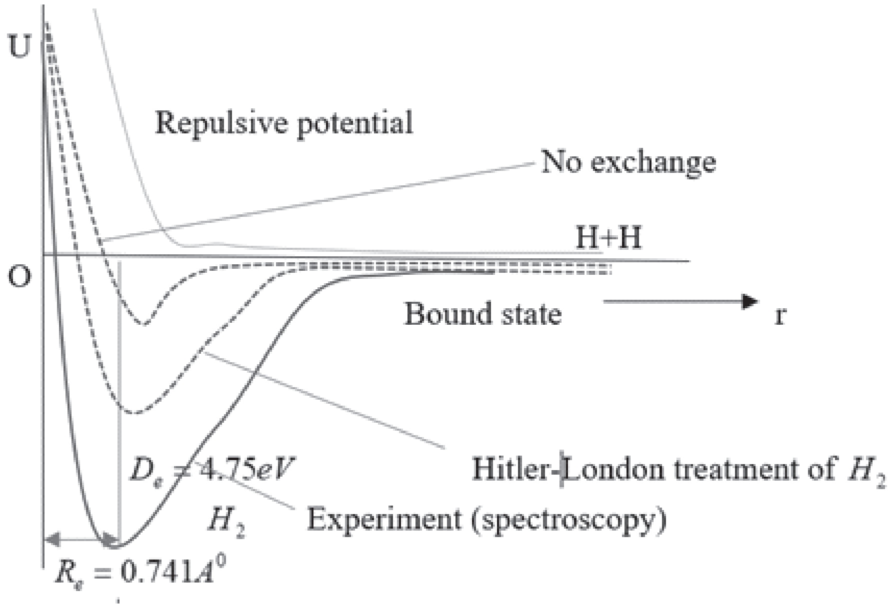

Fig.2.7. *Behavior of Diatomic Molecule with Heitlor-London Treatment*

Electron exchange between nuclei will occur only on one condition orbital overlap. We can calculate orbital overlap by the following expression. It is called overlap integral.

$$S = \int \psi_A \psi_B d\tau$$

Where, and is called valence orbital wave function for nuclei A and B respectively.

For the exchange of particle or exchange of electron between hydrogen atom $S \neq 0$.

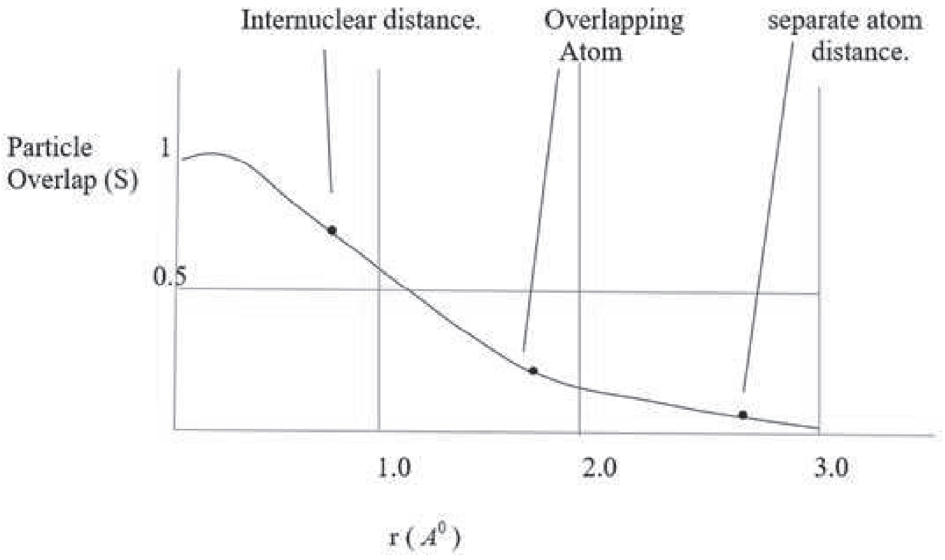

Fig.2.8*. Position of Nuclei when it would be Overlapping, when it is at Inter-Nuclear Distance and when they are not Bond Together*

2.4 WKB APPROXIMATION AND ITS APPLICATION TO ALPHA DECAY

In mathematical physics, the WKB approximation or WKB method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.

The abbreviation WKB approximation refers to Wentzel–Kramers–Brillouin, i.e., the WKB approximation method is named after physicists Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, who all developed it in 1926. In 1923, mathematician Harold Jeffreys had developed a general method of approximating solutions to linear, second order differential equations, a class that includes the Schrödinger equation. Early texts in quantum mechanics contain any number of combinations of their initials, including WBK, BWK, WKBJ, JWKB and BWKJ.

The WKB approximation is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrõdinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.

WKB Method

The WKB theory is a method typically used for approximating the solution of a differential equation whose highest derivative is multiplied by a small parameter ‘ε’. The method of approximation is as follows.

For a differential equation,

$$\varepsilon \frac{d^n y}{dx^n} + a(x)\frac{d^{n-1} y}{dx^{n-1}} + \cdots + k(x)\frac{dy}{dx} + m(x)y = 0,$$

Assume that following is the solution of the form of an asymptotic series expansion in the limit $\delta \rightarrow 0$,

$$y(x) \sim \exp\left[\frac{1}{\delta}\sum_{n=0}^{\infty}\delta^n S_n(x)\right]$$

The asymptotic scaling of δ in terms of ε will be determined by the equation,

$$\epsilon^2\left[\frac{1}{\delta^2}\left(\sum_{n=0}^{\infty}\delta^n S_n'\right)^2 + \frac{1}{\delta}\sum_{n=0}^{\infty}\delta^n S_n''\right] = Q(x).$$

WKB theory is a special case of multiple scale analysis.

Precision or Exactness of the Asymptotic Series

The asymptotic series for $y(x)$ is typically considered as a divergent series, whose general term $\delta^n S_n(x)$ starts to increase after a certain value $n = n_{\max}$. Therefore, the smallest error attained by the WKB method is the order of the last included term.

For the equation,

$$\epsilon^2 \frac{d^2 y}{dx^2} = Q(x) y$$

With $Q(x) < 0$ an analytic function, the value $n_{\max}$ and the magnitude of the last term can be estimated as follows:

$$n_{\max} \approx 2\epsilon^{-1} \left| \int_{x_0}^{x_*} \sqrt{-Q(z)}\, dz \right|,$$

$$\delta^{n_{\max}} S_{n_{\max}}(x_0) \approx \sqrt{\frac{2\pi}{n_{\max}}} \exp[-n_{\max}],$$

Where x_0 is the point at which $y(x_0)$ needs to be evaluated and x_* is the (complex) turning point where $Q(x_*) = 0$, closest to $x = x_0$.

The number $n_{\max}$ can be interpreted as the number of oscillations between x_0 and the closest turning point.

If $\in^{-1} Q(x)$ is a slowly changing function,

$$\epsilon \left| \frac{dQ}{dx} \right| \ll Q^2,$$

The number $n_{\max}$ will be large, and the minimum error of the asymptotic series will be exponentially small.

Derivation of the Schrödinger Equation

Solving the Schrödinger equation is one of the essential problems in quantum mechanics. Since a non-linear second order Ordinary Differential Equation (ODE) has, in general, no analytic solution, hence an approximation method is typically applied. Instead of starting with a simplified potential and adding small terms, which leads to perturbation theory, the WKB approximation makes an assumption of a slowly varying potential.

To derive the approximation, consider the Schrödinger equation,

$$\frac{d^2\psi}{dx^2} + k(x)^2 \psi = 0 \qquad \text{...(2.9)}$$

With the abbreviations,

$$k(x) = \left(\frac{2m}{\hbar^2}(E - V)\right)^{1/2} \quad \text{if} \quad \mathrm{E > V(x)}$$

$$k(x) = i\left(\frac{2m}{\hbar^2}(V - E)\right)^{1/2} = i\kappa(x) \quad \text{if} \quad \mathrm{E < V(x)} \qquad \text{...(2.10)}$$

If $k(x)$ = Constant is the function has the solution $\Psi(x) = e^{\pm ikx}$. If k is no longer constant but varies at a slow rate, then reasonably we can use the solution, with x dependent k,

$$e^{\pm i} \int k(t) dt \qquad \text{...(2.11)}$$

Substituting it in to the Schrödinger equation gives us,

$$\frac{d^2\psi}{dx^2} + k(x)^2\psi = (\frac{d^2}{dx^2} + k^2)e^{\pm i\int k(t)dt} = \pm ik'(x)e^{\pm i\int k(t)dt} \quad \text{...(2.12)}$$

Thus the solutions in Equation (2.11) solves the equation only when $k'(x)$ is equal to 0. However, Equation (2.12) suggests that Equation (2.11) remains a good approximation, if k' is negligible, or, more precisely, if

$$|k'| \ll k^2 \quad \text{...(2.13)}$$

This is the condition used in the derivation of the WKB approximation.

Application to Bound States

In quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space. The potential may be external or it may be the result of the presence of another particle; in the latter case, one can equivalently define a bound state as a state representing two or more particles whose interaction energy exceeds the total energy of each separate particle. One consequence is that, given a potential vanishing at infinity, negative-energy states must be bound. In general, the energy spectrum of the set of bound states is discrete, unlike free particles, which have a continuous spectrum.

In a bound state problem with potential $V(x)$, for a given energy E, we can divide space into classically allowed regions, for which $E > V(x)$, and classically forbidden regions for which $E < V(x)$. Assume that there are only three regions in total, classically forbidden for $x < a$ and $x > b$, and classically allowed for $a < x < b$.

In the classically allowed region $a < x < b$ the wave function will be oscillating and we can write it either as a superposition of right- and left-moving complex exponentials or as,

$$\psi(x) = \mathrm{A}\ k(x)\ \cos\int xk(x^2\ )dx^2\ + \phi$$

For the particular case of a well with infinite sides the solution must vanish at the boundaries, so (taking the lower limit of integration as a for definitness; any other choice just shifts ϕ) $\phi = (n' + 1\ 2)\pi$ and $\int abk(x')dx' + \phi = (n'' + 1\ 2)\pi$; in other words $\int abk(x')dx' = (n + 1)\pi$, with integer $n \geq 0$. Evidently for constant k this gives $k = n\pi/(b - a)$, which is exact.

For a more general potential, outside the classically allowed region we will have decaying exponentials. If we approximate the potential as linear we can solve the Schrödinger equation exactly (in terms of Airy functions). For WKB solutions in the locality of $x = a$ and $x = b$ gives the surprisingly simple result that inside the well, $\psi(x) = \mathrm{A}\ k(x)\ \cos\int axk(x')dx' - \pi/4$ and $\psi(x) = \mathrm{A}'\ k(x)\ \cos\int bxk(x')dx' + \pi/4$ which can only be satisfied if $\mathrm{A}' = \pm \mathrm{A}$ and $\int abk(x'\ )dx' = (n + 1\ 2)\pi$. This latter is the quantisation condition for a finite well; it is different from the infinite well because the solution can leak into the forbidden region. For a semi-infinite well, the condition is that the integral equal $(n + 3\ 4)\pi$. This is the appropriate form for the $l = 0$ solutions of a spherically symmetric well.

2.4.1 Applications to Alpha Decay

The WKB approximation can be used to calculate the bound state energy levels of a one-dimensional potential well. To study the penetration of a potential barrier, potential wells with several turning points. We will study with deep detail the alpha decay, we will find the energy values of the alpha particle in different Uranium isotopes. We will assume that the alpha particle is confined by a Coulomb barrier in a potential well of radius R. We will represent the potential of the strong nuclear binding as a simple potential well.

$$V(r) = \begin{cases} -V_0, & \text{if } r < R \\ \dfrac{1}{4\pi\varepsilon_0}\dfrac{2Ze^2}{r}, & \text{if } r > R. \end{cases} \qquad \text{... (2.14)}$$

For simplicity we assume we have s-waves and that we can write ψ (r) = 1/ r u (r), where the wave function is:

$$u(r) = N\begin{cases} \sin Kr, & \text{if } r < R \\ \dfrac{1}{\sqrt{\kappa_f(r)}}\left[Ae^{\int_R^r \kappa_f(x)\,dx} + Be^{-\int_R^r \kappa_f(x)\,dx}\right], & \text{if } R \leqslant r \leqslant b \\ \dfrac{1}{\sqrt{\kappa_a}}C\exp\left[i\int_b^r \kappa_a(x)\,dx\right] & \text{if } r > b, \end{cases} \qquad \text{... 2.15)}$$

$$\text{where } K = \sqrt{2m(E+V_0)}.$$

Figure 2.9 shown the four energy potentials are plotted versus the Uranium nuclear radius: Coulombic, Wood-Saxon, total potential, and WKB approximation as in Equation (2.14).

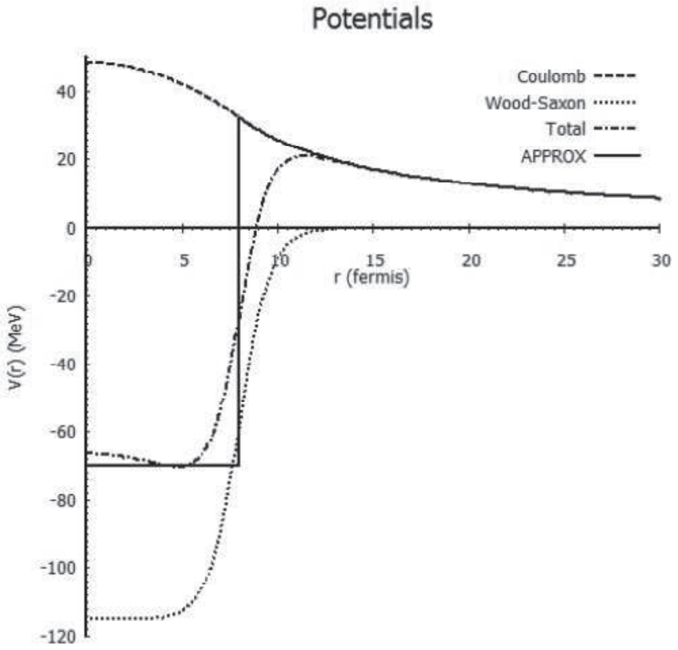

Fig. 2.9 *Four Energy Potentials are Plotted Versus the Uranium Nuclear Radius*

In Figure (2.9) a constant energy of $0 < E < V_{max}$ will intersect the approximation potential twice, thus creating three regions. Now we study the r = b: So if we are in region II, R 6 r 6 b we will use matching relations at the formulas described for when we are at the left of a classically allowed region and s will be negative. Notice that

$$\int_R^b \kappa_f(x)\,dx + \int_b^r \kappa_r(x)\,dx = \int_R^r \kappa_f(x)\,dx. \tag{2.16}$$

If we do the following changes of variables

$$\gamma = \int_R^b \kappa_f(x)\,dx \quad A' = Be^{-\gamma} \quad B' = Ae^{\gamma}, \tag{2.17}$$

The WKB will then be:

$$\frac{1}{\sqrt{\kappa_f(r)}}\left[A' e^{\int_r^b \kappa_f(x)\,dx} + B' e^{-\int_r^b \kappa_f(x)\,dx}\right] \tag{2.18}$$

And being the solution of $u_p(s) = aAi(\text{“}s) + bBi(\text{“}s)$, we have:

$$\begin{aligned} u_{WKB}(s) &\simeq A'(-s)^{-1/4}\exp\left(\frac{2}{3}(-s)^{3/2}\right) + B'(-s)^{-1/4}\exp\left(\frac{-2}{3}(-s)^{3/2}\right) \\ u_p(s) &\simeq \frac{1}{\sqrt{\pi}(-s)^{1/4}}\left[\frac{a}{2}\exp\left(\frac{-2}{3}(-s)^{3/2}\right) + b\exp\left(\frac{2}{3}(-s)^{3/2}\right)\right]. \end{aligned}$$

Thus $a = 2\sqrt{\pi}B'$ and $b = \sqrt{\pi}A'$. Now on the other side of point b, in region III, thus $s > 0$:

$$\begin{aligned} u_p(s) &\simeq= \frac{1}{2\sqrt{\pi}s^{1/4}}\left[(-ia+b)e^{i\pi/4}e^{i2/3s^{3/2}} + (ia+b)e^{-i\pi/4}e^{-i2/3s^{3/2}}\right] \\ u_{WKB} &= \frac{C}{s^{1/4}}\exp\left[i\frac{2}{3}s^{3/2}\right]. \end{aligned} \tag{2.19}$$

Thus we have that $ia + b = 0$ and $b = C\sqrt{\pi}e^{-i\pi/4}$, $a = iC\sqrt{\pi}e^{-i\pi/4}$. Therefore,

$$\begin{matrix} A' = Ce^{-i\pi/4} \\ 2B' = ie^{-i\pi/4} \end{matrix} \Rightarrow \begin{matrix} Ae^{\gamma} = \dfrac{iC}{2}e^{-i\pi/4} \\ Be^{-\gamma} = Ce^{-i\pi/4} \end{matrix} \Rightarrow A = \frac{iB}{2}e^{-2\gamma}. \tag{2.20}$$

By continuity of the wave function and its derivative at r = R:

$$\begin{matrix} \sin KR = \dfrac{A+B}{\sqrt{\kappa_f}} \\ \cos KR = \dfrac{\sqrt{\kappa_a}}{K}(A-B) \end{matrix} \Rightarrow \tan KR = \frac{A+B}{A-B}\frac{K}{\kappa_a}. \tag{2.21}$$

By substitution in Equation (2.20) we have

$$\frac{K}{\kappa_a} + \tan KR = \frac{ie^{-2\gamma}}{2}\left(\tan KR - \frac{K}{\kappa_a}\right) \tag{2.22}$$

The right-hand side of the last equation is extremely small. Furthermore, the first term of the left-hand side can be neglected since for high Coulomb barriers and lowlying states $K << \kappa_a(R)$. The real part of the eigenvalue will almost be the same as in the case of an infinite square well:

$\tan KR \simeq 0 \Rightarrow KR = n\pi \quad n \in \mathbb{N}$. And by the definition of K we find:

$$E_\alpha = \left(\frac{\hbar n\pi}{R}\right)^2 \frac{1}{2m} - V_0. \tag{2.23}$$

Notice that the constant well depth V_0 has an electrostatic component and a strong force component.

2.5 TIME-DEPENDENT PERTURBATION THEORY AND FERMI'S GOLDEN RULE

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional 'Perturbing' Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, then the various physical quantities associated with the perturbed system, for example its energy levels and eigenstates, can be expressed as 'Corrections' to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods, such as asymptotic series. The complicated system can consequently be studied based on the simpler one.

Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation $V(t)$ applied to a time independent Hamiltonian, H_0. Since the perturbed Hamiltonian is time dependent, accordingly are its energy levels and eigenstates. Thus, the goals of time dependent perturbation theory are slightly different from time independent perturbation theory. Following are the two significant quantities of the time dependent perturbation:

1. The time dependent expectation value of some observable A, for a given initial state.
2. The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

General Time Dependent Perturbations

Assume that the unperturbed energy eigenvalue problem is exactly of the form $H_0\phi_n = E_n\phi_n$.

To this is added a perturbation that depends on time, $v(t)$. To solve the time dependent problems we use the following time dependent Schrödinger equation.

$$(H_0 + \mathcal{V}(t))\,\psi(t) = i\hbar\frac{\partial\psi(t)}{\partial t}$$

Then we expand ψ in terms of the eigenfunctions as,

$$\psi(t) = \sum_k c_k(t)\phi_k e^{-iE_kt/\hbar} \text{ with } c_k(t)e^{-iE_kt/\hbar} = \langle\phi_k|\psi(t)\rangle\,.$$

The time dependent Schrödinger equations is then given as,

$$\begin{aligned}
\sum_k (H_0 + \mathcal{V}(t))\,c_k(t)e^{-iE_kt/\hbar}\phi_k &= i\hbar\sum_k \frac{\partial c_k(t)e^{-iE_kt/\hbar}}{\partial t}\phi_k \\
\sum_k c_k(t)e^{-iE_kt/\hbar}\,(E_k + \mathcal{V}(t))\,\phi_k &= \sum_k \left(i\hbar\frac{\partial c_k(t)}{\partial t} + E_k c_k(t)\right)e^{-iE_kt/\hbar}\phi_k \\
\sum_k \mathcal{V}(t)c_k(t)e^{-iE_kt/\hbar}\phi_k &= i\hbar\sum_k \frac{\partial c_k(t)}{\partial t}e^{-iE_kt/\hbar}\phi_k
\end{aligned}$$

Now dot $\langle\phi_n|$ into this equation to get the time dependence of one coefficient.

$$\begin{aligned}
\sum_k \mathcal{V}_{nk}(t)c_k(t)e^{-iE_kt/\hbar} &= i\hbar\frac{\partial c_n(t)}{\partial t}e^{-iE_nt/\hbar} \\
\frac{\partial c_n(t)}{\partial t} &= \frac{1}{i\hbar}\sum_k \mathcal{V}_{nk}(t)c_k(t)e^{i(E_n-E_k)t/\hbar}
\end{aligned}$$

Assuming that at $t = 0$, we are in an initial state $\psi(t=0) = \phi_i$ and hence all the other c_k are equal to zero as $c_k = \delta_{ki}$.

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)c_k(t)e^{i\omega_{nk}t}\right)$$

Next we calculate the transition rates. Considering that for the first order, all the $c_k(t)$ are small in comparison to $c_i(t) \approx= 1$, therefore the sum can be neglected.

$$\frac{\partial c_n^{(1)}(t)}{\partial t} = \frac{1}{i\hbar}\mathcal{V}_{ni}(t)e^{i\omega_{ni}t}$$

$$c_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{ni}t'}\mathcal{V}_{ni}(t')dt'$$

This equation is used to calculate transition probabilities for a general time dependent perturbation. This can also be used as a basis to calculate the transition rates for the specific problem of harmonic potentials.

Assuming again that 't' is small enough hence the c_i may not have changed much.

Remember that, if there is a large energy difference between the initial and the final states, then a slowly varying perturbation can average to zero.

Subsequently we can find that the perturbation may require frequency components that are compatible with ω_{ni} in order to cause transitions.

If the first order term is zero or higher accuracy is required, then the second order term can be calculated. In second order, first a transition is made to an intermediate state ϕ_k and then a transition to ϕ_n. We simply put the first order $c_k^{(1)}(t)$ into the sum.

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)c_k^{(1)}(t)e^{i\omega_{nk}t}\right)$$

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)\frac{1}{i\hbar}e^{i\omega_{nk}t}\int_0^t e^{i\omega_{ki}t'}\mathcal{V}_{ki}(t')dt'\right)$$

$$c_n^{(2)}(t) = \frac{-1}{\hbar^2}\sum_{k\neq i}\int_0^t dt''\mathcal{V}_{nk}(t'')e^{i\omega_{nk}t''}\int_0^{t''} dt' e^{i\omega_{ki}t'}\mathcal{V}_{ki}(t')$$

$$c_n^{(2)}(t) = \frac{-1}{\hbar^2}\sum_{k\neq i}\int_0^t dt''\mathcal{V}_{nk}(t'')e^{i\omega_{nk}t''}\int_0^{t''} dt' e^{i\omega_{ki}t'}\mathcal{V}_{ki}(t')$$

The Golden Rule and its Applications

In quantum physics, Fermi's golden rule is a formula that describes the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation. This transition rate is effectively independent of time (so long as the strength of the perturbation is independent of time) and is proportional to the strength of the coupling between the initial and final states of the system, typically described by the square of the matrix element of the perturbation, along with the density of states. It is also applicable when the final state is not part of a continuum if there is some de-coherence in the process, like relaxation of the atoms or like noise in the perturbation, in which case the density of states is replaced by the reciprocal of de-coherence bandwidth.

Fermi's Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ that is part of a continuum of states.

Fermi's golden rule describes a system which begins in an eigenstate, $|i\rangle$, of an unperturbed Hamiltonian, H_0 and considers the effect of a perturbing Hamiltonian, H' applied to the system. If H' is considered time independent, then the system goes only into those states in the continuum that have the same energy as the initial state. If H' is oscillating sinusoidally as a function of time, i.e., it is a harmonic perturbation, with an angular frequency É, then the transition is into states with energies that differ by 'É from the energy of the initial state.

In both cases, the transition probability per unit of time from the initial state $|i\rangle$ to a set of final states $|f\rangle$ is essentially constant. It is given, to first order approximation, by,

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\rho(E_f)$$

Where $\langle f|H'|i\rangle$ is the matrix element (in bra–ket notation) of the perturbation H' between the final and initial states and $\rho(E_f)$ is the density of states (number of continuum states in an infinitesimally small energy interval $E + dE$ at the energy E_f of the final states. This transition probability is also called 'Decay Probability' and is related to the inverse of the mean lifetime. Thus, the probability of finding the system in state $|f\rangle$ is proportional to $e^{-\Gamma_{i\to f}t}$.

The standard way to derive the equation is to start with time dependent perturbation theory and to take the limit for absorption under the assumption that the time of the measurement is much larger than the time needed for the transition.

Check Your Progress

1. State the Born–Oppenheimer (BO) approximation in quantum mechanics.
2. Define the subtractive orbital.
3. How does the formation of bonding molecular orbital produce attraction between the two nuclei?
4. State the Heitler-London theory.
5. State the WKB approximation.
6. What is WKB method?
7. What do you understand the perturbation theory?
8. Define the time-dependent perturbation theory.
9. What is Fermi's golden rule?

2.6 EMISSION AND ABSORPTION OF RADIATION

Semi-classical physics, or simply semi-classical refers to a theory in which one part of a system is described quantum-mechanically whereas the other is treated classically. For example, external fields will be constant, or when changing will be classically described. In general, it incorporates a development in powers of Planck's constant, resulting in the classical physics of power 0, and the first nontrivial approximation to the power of (–1). Thus, there is a clear link between the quantum-mechanical system and the associated semi-classical and classical approximations, as it is similar in appearance to the transition from physical optics to geometric optics.

Four examples of a semi-classical approximations include:

- WKB approximation: electrons in classical external electromagnetic fields.

- Semi-classical gravity: quantum field theory within a classical curved gravitational background (see general relativity).
- Quantum chaos: quantization of classical chaotic systems.
- Quantum field theory: only Feynman diagrams with at most a single closed loop are considered, which corresponds to the powers of Planck's constant.

The semi-classical radiation theory consists of two elements: the classical Maxwell equations that is satisfied by the electric 'E' and the magnetic 'B' fields, and the ordinary quantum mechanics that is based on the SchrQdinger equation of a single charged matter particle interacting with the electromagnetic field. The single particle SchrQdinger quantum mechanics can be modified to take into account spin or be replaced by the nonrelativistic quantum mechanics of many particles.

The distribution of energy in the spectrum of radiations of a hot body cannot be explained by applying the classical concepts of physics. Max Planck gave an explanation to this observation by his '***Quantum Theory of Radiation***'. His theory states that,

1. The 'Radiant Energy' is always in the form of tiny bundles of light called '**quanta**', i.e., the energy is absorbed or emitted discontinuously.
2. Each **quantum** has some definite energy 'E', which depends upon the frequency of the radiations as,

   $E = h\gamma$

Here, E is the energy of each quantum in Joules, γ is the frequency of the radiations in s^{-1}, h is known as Planck's constant (a fundamental constant), whose value is, $h = 6.626 \times 10^{-34}$ J-s.

Also, $E = hcw$, where w is known as wave number. $w = (1/\lambda)\ m^{-1}$.

From these equations, it is evident that $\gamma = c/\lambda = cw$.

The energy emitted or absorbed by a body is a multiple of a quantum, i.e., a body cannot absorb or emit energy in fractions of quantum. This concept is known as quantization of energy.

'Absorption' is the phenomenon when electrons in a substance take up energy from electromagnetic radiation or types of light. Whereas '***Emission'*** is the phenomenon when a substance gives off electromagnetic radiation. The electromagnetic radiation in both cases has some type of energy with a specific wavelength.

In our world of material, all the objects emit thermal radiation from its surface at any temperature. The radiation characteristics depend on the temperature and properties of the surface. As the surface temperature of the object increases, wavelength of the radiation goes from infrared to white region.

The thermally agitated accelerating particles emits the radiation and distributed the energies in continuous manner, as the result continuous spectrum of electromagnetic radiation emitted by the object. The classical theory of thermal radiation was inadequate, when one consider the distribution of wavelengths in the thermal radiation emitted by a ***blackbody.***

Fig. 2.10 *Absorption of radiations in a blackbody*

A blackbody is defined as it absorbs all the thermal radiations, whatever may be the wavelength incident on it. It neither reflects nor transmits any radiation, and appears black.

An isothermal enclosure behaves same as a blackbody. Let us consider a blackbody, placed in an isothermal enclosure. In thermal equilibrium, the body will emit the full radiations independent of the nature of the substance. The thermal radiations in an isothermal enclosure are, therefore, termed as 'Blackbody Radiations.'

2.7 EINSTEIN'S A & B COEFFICIENTS

Let us consider $E(v)$ as the energy density at equilibrium, where v is the frequency of photon.

If N_1 and N_2 are the number of atoms in the lower energy state (ground state) and higher energy state (excited state) respectively, then we can write,

$$N_1P_{12} = N_1B_{12}E(v) \quad \text{...(2.24)}$$

where P_{12} is the probability of absorption proportional to energy density $E(v)$ and B_{12} is the Einstein's coefficient of absorption.

Therefore, we can express the energy state of N_2 as follows:

$$N_2P_{21} = N_2[A_{21} + B_{21}\text{E}(v)] \quad \text{...(2.25)}$$

Where P_{21} is the probability (stimulated) proportional to energy density $\text{E}(v)$ with addition to A_{21}, A_{21} is the Einstein's coefficient of spontaneous and B_{21} is the Einstein's coefficient of stimulated emission.

When thermal equilibrium exists, we can say that the total absorption probability is equal to the total emission probability.

NOTES

So, from Equations (2.27) and (2.28), we have

$$N_1 B_{12} E(v) = N_2[A_{21} + B_{21}\mathrm{E}(v)]$$

or $$E(v) = \frac{A_{21}/B_{21}}{\left(\frac{N_1}{N_2}\right)\left(\frac{B_{12}}{B_{21}}\right)-1} \qquad ...(2.26)$$

According to Einstein's assumption, coefficient of stimulated absorption and coefficient of stimulated emission are equal, i.e., $B_{12} = B_{21} = B$ (say) and if we consider $A_{21} = A$ (say), then the Equation (2.26) reduces to,

$$E(v) = \frac{A/B}{\frac{N_1}{N_2}-1} \qquad ...(2.27)$$

A and *B* in the above equation are called Einstein's 'A' and 'B' coefficients.

According to Planck's radiation law, we know that

$$E(v) = \frac{8\pi h v^3}{c^3 e^{hv/KT} - 1} \qquad ...(2.28)$$

By comparing Equations (2.27) and (2.28), we can write,

$$\frac{N_1}{N_2} = e^{hv/KT}$$

And $$\frac{A}{B} = \frac{8\pi h v^3}{c^3}$$

(Ratio of coefficients of spontaneous and stimulated emission, i.e., ratio of Einstein's 'A' and 'B' Coefficient)

Where *h* is the Planck's Constant.
K is the Boltzman's Constant.
c is the Velocity of Light.
T is the Temperature in Kelvin.

2.8 EXCHANGE DEGENERACY OF INDISTINGUISHABLE PARTICLES

The coulomb potential, with the interaction of electron-electron and electron-nucleus interaction

$$V\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_z\right) = -\sum_{i=1}^{z} \frac{Ze^2}{\left|\vec{r}_i - \vec{R}\right|} + \sum_{i>j} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|}$$

It is invariant under the permutation of any electrons, the Hamiltonian is also invariant under such permutation. This symmetry also true for the orbital, spin, and angular momentum of an atom.

The N particles of any system said to be identical if the various observables of the system (for example Hamiltonian $\hat{H}$ angular momenta and so on) are symmetrical when any two particles are exchanged.

If these observables are not symmetric under particle interchange, then the particle would be distinguishable.

The Hamiltonian invariance under particle interchanges is not without physical implications: the eigen value $\hat{H}$ of are degenerate. The wave function corresponding to all possible electron permutations order will have the same energy E: $\hat{H}\psi = E\psi$. This is known as exchange degeneracy.

For more understanding, the degeneracy associated with the system of two identical particle is equal to 2, since $\psi(r_1, r_2)$ and $\psi(r_2, r_1)$ correspond the same energy E.

The Hamiltonian of system of N particles with the same masses $(m_i = m)$ is symmetric with respect to the coordinates of the system.

$$\hat{H}(r_1, \ldots, r_i, \ldots, r_j, \ldots r_N) = \sum_{k=1}^{N} \frac{p_k^2}{2m} + \hat{V}(r_1, \ldots, r_i, \ldots, r_j, \ldots r_N) = \hat{H}(r_1, \ldots, r_j, \ldots, r_i, \ldots r_N)$$

Because potential is invariant under the permutation of any pair of particles.

$$i \leftrightarrow j$$

$$\hat{V}(r_1, \ldots, r_i, \ldots, r_j, \ldots r_N) = \hat{V}(r_1, \ldots, r_j, \ldots, r_i, \ldots r_N)$$

Since $\hat{V}$ is invariant therefore particle interchange operator will commute with Hamiltonian.

$$\left[\hat{H}, \hat{P}_{ij}\right] = 0$$

Where, interchange operator $\hat{P}_{ij}$ is constant of motion.

2.8.1 Symmetrization Postulate

The wave function of a system of N-identical particles is either symmetric or anti-symmetric under the interchange of any pair of particles.

$$\psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_z) = \pm\psi(\vec{r}_1, \ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots, \vec{r}_z)$$

Experimentally, symmetrization postulate state that the system containing N particles are either totally symmetric or anti-symmetric under the interchange of any pairs of particle and state that mixed symmetry does not exist. Beside these there is two more postulate.

- Particles with integral spins, or bosons have symmetric state.
- Particle with half integral spins or fermions have antisymmetric state.

Fermions obey Fermi-Dirac statics and bosons obey Bose-Einstein static.

2.8.2 Constricting Symmetric and Antisymmetric Wave Function

According to postulate, the identical particle system will be totally symmetric or totally antisymmetric system.

Consider a system of two identical particles. Starting from any normalized asymmetric wave function $\psi(r_1, r_2)$, we can constrict a symmetric wave function $\psi_s(r_1, r_2)$ as

And antisymmetric wave function $\psi_a(r_1, r_2)$ as

$$\psi_s(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\psi(r_1, r_2) + \psi(r_2, r_1)\right]$$

Where $\frac{1}{\sqrt{2}}$ is normalization factor.

Similarly, for system of three identical particles, we can construct and from an asymmetric wave function as follows:

$$\psi_s(r_1, r_2, r_3) = \frac{1}{\sqrt{6}}\left[\psi(r_1, r_2, r_3)\psi(r_1, r_3, r_2)\psi(r_2, r_3, r_1) + \psi(r_2, r_1, r_3)\psi(r_3, r_1, r_2)\psi(r_3, r_2, r_1)\right]$$

And

$$\psi_a(r_1, r_2, r_3) = \frac{1}{\sqrt{6}}\left[\psi(r_1, r_2, r_3)\psi(r_1, r_3, r_2)\psi(r_2, r_3, r_1) - \psi(r_2, r_1, r_3)\psi(r_3, r_1, r_2)\psi(r_3, r_2, r_1)\right]$$

Similarly, we can construct symmetric and antisymmetric wave function for any system of N identical particle.

2.8.3 System of Identical Non-Interacting Indistinguishable Particle

A system of N noninteracting identical particles, with particles have equal masses $(m_i = m)$ and under same potential $\hat{V}_i(r_i) = \hat{V}(r_i)$, therefore the Schrodinger equation of the system separate into N identical one particle equations.

Where the energy will be given as $E_{n_1, n_2, \ldots, n_N} = \sum_{i=N}^{n} E_{n_i}$ but the function can not be given as product of wave function for individual identical particle for at least two reasons. First, the wave function cannot be given as product because the particle is identical and indistinguishable so there is no way to tell which particle in which state.

The second reason is that wavefunction of a system can is not given as because such product has no definite symmetry. Since it is a mandatory that a N identical particle system will be either totally symmetric or antisymmetric. We can construct completely symmetric and antisymmetric wave function form single particle state

2.8.4 Wave Function of Two Particle System

Wave function a symmetric and antisymmetric wave function for two identical non-interacting indistinguishable from a single particle state.

$$\psi_s(r_1,r_2)=\frac{1}{\sqrt{2}}\left[\psi_{n_1}(r_1)\psi_{n_2}(r_2)+\psi_{n_1}(r_2)\psi_{n_2}(r_1)\right]$$

$$\psi_a(r_1,r_2)=\frac{1}{\sqrt{2}}\left[\psi_{n_1}(r_1)\psi_{n_2}(r_2)-\psi_{n_1}(r_2)\psi_{n_2}(r_1)\right]$$

Here $n_1=n_2$. When $n_1=n_2=n$ the symmetric wave function is given by $\psi_s(r_1,r_2)=\left[\psi_n(r_1)\psi_n(r_2)\right]$ and the antisymmetric wave function will be zero.

The symmetric wave function can be written as

$$\psi_s(r_1,r_2)=\frac{1}{\sqrt{\lfloor 2}}\left[\sum_P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)\right]$$

Where $\hat{P}$ is permutation operator. Similarly, we can write ψ_a as

$$\psi_a(r_1,r_2)=\frac{1}{\sqrt{\lfloor 2}}\left[\sum_P (-1)^P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)\right]$$

Where $(-1)^P$ is positive for even permutation and negative for odd permutation. Now, again, rewrite ψ_a as

$$\psi_a(r_1,r_2)=\frac{1}{\sqrt{\lfloor 2}}\begin{bmatrix}\psi_{n_1}(r_1) & \psi_{n_1}(r_2)\\ \psi_{n_2}(r_1) & \psi_{n_2}(r_2)\end{bmatrix}$$

2.8.5 Wave Function of Three Particle System

For a system of three non-interacting identical and indistinguishable particle, the symmetric wave function is given by

$$\psi_s(r_1,r_2,r_3)=\frac{1}{\sqrt{\lfloor 3}}\left[\sum_P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)\psi_{n3}(r_3)\right]$$

Or by,

$$\psi_s(r_1,r_2,r_3)=\frac{1}{\sqrt{\lfloor 3}}\begin{bmatrix}\psi_{n_1}(r_1)\psi_{n_2}(r_2)\psi_{n3}(r_3)\\ +\psi_{n_1}(r_2)\psi_{n_2}(r_1)\psi_{n3}(r_3)\\ +\psi_{n_1}(r_2)\psi_{n_2}(r_3)\psi_{n3}(r_1)\\ +\psi_{n_1}(r_3)\psi_{n_2}(r_1)\psi_{n3}(r_2)\\ +\psi_{n_1}(r_3)\psi_{n_2}(r_2)\psi_{n3}(r_1)\\ +\psi_{n_1}(r_1)\psi_{n_2}(r_3)\psi_{n3}(r_2)\end{bmatrix}$$

And when the $n_1 \neq n_2 \neq n_3$, the antisymmetric wave function is given by

$$\psi_a(r_1, r_2, r_3) = \frac{1}{\sqrt{\underline{|3}}}\left[\sum_P (-1)^P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)\psi_{n3}(r_3)\right]$$

Or in the form of matrix as

$$\psi_a(r_1, r_2, r_3) = \frac{1}{\sqrt{\underline{|3}}}\begin{bmatrix} \psi_{n_1}(r_1) & \psi_{n_1}(r_2) & \psi_{n_1}(r_3) \\ \psi_{n_2}(r_1) & \psi_{n_2}(r_2) & \psi_{n_2}(r_3) \\ \psi_{n3}(r_1) & \psi_{n3}(r_2) & \psi_{n3}(r_3) \end{bmatrix}$$

If $n_1 = n_2 = n_3$ so $\psi_s(r_1, r_2, r_3) = \psi_n(r_1)\psi_n(r_2)\psi_n(r_3)$ and $\psi_a(r_1, r_2, r_3) = 0$.

2.8.6 Wave Function of Many Particles System

Write the symmetric and antisymmetric wave function for a system of N non-interacting identical particle as.

$$\psi_s(r_1, r_2, ..., r_N) = \frac{1}{\sqrt{N!}}\sum_P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)...\psi_{n_N}(r_N)$$

$$\psi_a(r_1, r_2, ..., r_N) = \frac{1}{\sqrt{N!}}\sum_P (-1)^P \hat{P}\psi_{n_1}(r_1)\psi_{n_2}(r_2)...\psi_{n_N}(r_N)$$

Or

$$\psi_a(r_1, r_2, ..., r_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{n_1}(r_1) & \psi_{n_1}(r_1) & ... & \psi_{n_1}(r_1) \\ \psi_{n_2}(r_2) & \psi_{n_2}(r_2) & ... & \psi_{n_2}(r_2) \\ . & . & & . \\ . & . & ... & . \\ . & . & & . \\ \psi_{n_N}(r_N) & \psi_{n_N}(r_N) & ... & \psi_{n_N}(r_N) \end{vmatrix}$$

This $N \times N$ determinant, which involve one-particle states only, is known as the Slater determinant. An interchange of any pair of particles correspond to an interchange of two columns of the determinant will introduce change in sign of determinant.

For even permutation we have $(-1)^P = 1$ and for odd permutation we have $(-1)^P = -1$.

If $n_1 = n_2 = ... = n_N$ then

$$\psi_s\left(r_1,r_2,r_3\right)=\prod_{i=1}^{N}\psi_n\left(r_i\right)=\psi_n\left(r_1\right)\psi_n\left(r_2\right)...\psi_{n_N}\left(r_N\right).$$

If there is multiplicity in numbers $n_1,n_2,...,n_N$ i.e., some of the n_i are repeated. We must be careful regarding this and avoid double counting.

For instance, if n_1 occur N_1 times in the sequence $n_1,n_2,...,n_N$ and if N_2 occur n_2 times and so on. The symmetric wave function will be.

$$\psi_s\left(r_1,r_2,...,r_N\right)=\sqrt{\frac{N_1!N_2!...N_N!}{N!}}\sum_P \hat{P}\psi_{n_1}\left(r_1\right)\psi_{n_2}\left(r_2\right)...\psi_{n_N}\left(r_N\right)$$

For example, take the case of three independent identical boson where $n_1=n_2=n$ and $n_3\neq n$, the multiplicity of n_1 is $N_1=2$. Hence ψ_s is given by

$$\begin{aligned}\psi_s\left(r_1,r_2,r_3\right)&=\sqrt{\frac{2!}{3!}}\sum_P \hat{P}\psi_n\left(r_1\right)\psi_n\left(r_2\right)\psi_n\left(r_3\right)\\&=\frac{1}{\sqrt{3}}\left[\psi_n\left(r_1\right)\psi_n\left(r_2\right)\psi_{n_3}\left(r_3\right)+\psi_n\left(r_1\right)\psi_{n_3}\left(r_2\right)\psi_n\left(r_3\right)+\psi_{n_3}\left(r_1\right)\psi_n\left(r_2\right)\psi_n\left(r_3\right)\right]\end{aligned}$$

In case of antisymmetric when among the numbers $n_1,n_2,...,n_N$, only two are equal, the antisymmetric wave function vanishes. For example, if $n_i=n_j$ therefore the *i*th and *j*th rows of determinant will be identical; hence the determinant vanishes identically. Antisymmetric wave functions, therefore, are nonzero only for those cases where all the numbers $n_1,n_2,...,n_N$ are different.

2.8.7 Pauli Exclusion Principle

It states that *in a system of N identical particles, no two fermions can occupy the same single-particle state at a time; every single-particle state can be occupied by at most one fermion*. This is the Pauli exclusion principle, first postulated in 1925 to explain the periodic table.

Pauli exclusion principle for periodic table states that no two electrons can occupy simultaneously the same (single particle) particle state on the same atom. Therefore, there can be only one electron occupying quantum state $n_i l_i m_{l_i} m_{s_i} : \psi_{n_i l_i m_{l_i} m_{s_i}}$. The Pauli exclusion principle has a direct effect on the spatial part of distribution of fermions.

When a Schrodinger equation include the spin, the wave function of a single particle state is equal to product of the spatial part and spin part- $\psi\left(\vec{r},\vec{S}\right)=\psi\left(\vec{r}\right)\chi\left(\vec{S}\right)$.

The wave function of a system of N particles, which have spins, is the product of the spatial part and spin part of the particle.

$$\psi\left(\vec{r}_1,\vec{S}_1;\vec{r}_2,\vec{S}_2;\ldots;\vec{r}_N,\vec{S}_N\right)=\psi\left(\vec{r}_1,\vec{r}_1,\ldots,\vec{r}_N\right)\chi\left(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N\right)$$

The wave function given above must satisfy the symmetry requirements when N particles are identical.

In the case of a system of N identical boson, the wave function must be symmetric; hence the spatial and spin parts must have the same parity.

$$\psi_s\left(\vec{r}_1,\vec{S}_1;\vec{r}_2,\vec{S}_2;\ldots;\vec{r}_N,\vec{S}_N\right)=\begin{cases}\psi_a\left(\vec{r}_1,\vec{r}_1,\ldots,\vec{r}_N\right)\chi_a\left(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N\right)\\ \psi_s\left(\vec{r}_1,\vec{r}_1,\ldots,\vec{r}_N\right)\chi_s\left(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N\right)\end{cases}$$

And when a system of N identical fermions, for fermions spin and spatial part must have different parity, to leading to the overall wave function antisymmetric:

$$\psi_a\left(\vec{r}_1,\vec{S}_1;\vec{r}_2,\vec{S}_2;\ldots;\vec{r}_N,\vec{S}_N\right)=\begin{cases}\psi_a\left(\vec{r}_1,\vec{r}_1,\ldots,\vec{r}_N\right)\chi_s\left(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N\right)\\ \psi_s\left(\vec{r}_1,\vec{r}_1,\ldots,\vec{r}_N\right)\chi_a\left(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N\right)\end{cases}$$

2.9 WAVE FUNCTION FOR MANY ELECTRON SYSTEM

For the case of matter waves, the function that make up the waves and by which we can describe the different characteristics and properties of the said waves is called wave function, denoted by ψ (psi). The value of the wave function (ψ) associated with a matter wave helps us in finding the particle at a particular time t in space.

Thus, a complete wave function ψ for a matter wave depends on the positions of all the particles associated with the wave and on time explicitly. From our above discussions, we can describe a wave function of a matter wave as:

$$\psi(r, t) = Ae^{i(K_r\bar{r}-\omega t)} \quad \ldots(2.29)$$

where ($\omega = 2\pi\nu$) is the angular frequency of the matter wave, $k_r = \dfrac{2\pi}{\lambda}$ is the wave propagation vector or wave number.

Physical Interpretation of y; Normalization, Probability, Density

The wave function ψ described above often takes complex value. The square of its magnitude, *i.e.*, $|\psi|^2 = \psi^* \psi$ is always real and positive, where ψ* is the complex conjugate of the wave function ψ. The quantity $|\psi|^2$ is proportional to the probability per unit volume of finding a particle associated with the wave function ψ at a given point at an instant t. The wave function ψ gives us all the information about the particle associated in it.

Let us consider the particles of the wave function ψ is propagating along x-direction. The wave function for that case is given by $\psi(x, t)$ and $|\psi(x, t)|^2 dx = \psi^*(x, t)\, \psi(x, t) dx$ is proportional to the probability of finding the particle associated with the wave function $\psi(x, t)$ in the position interval x to $x + dx$ at any instant t. The total probability of finding the particle in the position interval

x to $x + dx$ at any instant t anywhere along x-direction is given by

$$P \propto \int_{-\infty}^{\infty} |\psi(x, t)|^2 \, dx$$

$$\propto \int_{-\infty}^{\infty} \psi^*(x, t) \; \psi(x, t) \, dx \qquad ...(2.30)$$

The position *probability density* of a particle associated with the wave function $\psi(x, t)$ along x-direction in the interval x to $x + dx$ at any instant t is given by

$$p(x, t) = \frac{|\psi(x,t)|^2}{\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx} \qquad ...(2.31)$$

and hence the total probability will be

$$P = \int_{-\infty}^{\infty} p(x,t) dx$$

$$= \frac{\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx}{\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx} = 1 \qquad ...(2.32)$$

[*i.e.*, the total probability of any event must be one (1)].

Therefore, the particle must be somewhere along x-direction, the sum of the probabilities over all values of x must be equal to 1 (one). Let us consider a wave function as:

$$\psi_N(x, t) = A\psi(x, t) \qquad ...(2.33)$$

where A is a constant.

According to the definition of total probability and by equation (2.30), we can write

$$\int_{-\infty}^{\infty} |\psi_N(x,t)|^2 dx = A^2 \int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1 \qquad ...(2.34)$$

where $\psi_N(x, t)$ is called *normalized wave function* and A is called the *normalization constant*. From Equation (2.34), we can write

$$A^2 = \frac{1}{\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx} \qquad ...(2.35)$$

[**Note:** If we consider a complex number as $x = a + ib$, The complex conjugate of x will be $x^* = a - ib$. The product of a complex number and its complex conjugate is always real and positive. *i.e.*, $x^*x = (a - ib)(a + ib) = a^2 - (ib)^2 = a^2 + b^2$ as $i^2 = -1$].

Operators in Quantum Mechanics

The operator operates on a function (given) and gives an another function. An operator is often represented by ô.

For example, if $\frac{\partial}{\partial x}$ operates on a function x^3, then we can write

$$\frac{\partial}{\partial x}(x^3) = 3x^2.$$

Here, $\frac{\partial}{\partial x}$ is the operator that operates on the function x^3.

NOTES

In quantum mechanics, there are several dynamical variables or functions, such as position, momentum, energy those are represented by operators.

The Momentum Operator

Let us consider a wave function

$$\psi(x, t) = Ae^{i(K_x x - \omega t)}$$

$$\therefore \qquad \frac{\partial\psi(x,t)}{\partial x} = \frac{\partial}{\partial x}\{Ae^{i(K_x x - wt)}\}$$

$$= iK_x Ae^{i(K_x x - \omega t)} = iK_x\psi(x, t)$$

Multiplying both sides by $-i\hbar$, we get

$$-i\hbar\frac{\partial\psi(x,t)}{\psi x} = -i\hbar\{iK_x\psi(x, t)\} = \hbar K_x\psi(x, t)$$

$$\Rightarrow \qquad -i\hbar\frac{\partial\psi(x,t)}{\partial x} = P_x\psi(x, t)$$

[from de Broglie hypothesis, $P_x = \hbar K_x$]

Thus, the momentum operator P_x denoted by $\hat{P}_x$ is given by

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x} \qquad \text{[momentum operator along } x\text{-direction]}$$

Similarly, the momentum operator along y- and z-directions is given by

$$\hat{P}_y = -i\hbar\frac{\partial}{\partial y}$$

and $$\hat{P}_z = -i\hbar\frac{\partial}{\partial z}$$

In general, the momentum operator is given by

$$\hat{P} = i\hbar\frac{\partial}{\partial r} = i\hbar\overline{\nabla}$$

The Energy Operator

Let us consider a wave function

$$\psi(x, t) = Ae^{i(K_x x - \omega t)}$$

$$\therefore \qquad \frac{\partial\psi(x,t)}{\partial t} = \frac{\partial}{\partial t}\{Ae^{i(K_x . x - wt)}\}$$

$$= -i\omega Ae^{i(K_x x - \omega t)} = -i\omega\psi(x, t)$$

Multiplying both sides by $i\hbar$, we get

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = i\hbar\{-i\omega\psi(x, t)\} = \hbar\omega\psi(x, t)$$

$$\Rightarrow \quad i\hbar\frac{\partial\psi(x,t)}{\partial t} = E\psi(x,\ t)\ \text{[from de Broglie hypothesis, } E = \hbar\,\omega\text{]}$$

Thus, the energy operator E denoted by $\hat{E}$ is given by

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

The Commutator

If $\hat{a}$ and $\hat{b}$ are two operators, the commutator correspondence of these two operators is denoted by $[\,\hat{a},\ \hat{b}\,]$ and is defined as

$$[\,\hat{a},\ \hat{b}\,] = (\hat{a}\,\hat{b} - \hat{b}\,\hat{a})$$

If $[\,\hat{a},\ \hat{b}\,] = 0$, *i.e.*, $\hat{a}\,\hat{b} = \hat{b}\,\hat{a}$, then the two operators are said to be commutative.

If $[\,\hat{a},\ \hat{b}\,] \neq 0$, *i.e.*, $\hat{a}\,\hat{b} \neq \hat{b}\,\hat{a}$, then the two operators are said to be non-commutative.

The Expectation Values

We can calculate the expectation value or average value of a particle anywhere is space at any instant t by the following:

By considering $\psi^*(x,\ t)\ \psi(x,\ t)$ with the position probability density, the expectation value or average value of a particle along x-direction is given by

$$\langle x\rangle = \frac{\iiint x\ \psi^*(x,t)\psi(x,t)\ d\tau}{\iiint \psi^*(x,t)\psi(x,t)\ d\tau} \qquad ...(2.36)$$

where $d\tau$ is the volume element and we integrate it over the entire space.

As the particle is somewhere in space, we can say that the total probability of finding the particle in the entire space is unity (1). We can write it mathematically as

$$\iiint |\,\psi(x,t)\,|^2\ d\tau = \iiint \psi^*(x,t)\psi(x,t)\ d\tau = 1 \qquad ...(2.37)$$

[normalization condition]

From equations 9.8 and 9.9, we can write

$$\langle x\rangle = \iiint x\ \psi^*(x,t)\psi(x,t)\ d\tau$$

$$= \iiint \psi^*(x,t)\hat{x}\ \psi(x,t)\ d\tau \qquad ...(2.38)$$

(where $\hat{x}$ is the operator of position x)

In general, $\langle f(r)\rangle = \iiint \psi^*\hat{f}(r)\psi\ d\tau$ ...(2.39)

The expectation value of potential energy $V(r)$ is given by

$$\langle V(r)\rangle = \iiint \psi^*\hat{V}(r)\ \psi\ d\tau$$

The expectation value of momentum P is given by

$$\langle P\rangle = \iiint \psi^*\hat{P}\ \psi\ d\tau$$

$$= \iiint \psi^* \left(-i\hbar \frac{\partial}{\partial r}\right) \psi \, dx = \iiint \psi^* (-i\hbar \overline{\nabla}) \psi \, d\tau$$

The expectation value of energy E is given by

$$\langle E \rangle = \iiint \psi^* \hat{E} \, \psi \, d\tau$$

$$= \iiint \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, d\tau$$

We know that, $E = \frac{P^2}{2m} + V$

Thus, using operator symbol, we have

$$\langle E \rangle = \left\langle \frac{P^2}{2m} \right\rangle + \langle V \rangle$$

In terms of expectation value, we can write

$$\iiint \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, d\tau$$

$$= \iiint \psi^* \left(-\frac{\hbar^2}{2m} \nabla^2\right) \psi \, d\tau + \iiint \psi^* \hat{V}(r) \psi \, d\tau$$

where $\left\langle \frac{P^2}{2m} \right\rangle = \iiint \psi^* \left(-\frac{\hbar^2}{2m} \nabla^2\right) \psi \, d\tau$

Therefore, we can write

$$\langle Px \rangle = \iiint \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, d\tau$$

$$\langle Py \rangle = \iiint \psi^* \left(-i\hbar \frac{\partial}{\partial y}\right) \psi \, d\tau$$

$$\langle Pz \rangle = \iiint \psi^* \left(-\hbar \frac{\partial}{\partial z}\right) \psi \, d\tau$$

$$\langle P_x^2 \rangle = \iiint \psi^* \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \psi \, d\tau$$

$$\langle P_y^2 \rangle = \iiint \psi^* \left(-\hbar^2 \frac{\partial^2}{\partial y^2}\right) \psi \, d\tau$$

$$\langle P_z^2 \rangle = \iiint \psi^* \left(-\hbar^2 \frac{\partial^2}{\partial z^2}\right) \psi \, d\tau \qquad \text{...(2.40)}$$

$$\langle E \rangle = \iiint \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, d\tau$$

$$\langle V(r) \rangle = \iiint \psi^* \hat{V}(r) \psi \, d\tau$$

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and $\iiint \psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\psi\, d\tau$

$$= \iiint \psi^*\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi\, d\tau + \iiint \psi^* \hat{V}(r)\psi\, d\tau$$

The Probability Current Density

From equation (2.40), we can write

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \qquad ...(2.41)$$

and its complex conjugate

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* \qquad ...(2.42)$$

where the potential energy $V(r, t)$ is assumed to be a real quantity.

Multiplying equation (2.41) by ψ^* and equation (2.41) by ψ, we get

$$i\hbar\, \psi^*\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + \psi^* V\psi \qquad ...(2.43)$$

and $$-i\hbar\, \psi\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + \psi V\psi^* \qquad ...(2.43a)$$

Subtracting equation (2.43*a*) from equation (2.43), we get

$$i\hbar\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] = \frac{\hbar^2}{2m}[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*] \qquad ...(2.44)$$

Since $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and $$\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t} = \frac{\partial}{\partial t}(\psi^*\psi),$$

we can rewrite the equation (2.44) in the form

$$\frac{\partial}{\partial t}(\psi^*\psi) + \left[\frac{\partial Jx}{\partial x} + \frac{\partial Jy}{\partial y} + \frac{\partial Jz}{\partial z}\right] = 0 \qquad ...(2.45)$$

where $$Jx = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right]$$

$$Jy = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial y} - \psi^*\frac{\partial\psi}{\partial y}\right]$$

and $$Jz = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial z} - \psi^*\frac{\partial\psi}{\partial z}\right]$$

Now, we can rewrite equation (2.25) in the form

$$\frac{\partial P}{\partial t} + \vec{\nabla}.\vec{J} = 0 \qquad \text{...(2.46)}$$

where $\psi^*\psi = P$

and $$\vec{J} = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial r} - \psi^*\frac{\partial\psi}{\partial r}\right]$$

$$= \frac{i\hbar}{2m}[\psi\nabla\psi^* - \psi^*\nabla\psi]$$

Equation (2.46) is termed as equation of continuity in electro-magnetic theory. Here, P represents the charge density and $\vec{J}$ represents the current density.

2.9.1 Formation of Energy Bands in Solids

In the case of a single isolated atom, the electron in any orbit as shown in Figure 2.11 have a definite energy. As a result, they occupy discrete energy levels, as shown in Figure 2.12(a).

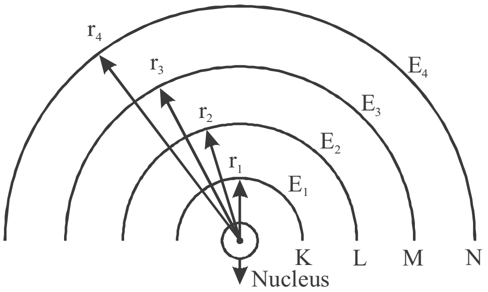

Fig. 2.11 *The energy levels of a single isolated atom*

The pauli exclusion principle allows each energy level to contain only two electrons. For example, the 2s level of a single atom contains one energy level with two electrons and 2p level contains 3 energy levels with two electrons in each level thus, with a total of six electrons as shown in Figure 2.12(a).

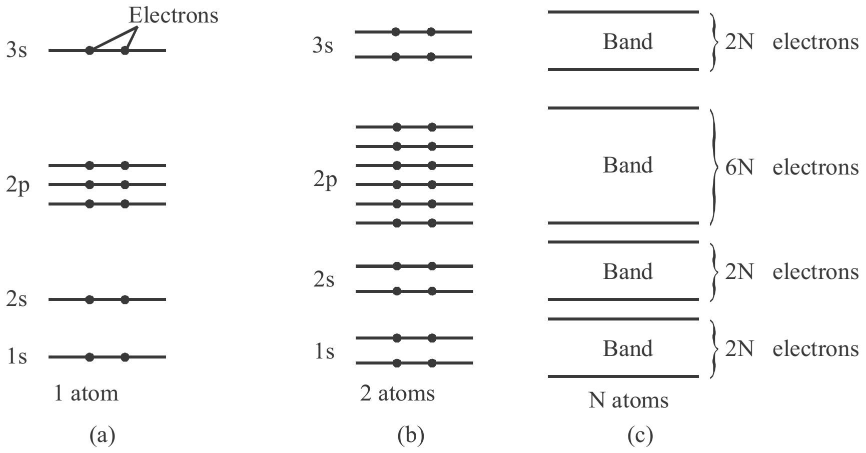

Fig. 2.12: *The energy levels broaden into energy bands*

Band Structure in Solid

Let us consider the formation of bands in a solid sodium.

The single energy level of an isolated sodium (Z = 11) based on the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ is shown in Figure 2.12(a).

When an another sodium is brought close to it, the electrons will be subjected to the effect of an additional field. As a result, each energy level is split in to two as shown in Figure 2.12(b). Similarly, when three atoms come close together, the original level splits into three levels and so on.

More generally, when a solid is formed by bringing N atoms together, the Pauli principle still demands that only two electrons in the entire solid should have the same energy. Hence, in a solid the different split energy levels of electrons come together to form continuous bands of energies as shown in Figure 2.12(c).

Consequently, the 2s band in a solid sodium contain N discrete energy levels and 2N electrons, two in each energy level. Similarly, each of the 2p level contain N energy levels and 2N electrons. Hence, a broad 2p band will contain 3N energy levels and 6N electrons since the three 2p bands overlap.

Hence in general, each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l + 1)$ N electrons.

[Each energy level can hold $2\ (2l + 1)$ electrons. 2 corresponds to the electrospin and $(2l + 1)$ corresponds to the orientation of the electron orbital angular momentum].

The result is that, electrons in any orbit of atom within a solid can have a range of energies rather than a single value. *Thus, the range of energies possessed by an electron in a solid is known as energy band.* i.e., Each energy level of an isolated atom becomes a band in a solid.

Check Your Progress

10. What do you understand by semi-classical physics?
11. State the semi-classical theory.
12. State quantum theory of radiation?
13. What is Einstein's coefficient of absorption?
14. State the symmetrization postulate.
15. Define the wave function.
16. What do you understand by energy band?

2.10 ANSWERS TO 'CHECK YOUR PROGRESS'

1. In quantum chemistry and molecular physics, the Born-Oppenheimer (BO) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the wave functions of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons.

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2. In this type of linear combination the positive lobe of ψ_A overlaps with the negative lobe (i.e., the lobe having-sign) of ψ_B and a molecular orbital is formed. This molecular orbital has higher energy than each of the two atomic orbital wave functions (ψ_A and ψ_B) (increase in energy) and hence the formation of this molecular orbital produces repulsion between the two nuclei of A and B.

3 The increase in electron charge density between the two positive nuclei shields (i.e., screens) the two nuclei from mutual repulsion, i.e., due to the increase in electron charge density, the two nuclei are attracted towards each other. Thus the formation of bonding molecular orbital produces attraction between the two nuclei and hence leads to the establishment of a stable chemical bond.

4. Heitler-London theory state the exchange of electron in orbital of H2 molecule and it was the first quantum-mechanical system which explains chemical bonding hydrogen molecule. Understand the Heitler-London theory; first we need to know about hydrogen molecule bonding as well as interaction between their electron and nuclei.

5. In mathematical physics, the WKB approximation or WKB method is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. It is typically used for a semi-classical calculation in quantum mechanics in which the wavefunction is recast as an exponential function, semi-classically expanded, and then either the amplitude or the phase is taken to be changing slowly.

6. The WKB theory is a method typically used for approximating the solution of a differential equation whose highest derivative is multiplied by a small parameter 'ε'.

7. In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional 'Perturbing' Hamiltonian representing a weak disturbance to the system.

8. Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation $V(t)$ applied to a time independent Hamiltonian, H_0.

9. In quantum physics, Fermi's golden rule is a formula that describes the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation. This transition rate is effectively independent of time (so long as the strength of the perturbation is independent of time) and is proportional to the strength of the coupling between the initial and final states of the system, typically described by the square of the matrix element of the perturbation, along with the density of states.

10. Semi-classical physics, or simply semi-classical refers to a theory in which one part of a system is described quantum-mechanically whereas the other is treated classically.

11. The semi-classical radiation theory consists of two elements: the classical Maxwell equations that is satisfied by the electric 'E' and the magnetic 'B' fields, and the ordinary quantum mechanics that is based on the SchrQdinger equation of a single charged matter particle interacting with the electromagnetic field.

12. The distribution of energy in the spectrum of radiations of a hot body cannot be explained by applying the classical concepts of physics. Max Planck gave an explanation to this observation by his '***Quantum Theory of Radiation***'. His theory states that,

    - The 'Radiant Energy' is always in the form of tiny bundles of light called '**quanta**', i.e., the energy is absorbed or emitted discontinuously.
    - Each **quantum** has some definite energy 'E', which depends upon the frequency of the radiations as,

    $E = h\gamma$

13. If N_1 and N_2 are the number of atoms in the lower energy state (ground state) and higher energy state (excited state) respectively, then we can write,

    $$N_1P_{12} = N_1B_{12}E(v)$$

    where P_{12} is the probability of absorption proportional to energy density $E(v)$ and B_{12} is the Einstein's coefficient of absorption.

14. Symmetrization postulate state that the system containing N particles are either totally symmetric or anti-symmetric under the interchange of any pairs of particle and state that mixed symmetry does not exist. Beside these there is two more postulate.

    - Particles with integral spins, or bosons have symmetric state.
    - Particle with half integral spins or fermions have antisymmetric state.

15. For the case of matter waves, the function that make up the waves and by which we can describe the different characteristics and properties of the said waves is called wave function, denoted by ψ (psi). The value of the wave function (ψ) associated.

16. The result is that, electrons in any orbit of atom within a solid can have a range of energies rather than a single value. *Thus, the range of energies possessed by an electron in a solid is known as energy band.* i.e., Each energy level of an isolated atom becomes a band in a solid

2.11 SUMMARY

- When nuclei of two atoms come close to each other, there election cloud interact and result in the formation of molecular orbitals.

- Each molecular orbital can be described by a wave function ψ^2, known as molecular orbital wave function ψ^2 represent the probability density or election density.
- According to linear combination of atomic orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals.
- In other words, the bonding molecular orbital has lower energy than each of the isolated atomic orbitals from which this molecular orbital is derived.
- The repulsion between the nuclei leads to an increase in the energy of the anti-bonding molecular orbital in the event of its being occupied by electrons.
- The abbreviation WKB approximation refers to Wentzel–Kramers–Brillouin, i.e., the WKB approximation method is named after physicists Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, who all developed it in 1926.

  The WKB approximation is specifically used for obtaining an approximate solution to a time independent one-dimensional differential equation, typically the Schrõdinger equation. Its principal applications include the calculations of bound state energies and tunnelling rates through barriers.
- The asymptotic series for $y(x)$ is typically considered as a divergent series, whose general term $\delta^n S_n(x)$ starts to increase after a certain value $n = n_{\max}$. Therefore, the smallest error attained by the WKB method is the order of the last included term.
- In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional 'Perturbing' Hamiltonian representing a weak disturbance to the system.
- The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.
- Fermi's Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ that is part of a continuum of states.
- The standard way to derive the equation is to start with time dependent perturbation theory and to take the limit for absorption under the assumption that the time of the measurement is much larger than the time needed for the transition.
- Thus, there is a clear link between the quantum-mechanical system and the associated semi-classical and classical approximations, as it is similar in appearance to the transition from physical optics to geometric optics.
- Quantum field theory: only Feynman diagrams with at most a single closed

loop are considered, which corresponds to the powers of Planck's constant.

- The single particle SchrQdinger quantum mechanics can be modified to take into account spin or be replaced by the nonrelativistic quantum mechanics of many particles.
- For the case of matter waves, the function that make up the waves and by which we can describe the different characteristics and properties of the said waves is called wave function, denoted by ψ (psi). The value of the wave function (ψ) associated The wave function ψ described above often takes complex value. The square of its magnitude, *i.e.*, $|\psi|^2 = \psi * \psi$ is always real and positive, where ψ* is the complex conjugate of the wave function ψ.
- More generally, when a solid is formed by bringing N atoms together, the Pauli principle still demands that only two electrons in the entire solid should have the same energy.
- Consequently, the 2s band in a solid sodium contain N discrete energy levels and 2N electrons, two in each energy level. Similarly, each of the 2p level contain N energy levels and 2N electrons. Hence, a broad 2p band will contain 3N energy levels and 6N electrons since the three 2p bands overlap.
- Hence in general, each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l + 1)$ N electrons.

2.12 KEY TERMS

- **Born–Oppenheimer (BO) approximation:** In quantum chemistry and molecular physics, the Born–Oppenheimer (BO) approximation is the best known mathematical approximation in molecular dynamics.
- **WKB approximation or WKB method:** It is a method for finding approximate solutions to linear differential equations with spatially varying coefficients. The WKB approximation refers to Wentzel–Kramers–Brillouin.
- **Bound state:** A bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space.
- **Time dependent perturbation theory:** It was developed by Paul Dirac that typically explains the effect of a time dependent perturbation V(t) applied to a time independent Hamiltonian, H_0.
- **Absorption and emission:** 'Absorption' is the phenomenon when electrons in a substance take up energy from electromagnetic radiation or types of light. Whereas 'Emission' is the phenomenon when a substance gives off electromagnetic radiation. The electromagnetic radiation in both cases has some type of energy with a specific wavelength.

2.13 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the Born-Oppenheimer approximation.
2. State the Heitler-London theory.
3. What do you understand by WKB approximation?
4. Define the Fermi's golden rule.
5. Give the phenomenon of emission and absorption of radiation.
6. What is Einstein A and B coefficient?
7. How will you define the exchange degeneracy?
8. State the Pauli exclusion principle.

Long-Answer Questions

1. Explain in detail about the Born-Oppenheimer approximation of LACO with appropriate examples.
2. Discuss about the Heitler-London theory of hydrogen atom.
3. Describe the WKB approximation and its applications to alpha decay.
4. Elaborate on the time dependent perturbation theory and Fermi's golden rule.
5. Analyse the Einstein A and B coefficient.
6. Interpret the exchange degeneracy of indistinguishable particle.
7. Explain the wave function for many electron systems with the help of examples.
8. Comprehend the Pauli exclusion principle.

2.14 FURTHER READING

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UNIT 3 ANGULAR MOMENTUM AND SPIN

Structure

3.0 INTRODUCTION

In linear algebra, an eigenvector is the characteristic vector which has linear transformation is a non-zero vector that changes at most by a scalar factor when that linear transformation is applied to it. Whereas the function is called an eigen function, and the resulting numerical value is called the eigenvalue. It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured.

Orbital angular momentum is a property of the electron's rotational motion, i.e., related to the shape of its orbital. In mathematics and physical science, spherical harmonics are special functions defined on the surface of a sphere. They are often employed in solving partial differential equations in many scientific fields.

An electron spin refers to a form of angular momentum of electrons. Moreover, it is a quantum property of electrons and its magnitude happens to be permanent. The spin quantum number provides information about an electron's unique quantum state. Also, the spins play an important role in quantum mechanics. The spin number describes how many symmetrical facets a particle has in one full rotation a spin of 1/2 it means that the particle must be rotated by two full turns (through 720°) before it has the same configuration as when it started.

The nuclear force (or nucleon–nucleon interaction, residual strong force, or, historically, strong nuclear force) is a force that acts between the protons and neutrons of atoms.

Clebsch-Gordan coefficients are mathematical symbol used to integrate products of three spherical harmonics. Clebsch-Gordan coefficients commonly arise in applications involving the addition of angular momentum in quantum mechanics.

In this unit, you will study about the eigenvalue and eigen vectors of angular momentum, angular momentum operator algebra, definitions and notation for the eigenvalues of $\hat{j}^2$ and $\hat{j}_z$, properties of the eigenvalues and eigenvectors of $\hat{j}^2$ and $\hat{j}_z$, spectrum of $\hat{j}^2$ and $\hat{j}_z$, orbital angular momentum and the spherical harmonics, spectrum of and , definition construction of spherical harmonics, rotation operators and angular momentum operators, rotational invariance and conservation of angular momentum, rotational degeneracy, electron spin, Pauli matrices, observable and wave function of spin ½ particles, vector fields and particles of spin 1, spin independent interaction of an atom, addition of angular momenta, eigenvectors of total angular momentum, Clebsch Gordan coefficients, two nucleon system and the application to the two nucleon system.

3.1 OBJECTIVES

- Understand the eigenvalue and eigen vectors of angular momentum
- Know about the angular momentum operator algebra
- Analyse the definitions and notation for the eigenvalues of $\hat{j}^2$ and $\hat{j}_z$
- Comprehend the properties of the eigenvalues and eigenvectors of $\hat{j}^2$ and $\hat{j}_z$
- Illustrate the spectrum of $\hat{j}^2$ and $\hat{j}_z$
- Interpret the orbital angular momentum and the spherical harmonics
- Explain the spectrum of and
- Discuss about the definition construction of spherical harmonics
- Describe the rotation operators and angular momentum operators
- Elaborate on the rotational invariance and conservation of angular momentum
- Define the rotational degeneracy
- Understand the electron spin and Pauli matrices
- Know about the observable and wave function of spin ½ particles

- Comprehend the vector fields, particles of spin 1and spin independent interaction of an atom
- Interpret the addition of angular momenta and eigenvectors of total angular momentum
- Calculate the Clebsch Gordan coefficients
- Know about the two nucleon system and their applications

3.2 EIGENVALUES AND EIGENVECTORS OF ANGULAR MOMENTUM

The ***eigenvalues*** of angular momentum states in quantum mechanics, we can solve the Hamiltonian and get the allowed energy levels of an object with angular momentum. The eigenvalues of the angular momentum are the possible values the angular momentum.

Derive eigen state equations with,

$$\beta_{\max} \text{ and } \beta_{\min}. \tag{3.1}$$

Note that $L^2 - L_z^2 = L_x^2 + L_y^2$, which is a positive number, so

$$L^2 - L_z^2 \geq 0 \tag{3.2}$$

That means,

$$<\alpha,\beta\left|\left(L^2 - L_z^2\right)\right|\alpha,\beta> \geq 0 \tag{3.3}$$

And substituting in Equation (3.2)

$$L^2\left|\alpha,\beta> = \alpha\hbar^2\right|\alpha,\beta> \text{ and } L_z^2\left|\alpha,\beta> = \beta\hbar\right|\alpha,\beta>, \tag{3.4}$$

And using the fact that the eigenstates are normalized, gives you Equation (3.5):

$$<\alpha,\beta\left|\left(L^2 - L_z^2\right)\right|\alpha,\beta> = \hbar^2\left(\alpha - \beta^2\right) \geq 0$$

$$\text{Therefore, } \alpha \geq \beta^2. \tag{3.5}$$

So there's a maximum possible value of β, which is also call β_{Max} because there has to be a state is:

$$|\alpha, \beta_{Max}>$$

If you apply the raising operator, we get zero:

$$L_+|\alpha, \beta_{Max}> = 0$$

Applying the lowering operator to this also gives you zero:

$$L_-L_+|\alpha, \beta_{Max}> = 0$$

And

$$L_-L_+ = L^2L_z^2 - \hbar L_z \tag{3.6}$$

That means,

$$\left(L^2 - L_z^2 - \hbar L_z\right)\left|\alpha, \beta_{max} >= 0\right. \qquad (3.7)$$

Putting in Equation (3.7)

$$L^2\left|\alpha, \beta_{max} >= \alpha\hbar^2\right. \text{ and } L_z\left|\alpha, \beta_{max} >= \beta_{max}\hbar\right|\alpha, \beta_{max} >$$

We get,

$$\left(\alpha - \beta_{max}{}^2 - \beta_{max}\right)\hbar^2 = 0$$

$$\alpha = \beta_{max}\left(\beta_{max} + 1\right) = 0$$

β_{max} as l and β as m, so $|\alpha, \beta >$ becomes $|l, m >$ and

- $L^2\left|l, m >= l(l+1)\hbar^2\right|l, m >$
- $L_z\left|l, m >= m\hbar\right|l, m >$

In addition to a β_{Max} there must also be a β_{Min}

Such that when apply the lowering operator, L_-, we get zero

$$\beta_{min} :$$

$$L_-\left|l, \beta_{min} >= 0\right.$$

And you can apply L_+ from Equation (3.6) on this as well:

$$L_+ L_-\left|l, \beta_{min} >= 0\right.$$

We also know that

$$\left(L^2 - L_z^2 + \hbar L_z\right)\left|\alpha, \beta_{min} >= 0\right.$$

This gives the following equations:

$$\left(\alpha - \beta_{min}^2 + \beta_{min}\right)\hbar^2 = 0$$

$$\alpha - \beta_{min}^2 + \beta_{min} = 0$$

$$\alpha = \beta_{min}^2 - \beta_{min}$$

$$\alpha = \beta_{min}\left(\beta_{min} - 1\right)$$

And comparing this equation to following equation’

$$\alpha = \beta_{max}\left(\beta_{max} + 1\right) = 0$$

We get

$$\beta_{Max} = -\beta_{Min}$$

So that,

$$|\alpha, \beta_{Min} >$$

By *n* successive applications of Equation (3.8)

$$L_- \text{ on } |\alpha, \beta_{Max} > \qquad (3.8)$$

We get the following equation:

$$\beta_{Max} = \beta_{Min} + n$$

Coupling these two equations gives

$$\beta_{Max} = n/2$$

Therefore, β_{Max} can be either an integer or half an integer (depending on whether *n* is even or odd).

$$l = \beta_{Max}, \ m = b$$

And *n* is a positive number, we can find that,

$$\mathbf{-l \leq m \leq l}$$

So now you have it:

The eigenstates are $| l, m >$.

The quantum number of the total angular momentum is l.

The quantum number of the angular momentum along the *z* axis is *m*.

- $L^2 |l, m >= \hbar^2 l(l+1) |l, m >$, where $l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$
- $L_z |l, m >= \hbar m |l, m >$, where $m = -l, -(l-1), \ldots, l-1, l.$
- $-l \leq m \leq l.$

For each l, there are 2l + 1 values of m. For example, if l = 2, then *m* can equal –2, –1, 0, 1, or 2.

If $l = \frac{5}{2}$, then m can equal $-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$.

You can see a representative L and L_z in the Figure 3.1 are following

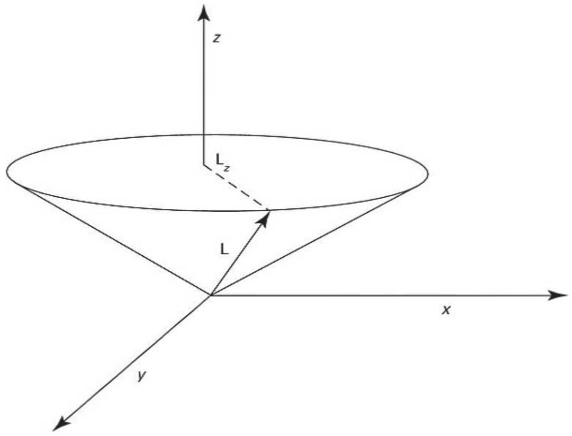


Fig.3.1 *L is the Total Angular Momentum and L_z is the Projection of Total Angular Momentum on the z Axis*

3.2.1 Angular Momentum Operator Algebra

Would be two different eigenvectors associated with the same eigenvalue a, which is incompatible with the hypothesis that is a non-degenerate eigenvalue. Therefore, we can write

$$\hat{C}|a,b\rangle = \gamma\left(\hat{B}|a,b\rangle\right) = \gamma\, b|a,b\rangle, \tag{3.9}$$

Because $\hat{B}|a,b\rangle = b|a,b\rangle$, and γ is a numerical constant. Multiplying by $\hat{B}$ both sides of this equation, we obtain:

$$\hat{B}\hat{C}|a,b\rangle = \gamma\, b\left(\hat{B}|a,b\rangle\right) = \gamma\, b^2|a,b\rangle. \tag{3.10}$$

On the other hand, applying $\hat{C}$ to both sides of

$$\hat{B}|a,b\rangle = b|a,b\rangle, \tag{3.11}$$

We find

$$\hat{C}\hat{B}|a,b\rangle = b\left(\hat{C}|a,b\rangle\right) = \gamma\, b^2|a,b\rangle, \tag{3.12}$$

Where (3.9) has been used. Subtracting (3.12) from (3.10) we obtain

$$\left[\hat{B},\hat{C}\right]|a,b\rangle = 0. \tag{3.13}$$

This equality cannot be true for all the basis vectors $\{|a,b\rangle\}$, because this would imply

$$\left[\hat{B},\hat{C}\right] = 0, \tag{3.14}$$

Therefore, the presupposition that the eigenvalue is non-degenerate cannot be valid for all eigenvalues of the operator **Â.** This means that Â has at least one degenerate eigenvalue.

3.2.2 Definitions and Notation for the Eigenvalues of $\hat{J}^2$ and $\hat{J}_z$

It follows that for any ket $|\psi\rangle$, the expectation value $\langle\psi|\hat{J}^2|\psi\rangle$ is non-negative, because

$$\langle\psi|\hat{J}^2|\psi\rangle = \langle\psi|\hat{J}_x^2|\psi\rangle + \langle\psi|\hat{J}_y^2|\psi\rangle + \langle\psi|\hat{J}_z^2|\psi\rangle$$

$$= \left\|\hat{J}_x|\psi\rangle\right\|^2 + \left\|\hat{J}_y|\psi\rangle\right\|^2 + \left\|\hat{J}_z|\psi\rangle\right\|^2 \geq 0, \tag{3.14}$$

The Eigenvalues of $\hat{J}^2$ and $\hat{J}_z$

Where $\langle\psi|\hat{J}^2|\psi\rangle = \langle\psi|\hat{J}_x^\dagger\hat{J}_x|\psi\rangle = ||\hat{J}_x|\psi\rangle||^2$, remember that $\hat{J}_x$ is Hermitian, therefore $\langle\psi|\hat{J}_x^\dagger = \langle\psi|\hat{J}_x)$. If $|\psi\rangle$ is an eigenvector of $\hat{J}^2$ associated with the eigenvalue $\lambda\hbar^2$ ($\hbar$ is thus dimensionless), then (3.14) implies:

$$\lambda \geq 0 \tag{3.15}$$

It is conventional (but not mandatory) to introduce a non-negative number $j \geq 0$ defined by Equation (3.16)

$$\lambda = j\,(j + 1) \qquad (3.16)$$

For $j \geq 0$ the function $j\,(j + 1)$ is positive or null and monotonically increasing, as shown in Figure 3.2.

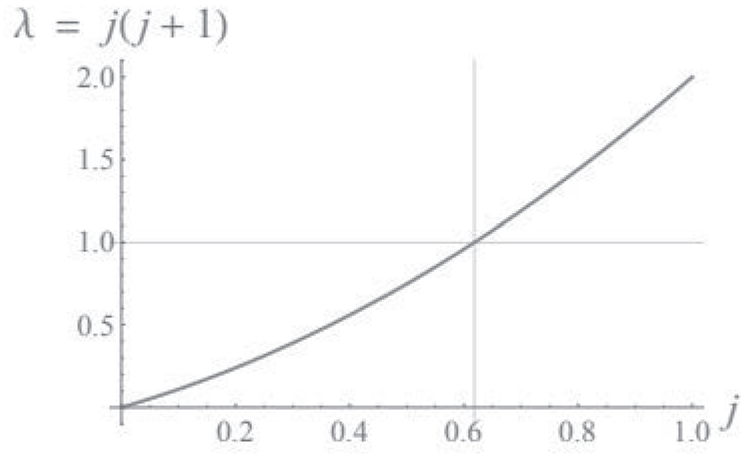


***Fig. 3.2** Graph of the Function λ = j (j + 1), for j ≥ 0. The vertical gray line mark the value j = (√5 − 1)/2, which gives λ = 1*

Therefore, if necessary, we can invert Equation (3.16) to obtain

$$j = \frac{1}{2}\left(\sqrt{4\lambda + 1} - 1\right) \qquad (3.17)$$

Since $\hat{J}^2$ and $\hat{J}_z$ commute, it is possible to find a set of common eigenvectors $\{|j,m\rangle\}$, such that

$$\hat{J}^2|j, m\rangle = j(j + 1)\hbar^2\,|j, m\rangle, \qquad (3.18a)$$

$$\hat{J}_z|j, m\rangle = m\hbar\,|j, m\rangle, \qquad (3.18b)$$

And,

$$\langle j\,', m\,'|j, m\rangle = \delta_{jj\,'}\delta_{mm\,'}, \qquad (3.19)$$

Only $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, it is not possible to build an additional (non-trivial) Hermitian operator commuting with both $\hat{J}^2$ and $\hat{J}_z$ This can be also rigorously demonstrated using group theory, but this is outside the scope of these lectures. In short, in the language of group theory, the set of the three Hermitian operators $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$. Since the $\hat{J}^2$ is compatible with $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, but $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, are reciprocally incompatible, we expect the eigenvalue $j\,(j + 1)\,\hbar^2$ to be degenerate.

3.2.3 Properties of the Eigenvalues and Eigenvectors of $\hat{J}^2$ and $\hat{J}_z$

Let $j(j + 1)\,\hbar^2$ and $m\,\hbar$ be the eigenvalues of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvector $|j, m\,\rangle$. Then j and m satisfy the following inequality

$$-j \leq m \leq j \tag{3.20}$$

To prove this assertion, consider first the two vectors $\hat{J}_+ |j, m\rangle$ and $\hat{J}_- |j, m\rangle$. By definition, their squared norms are non-negative, i.e.

$$\left\| \hat{J}_+ |j, m\rangle \right\|^2 = \langle j, m| \hat{J}_- \hat{J}_+ |j, m\rangle \geq 0, \tag{3.21a}$$

$$\left\| \hat{J}_- |j, m\rangle \right\|^2 = \langle j, m| \hat{J}_+ \hat{J}_- |j, m\rangle \geq 0, \tag{3.21b}$$

Where we have used $\hat{J}_- = (\hat{J}_+)^\dagger$.

$$\langle j, m| \hat{J}_- \hat{J}_+ |j, m\rangle = \langle j, m| \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z |j, m\rangle$$

$$= \left[j(j+1) - m(m+1) \right] \hbar^2 \langle j, m|j, m\rangle \geq 0, \tag{3.22a}$$

$$\langle j, m| \hat{J}_+ \hat{J}_- |j, m\rangle = \langle j, m| \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z |j, m\rangle$$

$$= \left[j(j+1) - m(m-1) \right] \hbar^2 \langle j, m|j, m\rangle \geq 0. \tag{3.22b}$$

These equations imply

$$j(j+1) - m(m+1) = (j-m)(j+m+1) \geq 0, \tag{3.23a}$$

$$j(j+1) - m(m-1) = (j+m)(j-m+1) \geq 0, \tag{3.23b}$$

Where to obtain the right sides we have added the null term jm − mj = 0 to the left sides. For example,

$$j(j+1) - m(m+1) = j(j+1) - m(m+1) + jm - mj$$

$$= j(j+1+m) - m(m+1+j)$$

$$= (j-m)(j+m+1). \tag{3.24}$$

Then, from Equations (3.23a) and (3.23b) it follows that:

$$-(j+1) \leq m \leq j, \tag{3.25a}$$

$$-j \leq m \leq j+1, \tag{3.25b}$$

Respectively From $j \geq 0$, it follows that $-(j+1) < -j \leq j < j+1$. Therefore, equations (3.25a) and (3.25b) are satisfied together only if m satisfies the inequality

$$-j \leq m \leq j \tag{3.26}$$

This proves in Equation (3.20).

A necessary and sufficient condition for a ket $|\psi\rangle$ to be a null vector, i.e., $|\psi\rangle = 0$, is that its norm vanishes: $\langle\psi|\psi\rangle = 0$. Therefore, from Equations (3.21a, 3.22a, 3.23a) it follows that

$$\hat{J}_{+}|j, m\rangle = 0 \quad \text{iff} \quad (j - m)(j + m + 1) = 0 \tag{3.27}$$

The solutions of the algebraic equation $(j - m)(j + m + 1) = 0$ are $m = j$ and $m = -j - 1 < -j$. Since the values of m are constrained by $-j \leq m \leq j$, only the solution $m = j$ is acceptable and Equation (3.27) implies:

$$\hat{J}_{+}|j, j\rangle = 0 \tag{3.28}$$

Similarly, from Equations (3.21b, 3.22b, and 3,23b) it follows that

$$\hat{J}_{-}|j, m\rangle = 0 \quad \text{iff} \quad (j + m)(j - m + 1) = 0, \tag{3.29}$$

Therefore,

$$\hat{J}_{-}|j, -j\rangle = 0 \tag{3.30}$$

The converse relations are also true, namely

$$\hat{J}_{\pm}|j, m\rangle = 0 \Rightarrow \qquad m = \pm j \tag{3.31}$$

This is easy to prove. Applying $\hat{J}_{\pm}$ to both sides of $\hat{J}_{\pm}|j, m\rangle = 0$ and using we obtain

$$\begin{aligned} \hat{J}_{\mp}\hat{J}_{\pm}|j,m\rangle &= \left(\hat{J}^2 - \hat{J}_z^2 \mp \hbar\hat{J}_z\right)|j,m\rangle \\ &= \hbar^2\left[j(j+1) - m(m \pm 1)\right]|j,m\rangle \\ &= \hbar^2\left[(j \mp m)(j \pm m + 1)\right]|j,m\rangle = 0. \end{aligned} \tag{3.32}$$

The last equality together with Equation (3.20) implies $m = \pm j$. Then, the following two statements are true:

1) If $m > -j$, $\hat{J}_{-}|j, m\rangle$ is a non-null eigenvector of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvalues $j(j + 1)\hbar^2$ and $(m - 1)\hbar^2$, respectively.

2) If $m < j$, $\hat{J}_{+}|j, m\rangle$ is a non-null eigenvector of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvalues $j(j + 1)\hbar^2$ and $(m + 1)\hbar^2$, respectively.

It follows that $\hat{J}_{-}|j, m\rangle$ is a non-null vector because its norm is positive for $m > -j$.

Then, we show that $\hat{J}_{-}|j, m\rangle$ is an eigenvector of $\hat{J}^2$.

$$\left[\hat{J}^2, \hat{J}_{-}\right]|j,m\rangle = 0. \tag{3.33}$$

This can be rewritten as

$$\begin{aligned} \hat{J}^2\left(\hat{J}_{-}|j,m\rangle\right) &= \hat{J}_{-}\hat{J}^2|j,m\rangle \\ &= j(j+1)\hbar^2\left(\hat{J}_{-}|j,m\rangle\right), \end{aligned} \tag{3.34}$$

Which signifies that $\hat{J}_-|j, m\rangle$ is an eigenvector of $\hat{J}^2$ associated with the eigenvalue $j(j + 1)\hbar^2$

Now, we prove that $\hat{J}_-|j, m\rangle$ is an eigenvector of $\hat{J}_z$ If we multiply from right both sides of $[\hat{J}_z - \hat{J}_- = -\hbar\hat{J}_-]$ by $|j, m\rangle$, we obtain

$$\left[\hat{J}_z, \hat{J}_-\right]|j, m\rangle = -\hbar\hat{J}_-|j, m\rangle, \tag{3.35}$$

Which is, equivalent to

$$\hat{J}_z\left(\hat{J}_-|j, m\rangle\right) = \hat{J}_-\hat{J}_z|j, m\rangle - \hbar\hat{J}_-|j, m\rangle$$
$$= (m-1)\hbar\left(\hat{J}_-|j, m\rangle\right). \tag{3.36}$$

This shows that $\hat{J}_-|j, m\rangle$ is an eigenvector of $\hat{J}_z$ with the eigenvalue $(m + 1)\hbar^2$. If $m < j$, we can use arguments similar to the ones leading to Equation (3.34) and (3.36), to prove statement 2). Of course, we must replace $\hat{J}_-|j, m\rangle$ with $\hat{J}_+|j, m\rangle$.

$$\hat{J}^2\left(\hat{J}_+|j, m\rangle\right) = j(j+1)\hbar^2\left(\hat{J}_+|j, m\rangle\right),$$
$$\hat{J}_z\left(\hat{J}_+|j, m\rangle\right) = (m+1)\hbar\left(\hat{J}_+|j, m\rangle\right). \tag{3.37}$$

These relations may be straightforwardly generalized to include powers of $\hat{J}_\pm$, that is $(\hat{J}_\pm)^n$, , where n = 1, 2, . . . is a positive integer. Specifically, we assert that

3) If $-j + n \leq m \leq j$, then $(\hat{J}_-)^n|j, m\rangle$ is an eigenvector of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvalues $j(j + 1)\hbar^2$ and $(m - n)\hbar^2$, respectively.

4) If $-j \leq m \leq j - n$, then $(\hat{J}_+)^n|j, m\rangle$ is an eigenvector of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvalues $j(j + 1)\hbar^2$ and $(m + n)\hbar^2$, respectively.

The proof is very simple,

$$\left[\hat{J}^2, \left(\hat{J}_\pm\right)^n\right]|j, m\rangle = 0, \tag{3.38}$$

This can be rewritten as,

$$\hat{J}^2\left[\left(\hat{J}_\pm\right)^n|j, m\rangle\right] = \left(\hat{J}_\pm\right)^n\hat{J}^2|j, m\rangle$$
$$= j(j+1)\hbar^2\left[\left(\hat{J}_\pm\right)^n|j, m\rangle\right]. \tag{3.39}$$

This relation means that $(\hat{J}_+)^n|j, m\rangle$is an eigenvector of $\hat{J}^2$ with eigenvalue $j(j + 1)\hbar^2$ Next, if we multiply from right both sides of equation by $|j, m\rangle$, is we obtain,

$$\left[\hat{J}_z, \left(\hat{J}_\pm\right)^n\right]|j, m\rangle = \pm n\hbar\left(\hat{J}_\pm\right)^n|j, m\rangle, \tag{3.40}$$

Namely,

$$\begin{aligned}\hat{J}_z\left[\left(\hat{J}_\pm\right)^n|j,m\rangle\right] &= \left(\hat{J}_\pm\right)^n\hat{J}_z|j,m\rangle \pm n\hbar\left(\hat{J}_\pm\right)^n|j,m\rangle \\ &= m\hbar\left(\hat{J}_\pm\right)^n|j,m\rangle \pm n\hbar\left(\hat{J}_\pm\right)^n|j,m\rangle \\ &= (m\pm n)\hbar\left[\left(\hat{J}_\pm\right)^n|j,m\rangle\right].\end{aligned} \tag{3.41}$$

Therefore, $(\hat{J}_\pm)^n|j, m\rangle$ is an eigenvector of $\hat{J}_z$ with eigenvalue (m + n) $\hbar$2However, since Equation (3.20) requires that $-j \leq m \leq j$, we must demand

$$\begin{aligned}-j \leq m+n \leq j \qquad &\Longleftrightarrow \qquad -j \leq m \leq j-n, \\ -j \leq m-n \leq j \qquad &\Longleftrightarrow \qquad -j+n \leq m \leq j.\end{aligned} \tag{3.42}$$

This concludes the demonstration of statements 3) and 4).

3.2.4 Spectrum of $\hat{J}^2$ and $\hat{J}_z$

Now we are able to determine the possible values of j and m, i.e., the spectrum of $\hat{J}^2$ and $\hat{J}_z$. According to our previous findings, since the set $\{\hat{J}^2$ and $\hat{J}_z\}$ is a CSCO, the knowledge of j and m uniquely identify the eigenvector $|j, m\rangle$ common to $\hat{J}^2$ and $\hat{J}_z$. Therefore, once we know the spectrum of $\hat{J}^2$ and $\hat{J}_z$ we also know the common eigenvectors. Thus, let $j(j + 1)\hbar^2$ and $m\hbar$ be the eigenvalues of $\hat{J}^2$ and $\hat{J}_z$ associated with the eigenvector $|j, m\rangle$. We do not make any hypothesis about the values of j and m; we only require, according to Equation (3.20), that j and m satisfy the inequality $-j \leq m \leq j$, with $j \geq 0$. So, at this stage m can be any real number between –j and j.

Consider the two vectors $(\hat{J}_+)^p|j, m\rangle$ and$(\hat{J}_-)^q|j, m\rangle$ where p and q are non-negative integers. According to 3) of the previously discussed, $(\hat{J}_-)^q|j, m\rangle$ is an eigenvector of $\hat{J}^2$ and $\hat{J}_z$ with the eigenvalues $j(j + 1)\hbar^2$ and (m-q) $\hbar$ respectively. Similarly, from 4) it follows that $(\hat{J}_+)^p|j, m\rangle$ is an eigenvector of $\hat{J}^2$ and $\hat{J}_z$ with the eigenvalues $j(j + 1)\hbar^2$ and (m-q) $\hbar$ respectively. As usual, in Equation (3.20) requires that

$$\begin{aligned}-j &\leq m-q, \\ m+p &\leq j.\end{aligned} \tag{3.43}$$

Now, let us choose p and q to be the greatest non-negative integers such that:

$$\begin{aligned}m-(q+1) &< -j, \\ m+(p+1) &> j,\end{aligned} \tag{3.44}$$

As illustrated in following Figure 3.3 showing th graphical representation of the inequalities of Equation (3.44) By hypothesis, the non-negative integers q and p are chosen to satisfy a = j+(m−q) < 1 and b = j−(m+p) <1. The intervals a and b are pictured as gray bands

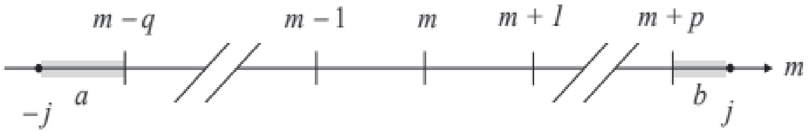


Fig. 3.3 Graphical representation of the inequalities of Equation (3.44)

The unnormalized eigenvectors of $\hat{J}^2$ and $\hat{J}_z$ with the eigenvalues of $\hat{J}_z$ proportional to

$$m - q, \ldots, m - 1, m, m + 1, \ldots, m + p,$$

Are, according to (3) and (4) of the as per previous discussed,

$$(\hat{J}_-)^q|j,m\rangle,\ \ldots,\ \hat{J}_-|j,m\rangle,\ |j,m\rangle,\ \hat{J}_+|j,m\rangle,\ \ldots,\ (\hat{J}_+)^p|j,m\rangle. \tag{3.45}$$

It is important to understand that these are the only possible vectors with these properties, because the pair (j, m) uniquely identify (up to an irrelevant multiplicative numerical constant) the eigenvector |j, m⟩. Given the leftmost and the rightmost vectors $(\hat{J}_+)^p|j, m\rangle$ and$(\hat{J}_-)^q|j, m\rangle$ we can calculate

$$\hat{J}_z\left[(\hat{J}_-)^{q+1}|j,m\rangle\right] = (m-q-1)\hbar\left[(\hat{J}_-)^{q+1}|j,m\rangle\right], \tag{3.46a}$$

$$\hat{J}_z\left[(\hat{J}_+)^{p+1}|j,m\rangle\right] = (m+p+1)\hbar\left[(\hat{J}_+)^{p+1}|j,m\rangle\right] \tag{3.46b}$$

According to Equation (3.46a), either $(\hat{J}_-)^{q+1}|j, m\rangle=0$ and $(\hat{J}_-)^{q+1}|j, m\rangle$ is an eigenvector of $\hat{J}_z$ with eigenvalue $m - q - 1$. However, from Equation (3.44) it follows that $m - q - 1 < -j$, in contradiction with Equation (3.20). Therefore, we conclude $(\hat{J}_-)^{q+1}|j, m\rangle=0$. An analogous argument yields to $(\hat{J}_+)^{p+1}|j, m\rangle=0$ When a vector is null, its norm is equal to zero, that is

$$\left\|(\hat{J}_-)^{q+1}|j,m\rangle\right\|^2 = \langle j,m|(\hat{J}_+)^{q+1}(\hat{J}_-)^{q+1}|j,m\rangle = 0,$$

$$\left\|(\hat{J}_+)^{p+1}|j,m\rangle\right\|^2 = \langle j,m|(\hat{J}_-)^{p+1}(\hat{J}_+)^{p+1}|j,m\rangle = 0. \tag{3.47}$$

It is convenient to rewrite these equations as:

$$\langle j,m|(\hat{J}_+)^{q+1}(\hat{J}_-)^{q+1}|j,m\rangle = \langle j,m|(\hat{J}_+)^{q}(\hat{J}_+\hat{J}_-)(\hat{J}_-)^{q}|j,m\rangle = 0,$$

$$\langle j,m|(\hat{J}_-)^{p+1}(\hat{J}_+)^{p+1}|j,m\rangle = \langle j,m|(\hat{J}_-)^{p}(\hat{J}_-\hat{J}_+)(\hat{J}_+)^{p}|j,m\rangle = 0. \tag{3.48}$$

We find,

$$\begin{aligned}
\langle\alpha|\hat{J}_+\hat{J}_-|\alpha\rangle &= \langle\alpha|\hat{J}^2 - \hat{J}_z^2 + \hbar\,\hat{J}_z|\alpha\rangle \\
&= \big[j(j+1) - (m-q)(m-q-1)\big]\hbar^2\langle\alpha|\alpha\rangle \\
&= 0, \\
\langle\beta|\hat{J}_-\hat{J}_+|\beta\rangle &= \langle\beta|\hat{J}^2 - \hat{J}_z^2 - \hbar\,\hat{J}_z|\beta\rangle \\
&= \big[j(j+1) - (m+p)(m+p+1)\big]\hbar^2\langle\beta|\beta\rangle \\
&= 0,
\end{aligned} \tag{3.49}$$

Where we have used the shorthand notation,

$$|\alpha\rangle \equiv \left(\hat{J}_-\right)^q|j,m\rangle, \qquad |\beta\rangle \equiv \left(\hat{J}_+\right)^p|j,m\rangle. \tag{3.49}$$

Equations (3.49) imply that:

$$\begin{aligned}
j(j+1) - (m-q)(m-q-1) &= (j+m-q)(j-m+q+1) = 0, \\
j(j+1) - (m+p)(m+p+1) &= (j-m-p)(j+m+p+1) = 0.
\end{aligned} \tag{3.50}$$

The solution of these two algebraic equations is:

$$\begin{aligned}
m &= q-j, \qquad \text{or} \qquad m = j + (q+1) > j, \\
m &= j-p, \qquad \text{or} \qquad m = -j - (p+1) < -j.
\end{aligned} \tag{3.51}$$

According to the condition (3.50), the only acceptable solutions are:

$$\begin{aligned}
m = q-j \quad &\Longleftrightarrow \quad m-q = -j, \\
m = j-p \quad &\Longleftrightarrow \quad m+p = j.
\end{aligned} \tag{3.52}$$

Clearly, these two equalities are satisfied simultaneously only if

$$q-j = j-p \qquad \Longleftrightarrow \qquad j = \frac{q+p}{2}. \tag{3.53}$$

Therefore, j is equal to a positive or zero integers (by hypothesis q and p are non-negative integers) divided by 2:

$$j = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ \ldots \tag{3.54}$$

Equations (3.52) imply that if j is an integer, all m values are integers; if j is a half-integer, all m values are half-integers. The allowed values of m for a given j are therefore:

$$-j = m - q, m - q + 1, \ldots, m + p - 1, m + p = j, \quad (3.55)$$

That is,

$$m = \underbrace{-j,\ -j+1,\ \ldots,\ j-1,\ j}_{2j+1 \text{ values}}. \quad (3.56)$$

3.3 ORBITAL ANGULAR MOMENTUM AND THE SPHERICAL HARMONICS

In quantum mechanics, we can easily understand the concept of orbital angular momentum if we already have an idea about the angular momentum in 'Classical Mechanics'. So in classical aspect, '**Angular Momentum'** is the rotational equivalent of linear momentum, thus used in systems involving rotational motion. We can denote it by the letter L in the general cases.

In the quantum mechanics, there is an analogous representation for it, which is the '**Orbital Angular Momentum'.** The key difference lies in the fact that in quantum mechanics, we use operator representation for physical quantities and this leads to the following:

In Classical: **L**= **r** × **p**

In Quantum: = $\hat{L}=\hat{r}\times\hat{p}$

So the quantization of **L**= **r**×**p** $\xrightarrow{yields} \hat{L}=\hat{r}\times(-i\frac{h}{2\pi}\vec{\nabla})$ (3.57)

In quantum mechanics, we have our orbital angular momentum as represented by $\hat{L}= (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ (in Cartesian coordinates). From Equation (3.57), we get:

$$\widehat{L_x}= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$

$$\widehat{L_y}=\hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

$$\widehat{L_z}= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

Since, $\hat{p}_x= -i\frac{h}{2\pi}\frac{\partial}{\partial x}$;

$$\hat{p}_y = -i\frac{h}{2\pi}\frac{\partial}{\partial y} \quad ;$$

$$\hat{p}_z=-i\frac{h}{2\pi}\frac{\partial}{\partial z}$$

Therefore, $\widehat{L_x}=-i\frac{h}{2\pi}(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y});$

$$\widehat{L_y}=-i\frac{h}{2\pi}(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z});$$

$$\widehat{L_z}= =-i\frac{h}{2\pi}(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

The commutator operation of the Orbital Angular Momentum can be calculated, and the same can be written as follows:

$$[\widehat{L_x},\widehat{L_y}]=i\frac{h}{2\pi}\widehat{L_z}$$

$$[\widehat{L_y},\widehat{L_z}]=i\frac{h}{2\pi}\widehat{L_x}$$

$$[\widehat{L_z},\widehat{L_x}]=i\frac{h}{2\pi}\widehat{L_y}$$

Now, after that we proceed to the **spherical harmonics** are defined as the **Eigen functions of the operator of the orbital angular momentum**. They play a really important role in 'Quantum Mechanics' and play a central role in the theory of orbital angular momentum. They are used in many problems but most importantly, spherical harmonics are used in the hydrogen atom problem.

Now since the phenomenon of the rotation is done by the angular momentum, when we perform rotation about x axis and y axis in one order and then again we perform rotation in reverse order, we do not get the same result.

From the concept of vector spaces, we already know if we get same results after reversing the order then it would be a commutative or Abelian group. But since they are not giving the same result, so they are Non Abelian, i.e., in quantum mechanics, orbital angular momentum is a non- commutative group or a ***non-Abelian*** group.

Therefore, after calculating the commutator bracket of the angular momentum, we find that it does not come out to be zero. This can be represented as follows. For that we need the **Laplacian operator** in spherical coordinates and can further proceed. With respect to the spherical coordinates, the Laplacian operator is written as:

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})+\frac{1}{r^2\sin^2\theta}(\frac{\partial^2}{\partial\Phi^2})$$

The mathematical form for the spherical harmonics can be understood by solving the quantum mechanical operations in spherical coordinates which lead us to our next topic.

3.3.1 Spectrum of L^2 and L_z

In the previous topic, we already defined the orbital angular momentum as L. We dealt with the orbital angular momentum in Cartesian coordinates but mostly it is more convenient to work in spherical coordinates rather than in the Cartesian coordinates.

Spherical coordinates, we know, are r, θ and Φ. Also:

$$x = r \sin\theta \cos\Phi \qquad (3.58)$$

$$y = r \sin\theta \sin\Phi \qquad (3.59)$$

$$z = r \cos\theta \qquad (3.60)$$

So, $r=\sqrt{(x^2+y^2+z^2)}$, $\theta=\cos^{-1}\frac{z}{\sqrt{(x^2+y^2+z^2)}}$, $\Phi=\tan^{-1}\frac{y}{x}$ (3.61)

Now, we already know that:

$$\widehat{L_z}==-i\frac{h}{2\pi}(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}) \tag{3.62}$$

So putting the expressions from Equartions (3.58),(3.59),(3.60) and (3.61) in (3.62), we get:

$$\widehat{L_z}=-i\frac{h}{2\pi}[r\ \sin\theta\cos\Phi\ (\sin\theta\sin\Phi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\Phi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\Phi}{r\sin\theta}\frac{\partial}{\partial\Phi})-r\ \sin\theta\sin\Phi\ (\sin\theta\cos\Phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\Phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\Phi}{r\sin\theta}\frac{\partial}{\partial\Phi})] \tag{3.63}$$

After solving (3.63), we are left with:

$$\widehat{L_z}=-i\frac{h}{2\pi}(cos^2\Phi+sin^2\Phi)\frac{\partial}{\partial\Phi}$$

$$\boldsymbol{\widehat{L_z}=-i\frac{h}{2\pi}\frac{\partial}{\partial\Phi}} \tag{3.64}$$

Now, similarly solving for and, we get:

$$\widehat{L_x}=i\frac{h}{2\pi}(\sin\Phi\frac{\partial}{\partial\theta}+\frac{\cos\Phi}{\tan\theta}\frac{\partial}{\partial\Phi}) \tag{3.65}$$

$$\widehat{L_y}=i\frac{h}{2\pi}(-\cos\Phi\frac{\partial}{\partial\theta}+\frac{\sin\Phi}{\tan\theta}\frac{\partial}{\partial\Phi}) \tag{3.66}$$

Calculating $\hat{L}^2=\widehat{L_x}^2+\widehat{L_y}^2+\widehat{L_z}^2$ (3.67)

We get, $\boldsymbol{\hat{L}^2=-(\frac{h}{2\pi})^2(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\Phi^2})}$ (3.68)

Also, $\widehat{L_+}=\widehat{L_x}+i\widehat{L_y}=\frac{h}{2\pi}e^{i\Phi}(\frac{\partial}{\partial\theta}+\frac{i}{\tan\theta}\frac{\partial}{\partial\Phi})$ (3.69)

$$\widehat{L_-}=\widehat{L_x}-i\widehat{L_y}=\frac{h}{2\pi}e^{-i\Phi}(-\frac{\partial}{\partial\theta}+\frac{i}{\tan\theta}\frac{\partial}{\partial\Phi}) \tag{3.70}$$

For eigenvalues equation, we have:

|l, m>=l (l+1) |l, m>   l=0, 1, 2… (3.71)

And, |l, m>=m () |l, m>   m=-l,-l+1… l-1, l (3.72)

So, from Equations (3.68) and (3.64) we have,

$$-(\frac{h}{2\pi})^2(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\Phi^2})\psi_{lm}(r,\theta,\Phi)=l(l+1)(\frac{h}{2\pi})^2\ \psi_{lm}(r,\theta,\Phi) \tag{3.73}$$

$$\boldsymbol{-i\frac{h}{2\pi}\frac{\partial}{\partial\Phi}}\psi_{lm}(r,\theta,\Phi)=m\ (\frac{h}{2\pi})\ \psi_{lm}(r,\theta,\Phi) \tag{3.74}$$

Thus, the spectra of $\hat{L}^2$ and $\widehat{L_z}$ has been discussed with the help of the spherical coordinates which again proved the importance of writing the orbital angular momentum equations in spherical coordinates. The calculations made above will be used in deriving further the Definition Construction of Spherical Harmonics.

3.3.2 Definition Construction of Spherical Harmonics

NOTES

As per previous knowledge, we know that the spherical harmonics are the **eigenfunctions of the operator of orbital angular momentum**. eigenfunction of angular momentum allows us to describe the states that correspond to the fixed quantized eigenvalues of the angular momentum. So to find out those eigenfunctions, we will proceed as follows:

(3.73) and (3.74) gives us the eigenvalues equations for $\widehat{L}^2$ and $\widehat{L_z}$ in spherical coordinates. One important thing to note here is that the operators in both of these equations only depend on the angles θ and Φ but don't depend on r, so we can have a separable trial solution for ψ.

Therefore, $\psi_{lm}(\mathrm{r}, \theta, \Phi) = \mathrm{f(r)} Y_l^m(\theta, \Phi)$ (3.75)

Putting (3.75) in (3.73), we get:

$$-\left(\frac{h}{2\pi}\right)^2\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\Phi^2}\right) \mathrm{f(r)} Y_l^m(\theta, \Phi) = \mathrm{l(l+1)}\left(\frac{h}{2\pi}\right)^2 \mathrm{f(r)} Y_l^m(\theta, \Phi)$$

The f(r) term cancels from both sides, we can rewrite the above equation as:

$$-\left(\frac{h}{2\pi}\right)^2\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\Phi^2}\right) Y_l^m(\theta, \Phi) = \mathrm{l(l+1)}\left(\frac{h}{2\pi}\right)^2 Y_l^m(\theta, \Phi) \tag{3.76}$$

Similarly, for $\widehat{L_z}$, we write:

$$-\mathrm{i}\frac{h}{2\pi}\frac{\partial}{\partial\Phi} Y_l^m(\theta, \Phi) = \mathrm{m}\left(\frac{h}{2\pi}\right) Y_l^m(\theta, \Phi) \tag{3.77}$$

So we have to figure out the (θ, Φ) of these two Equations (3.76) and (3.77) and further we are going to get something which is known as **Spherical Harmonics.**

In (3.77), we saw that the dependence is only on Φ which means that we can separate the eigenfunction Y_l^m (θ, Φ) as :

$$Y_l^m(\theta, \Phi) = A_l^m(\theta)\, B_l^m(\Phi) \tag{3.78}$$

Now using (3.78) in (3.77), we get:

$$-\mathrm{i}\frac{h}{2\pi}\frac{\partial}{\partial\Phi} A_l^m(\theta)\, B_l^m(\Phi) = \mathrm{m}\left(\frac{h}{2\pi}\right) A_l^m(\theta)\, B_l^m(\Phi)$$

Cancelling (θ) from both sides due to the non dependence on θ, we get the final expression as:

$$\frac{\partial}{\partial\Phi} B_l^m(\Phi) = \mathrm{im} B_l^m(\Phi)$$

Solving this first order differential solution, we get:

$$B_l^m(\Phi) = \mathrm{F}e^{im\Phi} \tag{3.79}$$

So, $Y_l^m(\theta, \Phi) = A_l^m(\theta)\, e^{im\Phi}$ (3.80)

The value of $A_l^m(\theta)$ can be calculated by the use of ladder operators as mentioned in Equations (3.69) and (3.70).

Putting m=l in $A_l^m(\theta)$ and then using the operator (3.69) on $A_l^m(\theta)$, after solving we get that:

$$A_l^l(\theta) = c_l(\sin\theta)^l$$

So, (3.24) can be rewritten as:

$$Y_l^l(\theta, \Phi) = c_l(\sin\theta)^l\, e^{il\Phi} \tag{3.81}$$

Now the normalization constant, after a long and exhausting calculation, we get:

$$c_l = \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)!}{4\pi}}$$

Therefore, $$Y_l^l(\theta, \Phi) = \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)!}{4\pi}}\,(\sin\theta)^l\, e^{il\Phi} \tag{3.82}$$

This is the eigenfunction $Y_l^m(\theta, \Phi)$ for l = m. For the rest of the eigenfunctions we can use operator in (3.70) and can get the eigenfunctions $Y_l^{l-1}(\theta, \Phi)$, $Y_l^{l-2}(\theta, \Phi)$ and so on.

After calculating these, we can get the eigenfunction $Y_l^m(\theta, \Phi)$ of the orbital angular momentum operators $\hat{L}^2$ and $\widehat{L_z}$ as:

$$\boldsymbol{Y_l^m}(\theta, \Phi) = \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}}\, e^{im\Phi}(\sin\theta)^{-m}\frac{d^{l-m}}{d(\cos\theta)^{l-m}}(\sin\theta)^{2l} \tag{3.83}$$

These eigenfunctions are called spherical harmonics.

Some of the spherical harmonics are written as follows, we can also calculate to find out the spherical harmonics using Equation (3.83) too.

For l=0 and m=0 we have: $Y_0^0(\theta, \Phi) = \sqrt{\frac{1}{4\pi}}$

For l=1, m=-1,0,1 we have: $Y_1^{-1}(\theta, \Phi) = \sqrt{\frac{3}{8\pi}}\, e^{-i\Phi}\sin\theta$

$$Y_1^0(\theta, \Phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1(\theta, \Phi) = -\sqrt{\frac{3}{8\pi}}\, e^{i\Phi}\sin\theta$$

And we can similarly find out the spherical harmonics for l=2, 3 and so on.

Check Your Progress

1. State the eigenvalue of angular momentum.
2. When two different eigenvectors associated with the same eigenvalue?
3. Give the solutions of the algebraic equation.
4. What is angular momentum in classical aspects?
5. Define the spherical harmonics.
6. Write a short note on spectra of $\hat{L}^2$ and $\widehat{L_z}$.
7. What do you understand the eigen function of angular momentum?

3.4 ANGULAR MOMENTUM AND ROTATION OPERATOR

We are already done defining the orbital angular momentum in spherical polar coordinates and it is found out that we are left with functions, purely of angular variables namely θ and Φ.

The commutation relation **L**×**L**=i $(\frac{h}{2\pi})$ **L** which implies that **L** does not commute with itself.

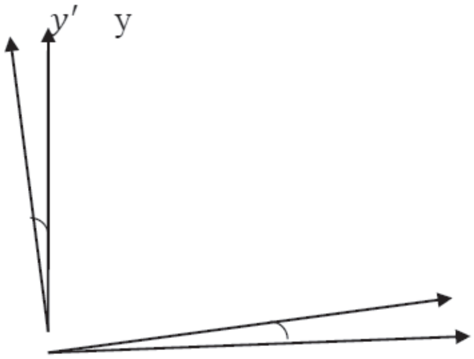
Also, $[L^2, L_{x,y,z}]$=0 which implies that there are simultaneous eigenfunction of and any component of **L.**

Angular momentum operators depend only on angular coordinates so any radial component f(r) will commute with L.

In general, any isolated system is taken invariant under rotation. Let $\widehat{O_R}$ be the rotation operator. After operating on ψ, let us say the ψ will become ψ, i.e. $\widehat{O_R}\,\psi = \psi'$

$< \psi'|\,\psi' > = < \widehat{O_R}\,\psi|\widehat{O_R}\,\psi > = < \psi|\widehat{O_R}^{+}\,\widehat{O_R}\,|\,\psi > = < \psi|\psi >$ (since rotation operator is unitary)

Rotation Operator represents rotation of coordinate system.



So, here $\widehat{O_R}\ \psi(\mathrm{x, y}) = \ \psi(x',\ y'\ )$

Here, x' = xcos($\Delta\theta$)+ysin($\Delta\theta$)

y' = -xsin($\Delta\theta$)+ycos($\Delta\theta$)

For the small angleθ, we get:

x' = x+ y$\Delta\theta$

y' = -x$\Delta\theta$+y

Therefore, $\widehat{O_R}\ \psi(\mathrm{x, y}) = \psi(\mathrm{x+ y}\Delta\theta, \mathrm{-x}\Delta\theta\mathrm{+y})$

$$= \psi(\mathrm{x, y}) + \mathrm{y}\Delta\theta\frac{\partial\psi}{\partial x} - \mathrm{x}\Delta\theta\frac{\partial\psi}{\partial y}$$

From (3.58), $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$ and can be written in the forms of momentum as follows:

$$\widehat{O_R}\ \psi(\mathrm{x, y}) = \psi(\mathrm{x, y}) + \frac{\mathrm{i}\Delta\theta}{\frac{h}{2\pi}}(\mathrm{y}\hat{p}_x - x\hat{p}_y)\ \psi$$

Since, $L_z = (\mathrm{y}\hat{p}_x - x\hat{p}_y)$

Therefore, $$\widehat{O_R}\ \psi(\mathrm{x, y}) = (1 - \frac{\mathrm{i}\Delta\theta L_z}{\frac{h}{2\pi}})\ \psi(\mathrm{x, y})$$

$$\boldsymbol{\widehat{O_R} = (1 - \frac{\mathrm{i}\Delta\theta L_z}{\frac{h}{2\pi}})} \qquad (3.84)$$

This is the Rotation Operator for small angle Δθ.

The operator for rotation through angle θ further given by:

$$\Delta\theta = \frac{\theta}{N}$$

We have to apply Equation (3.84) N times to get operator for rotation through angle θ:

$$\widehat{O_R}(\theta) = \lim_{N\to\infty}\left((1 - \frac{\mathrm{i}(\theta/N)L_z}{\frac{h}{2\pi}})\right)^N$$

Which gives, $$\boldsymbol{\widehat{O_R}}\ (\theta) = \ \boldsymbol{e}^{\frac{-\grave{i}L_z}{\left(\frac{h}{2\partial}\right)}} \qquad (3.85)$$

This is rotation about z axis through angle θ.

So, we saw the importance of Angular Momentum Operators in defining the Rotation Operators.

One important rotation operator is the rotation about **an axis**, which is given by:

$$\boldsymbol{\widehat{O_R}(\theta) = e^{\frac{-i\theta L_z}{(\frac{h}{2\pi})}}} \qquad (3.86)$$

In the next section, we will discuss about the rotational invariance and the conservation of angular momentum.

3.4.1 Rotational Invariance and Conservation of Angular Momentum

In general, any isolated system is taken invariant under rotation. Rotational invariance can be proved by the commutator relation of the rotational operator and the Hamiltonian of the system which is further given by:

$[\widehat{O_R}, H]$ = (to find)

Suppose, for an arbitrary operator, $\widehat{O_R}A = A'$

Then,

$$< \psi'|A'|\psi' > = < \psi|\widehat{O_R}^{+} A\, \widehat{O_R}\,|\,\psi > = < \psi|A\,|\,\psi >$$

Since expectation value remains invariant, as from Equation (3.83), therefore,

$$\widehat{O_R}^{+} A'\, \widehat{O_R} = A$$

Or, $$\widehat{O_R}^{+} A\, \widehat{O_R} = A'$$

If $$A \equiv H$$

Then, $$H' = \widehat{O_R}\, H\, \widehat{O_R}^{+} = H$$

Which gives, $$\widehat{O_R}\, H = H\widehat{O_R}$$

Therefore, $$[\widehat{O_R}\,, H] = 0 \qquad (3.87)$$

Also, If a system is invariant under rotation, then

$[\widehat{O_R}\,, H] = 0$

And since angular momentum is the generator for infinitesimal rotations and rotation by an angle, therefore it follows:

$$[\hat{\boldsymbol{L}}\,, H] = 0 \text{ and } [\boldsymbol{L}^2, H] = 0 \qquad (3.88)$$

Thus rotational invariance is proved.

Now,

Conservation laws in quantum mechanics tell us that if a quantity does not explicitly depend on time and it commutes with H, then it is a conserved quantity.

And here, The Angular Momentum does not explicitly depend on time and from Equation (3.88) it is clear that the angular momentum commutes with H and therefore the conservation of Angular Momentum is proved.

3.4.2 Rotational Degeneracy

In this section, we will discuss about the degeneracy in rotating systems in quantum mechanics. We already know that the angular momentum operators are used in defining the rotation operators, thus representing rotating systems. Now using the orbital angular momentum, the spherical harmonics have been discussed which plays an important role in hydrogen atom. It has been noticed that there is degeneracy of energy associated with the hydrogen atom which can be explained by discussing the angular momentum operators and their degeneracy. We dealt with the orbital angular momentum and then with the important idea of spin angular momentum in quantum systems.

So, for discussing rotational degeneracy, we will take the example of hydrogen atom as its spherical harmonics are derived from the angular momentum operators which are the operators for the rotation phenomenon in quantum mechanics.

There are two types of degeneracy in Hydrogen Atom: 'Without Spin' and 'With Spin'.

For discussing the case of degeneracy (without spin) case of hydrogen atom:

The total quantum number n takes only non-zero values i.e. n = 1,2,3,4… For a given n, the quantum number l can vary from 0 to n-1, and for each 'l', the value of 'm' can take the (2l+1) values since m can vary from –l,-l+1,….l-1,l as we know from Equations (3.71) and (3.72), so the rotational degeneracy is (2l+1) in this case, and the degeneracy of the state n which is specified by the total no. of different states associated with n is given by:

$$g_n = \sum_{l=0}^{n-1}(2l+1) = n^2 \tag{3.89}$$

When we consider degeneracy with spin then:

We know that the state of the hydrogen atom is denoted by the three quantum numbers n, l and m which are called the single particle states. According to the spectroscopic notation, we get that the states corresponding to the numerical values l=0,1,2,3,4,5…. are called the s,p,d,f,g,h,… states.

For l = 0, we have s;

For l = 1, we have p;

For l = 2, we have d;

For l = 3, we have f and so on.

And the letters s, p, d, f refers to the sharp, principle, diffuse and fundamental levels respectively.

Therefore, for a given or fixed n,

We have: s state with 1 orbital i.e. |n,0,0>

p state with 3 orbitals |n,1,m> with m=-1, 0, 1

d state with 5 orbitals |n,2,m> with m=-2,-1,0,1,2

Therefore, after including the spin, the degeneracy of the energy level of the hydrogen becomes:

$$g_n = 2\sum_{l=0}^{n-1}(2l+1) = 2n^2 \tag{3.90}$$

The inclusion of spin results in doubly degenerate levels.

For example, the ground state of the atom becomes doubly degenerate for the same energy value with wave functions $\psi(\mathbf{r})_{100\frac{-1}{2}}$ and $\psi(\mathbf{r})_{100\frac{1}{2}}$ which corresponds to the same energy value and thus called doubly degenerate ground state when the spin is included.

Also, the first state becomes eight fold degenerate as n = 2 which gives gn = 8.

3.5 ELECTRON SPIN AND SPIN 1/2

In quantum mechanics, there is an analogous quantity of the classical spin. In classical aspect, spin S=I w is associated with the motion about the centre of mass of the rigid object whereas in quantum mechanics, especially when we talk about the electron spin, added together to the orbital angular momentum which is linked with the motion of the electron that is around the nucleus, the electron has another type of angular momentum which does nothing with the motion in space but it is analogous to the classical spin but electron is without any structure and a point particle, so we say that electron has intrinsic angular momentum (S) and extrinsic angular momentum (L).

The algebra of spin is the carbon copy of that of the orbital angular momentum and is given by:

$$[\widehat{S}_x, \widehat{S}_y] = i\frac{h}{2\pi}\widehat{S}_z \qquad (3.91)$$

$$[\widehat{S}_y, \widehat{S}_z] = i\frac{h}{2\pi}\widehat{S}_x \qquad (3.92)$$

$$[\widehat{S}_z, \widehat{S}_x] = i\frac{h}{2\pi}\widehat{S}_y \qquad (3.93)$$

Also the eigenvectors of S^2 and S_z are given by:

$$\hat{S}^2 |s, m\rangle = s(s+1)\left(\frac{h}{2\pi}\right)^2 |s, m\rangle \quad , s=0, ½, 1, 3/2 \qquad (3.94)$$

$$\widehat{S}_z |s, m\rangle = m\left(\frac{h}{2\pi}\right) |s, m\rangle \quad , m=-s,-s+1\ldots s-1, s \qquad (3.95)$$

And, $$S_{\pm} |s, m\rangle = \left(\frac{h}{2\pi}\right)\sqrt{s(s+1)-m(m\pm1)}\, |s, (m\pm1)\rangle \qquad (3.96)$$

Where, $S_{\pm} = S_x \pm i S_y$

Here one thing to note is that the eigenvectors are not the spherical harmonics and s are allowed with the half integer spins.

Every particle has its own value of s, for pi meson the value of s is 0 and here the particle of concern is **electron**, and the spin of the electron is s=1/2, i.e., electron is a spin-half particle.

Once we understand the algebra of spin-half particles, dealing with the higher spins become easier. For spin half particles, we have only two eigenstates, i.e., spin up eigenstate which is written as $|\frac{1}{2}, \frac{1}{2}\rangle$ and another one is the spin down eigenstate i.e., $|\frac{1}{2}, \frac{-1}{2}\rangle$ since s is fixed and its value for electron is ½ and for m, we get $m = \frac{1}{2} \textit{ and } \frac{-1}{2}$.

Solving further will get us our next important topic in the domain of quantum mechanics, famously known as the Pauli Matrices.

Spin 1/2

In quantum mechanics, spin is an intrinsic property of all ‘Elementary Particles’. All known *fermions*, the particles that constitute ordinary matter, have a spin of 1/2. The spin number describes how many symmetrical facets a particle has in one full rotation; a spin of ½ it means that the particle must be rotated by two full turns (through 720°) before it has the same configuration as when it started. Particles having net spin 1/2 include the proton, neutron, electron, neutrino, and quarks. The dynamics of spin- objects cannot be accurately described using classical physics; they are among the simplest systems which require quantum mechanics to describe them. As such, the study of the behaviour of spin-1/2 systems forms a central part of quantum mechanics.

General Properties

Spin-1/2 objects are all fermions (a fact explained by the spin–statistics theorem) and satisfy the **Pauli exclusion principle.** Spin- particles can have a permanent magnetic moment along the direction of their spin, and this magnetic moment gives rise to electromagnetic interactions that depend on the spin. One such effect that was important in the discovery of spin is the Zeeman effect, the splitting of a spectral line into several components in the presence of a static magnetic field. Unlike in more complicated quantum mechanical systems, the spin of a spin-1/2 particle can be expressed as a linear combination of just two eigenstates, or eigenspinors. These are traditionally labeled spin up and spin down. Because of this, the quantum-mechanical spin operators can be represented as simple 2 × 2 matrices. These matrices are called the Pauli matrices. Creation and annihilation operators can be constructed for spin-1/2 objects; these obey the same commutation relations as other angular momentum operators.

Mathematical Description: A spin-1/2 particle is characterized by an angular momentum quantum number for spin s of 1/2. In solutions of the Schrödinger equation, angular momentum is quantized according to this number, so that total spins angular momentum

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

However, the observed fine structure when the electron is observed along one axis, such as the z-axis, is quantized in terms of a magnetic quantum number, which can be viewed as a quantization of a vector component of this total angular momentum, which can have only the values of ±1/2 ‘. Note that these values for angular momentum are functions only of the reduced Planck constant (the angular momentum of any photon), with no dependence on mass or charge.

3.5.1 Pauli Matrices

After getting the two eigenfunctions, namely spin up and spin down, the general state of the spin ½ particle can be written as a two element column matrix also called the spin or as follows:

NOTES

$$\text{X}=\begin{pmatrix} q \\ r \end{pmatrix} = \text{q}\,X_{+} + \text{r}\,X_{-}$$

Where, $X_{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

This is the spin up operator.

And, $X_{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

This is the spin down operator.

Now, we are getting a 2×2 matrix, which we can work it out by taking a note of their operation on X_{+} and X_{-} and from Equation (3.94) we get:

$$\hat{S}^2 X_{+} = \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 X_{+} \tag{3.97}$$

And, $$\hat{S}^2 X_{-} = \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 X_{-} \tag{3.98}$$

Let us write $\hat{S}^2$ in terms of a matrix, we get:

$$\hat{S}^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix}$$

From Equations (3.97) and (3.98), we get:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Or, $$\begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 \\ 0 \end{pmatrix}$$

Also, we get:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Or, $$\begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 \end{pmatrix}$$

O, finally the result that we get is:

$$\hat{\boldsymbol{S}}^2 = \frac{3}{4}\left(\frac{\boldsymbol{h}}{2\boldsymbol{\pi}}\right)^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{3.99}$$

Similarly, $S_z X_+ = \frac{1}{2}\left(\frac{h}{2\pi}\right) X_+$

and, $S_z X_- = -\frac{1}{2}\left(\frac{h}{2\pi}\right) X_-$

Solving this, we get:

$$\boldsymbol{S}_z = \frac{1}{2}\left(\frac{\boldsymbol{h}}{2\boldsymbol{\pi}}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.100}$$

From (3.99), we get that:

$\boldsymbol{S}_+ X_- = \left(\frac{h}{2\pi}\right) X_+$

And, $\boldsymbol{S}_- X_+ = \left(\frac{h}{2\pi}\right) X_-$

i.e., $\boldsymbol{S}_+ X_+ = \boldsymbol{S}_- X_- = 0$

Therefore, $S_+ = \frac{h}{2\pi}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ and $S_- = \frac{h}{2\pi}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

Also, $S_\pm = S_x \pm \mathrm{i} S_y$

So, $S_x = \frac{1}{2}(S_+ + S_-)$

And, $S_y = \frac{1}{2i}(S_+ - S_y)$

Therefore,

$$\boldsymbol{S}_x = \frac{1}{2}\ (\frac{\boldsymbol{h}}{2\boldsymbol{\pi}})\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{3.101}$$

And, $$\boldsymbol{S}_y = \frac{1}{2}\ (\frac{\boldsymbol{h}}{2\boldsymbol{\pi}})\begin{pmatrix} 0 & -\boldsymbol{i} \\ \boldsymbol{i} & 0 \end{pmatrix} \tag{3.102}$$

Let us denote

$$\mathrm{S} = \frac{1}{2}\ (\frac{h}{2\pi})\sigma$$

Therefore, $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

These σ_x, σ_y and σ_z are famously known as the **Pauli Spin Matrices.**

3.5.2 Observable and Wave Function Of Spin ½ Particles

We can describe the quantum state of a spin ½ particles by a two-component vector which is complex-value and is called a spinor. The spin operators S_x, S_y, and S_z are used to find the observable states of the particle and S is considered as the total spin operator.

The Observables are: We already know that when spinors are used to describe the quantum states, the three spin operators (S_x, S_y, S_z,) is described by the 2 × 2 matrices called the Pauli matrices whose eigenvalues are $\pm\frac{1}{2}\left(\frac{h}{2\pi}\right)$.

For example, we have the spin projection operator S_z. It is responsible for altering the measurement of the spin in the z direction.

$$S_z = \frac{1}{2}\left(\frac{h}{2\pi}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We know that $\pm\frac{1}{2}\left(\frac{h}{2\pi}\right)$ are the two eigenvalues of S_z, and they give us the following eigenspinors:

$$X_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$X_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

To describe the spin1/2 particle, we get these eigenspinors which form a complete basis for the Hilbert space. Thus, all of the possible states of the spin can be represented by the linear combinations of these two states, in which the x- and y-directions are also included.

Also, the ladder operators are:

$$S_+ = \left(\frac{h}{2\pi}\right)\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- = \left(\frac{h}{2\pi}\right)\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

We know that:

$S_{\pm} = S_x \pm i\, S_y$ and it results in:

$S_x = 1/2\ (S_+ + S_„)$ and $S_y = (1/2i)(S_+ - S_„)$.

Thus:

$$S_x = \frac{1}{2}\ (\frac{h}{2\pi})\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{1}{2}\ (\frac{h}{2\pi})\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

The eigenspinors for these which are also normalized, they are found as follows.

For S_x, they are:

$$X_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$X_- = \left(\frac{1}{\sqrt{2}}\right)\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

For S_y, they are:

$$X_+ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$$

$$X_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Thus the observables and the wave functions of the spin ½ particles have been described as above. The previous Pauli matrices part was already covered in the previous section which boosted up in this section.

Spin of Field

Spin field may refer to: Spinor field, assignment of a spinor to every point in space, used in quantum mechanics and quantum field theory. A kind of Torsion field, used in pseudophysics. In differential geometry, given a spin structure on an n-dimensional orientable Riemannian manifold (M, g), a section of the spinor bundle S is called a **spinor field**. A spinor bundle is the complex vector bundle $\pi_{\mathbf{s}}\mathbf{: S} \rightarrow \mathrm{M}$.

Associated to the corresponding principal bundle $\pi_{\mathbf{p}}\mathbf{: P} \rightarrow \mathrm{M}$ of spin frames over M via the spin representation of its structure group Spin(n) on the space of spinors Δ_n.

In particle physics, particles with spin s are described by a 2s-dimensional spinor field, where s is an integer or a half-integer. Fermions are described by spinor field, while bosons by tensor field.

Formal Definition

Let (P, F_P) be a spin structure on a Riemannian manifold (M, g) that is, an equivariant lift of the oriented orthonormal frame bundle $F_{SO}(M) \rightarrow M$ with respect to the double covering ρ: Spin(n) → SO(n),.

One usually defines the spinor bundle $\pi_s\mathbf{: S \rightarrow M}$ to be the complex vector bundle

$$\mathbf{S = P \times_{\kappa} \Delta_n}$$

3.5.3 Vector Fields and Particles of Spin 1

To find the nature of the spin property as we do for the mass and the charge also describing, how it interacts with the other forces and particles in the universe, experiments have been performed. And we found out that the spin behaves weirdly too when taken into consideration.

For one, the value of the same type of the particle's spin is fixed. By definition, electrons have a spin equal to 1/2. Other particles may have the spins of 3/2, 2, 0 or even 1. Also the value of a particle's spin decides the directions of the spin which we can measure actually.

For example, an electron is a spin half particle and they give the up and down spins or the deflections in the Stern-Gerlach experiment, and it can only be measured to have the values -1/2 or +1/2,. A spin 1 particle, such as a photon, when measured, it results to only have the directions -1, 0, or +1.

The spin 1 particles such as the photon are again related to the vector field and this topic is of hot discussions among the physicists, that the description of the spin 1 particles is done by the vector field.

Vector field as we know in vector calculus and physics, a vector field is to assign a vector to each point in a subset of space. For example, in a plane, a vector field can be envisioned as a collection of the arrows with a fixed given magnitude and direction, where each of them is attached to a point in that plane.

3.5.4 Spin Independent Interaction of an Atom

Earlier when the concept of spin was not known to people, then the interaction of an atom was studied under the spin independent consideration.

With spin consideration we get the total angular momentum as:

$$J = L + S$$

And without the spin consideration, we are left with the orbital angular momentum which has been discussed in details above; it is generally represented by the letter L.

One important rule that we had noticed about the inclusion of the spin which in turn generated the total angular momentum J i.e. when we wrote the eigenvalue equation of that of the total angular momentum, then the results are as follows:

$$\hat{J}^2 |j, m>= j\,(j+1)\left(\frac{h}{2\pi}\right)^2 |j, m> \quad , j=0, ½, 1, 3/2$$

$$\widehat{J_z}\ |j, m>= m\,(\frac{h}{2\pi})\ |j, m> \quad , m=-j,-j+1\ldots j-1, j$$

And, $$J_{\pm}\ |j, m> = (\frac{h}{2\pi})\sqrt{j(j+1)-m(m\pm 1)}\ |j, (m\pm 1)>$$

Where, $$J_{\pm} = J_x \pm i J_y$$

Here, the eigenvalue equation of J^2 has j in its eigenvalue equation which takes the values of half integrals due to the consideration of the spin but if the spin is not included, the after considering the orbital angular momentum, we get the eigenvalue equation of the L^2 as follows:

$$\hat{L}^2 |l, m>= l\,(l+1)\left(\frac{h}{2\pi}\right)^2 |l, m> \quad , l=0, 1, 2,\ldots$$

$$\hat{L}\ |l, m>= m\,(\frac{h}{2\pi})\ |l, m> \quad , m=-l,-l+1\ldots l-1, l$$

And, $$L_{\pm}\ |l, m> = (\frac{h}{2\pi})\sqrt{l(l+1)-m(m\pm 1)}\ |l, (m\pm 1)>$$

Where, $$L_{\pm} = L_x \pm i L_y$$

Here, we noticed that the l included in the eigenvalue equation of L^2 takes only the integral value because it's a spin independent consideration which has been taken into the account here.

This makes us ponder more about the difference that spin can create while dealing with the atomic systems further.

3.6 ADDITION OF ANGULAR MOMENTA

Let us suppose there is a system of two spin 1/2 particles, for example: electron and proton. Each one of them can have a spin up or a spin down state, so we come up with four different possibilities, i.e.:

$$\downarrow\uparrow, \uparrow\downarrow, \uparrow\uparrow, \downarrow\downarrow$$

Here, the first arrow is for electron and the second is for the proton. So we have to find the total angular momentum of the system and for that we use the concept of the addition of the angular momentum which is as follows:

$$S= \boldsymbol{S}^{(1)} + \boldsymbol{S}^{(2)}$$

Here, each one of the four states is the composite state is an eigenstate of S_z and now adding the z components which simply adds, gives us:

$$S_z X_1 X_2 = (S_z^{(1)} + S_z^{(2)})\ X_1 X_2 = (S_z^{(1)}\ X_1) X_2 + X_1\ (S_z^{(2)} X_2) \qquad (3.103)$$

$$= ((\frac{h}{2\pi})\, m_1 X_1)\ X_2 + X_1\ ((\frac{h}{2\pi})\, m_2 X_2)$$

$$(\frac{h}{2\pi})(m_1 + m_2)\ X_1 X_2$$

We saw that m= $m_1 + m_2$ i.e.:

$\downarrow\uparrow$: m=0

$\uparrow\downarrow$: m=0

$\uparrow\uparrow$: m=1

$\downarrow\downarrow$: m=-1

Now after applying the lowering operator, we can proceed as follows:

$S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$ and then using the (3.103), we get:

$$S_-(\uparrow\uparrow) = (S_-^{(1)}\ \uparrow)\uparrow + \uparrow\left(S_-^{(2)}\uparrow\right)$$

$$= (\frac{h}{2\pi}\downarrow)\uparrow + \uparrow(\frac{h}{2\pi}\downarrow)$$

$$= \frac{h}{2\pi}(\downarrow\uparrow + \uparrow\downarrow)$$

We are having the notation |s, m>, and the evident states for s=1 is the three states as follows:

$|1, 0> = \uparrow\uparrow$

$|1, 1> = \frac{1}{\sqrt{2}}(\downarrow\uparrow + \uparrow\downarrow)$

$|1,-1> = \downarrow\downarrow$

So we get a triplet for the spin s=1 and it is known as the triplet because we got three states for s=1.

If we do the same for s=0, we get a singlet i.e. a single state which is given as follows:

Since for s=0, we get m=0 and thus the state is given by:

$$|0, 0> = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow).$$

This is singlet for s=0. If we apply lowering or raising operator to this state, we will get zero in this case.

So, in other words we can say that the combination of the two spin ½ particles can carry in total a spin of 0 or 1 and it depends on whether they occupy the singlet or the triplet in configuration.

To confirm this, we have to show that the eigenvalue of the triplet state is $2\left(\frac{\boldsymbol{h}}{2\pi}\right)^2$ and the triplet states are the eigenvectors of S^2. Also, the singlet is the eigenvector of S^2 with the eigenvalue 0. Now,

$$S^2 = (S^{(1)} + S^{(2)}) \cdot (S^{(1)} + S^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\, S^{(1)} \cdot S^{(2)}$$

$$S^{(1)} \cdot S^{(2)} (\uparrow\downarrow) = (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow)$$

$$= \frac{1}{4}\left(\frac{h}{2\pi}\right)^2 (2\downarrow\uparrow - \uparrow\downarrow)$$

Similarly, we can get:

$$\boldsymbol{S}^{(1)} \cdot \boldsymbol{S}^{(2)} (\downarrow\uparrow) = \frac{1}{4}\left(\frac{\boldsymbol{h}}{2\pi}\right)^2 (2\uparrow\downarrow - \downarrow\uparrow)$$

Which further gives, $\boldsymbol{S}^{(1)} \cdot \boldsymbol{S}^{(2)} |1, 0>$

$$= \frac{1}{4}\left(\frac{\boldsymbol{h}}{2\pi}\right)^2 \frac{1}{\sqrt{2}} (2\downarrow\uparrow - \uparrow\downarrow + 2\uparrow\downarrow - \downarrow\uparrow) = \frac{1}{4}\left(\frac{\boldsymbol{h}}{2\pi}\right)^2 |1, 0>$$

Also, $\boldsymbol{S}^{(1)} . \boldsymbol{S}^{(2)} |0, 0> = \frac{1}{4}\left(\frac{\boldsymbol{h}}{2\pi}\right)^2 \frac{1}{\sqrt{2}} (2\downarrow\uparrow - \uparrow\downarrow - 2\uparrow\downarrow + \downarrow\uparrow)$

$$= -\frac{3}{4}\left(\frac{h}{2\pi}\right)^2 |0, 0>$$

$$S^2 |1, 0> = \left(\left(\frac{3}{4}\left(\frac{h}{2\pi}\right)^2 + \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 + \frac{2}{4}\left(\frac{h}{2\pi}\right)^2\right) |1, 0> = 2\left(\frac{h}{2\pi}\right)^2 |1, 0>$$

So, we showed that |1, 0> is the eigenvector of S^2 with the eigenvalue $2\left(\frac{h}{2\pi}\right)^2$.

Now, $S^2 |0, 0> = \left(\left(\frac{3}{4}\left(\frac{h}{2\pi}\right)^2 + \frac{3}{4}\left(\frac{h}{2\pi}\right)^2 - 3\left(\frac{2}{4}\right)\left(\frac{h}{2\pi}\right)^2\right) |0, 0> = 0$

Therefore, it is evident from the above proof that the |0, 0> is the eigenstate of the S^2 with the eigenvalue 0.

So, we just saw that the combination of the two spin ½ particles can carry in total a spin of 0 or 1. It was one of the examples but now, if we are given spins s_1 and s_2 and we are said to combine spin s_1 with s_2, then what is the total spins do we get is given by the following:

$$S = (\boldsymbol{s}_1 + \boldsymbol{s}_2),\ (\boldsymbol{s}_1 + \boldsymbol{s}_2 - 1),\ (\boldsymbol{s}_1 + \boldsymbol{s}_2 - 2)\ldots\ |\boldsymbol{s}_1 + \boldsymbol{s}_2|$$

The highest total spin forms when the individual spins are aligned parallel to each other and the lowest total spin forms when the individual spins are aligned anti parallel.

3.6.1 Eigenvectors of Total Angular Momentum

Firstly, we define the total angular momentum. The total angular momentum $J = (J_x, J_y, J_z)$ combines both the spin and orbital angular momentum of a particle or system:

$$J = L + S$$

The conservation of the angular momentum states that for a closed system, **J** is conserved, or **J** is conserved for the whole universe. The **L** and **S** are *not* generally conserved.

We can define the angular momentum and also generalize it in quantum mechanics as the observable $J\,(J_x, J_y, J_z)$ which satisfies the following commutation relations:

$$[J_i, J_j] = \varepsilon_{ijk} i\hbar J_k \ .$$

By defining that, now we declare the operator $J^2 = J_x^{\,2} + J_y^{\,2} + J_z^{\,2}$, then using $[J_i, J_j] = \varepsilon_{ijk} i\hbar J_k$, we can show, that $[J^2, J_x] = [J^2, J_y] = [J^2, J_z] = 0$. This is often expressed as $[J^2, J] = 0$.

Now we have to find the simultaneous eigenstates of the J^2 and J_x operators or J^2 and J_y operators or J^2 and J_z operators but we cannot find that of J^2, J_z, J_x, and J_y since we already know that J_z, J_x, and J_y do not commute.

To find the simultaneous eigenstates of the operators J^2 and J_z, we are going to define the eigenstates with their respective eigenvalues. We know that the $\lambda\left(\dfrac{h}{2\pi}\right)^2$ is the set of the eigenvalues of operator J^2 and the $(m\dfrac{h}{2\pi})$ is the set of the eigenvalues of the operator J_z. Let us label the eigenstates by $|k, \lambda, m>$. We have:

$$J^2|k, \lambda, m> = \lambda\hbar^2|k, \lambda, m>, \qquad J_z|k, \lambda, m> = m\hbar|k, \lambda, m>$$

J^2 and J_z in general don't constitute a complete set of commuting observables, i.e. the eigenvalues of J^2 and J_z do not completely specify the state. For example, for a particle without spin in a central potential H, L^2 and L_z makes a CSCO i.e. complete set of commuting operators only if we specify the eigenvalues of H, L^2 and L_z are the eigenstates which are no longer degenerate. In order to distinguish between the degenerate eigenvectors having the same λ and m, the k is used by us above.

The eigenvalues of J^2 are >=0.

Let $|\psi>$ be an eigenstate of J^2.

$<\psi|\psi> = \|\,|\psi>\|^2 >= 0$

$<\psi|J^2|\psi> = \lambda\hbar^2 <\psi|\psi>$.

But we also know that:

$$\langle\psi|J^2|\psi\rangle = \langle\psi|J_x^2|\psi\rangle + \langle\psi|J_y^2|\psi\rangle + \langle\psi|J_z^2|\psi\rangle = \|J_x|\psi\rangle\|^2 + \|J_y|\psi\rangle\|^2 + \|J_z|\psi\rangle\|^2 \geq 0.$$

Therefore, it is obvious that $\lambda\hbar^2 \geq 0$. We write $\lambda = j(j+1)$, with $j \geq 0$ and so we showed the eigenstates of J^2 and J_z by $|k, j, m>$. So now we have:

$$J^2|k,j,m> = j(j+1)\hbar^2|k,j,m>, \quad J_z|k,j,m> = m\hbar|k,j,m>.$$

Also, the eigenvalues of J_z are $(m\frac{h}{2\pi})$ with –jd” m d”j.

Let us now introduce the operators $J_+ = J_x + iJ_y$ and $J_- = J_x - iJ_y$. These operators commute with J^2, but they do not commute with the J_z and also with each other.

$$[J^2, J_+] = [J^2, J_-] = 0, \quad [J_z, J_+] = \hbar J_+, \quad [J_z, J_-] = -\hbar J_-, \quad [J_+, J_-] = 2\hbar J_z.$$

After the multiplication, we find the products as follows:

$$J_+J_- = J_x^2 + J_y^2 + \hbar J_z = J^2 - J_z^2 + \hbar J_z, \quad J_-J_+ = J_x^2 + J_y^2 - \hbar J_z = J^2 - J_z^2 - \hbar J_z$$

and

$$J^2 = \tfrac{1}{2}(J_+J_- + J_-J_+) + J_z^2.$$

Also, the norm of the vectors $J_+|kjm>$ and $J_-|kjm>$ is ≥ 0.

Therefore,

$$\|J_+|k,j,m>\|^2 = <k,j,m|J_+^T J_+|k,j,m> = <k,j,m|J_-J_+|k,j,m> \geq 0,$$ and

$$\|J_-|k,j,m>\|^2 = \langle k,j,m|J_-^T J_-|k,j,m\rangle = \langle k,j,m|J_+J_-|k,j,m\rangle \geq 0.$$

But we also do have:

$$\langle k,j,m|J_-J_+|k,j,m\rangle = \langle k,,jm|J^2 - J_z^2 - \hbar J_z|k,j,m\rangle = j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2$$

And

$$\langle k,j,m|J_+J_-|k,j,m\rangle = \langle k,j,m|J^2 - J_z^2 + \hbar J_z|k,j,m\rangle = j(j+1)\hbar^2 - m^2\hbar^2 + m\hbar^2.$$

Therefore we have

$$j(j+1) - m(m+1) \geq 0 \quad \text{or} \quad (j-m)(j+m+1) \geq 0 \quad \text{or} \quad -(j+1) \leq m \leq j$$

And

$$j(j+1) - m(m-1) \geq 0 \quad \text{or} \quad (j+m)(j-m+1) \geq 0 \quad \text{or} \quad -j \leq m \leq j+1.$$

To simultaneously satisfy both conditions we need $\underline{-j \leq m \leq j}$.

If m=-j then $J_-|k, j, -j> = 0$.

$$\|J_-|k,j,m>\|^2 = \hbar^2\big(j(j+1) - m(m-1)\big), \quad \|J_-|k,j,-j>\|^2 = \hbar^2\big(j(j+1) + j(-j-1)\big) = 0$$

When we find out the norm of a null vector, we get only zero as a result every time.

If $m \neq -j$ then $||J_-|k,j,m>||^2 \neq 0$ and $J_-|k,j,m>$ is a non-zero vector.

$J^2J_-|k,j,m> = J_-J^2|k,j,m> = j(j+1)\hbar^2J_-|k,j,m>$. $J_-|k,j,m>$

Is an eigenvector of J^2 with eigenvalue $j(j+1)\hbar^2$.

$J_zJ_-|k,j,m> = J_-J_z|k,j,m> - \hbar J_-|k,j,m> = (m-1)\hbar J_-|k,j,m>$. $J_-|k,j,m>$

Is eigenvector of J_z with eigenvalue $(m-1)\hbar$. So, then $J_-|k,j,m> \propto |k,j,(m-1)>$.

If m=j then J_+|k, j,-j>=0.

$||J_+|k,j,m>||^2 = \hbar^2\Big(j(j+1)-m(m+1)\Big)$, $||J_+|k,j,j>||^2 = \hbar^2\Big(j(j+1)-j(j+1)\Big) = 0$.

So as we find out the norm of a null vector, we get only zero as a result every time.

If $m \neq j$ then $||J_+|k,j,m>||^2 \neq 0$ and $J_+|k,j,m>$ is a non-zero vector.

$J^2J_+|k,j,m> = J_+J^2|k,j,m> = j(j+1)\hbar^2J_+|k,j,m>$. $J_+|k,j,m>$ is an eigenvector of J^2 with eigenvalue $j(j+1)\hbar^2$.

$J_zJ_+|k,j,m> = J_+J_z|k,j,m> + \hbar J_+|k,j,m> = (m+1)\hbar J_+|k,j,m>$. $J_+|k,j,m>$ is an eigenvector of J_z with eigenvalue $(m+1)\hbar$. So, $J_+|k,j,m> \propto |k,j,(m+1)>$.

The eigenvalues of J^2 are $j(j+1)\hbar^2$, where j is a non-negative integer divided by 2.

After we considered the |k, j, m> as a non-zero eigenvector of J^2 and J_z. $J_-|k,j,m> \propto |k,j,(m-1)>$, then $J_-^p|k,j,m> \propto |k,j,(m-p)>$ if $m-p \geq -j$. If $m-p \geq -j$ but $m-p-1 < -j$ then

$J_-|k,j,m-p>$ This has to be zero, since an eigenstate with the value of m' = (m-p-1) < -j is not allowed, except of cases:

$J_-|k,j,m-p>$ is only zero if m-p = -j.

Similarly, $J_+^p|k,j,m> \propto |k,j,(m+q)>$ if $m+q \leq j$. If $m+q \leq j$ but $m+q+1 > j$ then

$J_+|k,j,m+q>$ Must then be zero, since an eigenstate with m' = m+q+1 > j is not allowed. But $J_+|k,j,m+q>$ is only zero if m + q= j. We therefore have m + q - m + p=2j and j= (q +p)/2;

Where j is a non-negative integer divided by two.

The conclusion that can be drawn from the above discussion is that let us assume that J be an arbitrary angular momentum operator, obeying the commutation relations $[J_i, J_j] = \varepsilon_{ijk} i\hbar J_k$. If $j(j+1)\hbar^2$ defines the eigenvalues of the operator J^2 and $m\frac{h}{2\pi}$ defines the eigenvalues of the operator J_z, after that:

The non-negative half integers are the only possible values for the j and they are $(0, \frac{1}{2}, 1\,\frac{3}{2}, 2, \cdots)$.

For the fixed j, the only possible values of the m will be the **(2j+1)** $(-j, -j+1, -j+2, \cdots j-1, j)$, where m will be an integer whenever the j will be an integer, and m will be a half integer whenever the j be of half integral value.

NOTES

3.6.2 Clebsch Gordan Coefficients

Firstly, we will define it. In the quantum mechanics, the **Clebsch–Gordan** (**CG**) **coefficients** are those numbers that comes to the notice when we talk about coupling of the angular momentum. They appear to us as the expansion coefficients of the total angular momentum eigenstates in an uncoupled basis of tensor product. More in the terms of being mathematical, the CG coefficients are extensively used in compact Lie groups, to be able to do the explicit direct sum decomposition of the multiplication of tensors, i.e., tensor product of the two representations which cannot be reduced. This name found its origin from those of the German mathematicians whose names are Alfred Clebsch and Paul Gordan.

So, we already studied that the combinations of the two spin ½ particles can carry in total a spin of 0 or 1. Also, if we are given spins and and we are said to combine spin with, then the total spins that we get, is given by the following:

$$S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2) \ldots |s_1 + s_2|$$

We also know that the highest total spin forms when the individual spins are aligned parallel to each other and the lowest total spin forms when the individual spins(of the electron and the proton) are aligned anti parallel. If we take an example, if we put together a particle of spin 2 with a particle of spin 3/2, then we will get a total spin of 5/2, 7/2, 1/2 or 3/2 depending on the configuration. Now, if we take the example of hydrogen atom, suppose it is in the state, then the net angular momentum is l+1/2 or l-1/2, if we also consider the spin of the proton, then the total quantum number of the angular momentum of the atom is l+1 or l-1

So, if we combine the state, the combined state will be |s, m> with the total spin as s and the z-component will be m and they will be the linear combination of the state |s1, m1> |s2, m2>:

Therefore, the combined state is written as:

$$|s, m\rangle = \sum_{m1+m2=m} C^{s1s2s}_{m1m2m} \; |s1\ m1\rangle\, |s2\ m2\rangle$$

Here, the constants C^{s1s2s}_{m1m2m} are known as the Clebsch-Gordan Coefficients.

$|3, 0\rangle = \frac{1}{\sqrt{5}}\, |2, 1\rangle|1, -1\rangle + \frac{\sqrt{3}}{\sqrt{5}}\, |2, 0\rangle|1, 0\rangle + \frac{1}{\sqrt{5}}\, |2, -1\rangle|1, 1\rangle$ is also another example for the illustration of the Clebsch-Gordan coefficients.

3.6.3 Two Nucleon System and the Application to the Two Nucleon System

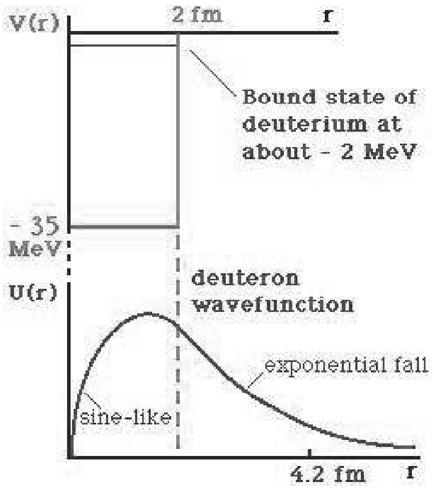
Protons and neutrons are said to be the bound states of the lowest energy of the quarks and the gluons. When we try to put two or more of these protons and neutrons all together, they interact, scatter and they form the bound states because of the strong interactions. If we want to invest our time in the low-energy region. This is the place where the nucleons generally do not get excited internally, we can say that those nucleons are inert, structure less fundamental particles, and by studying the nucleon-nucleon interactions we can realize many of the properties of the multi-nucleon systems. The interaction of the non-relativistic nucleons can be described with the help of a potential. QCD is the fundamental theory which describes the interaction of nucleon-nucleon. The interactions can be calculated from the physics of that of quarks and gluons. Nonetheless, this problem is not easy to deal with and less amount of progress is done from the 1st principles so far. Therefore, we are going to take the pretty good approach which is as follows: Firstly, we have to extract the interaction of the nucleon-nucleon from scattering data of the nucleon-nucleon or some of the properties of the nucleon, and after that we will try to make the predictions further for the nuclear many-body system by making the use of these interactions. In order to proceed in the discussions of the nuclear forces firstly we have to make a point of all the differences between the electrons in the atoms and the nucleons in the nuclei.

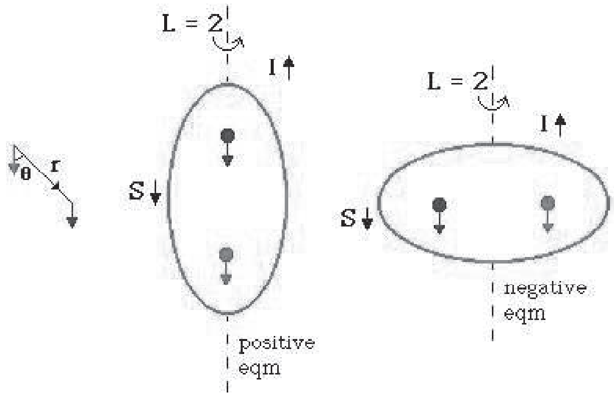
The deuteron properties, neutron-proton and the proton-proton scattering can be studied to know about the two nucleon system which can further be studied for the many body systems too:

The deuteron:

Properties:

Constituents	**1 proton 1 neutron**
Mass	**2.014732 u**
Binding energy	**2.224589 +/- 0.000002 MeV**
Angular momentum	**1 (h-bar)**
Magnetic moment	**0.85741 +/- 0.00002 nuclear magnetons**
Electric quadruple moment	**+2.88 x 10^{-3} barn**
RMS separation	**4.2 fm**

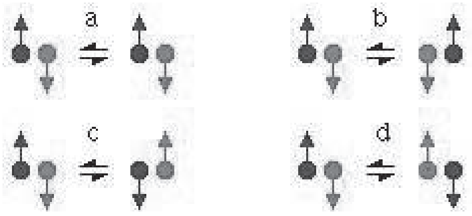




The above figure shows us the two nucleon system configuration.

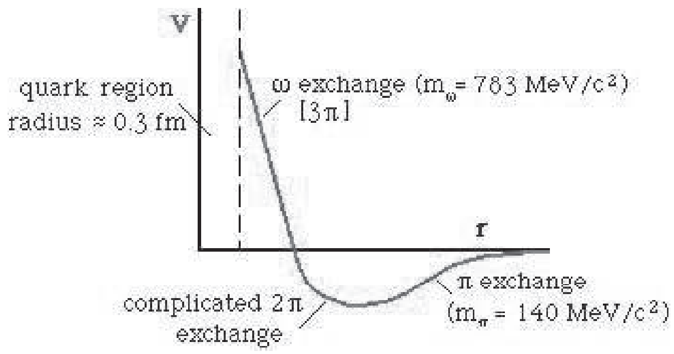
An isospin singlet is an example of the two nucleon system (**T = 0**) or the triplet (**T = 1**).

isospin triplet	isospin singlet
(combines with parallel normal spin only)	(combines with antiparallel normal spin only)
T = 1	**T = 0**
$T_3 = 1$ (pp)	
$T_3 = 0$ (pn + np)	**$T_3 = 0$ (pn - np)**
$T_3 = -1$ (nn)	



Here the red arrows denote the protons and the blue arrows show us the neutrons and their spin states are indicated by the arrows that are stacked to them.

In the graph below, we have shown a rough sketch of the nucleon-nucleon potential which shows some kind of the particles that exchange and which of them are supposed to take contribution:



NOTES

Check Your Progress

8. What do you understand the conservation law in quantum mechanics?
9. Define the spin 1/2.
10. What is Pauli matrix?
11. What do you understand by spin field?
12. Define the Clebsch–Gordan (CG) coefficients.

3.7 ANSWER TO CHECK YOUR PROGRESS

1. The eigenvalues of angular momentum states in quantum mechanics, we can solve the Hamiltonian and get the allowed energy levels of an object with angular momentum. The eigenvalues of the angular momentum are the possible values the angular momentum.
2. The two different eigenvectors associated with the same eigenvalue a, which is incompatible with the hypothesis that is a non-degenerate eigenvalue.
3. The solutions of the algebraic equation $(j-m)(j+m+1)=0$ are $m=j$ and $m=-j-1<-j$.
4. In classical aspect, 'Angular Momentum' is the rotational equivalent of linear momentum, thus used in systems involving rotational motion. We can denote it by the letter L in the general cases.
5. Spherical harmonics are defined as the Eigen functions of the operator of the orbital angular momentum. They play a really important role in 'Quantum Mechanics' and play a central role in the theory of orbital angular momentum. They are used in many problems but most importantly, spherical harmonics are used in the hydrogen atom problem.
6. The spectra of $\hat{L}^2$ and $\widehat{L_z}$ has been discussed with the help of the spherical coordinates which again proved the importance of writing the orbital angular momentum equations in spherical coordinates.
7. Eigen function of angular momentum allows us to describe the states that correspond to the fixed quantized eigenvalues of the angular momentum.
8. Conservation laws in quantum mechanics tell us that if a quantity does not explicitly depend on time and it commutes with H, then it is a conserved quantity.
9. In quantum mechanics, spin is an intrinsic property of all 'Elementary Particles'. All known *fermions*, the particles that constitute ordinary matter, have a spin of 1/2. The spin number describes how many symmetrical facets a particle has in one full rotation; a spin of ½ it means that the particle must be rotated by two full turns (through 720°) before it has the same configuration as when it started.

10. The quantum-mechanical spin operators can be represented as simple 2 × 2 matrices. These matrices are called the Pauli matrices.

11. Spin field may refer to: Spinor field, assignment of a spinor to every point in space, used in quantum mechanics and quantum field theory. A kind of Torsion field, used in pseudophysics. In differential geometry, given a spin structure on an n-dimensional orientable Riemannian manifold (M , g), a section of the spinor bundle S is called a **spinor field**. A spinor bundle is the complex vector bundle $\pi_s: \mathbf{S} \rightarrow \mathrm{M}$.

12. In the quantum mechanics, the Clebsch–Gordan (CG) coefficients are those numbers that comes to the notice when we talk about coupling of the angular momentum. They appear to us as the expansion coefficients of the total angular momentum eigenstates in an uncoupled basis of tensor product.

3.8 SUMMARY

- The eigenvalues of angular momentum states in quantum mechanics, we can solve the Hamiltonian and get the allowed energy levels of an object with angular momentum. The eigenvalues of the angular momentum are the possible values the angular momentum.
- The presupposition that the eigenvalue is non-degenerate cannot be valid for all eigenvalues of the operator $\hat{A}$. This means that $\hat{A}$ has at least one degenerate eigenvalue.
- The language of group theory, the set of the three Hermitian operators $\hat{j}_x$, $\hat{j}_y$ and $\hat{j}_z$. Since the $\hat{j}^2$ is compatible with $\hat{j}_x$, $\hat{j}_y$ and $\hat{j}_z$, but $\hat{j}_x$, $\hat{j}_y$ and $\hat{j}_z$, are reciprocally incompatible, we expect the eigenvalue $j(j+1)h^2$ to be degenerate.
- It is important to understand that these are the only possible vectors with these properties, because the pair (j, m) uniquely identify (up to an irrelevant multiplicative numerical constant) the eigenvector $|j, m\rangle$.
- $j(j+1)\hbar^2$ and $m\hbar$ be the eigenvalues of $\hat{j}^2$ and $\hat{j}_z$ associated with the eigenvector $|j, m\rangle$
- It is important to understand that these are the only possible vectors with these properties, because the pair (j, m) uniquely identify (up to an irrelevant multiplicative numerical constant) the eigenvector $|j, m\rangle$.
- In the quantum mechanics, there is an analogous representation for it, which is the 'Orbital Angular Momentum'.
- Therefore, after calculating the commutator bracket of the angular momentum, we find that it does not come out to be zero. This can be represented as

follows. For that we need the Laplacian operator in spherical coordinates and can further proceed.

- Angular momentum operators depend only on angular coordinates so any radial component f(r) will commute with L.
- The spherical harmonics have been discussed which plays an important role in hydrogen atom. It has been noticed that there is degeneracy of energy associated with the hydrogen atom which can be explained by discussing the angular momentum operators and their degeneracy.
- The hydrogen atom as its spherical harmonics are derived from the angular momentum operators which are the operators for the rotation phenomenon in quantum mechanics.
- The motion of the electron that is around the nucleus, the electron has another type of angular momentum which does nothing with the motion in space but it is analogous to the classical spin but electron is without any structure and a point particle, so we say that electron has intrinsic angular momentum (S) and extrinsic angular momentum (L).
- Every particle has its own value of s, for pi meson the value of s is 0 and here the particle of concern is electron, and the spin of the electron is s=1/2, i.e., electron is a spin-half particle.
- Particles having net spin 1/2 include the proton, neutron, electron, neutrino, and quarks. The dynamics of spin- objects cannot be accurately described using classical physics; they are among the simplest systems which require quantum mechanics to describe them.
- Spin-1/2 objects are all fermions (a fact explained by the spin–statistics theorem) and satisfy the Pauli exclusion principle. Spin- particles can have a permanent magnetic moment along the direction of their spin, and this magnetic moment gives rise to electromagnetic interactions that depend on the spin.
- A spin-1/2 particle is characterized by an angular momentum quantum number for spin s of 1/2.
- The value of the same type of the particle's spin is fixed. By definition, electrons have a spin equal to 1/2. Other particles may have the spins of 3/2, 2, 0 or even 1. Also the value of a particle's spin decides the directions of the spin which we can measure actually.
- Vector field as we know in vector calculus and physics, a vector field is to assign a vector to each point in a subset of space.
- The highest total spin forms when the individual spins are aligned parallel to each other and the lowest total spin forms when the individual spins(of the electron and the proton) are aligned anti parallel.

- Protons and neutrons are said to be the bound states of the lowest energy of the quarks and the gluons. When we try to put two or more of these protons and neutrons all together, they interact, scatter and they form the bound states because of the strong interactions.

3.9 KEY TERMS

- **Non-degenerate eigenvalue:** The two different eigenvectors associated with the same eigenvalue a, which is incompatible with the hypothesis that is a non-degenerate eigenvalue.
- **Spherical harmonics:** Spherical harmonics are defined as the Eigen functions of the operator of the orbital angular momentum. They play a really important role in 'Quantum Mechanics' and play a central role in the theory of orbital angular momentum. They are used in many problems but most importantly, spherical harmonics are used in the hydrogen atom problem.
- **Spin:** The spin number describes how many symmetrical facets a particle has in one full rotation; a spin of ½ it means that the particle must be rotated by two full turns (through 720°) before it has the same configuration as when it started.
- **Pauli matrices:** The quantum-mechanical spin operators can be represented as simple 2 × 2 matrices. These matrices are called the Pauli matrices.
- **Clebsch–Gordan (CG) coefficients:** In the quantum mechanics, the Clebsch–Gordan (CG) coefficients are those numbers that comes to the notice when we talk about coupling of the angular momentum.

3.10 SELF-ASSESMENT QUESTIONS AND EXCERCISES

Short-Answer Questions

1. What do you understand by eigenvalue of angular momentum?
2. Give the properties of J^2 and J_z.
3. Define the spherical harmonic in quantum mechanics.
4. What is electron spin?
5. Define the spin field.
6. What is Clebsch–Gordan (CG) coefficients?
7. Give the applications of two nucleon system.

Long-Answer Questions

1. State and prove the eigenvalue and eigenvector of angular momentum.
2. Illustrate the spectrum of J^2 and J_z.
3. Explain in detail about the angular momentum and rotation operator.

4. Discuss about the electron spin and spin ½ with appropriate examples.
5. Analyse the spin independent interaction of an atom.
6. Describe the spin independent nucleon -nucleon interaction and giving applications.

3.11 FURTHER READING

Rajasekar, S. and R. Velusamy. 2014. *Quantum Mechanics I: The Fundamentals*, 1st Edition. United States: CRC Press.

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Mathews, P. M. and K. Venkatesan. 1978. *A Textbook of Quantum Mechanics*. New Delhi: Tata McGraw-Hill.

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UNIT 4 SCATTERING THEORY

NOTES

Structure

4.0 INTRODUCTION

In mathematics and physics, scattering theory is a framework for studying and understanding the scattering of waves and particles. In physics, the cross section is a measure of the probability that a specific process will take place when some kind of radiant excitation intersects a localized phenomenon. Standing wave, also called stationary wave, combination of two waves moving in opposite directions, each having the same amplitude and frequency. A wave packet refers to the case where two (or more) waves exist simultaneously. The centre of mass is a position defined relative to an object or system of objects.

They are the systems that have a central potential, i.e., a potential energy that depends only on the distance r from the origin: V (r) = V (r). Partial-wave analysis, in the context of quantum mechanics, refers to a technique for solving scattering problems by decomposing each wave into its constituent angular-momentum components and solving using boundary conditions. With the method of partial waves the scattering amplitudes are then obtained from the phase shifts for spherically symmetric potentials. The impact parameter perpendicular distance from the original centre of a set of scattering particles to the original line of motion of a particle being scattered.

Elastic scattering of a particle by an atomic nucleus at an energy of the incident particle for which the scattering cross-section is large compared with that for adjacent values of the energy; also called resonant scattering. The finite potential well (also known as the finite square well) is a concept from quantum mechanics. It is an extension of the infinite potential well, in which a particle is confined to a 'Box', but one which has finite potential 'Walls'. Metastable state, in physics and chemistry, particular excited state of an atom, nucleus, or other system that has a longer lifetime than the ordinary excited states and that generally has a shorter lifetime than the lowest, often stable, energy state, called the ground state.

Generally in scattering theory and in particular in quantum mechanics, the Born approximation consists of taking the incident field in place of the total field as the driving field at each point in the scatterer. Effective range may describe a distance between two points where one point is subject to an energy release at the other point. The Bethe formula or Bethe-Bloch formula describes the mean energy loss per distance travelled of swift charged particles (protons, alpha particles, atomic ions) traversing matter (or alternatively the stopping power of the material).

In this unit, you will study about the scattering theory, cross section, stationary wave, wave packet, laboratory system and centre of mass, scattering by central potential, partial wave analysis and phase shift method, impact parameter, relation between phase shift and logarithmic derivatives, behaviour of phase shift at low energies scattering by hard sphere, scattering resonance, scattering by deep square well, metastable state, integral representation of phase shift, dependence upon potential, sign of phase shift, Born approximation, effective range theory, Bethe formula.

4.1 OBJECTIVES

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

- Explain the scattering theory
- Describe the laboratory system and centre of mass
- Discuss the scattering by central potential
- Explain the partial wave analysis and phase shift method
- Explain the impact parameter
- Describe the relation between phase shift and logarithmic derivatives
- Discuss the behaviour of phase shift at low energies scattering by hard sphere
- Elaborate on the scattering resonance and scattering by deep square well
- Analyse the Born approximation
- State the effective range theory and Bethe formula

4.2 AN INTRODUCTION TO SCATTERING THEORY

The 'Scattering Theory' is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics. Typically the wave scattering corresponds to the collision and scattering of a wave with some material object, for example formation of rainbow is resultant of sunlight scattered by rain drops. Latest technology of ultrasonic testing is another example of scattering theory which is used in medical imaging, non-destructive testing of metals and quantum field theory.

Rayleigh scattering is one commonly known type of scattering which mainly consists of scattering from atmospheric gases, it occurs when the particles causing scattering are smaller in size than the radiation wavelengths in contact with them.

Mie scattering, and non-selective scattering are the two other types of wave scattering. Principally, the Mie scattering is considered to be elastic scattered light of particles that have a diameter similar to or larger than the wavelength of the incident light. The Mie signal is proportional to the square of the particle diameter, where as in case of non-selective scattering also known as Raman scattering, it occurs in all wavelengths of electromagnetic radiation equally in the atmosphere and is usually caused by particles which are much larger than the energy wavelengths.

Definitions of Scattering

1. Scattering, in physics, is defined as a change in the direction of motion of a particle because of a collision with another particle. As defined in physics, a collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.
2. Scattering occurs when light or other energy waves pass through an imperfect medium, such as air filled with particles of some sort, and are deflected from a straight path. The light is deflected off of its straight path and scatters in many directions.
3. Scattering is a general physical process where some forms of radiation, such as light, sound, or moving particles, are forced to deviate from a straight trajectory by one or more paths due to localized non-uniformities in the medium through which they pass.
4. As per the Encyclopaedia Britannica, the 'Scattering, in physics, a change in the direction of motion of a particle because of a collision with another particle. A collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.

The physicist Ernest Rutherford passed a stream of alpha particles through a thin sheet of gold foil. The alpha particles were emitted by a radioactive material and had enough energy to penetrate an atom; although most passed right through the gold foil, some were deflected in a way that indicated that the scattering was produced by a Coulomb force. Because the alpha particles are positively charged and the electrons in the atom are negatively charged, it followed that there must be a large positive charge inside the atom to create the Coulomb force by interacting with the alpha particles. In this way the nucleus of the atom was discovered.

Elastic and Inelastic Scattering

The term 'Elastic Scattering' implies that the internal states of the scattering particles do not change, and hence they emerge unchanged from the scattering process. In inelastic scattering, by contrast, the particles' internal state is changed, which may amount to exciting some of the electrons of a scattering atom, or the complete annihilation of a scattering particle and the creation of entirely new particles.

When two atoms are scattered off one another, one can understand them as being the bound state solutions of some differential equation. Thus, for example, the hydrogen atom corresponds to a solution to the Schrödinger equation with a negative inverse-power, i.e., attractive Coulombic, central potential. The scattering of two hydrogen atoms will disturb the state of each atom, resulting in one or both becoming excited, or even ionized, representing an inelastic scattering process.

4.2.1 Rayleigh Scattering

Rayleigh scattering is named after the nineteenth-century British physicist Lord Rayleigh (John William Strutt). It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process. The particles may be individual atoms or molecules. It can occur when light travels through transparent solids and liquids, and is most prominently seen in gases. Rayleigh scattering results from the electric polarizability of the particles. The oscillating electric field of a light wave acts on the charges within a particle, causing them to move at the same frequency. The particle therefore becomes a small radiating dipole whose radiation we see as scattered light. This radiation is an integral part of the photon and no excitation or de-excitation occurs.

Rayleigh scattering of sunlight in Earth's atmosphere causes diffuse sky radiation, which is the reason for the blue colour of the daytime and twilight sky, as well as the yellowish to reddish hue of the low Sun.

For wave frequencies that are below the resonance frequency of the scattering particle (normal dispersion regime), the amount of scattering is inversely proportional to the fourth power of the wavelength.

Rayleigh scattering of molecular nitrogen and oxygen in the atmosphere includes elastic scattering as well as the inelastic contribution from rotational Raman scattering in air, since the changes in wavenumber of the scattered photon are typically smaller than 50 cm^{-1}. This can lead to changes in the rotational state of the molecules. Furthermore, the inelastic contribution has the same wavelengths dependency as the elastic part.

Scattering by particles similar to, or larger than, the wavelength of light is typically treated by the Mie scattering theory, the discrete dipole approximation and other computational techniques. Rayleigh scattering applies to particles that are small with respect to wavelengths of light, and that are optically 'soft' (i.e., with a refractive index close to 1).

In 1871, Lord Rayleigh published two papers on the colour and polarization of skylight to quantify Tyndall's effect in water droplets in terms of the tiny particulates' volumes and refractive indices. In 1881 with the help of James Clerk Maxwell's 1865 proof of the electromagnetic nature of light, he exhibited that his equations followed from electromagnetism.

NOTES

Small Size Parameter Approximation

The size of a scattering particle is often parameterized by the ratio,

$$x = \frac{2\pi r}{\lambda}$$

Where r is its characteristic length (radius) and λ is the wavelength of the light. The amplitude of light scattered from within any transparent dielectric is proportional to the inverse square of its wavelength and to the volume of material that is to the cube of its characteristic length. The wavelength dependence is characteristic of dipole scattering and the volume dependence will apply to any scattering mechanism. Objects with $x >> 1$ act as geometric shapes, scattering light according to their projected area. At the intermediate $x \simeq 1$ of Mie scattering, interference effects develop through phase variations over the object's surface. Rayleigh scattering applies to the case when the scattering particle is very small, i.e., $x << 1$, with a particle size < 1 /10 wavelength, and the whole surface re-radiates with the same phase. Because the particles are randomly positioned, the scattered light arrives at a particular point with a random collection of phases; it is incoherent and the resulting intensity is just the sum of the squares of the amplitudes from each particle and therefore proportional to the inverse fourth power of the wavelength and the sixth power of its size.

In detail, the intensity I of light scattered by any one of the small spheres of diameter d and refractive index n from a beam of unpolarized light of wavelength » and intensity I_0 is given by,

$$I = I_0 \frac{1+\cos^2\theta}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

Where R is the distance to the particle and θ is the scattering angle. Averaging this over all angles gives the Rayleigh scattering cross-section,

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2$$

The fraction of light scattered by a group of scattering particles is the number of particles per unit volume N times the cross-section. For example, the major constituent of the atmosphere, nitrogen, has a Rayleigh cross section of 5.1×10^{-31} m^2 at a wavelength of 532 nm (green light). This means that at atmospheric pressure, where there are about 2×10^{25} molecules per cubic meter, about a fraction 10^{-5} of the light will be scattered for every meter of travel.

The strong wavelength dependence of the scattering ($\sim\lambda^{-4}$) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths.

From Molecules

The above expression can also be written in terms of individual molecules by expressing the dependence on refractive index in terms of the molecular polarizability 'α', proportional to the dipole moment induced by the electric field of the light. In this case, the Rayleigh scattering intensity for a single particle is given in CGS units by,

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2}(1 + \cos^2 \theta).$$

The Rayleigh scattering gives the atmosphere its blue colour as shown in Figure (4.1).

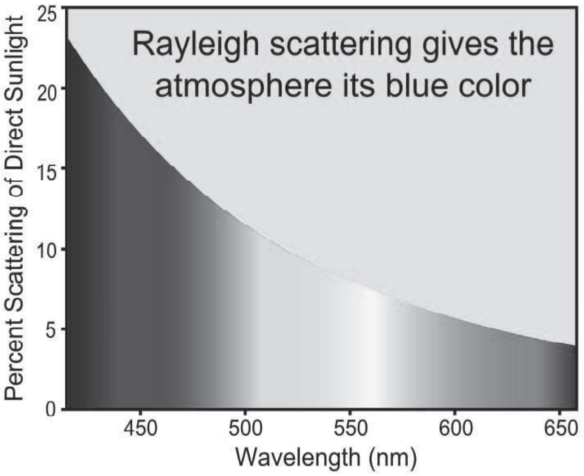

Fig. 4.1 *Blue Light Scattered by the Atmosphere Relative to Red Light*

The Rayleigh scattering is mostly seen occurring in nature, and therefore it is considered to be one of the most commonly observed optical phenomena. Foremost example for this phenomena is that the sky looks blue because of the intensity of light scattered by a molecule is inversely proportional to the fourth power of the wavelength of the incident light, which means that 10 times more blue light than red light gets scattered from a molecule. As such, sunlight incident on gas molecules in the air gets scattered as blue light in every direction, and the sky looks blue. Therefore, the Rayleigh scattering is the elastic scattering of light by particles which are much smaller than the wavelength of the light.

Figure (4.1) illustrates the greater proportion of blue light scattered by the atmosphere relative to red light. This phenomena occurs when radiation or beam of light interacts with molecules and particles in the atmosphere which happen to be smaller in diameter than the wavelength of the incoming radiation. Shorter wavelengths are more quickly and promptly scattered than the longer wavelengths. Light at shorter wavelengths (blue and violet) are scattered by small particles that include NO_2 and O_2. Since blue light is at the short wavelength end of the visible spectrum, it is more strongly scattered in the atmosphere than longer wavelength red light. This results in the blue colour of the sky. Rayleigh scatter is also responsible for haze in the photographic images. In aerial photography special filters are used to filter out the scatter blue light to reduce haze. In digital images there are different techniques used to minimize the impacts of Rayleigh scatter.

Effect of Fluctuations

When the dielectric constant $\in$ of a certain region of volume V is different from the average dielectric constant of the medium $\overline{\in}$, then any incident light will be scattered according to the following equation,

$$I = I_0 \frac{\pi^2 V^2 \sigma_\epsilon^2}{2\lambda^4 R^2}\left(1 + \cos^2\theta\right)$$

Where σ_ϵ^2 represents the variance of the fluctuation in the dielectric constant $\in$.

Rayleigh Scattering Theory

Rayleigh scattering theory refers to the scattering of light off of the molecules of the air, and can be extended to scattering from particles up to about a tenth of the wavelength of the light. It is Rayleigh scattering off the molecules of the air which gives us the blue sky. Lord Rayleigh calculated the scattered intensity from dipole scatterers much smaller than the wavelength to be:

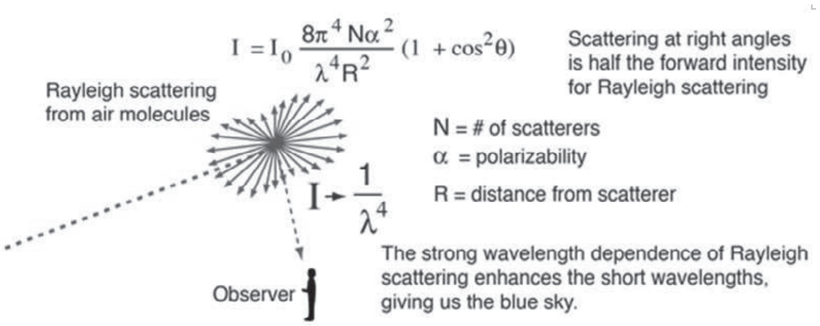

Fig. 4.2 *Rayleigh Scattering Theory*

Figure (4.2) illustrates Rayleigh scattering theory considering an air molecule. The Rayleigh scattering can be considered to be elastic scattering since the photon energies of the scattered photons is not changed. Scattering in which the scattered photons have either a higher or lower photon energy is called **Raman scattering.** Usually this kind of scattering involves exciting some vibrational mode of the molecules, giving a lower scattered photon energy, or scattering off an excited vibrational state of a molecule which adds its vibrational energy to the incident photon.

Advantages of Rayleigh Scattering

- It is an easy technique.
- Arbitrary laser wavelength can be used, but shorter wavelengths leads to stronger signal (the λ^{-4}-dependence).
- Signal is proportional to number concentration → N and/or 1/T.

- Signal is proportional to laser pulse energy, i.e., no quenching or saturation effects.

Limitations of Rayleigh Scattering

- The technique is not species selective, since all atoms/molecules/particles scatter at the same wavelength.
- For accurate thermometry, the Rayleigh cross-sections for individual species must be taken into account, since the mole fraction distribution must be known in every point.
- It is an incoherent technique.
- Stray light from particles, optics and surfaces can interfere with the Rayleigh signal.

4.2.2 Raman Scattering

Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect.

When photons are scattered by a material, most of them are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency and wavelength) as the incident photons but different direction. However, a small fraction of the scattered photons (approximately 1 in 10 million) are scattered in-elastically, with the scattered photons having an energy different from, and usually lower than, those of the incident photons—these are Raman scattered photons. Because of conservation of energy, the material either gains or loses energy in the process. Typically this is vibrational energy and the incident photons are of visible light, although rotational energy (if gas samples are used) and electronic energy levels (if an X-ray source is used) may also be investigated. The Raman effect forms the basis for Raman spectroscopy which is used by chemists and physicists to gain information about materials.

It is also possible to observe molecular vibrations by an inelastic scattering process. In the inelastic (Raman) scattering, an absorbed photon is re-emitted with lower energy; the difference in energy between the incident photons and scattered photons corresponds to the energy required to excite a molecule to a higher vibrational mode.

Typically, in Raman spectroscopy high intensity laser radiation with wavelengths in either the visible or near-infrared regions of the spectrum is passed through a sample. Photons from the laser beam produce an oscillating polarization in the molecules, exciting them to a virtual energy state. The oscillating polarization of the molecule can couple with other possible polarizations of the molecule, including vibrational and electronic excitations. If the polarization in the molecule does not couple to these other possible polarizations, then it will not change the vibrational state that the molecule started in and the scattered photon will have the same energy as the original photon. This type of scattering is known as Rayleigh scattering.

When the polarization in the molecules couples to a vibrational state that is higher in energy than the state they started in, then the original photon and the scattered photon differ in energy by the amount required to vibrationally excite the molecule. In perturbation theory, the Raman effect corresponds to the absorption and subsequent emission of a photon via an intermediate quantum state of a material. The intermediate state can be either a ‘Real’, i.e., stationary state, or a virtual state.

Stokes and Anti-Stokes

The Raman interaction leads to following two possible outcomes:

1. The material absorbs energy and the emitted photon has a lower energy than the incident photon. This outcome is labeled Stokes Raman scattering in honour of George Stokes who showed in 1852 that fluorescence is due to light emission at longer wavelength, now known to correspond to lower energy, than the absorbed incident light.
2. The material loses energy and the emitted photon has a higher energy than the absorbed photon. This outcome is labeled anti-Stokes Raman scattering.

The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the material and is independent of the absolute energy of the photon.

The spectrum of the scattered photons is termed the Raman spectrum. It shows the intensity of the scattered light as a function of its frequency difference ”½ to the incident photons. The locations of corresponding Stokes and anti-Stokes peaks form a symmetric pattern around $\Delta v = 0$.

The frequency shifts are symmetric because they correspond to the energy difference between the same upper and lower resonant states. The intensities of the pairs of features will typically differ, though. They depend on the populations of the initial states of the material, which in turn depend on the temperature. In thermodynamic equilibrium, the lower state will be more populated than the upper state. Therefore, the rate of transitions from the more populated lower state to the upper state, the ‘Stokes Transitions’ will be higher than in the opposite direction, the ‘Anti-Stokes Transitions’. Correspondingly, Stokes scattering peaks are stronger than anti-Stokes scattering peaks. Their ratio depends on the temperature, and can therefore be exploited to measure it.

Raman Spectroscopy

Raman spectroscopy is named after Indian physicist Sir C. V. Raman. It is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. Figure 4.3 illustrates the Energy-level diagram showing the states involved in Raman spectra.

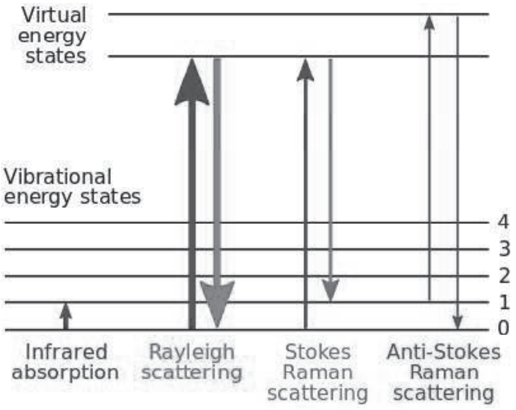

Fig. 4.3 *Energy-Level Diagram Showing the States Involved in Raman Spectra*

Raman spectroscopy relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Distinction from Fluorescence

The Raman effect differs from the process of fluorescence in that it is a scattering process. For fluorescence, the incident light is completely absorbed, transferring the system to an excited state. After a certain resonance lifetime, the system de-excites to lower energy states via emission of photons. The result of both processes is in essence the same.

A photon with a frequency different from that of the incident photon is produced and the molecule is brought to a higher or lower energy level. But the major difference is that the Raman effect can take place for any frequency of incident light. In contrast to the fluorescence effect, the Raman effect is therefore not a resonant effect. In practice, this means that a fluorescence peak is anchored at a specific frequency, whereas a Raman peak maintains a constant separation from the excitation frequency.

Selection Rules

A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different. For a vibration, this means that the derivative of the polarizability with respect to the normal coordinate associated to the vibration is non-zero:

$$\frac{\partial \alpha}{\partial Q} \neq 0.$$

In general, a normal mode is Raman active if it transforms with the same symmetry of the quadratic forms, $(x^2, y^2, z^2, xy, xz, yz)$, which can be verified from the character table of the molecule's symmetry group.

The specific selection rules state that the allowed rotational transitions are $\Delta J = \pm 2$, where '*J*' is the rotational state.

The allowed vibrational transitions are $\Delta \nu = \pm 1$, where 'u' is the vibrational state.

Advantages of Raman Effect

- Organic and inorganic materials are suitable for Raman analysis. These can be solids, liquids, polymers or vapours.
- No sample preparation is required.
- It is not interfered by water.
- It is a non-destructive application.
- It is highly specific like a chemical fingerprint of a material.
- Raman spectra are acquired quickly within seconds.
- Samples can be analyzed through glass or a polymer packaging.
- Laser light and Raman scattered light can be transmitted by optical fibers over long distances for remote analysis.
- In Raman spectroscopy, the region from 4000 cm^{-1} to 50 cm^{-1} can be covered by a single recording.
- Raman spectra can be collected from a very small volume (< 1 ¼m in diameter).
- Inorganic materials are easily analysable with Raman spectroscopy.

Disadvantages of Raman Effect

- This cannot be used for metals or alloys.
- Raman effect is very weak. The detection needs a sensitive and highly optimized instrumentation.
- Fluorescence of impurities or of the sample itself can hide the Raman spectrum. Some compounds fluoresce when irradiated by the laser beam.
- Sample heating through the intense laser radiation can destroy the sample or cover the Raman spectrum.

4.3 DEFINITION AND CALCULATION OF CROSS SECTION

Let us consider a beam of particles having a mass m and it is travelling along the z direction with velocity v. A target has a potential V centred at the origin. The travelling beam experience a force only when they are in the range of potential V. When the beam of particles interact with the scattering potential, the incident beam of particles get scattered in all the directions. After leaving the target again they travel in a straight line. The angle is measured between incident and the scattered lines and it is known as scattering angle θ (Refer Figure 4.4).

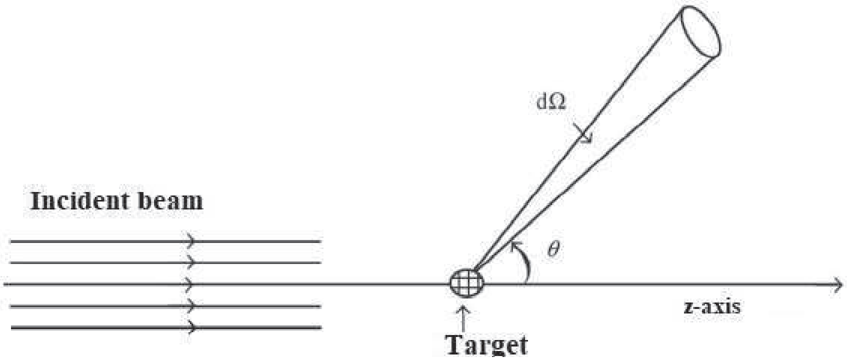

***Fig. 4.4** Incident and the Scattered Lines Scattering Angle è*

Let N number particles is crossing unit area normal to the beam in unit time. In that, n is the number of particles scattered into the solid angle $d\Omega$ in the direction (θ,ϕ). Experimental results on scattering are expressed in terms of differential cross section. Let, $\sigma(\theta,\phi)$ represents the differential scattering cross section and it is defined as

$$\sigma(\theta,\phi)=\frac{n/d\Omega}{N} \quad \text{...(4.1)}$$

The numerator term in the Equation (4.1) gives the number of particles scattered per unit solid angle.

The solid angle is defined using spherical coordinate.

$$d\Omega=\frac{r^2\sin\theta d\theta d\phi}{r^2}=\sin\theta d\theta d\phi \quad \text{... (4.2)}$$

The total cross section can be found by integrating the differential cross section.

$$\sigma=\int\sigma(\theta,\phi)d\Omega$$

$$\sigma=\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}\sigma(\theta,\phi)d\phi \quad \text{... (4.3)}$$

Here σ is the total cross section.

Total cross section and the differential cross section have the dimension of area. If the potential is spherically symmetric, then differential cross section is independent of ϕ. The total cross section becomes

$$\sigma=2\pi\int_0^{\pi}\sigma(\theta)\sin\theta d\theta \quad \text{... (4.4)}$$

The Equation (4.4) shows that, when the targets potential is spherically symmetric, the cross section depends only on scattering angle. The scattering cross section gives the idea of the nature of target. It is not equal to the exact spatial area of the target. Usually, cross sections are measured in barns, where $1\text{ barn}=10^{-24}\text{ cm}^2$.

4.4 LABORATORY AND CENTRE OF MASS SYSTEM

Experimental observations are done using laboratory coordinate system. But centre of mass coordinate system reduces the two body problem into one body problem. In these way degrees of freedom reduces by half. Thus centre of mass coordinate system is more convenient for the calculation of scattering problem. In the laboratory coordinate system scattering centre is initially at rest. In the centre of mass coordinate system, the two interacting particles are always at rest. So the coordinate systems move relative to each other and its velocity is equal to the velocity of centre of mass in the laboratory coordinate system. Hence the total momentum is always zero.

Let us consider a particle of mass m is moving in the positive z direction with the velocity v_L and it is colliding with another particle of mass M at rest at the origin. After the collision, incident particle gets scattered in the direction (θ_L, ϕ_L).

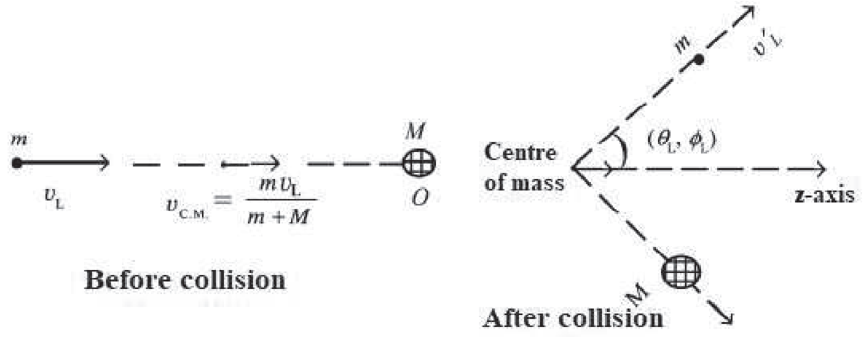

Fig. 4.5 *Centre of Mass Before and After Collision*

The velocity of the centre of mass is given by

$$v_{C.M} = \frac{mv_L}{m+M} \qquad \ldots (4.5)$$

When the observer is at centre of mass, he sees the particle M approaching him from right with the velocity $-\frac{mv_L}{m+M}$ and the particle m approaching him from left with velocity

$$v_C = v_L - v_{C.M}$$

$$v_C = v_L - \frac{mv_L}{m+M}$$

$$v_C = \frac{Mv_L}{m+M} \qquad \ldots (4.6)$$

To keep the centre of mass at rest, the two particles must be scatter in opposite direction just after the collision in opposite directions. The speed of the particles must be unchanged.

NOTES

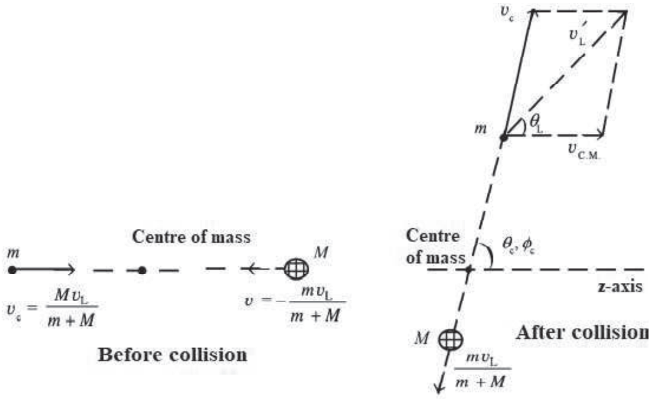

Fig. 4.6 *Two Particles Scattered in Opposite Direction*

From the above Figure 4.6, the two systems move relative to one another with $v_{C.M}$

$$v'_L \cos\theta_L = v_C \cos\theta_C + v_{C.M}$$

$$v'_L \sin\theta_L = v_C \sin\theta_C$$

$$\phi_L = \phi_C \qquad \ldots (4.7)$$

And it follows that

$$\tan\theta_L = \frac{\sin\theta_C}{\cos\theta_C + (v_{C.M}/v_C)}$$

$$\tan\theta_L = \frac{\sin\theta_C}{\cos\theta_C + \alpha} \qquad \ldots (4.8)$$

Here, $\alpha = m/M$. If M is infinitely large in comparison with m, then $\theta_L = \theta_C$

In this condition, the scatterer behaves like a fixed one.

Let $\sigma_C(\theta_C, \phi_C)$ and $\sigma_L(\theta_L, \phi_L)$ are the differential cross sections in centre off mass and the laboratory systems respectively. The relations can be obtained by imposing the condition that the number of particles scattered into the given solid angle must be the same in both the systems.

$$N\sigma_C(\theta_C, \phi_C)d\Omega_C = N\sigma_L(\theta_L, \phi_L)d\Omega_L \qquad \ldots (4.9)$$

By substituting for solid angle we get,

$$\sigma_C(\theta_C, \phi_C)\sin\theta_C d\theta_C d\phi_C = \sigma_L(\theta_L, \phi_L)\sin\theta_L d\theta_L d\phi_L \qquad \ldots (4.10)$$

From Equation (4.7) and Equation (4.8),

$$\frac{\sin^2\theta_L}{\cos^2\theta_L} = \frac{\sin^2\theta_C}{(\cos\theta_C + \alpha)^2}$$

By simplifying we get,

$$\frac{1}{\cos^2\theta_L} = \frac{\sin^2\theta_C + (\cos\theta_C + \alpha)^2}{(\cos\theta_C + \alpha)^2}$$

$$\frac{1}{\cos^2\theta_L} = \frac{1+2\alpha\cos\theta_C+\alpha^2}{(\cos\theta_C+\alpha)^2}$$

$$\cos\theta_L = \frac{|\alpha+\cos\theta_C|}{\left(1+\alpha^2+2\alpha\cos\theta_c\right)^{1/2}}$$

By differentiating, we get

$$\sin\theta_L d\theta_L = \frac{|\alpha+\cos\theta_C|}{\left(1+\alpha^2+2\alpha\cos\theta_C\right)^{3/2}}\sin\theta_C d\theta_C$$

$$\Rightarrow \sigma_L(\theta_L,\phi_L) = \frac{\left(1+\alpha^2+2\alpha\cos\theta_C\right)^{3/2}}{|1+\alpha\cos\theta_C|}\sigma_C(\theta_C,\phi_C) \qquad \dots (4.11)$$

The Equation (4.11) gives the relation between differential scattering cross section of centre of mass and the laboratory system.

If $M >> m$, $\alpha \cong 0$

$\sigma_L(\theta_L,\phi_L) = \sigma_C(\theta_C,\phi_C)$

If $M = m$, $\alpha = 1$

From Equation (4.7), $\theta_L = \theta_C/2$,

$\sigma_L(\theta_L,\phi_L) = 4\sigma_C(2\theta_C,\phi_C)\cos\theta_L$.

4.5 SCATTERING BY A CENTRAL POTENTIAL

The method of partial wave is best for the analysis of elastic scattering. The Schrodinger equation which represents the scattering is given by

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\psi = E\psi \qquad \dots (4.12)$$

Solution of the Schrodinger equation will have radial and angular part. Central potential is a symmetric one. So, angular part must be independent of ϕ, as the incident wave is along the z-axis. By variable separable method, the solution of the equation (4.12) is

$$\psi(r,\theta) = R_l(r)P_l(\cos\theta), \quad \text{where, } l = 0,1,2,.... \qquad \dots (4.13)$$

Here, $R_l(r)$ is the radial part and it satisfies the radial equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right) + \left[\frac{2\mu E}{\hbar^2} - \frac{2\mu V}{\hbar^2} - \frac{l(l+1)}{r^2}\right]R_l = 0 \qquad \dots (4.14)$$

When the wave is far away from the central potential, the equation reduces to the free particle equation.

$$\frac{d^2R_l}{dr^2} + \left(\frac{2}{r}\frac{dR_l}{dr}\right) + \left[k^2 - \frac{l(l+1)}{r^2}\right]R_l = 0 \qquad \dots (4.15)$$

Where, $k^2 = \dfrac{2\mu E}{\hbar^2}$ … (4.16)

The differential equation (4.15) has two independent solutions. One is $j_l(kr)$, is spherical Bessel function and another one is $n_l(kr)$, is spherical Neumann function.

So, the general solution to the equation (4.15) is given by

$$R_l(kr) = A^{'} j_l(kr) - B^{'} n_l(kr) \quad \text{… (4.17)}$$

Here $A^{'}$ and $B^{'}$ are constants. When the wave is far away from the central potential ($r \to \infty$), asymptotically, the radial part of the free particle wave equation is given by

$$R_l(kr) = \frac{A'}{kr}\sin\left(kr - \frac{l\pi}{2}\right) + \frac{B'}{kr}\cos\left(kr - \frac{l\pi}{2}\right) \quad \text{… (4.18)}$$

Now the wave enters the potential region where $V(r) \neq 0$. The value of ratio of the constants $\dfrac{B^{'}}{A^{'}}$ must be determined using equation (4.14) by applying the boundary conditions. Then the value is matched with the asymptotic solution, equation (4.18). We can write,

$A^{'} = A_l \cos\delta_l$ and $B^{'} = A_l \sin\delta_l$, where A_l and δ_l are constants.

Now we can write the asymptotic solution of equation (4.14) as

$$R_l(kr) = \frac{A'}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right), \quad l = 0, 1, 2, \ldots \quad \text{… (4.19)}$$

Here, A_l is the asymptotic amplitude and δ_l is called phase shift. It is measures the phase shift of the radial function for angular momentum quantum number l for the case between $V(r) \neq 0$ and $V(r) = 0$. From the equation (4.13), the general asymptotic solution is given by

$$\psi(r,\theta) = \sum_{l=0}^{\infty} \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) P_l(\cos\theta) \quad \text{… (4.20)}$$

We know that, when particle is far away from the central potential its asymptotic solution can be found using Schrödinger equation (4.12) and that is given by

$$\psi(r,\theta) = e^{ikz} + f(\theta)\frac{e^{ikr}}{r} \quad \text{… (4.21)}$$

The two asymptotic solutions, equation (4.20) and (4.21) are equal.

$$e^{ikz} + f(\theta)\frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) P_l(\cos\theta) \quad \text{… (4.22)}$$

Replacing the e^{ikz}, we get

$$\sum_{l=0}^{\infty} \frac{(2l+1)i^l}{kr}\sin\left(kr - \frac{l\pi}{2}\right) P_l(\cos\theta) + f(\theta)\frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} \frac{A_l}{kr}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) P_l(\cos\theta)$$

… (4.23)

By rewriting the sin function in terms of exponential form and comparing the coefficient of exponential terms we get,

$$\sum_{l=0}^{\infty}\frac{(2l+1)i^l e^{-il\pi/2}}{2ikr}P_l(\cos\theta)+\frac{f(\theta)}{r}=\sum_{l=0}^{\infty}\frac{(2l+1)i^l e^{2i\delta_l}}{2ikr}e^{-il\pi/2}P_l(\cos\theta) \quad \dots (4.24)$$

$$f(\theta)=\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)i^l e^{-il\pi/2}\left[\exp(2i\delta_l)-1\right]P_l(\cos\theta) \quad \dots (4.25)$$

We know that, $i^l = e^{\frac{il\pi}{2}}$

And, $\exp(2i\delta_l)-1=\exp(i\delta_l)[\exp(i\delta_l)-\exp(-i\delta_l)]$

$$\exp(2i\delta_l)-1=2i\exp(i\delta_l)\sin\delta_l \quad \dots (4.26)$$

Thus equation (4.25) can be written as

$$f(\theta)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)P_l(\cos\theta)\sin\delta_l \quad \dots (4.27)$$

Here equation (4.27) represents the result of partial wave analysis. The wave equation contains an exponential term which allows us to do the physical interpretations. The scattering potential shift the phase of scattered waves relative to the incident waves.

The differential cross section is given by, $\sigma(\theta)=|f(\theta)|^2$

From equation (4.27) we get

$$\sigma(\theta)=\frac{1}{k^2}\left|\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)P_l(\cos\theta)\sin\delta_l\right|^2 \quad \dots (4.28)$$

By using orthogonal property of Legendre polynomial we can find total cross-section.

$$\sigma=\int_0^{\pi}\sigma(\theta)d\Omega$$

$$\sigma=\int_0^{\pi}\sigma(\theta)(2\pi\sin\theta)d\theta$$

$$\sigma=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l \quad \dots (4.29)$$

The differential cross section (Equation (4.28)) and total cross section (Equation (4.29)) depends on phase shift δ_l of the partial wave.

4.6 PARTIAL WAVE ANALYSIS AND PHASE SHIFT METHOD

In scattering experiment the detector is far away from the target. The intensity of scattered wave depends only on θ and ϕ in spherical coordinate, the spherically diverging scattered wave amplitude is denoted by $f(\theta)$ and it is called as scattering amplitude. Scattering amplitude depends on. This can be found using partial wave analysis.

We know that the plane wave can be rewritten by expanding as a linear combination of spherical waves as

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \qquad \ldots (4.30)$$

Here, are the Legendre polynomials and is the spherical Bessel function. So each term in the Equation (4.30), that is and represents the spherical waves. Thus, the plane wave is equivalent to the linear combination of infinite number of spherical waves. The each individual waves are known as partial waves.

Here, and when, it is called s-wave, is known as p-wave and gives the d-wave and so on. Asymptotically we can write the spherical Bessel function as

$$j_l(kr) \rightarrow \frac{1}{kr}\sin(kr - \frac{l\pi}{2}) \qquad \ldots (4.31)$$

We can write the sin function in terms of exponentials.

$$j_l(kr) \rightarrow \frac{1}{2ikr}\left[\exp(ikr - i\frac{l\pi}{2}) - \exp(-ikr + i\frac{l\pi}{2}\right] \qquad \ldots (4.32)$$

Then substitute spherical Bessel function into the Equation (4.30), we get

$$e^{ikz} = \sum_{l=0}^{\infty} \frac{i^l(2l+1)}{2ik} P_l(\cos\theta)\frac{1}{r}\left[\exp(ikr - i\frac{l\pi}{2}) - \exp(-ikr + i\frac{l\pi}{2}\right] \qquad \ldots (4.33)$$

The Equation (4.33) shows that every partial wave can be represented as sum of incoming and a scattered spherical wave. The second exponential term indicates the incoming wave and the outgoing wave is indicated by the first exponential term in the bracket.

$$e^{ikz} = \sum_{l=0}^{\infty} A_l P_l(\cos\theta)\frac{1}{r}\left[\exp(ikr - i\frac{l\pi}{2}) - \exp(-ikr + i\frac{l\pi}{2}\right] \qquad \ldots (4.34)$$

Where, $A_l = \frac{(2l+1)i^l}{2ik}$

Momentums of the incoming and outgoing partial wave are conserved (equal) and the wavelength of the oscillation does not change in this process. So we can multiply the amplitude of each outgoing partial waves in the Equation (4.34) by a complex number, that is. Here represents the phase shift of the outgoing wave and it is depends only on. So, the scattered wave is shifted by an amount of when compared it to the incident wave.

4.7 IMPACT PARAMETER

According to the classical scattering theory, let us say particle incident on some scattering centre (we can say target), it comes with some enrgy E and it will get deviated. We can assume that the target is heavy and recoil of target substance is negligible.

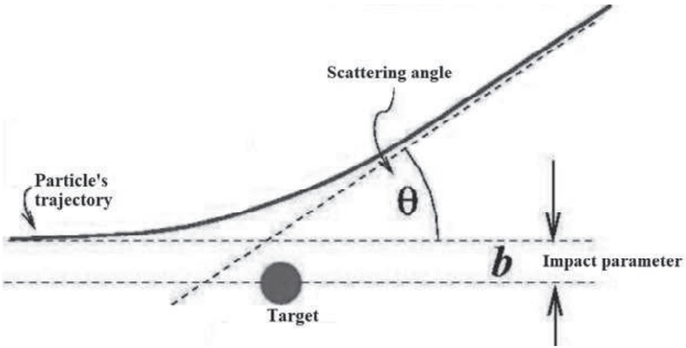

Fig. 4.7 *Tanget to the Trajectory of Scattered Particle*

In the Figure 4.7 we have a target and particle's trajectory is shown. When we draw a tanget to the trajectory of scattered particle, it will cut the horizontal line and makes an angle . This angle is known as scattering angle. The distance between two horizontal line (as shown in the figure, one line is going through the centre of the target) is called impact parameter. The particles which are moving in this regoin will only get scattered. The particle's which are moving above this region will not get deviated. The imapact parameter is denoted by . In general, the scattering angle increases when impact parameter decreases.

Let us find the relation between scattering angle and the impact parameter.

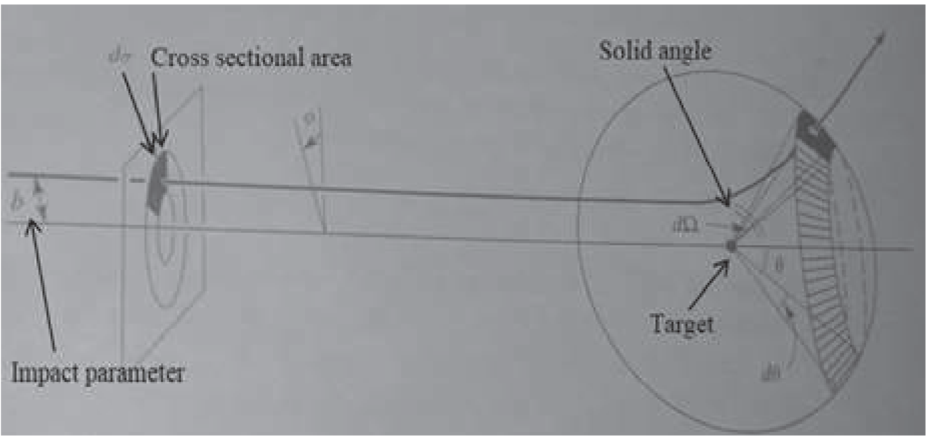

Fig. 4.8 *Incident within the Small Patch of Cross Sectional Area*

In the above Figure 4.8, let us say particles incident within the small patch of cross sectional area (Refer Figure 4.8) will scatter into the small angle and we call it as a solid angle. Obviously larger will lead to the greater in the. So we can write

$$d\sigma \prec d\Omega$$

So here we can define a proportionality factor,

$$d\sigma = D(\theta)d\Omega \qquad \dots (4.35)$$

By referring to the above Figure 4.8 we can write cross sectional area and solid angle using spherical coordinate as

$$d\sigma = bdbd\phi \qquad \dots (4.36)$$

And, $d\Omega = \sin\theta d\theta d\phi$ … (4.37)

By substituting Equations (4.36) and (4.37) in Equation (4.35), we get

$$bdbd\phi = D(\theta)\sin\theta d\theta d\phi$$

$$bdb = D(\theta)\sin\theta d\theta$$

$$\Rightarrow D(\theta) = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right| \quad \ldots (4.38)$$

Equation (4.38) gives the relation between impact parameter and the scattering angle. Here angle is decreasing function of. So its derivative will have a negative sign, hence the absolute value sign is used.

4.8 RELATION BETWEEN PHASE SHIFT AND LOGARITHMIC DERIVATIVE

Radial wave equation is given by $\frac{d^2R_l}{dr^2}+\frac{2}{r}\frac{dR_l}{dr}+[k^2-\frac{l(l+1)}{r^2}]R_l=0$

We can write above equation for $r < R$

$$\chi_l\,''+\left[k^2-\frac{l(l+1)}{r^2}-2mV(r)\right]\chi_l=0\,,\ \chi_l=rR_l \quad \ldots (4.39)$$

The wave function and its derivative on the sphere are continuous. Hence, we can write the equation for wave function continuity as

$$R_l(k,R)=j_l(kR)+\frac{1}{2}\alpha_l h_l^{(1)}(kR) \quad \ldots (4.40)$$

By deriving the wave at ,

$$\left.\frac{dR_l(k,r)}{dr}\right|_{r=R}=k\left[j'_l(kR)+\frac{1}{2}\alpha_l h_l^{(1)}{}'(kR)\right] \quad \ldots (4.41)$$

Prime notation in the Equation (4.41) denotes the derivative with respect to the argument of the function.

Divide Equation (4.41) by Equation (4.40) we get,

$$\left.\frac{\frac{dR_l(k,r)}{dr}}{R_l(k,R)}\right|_{r=R}=\frac{k\left[j'_l(x)+\frac{1}{2}\alpha_l h_l^{(1)}{}'(x)\right]}{j_l(x)+\frac{1}{2}\alpha_l h_l^{(1)}(x)}\,,\quad x=kR \quad \ldots (4.42)$$

By considering $dr = rd\log r$

We can rewrite the above Equation (4.42) as

$$L_l\equiv\left.\frac{d\log R_l(k,r)}{d\log r}\right|_{r=R}=\frac{x\left[j'_l(x)+\frac{1}{2}\alpha_l h_l^{(1)}{}'(x)\right]}{j_l(x)+\frac{1}{2}\alpha_l h_l^{(1)}(x)} \quad \ldots (4.43)$$

Here is the logarithmic derivative. Rewrite the above Equation (4.43) in terms ofby considering

$$\alpha_l = e^{2i\delta_l} - 1 \qquad \ldots (4.44)$$

$$L_l = \frac{\left[xj'_l(x) + \frac{1}{2} x\alpha_l h_l^{(1)}{}'(x) \right]}{j_l(x) + \frac{1}{2}\alpha_l h_l^{(1)}(x)} \qquad \ldots (4.45)$$

$$L_l j_l(x) - xj'_l(x) = \frac{1}{2} x\alpha_l h_l^{(1)}{}'(x) - \frac{1}{2} L_l \alpha_l h_l^{(1)}(x)$$

By solving for we get

… (4.46)

Hence, the Equation (4.46) shows the relation between phase shift and the logarithmic derivative. If logarithmic derivative is known, we can find the phase shift using the Equation (4.46).

4.8.1 Behaviour of Phase Shift at Low Energy Scattering By Hard Sphere

Consider a wave is scattering by a hard sphere of radius.

The potential is given by ∞ at $r \le a$, and 0 at $r > a$.

When potential is infinity, the wave function will be zero.

At $r = a$, $\psi(a, \theta) = 0$ … (4.47)

The wave function from the partial wave analysis is given by

$$\psi(r,\theta) = A\left\{ e^{ikz} + k\sum_{l=0}^{\infty} i^{l+1}(2l+1)a_l h_l^{(1)}(kr) P_l(\cos\theta) \right\} \qquad \ldots (4.48)$$

The wave function in the exterior region (that is, $r > a$) is

$$\psi(r,\theta) = A\left\{ \sum_{l=0}^{\infty} i^l (2l+1)[j_l(kr) + ika_l h_l^{(1)}(kr)] P_l(\cos\theta) \right\}$$

So, $\psi(r,\theta) = \left\{ \sum_{l=0}^{\infty} i^l (2l+1)[j_l(kr) + ika_l h_l^{(1)}(kr)] P_l(\cos\theta) \right\} = 0$

... (4.49)

Here, is the partial wave amplitude. By using orthogonal property of Legendre polynomials, the coefficients with different values of l must separately vanish. So in this situation partial wave amplitude is

$$a_l = i\frac{j_l(ka)}{kh_l^{(1)}(ka)} \qquad \ldots (4.50)$$

From partial wave analysis, the total cross section is given by

$$\sigma = \frac{4\pi}{k^2}\sum_{l-0}^{\infty}(2l+1)\left| \frac{j_l(ka)}{h_l^{(1)}(ka)} \right|^2 \qquad \ldots (4.51)$$

NOTES

At low energy scattering, $ka << 1$. Here the wavelength is much greater than the radius of the sphere.

We know that, $\dfrac{j_l(z)}{h_l^{(1)}(z)} = \dfrac{j_l(z)}{j_l(z) + in_l(z)}$ … (4.52)

For a small, Neumann function is larger than the $j_l(z)$.

$$\frac{j_l(z)}{j_l(z)+in_l(z)} \approx -i\frac{j_l(z)}{n_l(z)}$$

$$\approx -i\frac{2^l l!z^l/(2l+1)!}{-(2l)!z^{-l-1}/2^l l!} = \frac{i}{2l+1}\left[\frac{2^l l!}{(2l)!}\right]^2 z^{2l+1}$$

Thus,

$$\sigma \approx \frac{4\pi}{k^2}\sum_{l=0}^{\infty}\frac{1}{2l+1}\left[\frac{2^l l!}{(2l)!}\right]^4 (ka)^{4l+2} \quad \text{… (4.53)}$$

For low energy scattering $ka << 1$, so the higher order powers are too small and it is negligible. In this situation $l = 0$ terms is dominating and it is called S-wave scattering.

Hence, $l = 0$ in the Equation (4.53) gives

$$\sigma \approx \frac{4\pi}{k^2}\left[\frac{2^0}{(0)!}\right]^4 (ka)^2$$

$$\sigma \approx \frac{4\pi}{k^2}(ka)^2$$

Thus total cross section is

$$\sigma \approx 4\pi a^2 \quad \text{… (4.53)}$$

Here total cross section is equal to the total surface area of the hard sphere. In quantum scattering, waves feel their way around the whole sphere. But in case of classical scattering, the particles can see the head on cross section or a head on surface area.

Check Your Progress

1. State the scattering theory.
2. Define the elastic scattering.
3. State the Rayleigh scattering theory.
4. What do you mean by Raman scattered photons?
5. Define the scattering angle.
6. What do you understand by scattering cross section?
7. What is centre of mass coordinate system?
8. Define the scattering amplitude.

4.9 RESONANCE SCATTERING

NOTES

By solving the radial part of the Schrödinger equation we can explain the s-wave scattering by an attractive square well potential. Let us consider an equation from the scattering by an attractive square well potential

$$\tan(ka+\delta_0)=\frac{k}{k_1}\tan(k_1a) \qquad \ldots (4.55)$$

Let us consider the situation of very low energy scattering by attractive square well potential. By expanding tan function and rearranging, we get

$$\left[1+\frac{k}{k_1}\tan(ka)\tan(k_1a)\right]\tan\delta_0=\frac{k}{k_1}\tan(k_1a)-\tan(ka) \qquad \ldots (4.56)$$

When the potential is shallow, the ratio k/k_1 is very small (if potential is shallow, k_1 is large) for very low energy scattering. So $ka<<1$ then $\tan(ka)\approx ka$

If k/k_1 is too small, then the factor in square bracket (in Equation (4.56)) is nearly equal to 1. So we can rewrite the Equation (4.56) as

$$\tan\delta_0=ka\left[\frac{\tan(k_1a)}{k_1a}-1\right] \qquad \ldots (4.57)$$

The value of k_1a will be less than $\pi/2$. By increasing the value of k_1 we can increase the value of k_1a to $\pi/2$. If depth of the potential is increased to a certain stage, k_1 increases and angle k_1a will be equal to $\pi/2$.

As, $k_1a\to\pi/2$ $\tan\delta_0\to\infty$ (because, $\tan 90\to\infty$)

In this case total cross section can be found using the formula from the central potential scattering.

So, the total cross section is given by

$$\sigma=\frac{4\pi}{k^2} \qquad \ldots (4.58)$$

Equation (4.40) is the maximum value of the total cross section. If there is a bound state then phase shift δ_0 will take the value $\pi/2$ and the cross section will attain the maximum value. This is known as resonance. The total cross section at the resonance depends on k^2 (where, $k=\frac{2\mu E}{\hbar^2}$). The Breit-Wigner formula will talk about the behaviour of the cross section near resonance.

4.10 SCATTERING BY A DEEP SQUARE WELL

The *finite potential well* (also known as the finite square well) is a concept from quantum mechanics. It is an extension of the infinite potential well, in which a particle is confined to a 'Box', but one which has finite potential 'Walls'. Unlike the infinite potential well, there is a probability associated with the particle being found outside the box. The quantum mechanical interpretation is unlike the classical interpretation, where if the total energy of the particle is less than the potential energy barrier of the walls it cannot be found outside the box. In the quantum interpretation, there is a non-zero probability of the particle being outside the box even when the energy of the particle is less than the potential energy barrier of the walls (cf quantum tunnelling).

Asymmetric Square Well

Consider a particle of mass m moving in a one-dimensional infinitely deep asymmetric potential well as shown in the Figure (4.9), the potential function $V(x)$ being of the form,

$$V(x) = +\infty$$

for $x < 0$ [Region I]

$$= 0$$

for $0 \leq x \leq a$ [Region II]

$$= +\infty$$

for $x > a$ [Region III]

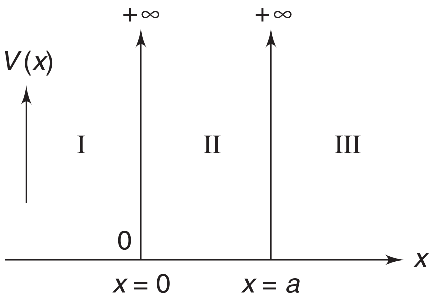

Fig. 4.9 *Asymmetric Square Well*

Classically, the particle remains confined within the well and moves with constant momentum back and forth as a result of repeated reflections from the walls of the well at $x = 0$ and at $x = a$.

Since $V(x) = +\infty$ for $x < 0$ (i.e., in Region I) as well as for $x > a$ (i.e., in Region III), the wavefunctions of the particle in these two regions are zero, i.e.,

$$\psi(x = 0) = 0 = \psi(x = a) \qquad ...(4.59)$$

If $\psi(x)$ represents the wavefunction for the particle inside the well $(0 \leq x \leq a)$, we have the Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\,\psi(x) = 0$$

NOTES

Or $$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad ...(4.60)$$

Where $$k = \sqrt{\frac{2m}{\hbar^2} E} \qquad ...(4.61)$$

The general solutions of Equation (4.60) are

$$\psi(x) = C\,e^{ikx} + De^{-ikx}$$

Or $$\psi(x) = A \sin kx + B \cos kx \qquad ...(4.62)$$

where A and B are constants.

Using the boundary condition given by Equation (4.59), namely $\psi(0) = 0$ in Equation (4.62) we get

$$B = 0$$

so that the solution becomes

$$\psi(x) = A \sin kx \qquad ...(4.63)$$

Further, applying the other boundary condition namely $\psi(a) = 0$, we get from Equation (4.63)

$$A \sin ka = 0$$

The above gives either $A = 0$ or $\sin ka = 0$. However, $A = 0$ leads to $\psi(x) = 0$ everywhere which is not possible. Hence, we obtain

$$\sin ka = 0$$

The above gives

$$ka = n\pi; \quad n = \text{A positive integer}$$

$$= 1, 2, 3, ... \qquad ... (4.64)$$

We may note that n cannot be 0 because that would make $k = 0$ so that wavefunction would vanish everywhere.

From Equation (4.64) we thus get

$$k = \frac{n\pi}{a} \qquad ...(4.65)$$

Using Equation (4.65) in Equation (4.63) we get the energy eigenfunctions of the particle to be given by

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a} x\right) \quad ; n = 1, 2, ... \qquad ...(4.66)$$

NOTES

Constant A can be determined from the requirement that the eigenfunctions are normalized, i.e.,

$$\int_0^a \psi_n^*(x)\,\psi_n(x)\,dx = 1$$

The above gives,

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

Or $$A^2\,\frac{a}{2} = 1$$

Or $$A = \sqrt{\frac{2}{a}} \qquad \text{...(4.67)}$$

The energy eigenfunctions are thus

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right); \quad n = 1, 2, ... \qquad \text{...(4.68)}$$

Using Equation (4.68) we get the energy eigenvalues of the particle to be given by

$$\sqrt{\frac{2m}{\hbar^2}E_n} = \frac{n\pi}{a}$$

Or $$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2, \quad n = 1, 2, ... \qquad \text{...(4.69)}$$

We find the energy to be quantized, only certain values of energy are permitted. This is as expected because the states of a particle which are confined within a limited region of space are bound states and the energy eigenvalue spectrum is discrete. This result is in sharp contrast to the result in classical physics in which the energy of the particle given by $E = \frac{p^2}{2m}$ (p being the momentum of the particle) can assume any value continuously from a minimum to a maximum.

From Equation (4.69) we get

$$E_{n+1} - E_n = \frac{\hbar^2\pi^2}{2ma^2}(2n+1) \qquad \text{...(4.70)}$$

Clearly, the energy levels are not equispaced.

We have

$$\frac{E_{n+1} - E_n}{E_n} = \frac{2n+1}{n^2} = \frac{2}{n} + \frac{1}{n^2}$$

Clearly, in the classical limit, the above gives,

$$\operatorname*{Lt}_{n\to\infty}\left(\frac{E_{n+1}-E_n}{E_n}\right)=\operatorname*{Lt}_{n\to\infty}\left(\frac{2}{n}+\frac{1}{n^2}\right)=0 \qquad ...(4.71)$$

meaning that the levels become so close together that they become practically indistinguishable forming a continuum.

The lowest energy state or the ground state corresponds to $n = 1$. The ground state energy is given by,

$$E_1 = \frac{\hbar^2\pi^2}{2ma^2} \qquad ...(4.72)$$

And the ground state wavefunction is given by,

$$\psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right) \qquad ...(4.73)$$

Energy given by Equation (4.72) is called the zero point energy because there exists no state with zero energy.

The plot of some of the eigenfunctions with x are shown in Figure (4.10). We observe from the plots that the eigenfunction $\psi_n(x)$ has $(n-1)$ nodes.

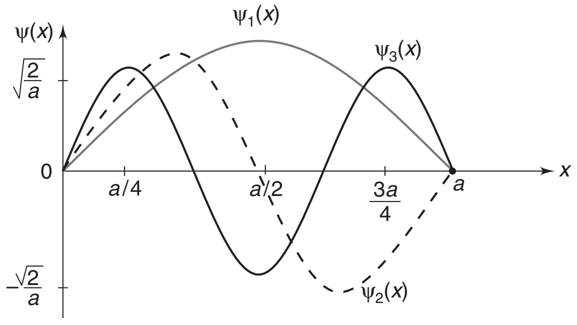

Fig. 4.10 *Plot of Engenfunctions*

Discussion on Zero Point Energy

If the particle inside the well has zero energy then it will come to rest and will be localized within the limited region defining the well. Heisenberg's uncertainty relation then will require the particle to acquire a finite momentum and hence a minimum kinetic energy. Since the particle is confined in the region $0 < x < a$, it has a maximum position uncertainty $\Delta x = a$ and hence a minimum momentum uncertainty $\Delta p \sim \frac{\hbar}{a}$ which in turn corresponds to a minimum kinetic energy $\frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2ma^2}$ which is in qualitative agreement with the exact value $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$.

The minimum momentum uncertainty given by $\Delta p \sim \frac{\hbar}{a}$, is inversely proportional to the width of the well. Smaller the width, more the particle becomes localized, and Δp increases. This causes the particle to move faster thereby increasing the zero point energy. If on the other hand, width of the well increases, the zero point energy decreases but never becomes zero. Thus localization of a particle forces a minimum motion and hence a minimum energy to the particle.

Symmetric Square-Well Potential of Infinite Depth

A symmetric infinite square well potential is defined as

$$\begin{aligned} V(x) &= +\infty \quad \text{for} \quad x < -a \\ &= 0 \qquad \text{for} \quad -a \le x \le a \\ &= +\infty \quad \text{for} \quad x > a \end{aligned}$$

and is represented in the Figure (4.11)

Consider the motion of a particle of mass m in the one-dimensional potential described above.

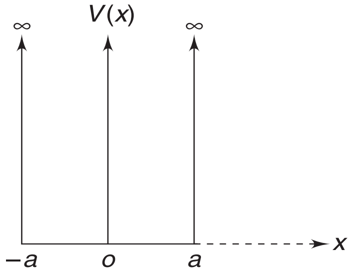

Fig. 4.11 *Symmetric Infinite Square*

If $\psi(x)$ is the wavefunction describing the state of the particle in the region $-a \le x \le a$ then it satisfies the time-independent Schrödinger equation,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\,\psi(x) = 0$$

Or $$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad \text{...(4.74)}$$

Where $$k = \sqrt{\frac{2m}{\hbar^2} E} \qquad \text{...(4.75)}$$

The most general solution of Equation (4.74) is given by,

$$\psi(x) = A\sin(kx) + B\cos(kx) \qquad \text{...(4.76)}$$

Where A and B are constants.

Since $V(x) = \infty$ for $x < -a$ and $x > a$, the wavefunctions in these two regions vanish giving,

$$\psi(-a) = 0 \quad \text{and} \quad \psi(+a) = 0 \qquad \text{...(4.77)}$$

Using the conditions given by Equation (4.77) in Equation (4.78) we get

$$A\sin ka + B\cos ka = 0 \qquad \text{...(4.78)}$$

and

$$-A \sin ka + B \cos ka = 0 \qquad ...(4.79)$$

For the above two equations to hold simultaneously we must have

$$A \sin ka = 0 \qquad ...(4.80)$$

and $$B \cos ka = 0 \qquad ...(4.81)$$

In view of Eqations (4.80) and (4.81) we may have $A = 0$ and $B = 0$ but these are physically unacceptable because $\psi(x)$ given by Equation (4.76) would then vanish.

Since $B \neq 0$, we have from Equation (4.81),

$$\cos ka = 0 = \cos \frac{n\pi}{2}, \quad n = 1, 3, 5, ...$$

or $$ka = \frac{n\pi}{2} \quad \text{or} \quad k = \frac{n\pi}{2a} \qquad ...(4.82)$$

Using Equation (4.82) in the above we obtain the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} = \frac{\pi^2\hbar^2}{8ma^2} n^2, \quad n = 1, 3, 5, ... \qquad ...(4.83)$$

The energy eigenfunctions corresponding to the above energy eigenvalues are

$$\psi_n(x) = B \cos kx = B \cos\left(\frac{n\pi}{2a} x\right), \quad n = 1, 3, 5 \qquad ...(4.84)$$

The condition given by Equation (4.80) gives

$$\sin ka = 0 = \sin n\pi \qquad (\text{since } A \neq 0)$$

Or $$ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}, \quad n = 2, 4, 6 \qquad ...(4.85)$$

Using the above value of k in Equation (4.75) we get the energy eigenvalues

$$E_n = \frac{\hbar^2}{2m} k^2 = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \quad n = 2, 4, 6, ... \qquad ...(4.86)$$

The corresponding energy eigenfunctions are

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{2a}\right), \quad n = 2, 4, 6, ... \qquad ...(4.87)$$

The normalization conditions of the wavefunctions,

$$\int_{-a}^{+a} \psi_n^*(x)\, \psi_n(x)\, dx = 1$$

lead to

$$A = \frac{1}{\sqrt{a}}, B = \frac{1}{\sqrt{a}} \qquad ...(4.88)$$

We can thus write the set of energy eigenfunctions for the particle in the symmetric infinite square well potential as,

$$\psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a} x\right), \quad n = 2, 4, \ldots \qquad \ldots(4.89)$$

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a} x\right), \quad n = 1, 3, 5, \ldots \qquad \ldots(4.90)$$

and the discrete set of energy eigenvalues as

$$E_n = \frac{\pi^2 \hbar^2}{8ma^2} n^2, \quad n = 1, 2, 3, \ldots \qquad \ldots(4.91)$$

Discussion

The wavefunctions corresponding to $n = 1, 3, 5, \ldots$, i.e., corresponding to odd quantum numbers are symmetric, $\psi(-x) = \psi(x)$.

- The wavefunctions corresponding to $n = 2, 4, 6, \ldots$ i.e., corresponding to even quantum numbers are antisymmetric, $\psi(-x) = -\psi(x)$
- In other words, for symmetric potentials $V(-x) = V(x)$, the wavefunctions of bound states are either even (symmetric) or odd (antisymmetric).
- The energy spectrum for the particle is discrete and non-degenerate.
- The ground state energy or the zero point energy is,

$$E_1 = \frac{\pi^2 \hbar^2}{8ma^2}$$

Corresponding to the eigenfunction,

$$\psi_1(x) = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}$$

Symmetric Square-Well Potential of Finite Depth

A symmetric square well potential of finite depth is described by potential function $V(x)$ of the form

$$\begin{aligned} V(z) &= V_0 \quad \text{for} \quad x < -a && \text{(Region I)} \\ &= 0 \text{for} \quad -a \le x \le a && \text{(Region II)} \\ &= V_0 \quad \text{for} \quad x > a && \text{(Region III)} \end{aligned}$$

The potential function is shown in the Figure (4.12)

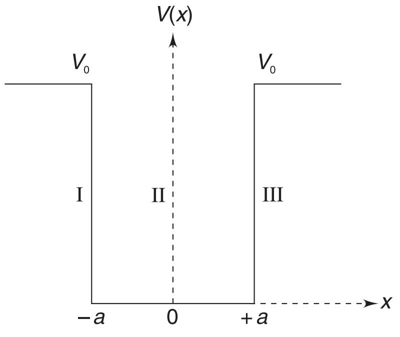

Fig. 4.12 Potential Function

Consider the motion of a particle of mass m in the potential well described above.

The Schrödinger equation in Regions I and III is,

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x)$$

or
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\,\psi(x) = 0 \qquad ...(4.92)$$

In Region II the Schrödinger equation is,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\,\psi(x) = 0$$

which can be put in the form

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad ...(4.93)$$

where
$$k = \sqrt{\frac{2m}{\hbar^2}E} \qquad ...(4.94)$$

Let us consider the cases where: $E < V_0$, and $E > V_0$

Case $E < V_0$: We may write Equation (4.92) in the form

$$\frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) = 0 \qquad ...(4.95)$$

where $\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$ is real positive ...(4.96)

The most general solution of Equation (4.95) is

$$\psi(x) = Ae^{+\alpha x} + Be^{-\alpha x}, \quad A \text{ and } B \text{ are constants} \qquad ...(4.97)$$

Specific solution in Region I $\psi_1(x) = A\,e^{\alpha x}$ ...(4.98)

Specific solution in Region III $\psi_3(x) = B\,e^{-\alpha x}$ ...(4.99)

Solution of Equation (4.93) gives the wavefunction in region II

$$\psi_2(x) = C\sin(kx) + D\cos(kx) \qquad ...(4.100)$$

$\psi_2(x)$ is either symmetric or antisymmetric about $x = 0$. The first term in Equation (4.107) is antisymmetric because $\sin(kx) = -\sin(-kx)$. The second term is symmetric because $\cos(kx) = \cos(-kx)$.

For the *symmetric function* in Region II, the coefficient $C = 0$ so that we may write the symmetric wavefunction in Region II as

$$(\psi_2(x))_{\text{symmetric}} = D\cos(kx) \qquad ...(4.101)$$

At $x = \pm a$, we have, using the single valuedness of wavefunction

$$Ae^{-\alpha a} = D\cos ka \qquad ...(4.102)$$

$$Be^{-\alpha a} = D\cos ka \qquad ...(4.103)$$

Similarly, using the continuity of wavefunction at $x = \pm a$ gives

$$\alpha A\, e^{-\alpha a} = +D\, k\sin(ka) \qquad ...(4.104)$$

$$+\alpha B\, e^{-\alpha a} = D\, k\sin(ka) \qquad ...(4.105)$$

The above equations give

$$A = B \qquad ...(4.106)$$

and $$k\tan ka = \alpha \qquad ...(4.107)$$

Let us now consider the antisymmetric wavefunctions in Region II. In the case $D = 0$ so that we may write the antisymmetric wavefunction in Region II as

$$(\psi_2(x))_{\text{antisymmetric}} = C\sin(kx) \qquad ...(4.108)$$

Using the single valuedness and continuity of wavefunction at the boundaries at $x = \pm a$ we get

$$A\, e^{-\alpha a} = -C\sin(ka) \qquad ...(4.109)$$

$$B\, e^{-\alpha a} = C\sin(ka) \qquad ...(4.110)$$

$$\alpha A\, e^{-\alpha a} = -C\, k\cos(ka) \qquad ...(4.111)$$

$$-\alpha Be^{-\alpha a} = C\, k\cos(ka) \qquad ...(4.112)$$

From the above four equations, we obtain

$$A = -B \qquad ...(4.113)$$

and

$$k\cot ka = -\alpha \qquad ...(4.114)$$

The energy eigenvalues for the particle can be obtained by solving Equations (4.107) and (4.114) graphically as explained in the following:

Let us put $$ka = x \qquad ...(4.115)$$

$$\alpha a = y \qquad ...(4.116)$$

From the above we get

$$x^2 + y^2 = (k^2 + \alpha^2)\, a^2$$

Substituting for k and α from Equations (4.94) and (4.96), the above becomes

$$x^2 + y^2 = \left[\frac{2m}{\hbar^2}E + \frac{2m}{\hbar^2}(V_0 - E)\right]a^2$$

or $$x^2 + y^2 = \frac{2ma^2}{\hbar^2}V_0 \qquad ...(4.117)$$

Substituting Equations (4.115) and (4.16) in Eqations (4.107) and (4.114), respectively, we obtain

$$x \tan x = y \qquad ...(4.118)$$

$$-x \cot x = y \qquad ...(4.119)$$

We plot x tan x against x, x cot x against x and $x^2 + y^2$ for different values of $V_0 a^2$ (which are circles of different radii). Since both x and y can take only positive values, the sections of the circles have been shown in the first quadrant only in Figure (4.13).

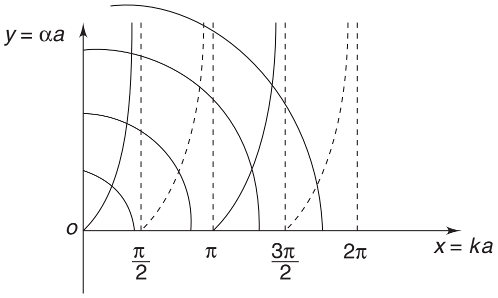

Fig. 4.13 *Graph*

In the Figure 4.13,

Full line curves → x tan x against x plots

Dashed curves → $-x$ cot x against x plots

Circular sections → Different values of $V_0 a^2$

The energy levels and the energy eigenvalues for the symmetric wavefunction are given by the intersections of the x tan x against x curves and the circular sections. Similarly, the energy eigenfunctions and the energy eigenvalues when the wavefunction in the well is antisymmetric are given by the intersections of $-x$ cot x against x curves and the circular sections.

If the intersections of x tan x against x curves and circles occur at values of x equal to $x_1, x_2, ..., x_n, ...$ then we get

$$x_n^2 = k^2 a^2 = \frac{2mE_n}{\hbar^2} a^2$$

Or $$E_n = \frac{\hbar^2}{2ma^2} x_n^2, \quad n = 1, 3, 5, ...$$

Similarly, if the intersections of $-x$ cot x against x curves and the circles occur at values of x equal to $x_{1'}, x_{2'}, ... x_{n'} ...$, then we get

$$x_{n'}^2 = k^2 a^2 = \frac{2mE_{n'}}{\hbar^2} a^2$$

Or $$E_{n'} = \frac{\hbar^2}{2ma^2} x_{n'}^2; \quad n' = 2, 4, 6, ...$$

The number of bound states are seen to depend upon the height V_0 and the width a of the well through the factor V_0a^2. From the Figure (4.13) we find the following

(i) Only one energy level of symmetric type, if $0 < V_0a^2 < \frac{\pi^2\hbar^2}{8m}$

(ii) Two energy levels of which one is of symmetric type and the other of antisymmetric type, if $\frac{\pi^2\hbar^2}{8m} < V_0a^2 < \frac{4\pi^2\hbar^2}{8m}$

(iii) Three energy levels of which two are of symmetric type and one of antisymmetric type, if $\frac{4\pi^2\hbar^2}{8m} < V_0a^2 < \frac{9\pi^2\hbar^2}{8m}$ and so on.

Some of the energy eigenfunctions corresponding to bound states are shown in the Figure (4.14).

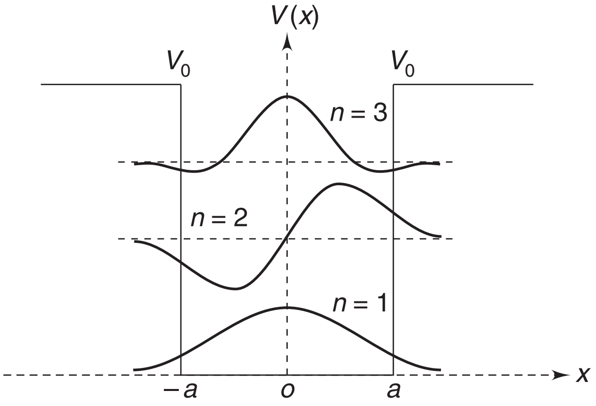

Fig. 4.14 Eigenfunctions for Bound State

Unlike in the case of infinite potential well, both the symmetric as well as the antisymmetric eigenfunctions extend beyond the well, i.e., in the regions $x < -a$ and $x > a$ which define the classical turning points. Clearly, there exists finite probability of finding the particle outside the well. This is a quantum mechanical effect.

Case $E > V_0$:

The Schordinger equation in Regions I and III is given by,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\,\psi(x) = 0$$

Since E is greater than V_0, $\frac{2m}{\hbar^2}(E - V_0)$ is a real positive quantity. As such the solution of the above equation is sinusoidal in nature. The probability density for the particle is distributed over all space in regions I and III. It is also distributed in Region II, i.e., within the well. Thus we do not get bound state for the particle.

4.11 DEPENDENCE UPON POTENTIAL

NOTES

To derive expression for phase shift, we have to consider the radial part of the Schrodinger wave equation that describes the scattering,

$$\frac{d^2u_l(r)}{dr^2}+\left[\frac{2\mu E}{\hbar^2}-\frac{2\mu V}{\hbar^2}-\frac{l(l+1)}{r^2}\right]u_l(r)=0 \qquad \text{...... (4.120)}$$

Here, $u_l = rR_l(r)$ and wave is coming from the region where the potential is zero that is, $V=0$

$$\frac{d^2u_l}{dr^2}+\left[k^2-\frac{l(l+1)}{r^2}\right]u_l(r)=0$$

And $k^2=\frac{2\mu E}{\hbar^2}$ ...... (4.121)

The solution of the above differential equation is

$$u_l(kr)=krj_l(kr) \qquad \text{...... (4.122)}$$

Asymptotic solution is,

$$u_l(kr)\xrightarrow[r\to\infty]{}\sin\left(kr-\frac{l\pi}{2}\right) \qquad \text{...... (4.123)}$$

In the same way, the asymptotic solution of

$$\frac{d^2v_l}{dr^2}+\left[k^2-\frac{2\mu V}{\hbar^2}-\frac{l(l+1)}{r^2}\right]v_l=0 \qquad \text{...... (4.124)}$$

Is,

$$v_l(kr)\xrightarrow[r\to\infty]{}\sin\left(kr-\frac{l\pi}{2}+\delta_l\right) \qquad \text{...... (4.125)}$$

Multiplying the Equation (4.121) by and Equation (4.124) by. Then subtracting, we get

$$v_l\frac{d^2u_l}{dr^2}-u_l\frac{d^2v_l}{dr^2}=-\frac{2\mu V}{\hbar^2}u_lv_l \qquad \text{...... (4.126)}$$

At $r=0$ the functions $u_l(r)$ and $v_l(r)$ are equal to zero. By integrating the equation (4.108) from to we get,

$$v_l\frac{du_l}{dr}-u_l\frac{dv_l}{dr}=-\frac{2\mu}{\hbar^2}\int_0^r V(r')u_l(r')v_l(r')dr' \qquad \text{...... (4.127)}$$

Now expanding the region of *r* to ∞, from Equations (4.123) and (4.124) we get

$$k\sin\left(kr-\frac{l\pi}{2}+\delta_l\right)\cos\left(kr-\frac{l\pi}{2}\right)-k\sin\left(kr-\frac{l\pi}{2}\right)\cos\left(kr-\frac{l\pi}{2}+\delta_l\right)=-\frac{2\mu}{\hbar^2}\int_0^\infty V(r)u_l(kr)v_l(kr)dr \quad \text{...... (4.128)}$$

$$k\sin\delta_l=-\frac{2\mu}{\hbar^2}\int_0^\infty V(r)u_l(kr)v_l(kr)dr \quad \text{...... (4.129)}$$

At very high energies for weak potential, the phase shift is very small and we can do the following approximations

$$u_l(kr)\cong v_l(kr)\cong krj_l(kr)$$

The relation between spherical Bessel function and the ordinary Bessel function is,

$$j_l(kr)=\left(\frac{\pi}{2kr}\right)^{1/2} J_{l+(1/2)}(kr) \quad \text{...... (4.130)}$$

Hence,

$$k\sin\delta_l=-\frac{2\mu k^2}{\hbar^2}\int_0^\infty V(r)j^2{}_l(kr)r^2dr$$

From Equation (4.131) we get,

$$\sin\delta_l=-\frac{2\mu k}{\hbar^2}\int_0^\infty V(r)\left[\left(\frac{\pi}{2kr}\right)^{1/2} J_{l+(1/2)}(kr)\right]^2 r^2dr$$

By simplifying we get,

$$\delta_l=-\frac{\mu\pi}{\hbar^2}\int_0^\infty V(r)\left[J_{l+(1/2)}(kr)\right]^2 rdr \quad \text{...... (4.131)}$$

This expression is only valid for weak potentials. The Equation (4.131) gives the expression for phase shift for weak potentials.

4.12 SIGN OF THE PHASE SHIFT

In scattering theory the phase shift is very important. Phase shift is measured by comparing the incoming wave and the scattered wave. When wave is scattered from the target (potential) there will be a change in the phase, in other words the scattered wave is delayed compared to the incident wave. At high energy for low potential, the phase shift is very small. The sign of the phase shift is depends on the potential. Let us consider equation for phase shift

$$\delta_l=-\frac{\mu\pi}{\hbar^2}\int_0^\infty V(r)\left[J_{l+(1/2)}(kr)\right]^2 rdr \quad \text{...... (4.132)}$$

This expression is also known as **Born approximation** for phase shift. This expression is only valid for weak potentials. If value of potential is, it is known as repulsive potential and in this case phase shift is negative. If value of potential is, it is known as ***attractive potential*** and in this case phase shift is positive.

4.12.1 Born Approximation

Generally in scattering theory and in particular in quantum mechanics, the ***Born approximation*** consists of taking the incident field in place of the total field as the driving field at each point in the scatterer. The Born approximation is named after Max Born who proposed this approximation in early days of quantum theory development. It is the perturbation method applied to scattering by an extended body. It is accurate if the scattered field is small compared to the incident field on the **scatterer**.

For example, the scattering of radio waves by a light styrofoam column can be approximated by assuming that each part of the plastic is polarized by the same electric field that would be present at that point without the column, and then calculating the scattering as a radiation integral over that polarisation distribution.

Born Approximation to the Lippmann–Schwinger Equation

The Lippmann–Schwinger equation for the scattering state $|\Psi_{\mathbf{p}}^{(\pm)}\rangle$ with a momentum p and out-going (+) or in-going (–) boundary conditions is,

$$|\Psi_{\mathbf{p}}^{(\pm)}\rangle = |\Psi_{\mathbf{p}}^{\circ}\rangle + G^{\circ}(E_p \pm i\epsilon)V|\Psi_{\mathbf{p}}^{(\pm)}\rangle,$$

Where G^0 is the free particle Green's function, ε is a positive infinitesimal quantity, and V the interaction potential. $|\Psi_{\mathbf{p}}^{\circ}\rangle$ is the corresponding free scattering solution sometimes called the incident field. The factor $|\Psi_{\mathbf{p}}^{(\pm)}\rangle$ on the right hand side is sometimes called the driving field.

Within the Born approximation, the above equation is expressed as:

$$|\Psi_{\mathbf{p}}^{(\pm)}\rangle = |\Psi_{\mathbf{p}}^{\circ}\rangle + G^{\circ}(E_p \pm i\epsilon)V|\Psi_{\mathbf{p}}^{\circ}\rangle,$$

Which is, much easier to solve since the right hand side no longer depends on the unknown state $|\Psi_{\mathbf{p}}^{(\pm)}\rangle$.

The obtained solution is the starting point of the Born series.

Born Approximation to the Scattering Amplitude

Using the outgoing free Green's function for a particle with mass ***m*** in coordinate space,

$$G^{(+)}(\mathbf{r},\mathbf{r}') = -\frac{2m}{\hbar^2}\frac{e^{+ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}$$

One can extract the Born approximation to the scattering amplitude from the Born approximation to the Lippmann–Schwinger equation above,

$$f_{\text{Born}}(\theta) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3r e^{i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r}) ,$$

Where q is the transferred momentum.

NOTES

The Born–Oppenheimer (B-O) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927, in the early period of quantum mechanics.

The approximation is widely used in quantum chemistry to speed up the computation of molecular wave functions and other properties for large molecules. There are cases where the assumption of separable motion no longer holds, which make the approximation lose validity, it is said to 'break down', but is then often used as a starting point for more refined methods.

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms, for example:

$$\mathbf{E}_{\mathbf{Total}} = \mathbf{E}_{\mathbf{Electronic}} + \mathbf{E}_{\mathbf{Vibrational}} + \mathbf{E}_{\mathbf{Rotational}} + \mathbf{E}_{\mathbf{Nuclear\ Spin}}$$

These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies $\mathbf{E}_{\mathbf{Electronic}}$ consist of kinetic energies, interelectronic repulsions, internuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

The benzene molecule consists of 12 nuclei and 42 electrons. The Schrödinger equation, which must be solved to obtain the energy levels and wave function of this molecule, is a partial differential eigenvalue equation in the three-dimensional coordinates of the nuclei and electrons, giving 3 × 12 + 3 × 42 = 36 Nuclear + 126 Electronic = 162 Variables for the wave function. The computational complexity, i.e., the computational power required to solve an eigenvalue equation, increases faster than the square of the number of coordinates.

When applying the Born–Oppenheimer (B-O) approximation, the following two consecutive steps are significant:

For a given position of the nuclei, the electronic Schrödinger equation is solved, while treating the nuclei as stationary (not "coupled" with the dynamics of the electrons). This corresponding eigenvalue problem then consists only of the 126 electronic coordinates. This electronic computation is then repeated for other possible positions of the nuclei, i.e. deformations of the molecule. For benzene, this could be done using a grid of 36 possible nuclear position coordinates. The electronic energies on this grid are then connected to give a potential energy surface for the nuclei. This potential is then used for a second Schrödinger equation containing only the 36 coordinates of the nuclei.

The slope of the potential energy surface can be used to simulate molecular dynamics, using it to express the mean force on the nuclei caused by the electrons and thereby skipping the calculation of the nuclear Schrödinger equation.

Principally, the Born-Oppenheimer (B-O) approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions. Following are the assumptions:

1. The electronic wavefunction depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
2. The nuclear motion, for example rotation, vibration, observes a smeared out potential from the speedy electrons.

If a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being,

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$, where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of H_1 and H_2 with eigenvalues E_1 and E_2, then,

$$\begin{aligned} H\psi(q_1, q_2) &= (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) \\ &= H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) \\ &= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\ &= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\ &= E\psi(q_1, q_2) \end{aligned}$$

Thus the eigenfunctions of H are products of the eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2.

The eigenfunctions and eigenvalues of this Hamiltonian can be given by solution of the time-independent Schrödinger equation of the form,

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})]\,\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

Using the Born-Oppenheimer approximation considering that there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be broken by assuming a quasi-separable form,

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

Where $\phi_N(\mathbf{R})$ is a nuclear wave function and $\phi_e(\mathbf{x},\mathbf{R})$ is an electronic wave function that depends parametrically on the nuclear positions.

Fundamentally, the Born-Oppenheimer (B-O) approximation is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. The electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are 'dragged' along with the nuclei without requiring a finite relaxation time. This, certainly, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this 'instantaneous' method, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

The B-O approximation recognizes the large difference between the electron mass and the masses of atomic nuclei, and correspondingly the time scales of their motion. Given the same amount of kinetic energy, the nuclei move much more slowly than the electrons. In mathematical terms, the BO approximation consists of expressing the wavefunction of a molecule as the product of an electronic wavefunction and a nuclear (vibrational, rotational) wavefunction. This enables a separation of the Hamiltonian operator into electronic and nuclear terms, where cross-terms between electrons and nuclei are neglected, so that the two smaller and decoupled systems can be solved more efficiently.

The Born approximation is used in several different physical contexts.

In neutron scattering, the first-order Born approximation is almost always adequate, except for neutron optical phenomena like internal total reflection in a neutron guide, or grazing-incidence small-angle scattering. The Born approximation has also been used to calculate conductivity in bilayer graphene and to approximate the propagation of long-wavelength waves in elastic media. The same ideas have also been applied to studying the movements of seismic waves through the Earth.

4.13 EFFECTIVE RANGE THEORY

We can study the energy dependence of low energy scattering by defining the effective range. To get the scattering cross section we need phase shift δ_l, where $l-0,1,2,\ldots$. For a low ebergy scattering s-wave ($l=0$) is dominating. Let us consider that the range of the potential is very small and only s-wave is involved in the scattering. Let E or kr_0 is very low, where r_0 is the range of the potential.

We know that scattering amplitude is given by

$$f(\theta)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)P_l(\cos\theta)\sin\delta_l \qquad \ldots\ldots (4.133)$$

For s-wave, $l = 0$.

$$f_0(\theta) = \frac{1}{k}\exp(i\delta_0)\sin\delta_0 \qquad \text{...... (4.134)}$$

The limiting value of energy is zero (this limiting value is derived from differential scattering cross section foe s-wave). Thus, as $E \to 0 - f(\theta) = a$, where is called *scattering length or effective range*. Thus Equation (4.116) can be written as

$$a = \lim_{E\to 0}\left[-f(\theta)\right] = -\lim_{E\to 0}\frac{1}{k}\exp(i\delta_0)\sin\delta_0 \qquad \text{...... (4.135)}$$

The zero energy cross section is given by, $\sigma_0 = 4\pi a^2$ ...... (4.136)

A small range of potential means $V(r)$ is weak and δ_0 (the phase shift) will be very small. Thus we can say $\exp(i\delta_0) = 1$ and $\sin\delta_0 \cong \delta_0$

$$a = \lim_{E\to 0}(-\frac{\delta_0}{k}) \qquad \text{...... (4.137)}$$

$$a = -\frac{\delta_0}{k}$$

$$\Rightarrow \delta_0 = -ka \qquad \text{...... (4.138)}$$

Hence, the phase shift of s-wave in zero energy limit depends on *scattering length* or *effective range*. This concept is used in the investigation of scattering of thermal neutrons.

4.13.1 Bethe Formula

The ***Bethe formula*** or ***Bethe-Bloch formula*** describes the mean energy loss per distance travelled of swift charged particles (protons, alpha particles, atomic ions) traversing matter (or alternatively the stopping power of the material). For electrons the energy loss is slightly different due to their small mass (requiring relativistic corrections) and their indistinguishability, and since they suffer much larger losses by Bremsstrahlung, terms must be added to account for this. Fast charged particles moving through matter interact with the electrons of atoms in the material. The interaction excites or ionizes the atoms, leading to an energy loss of the traveling particle. The non-relativistic version was found by Hans Bethe in 1930; the relativistic version is the most probable energy loss differs from the mean energy loss and is described by the ***Landau-Vavilov distribution***.

The Formula

For a particle with speed ***v***, charge ***z*** (in multiples of the electron charge), and energy ***E***, traveling a distance ***x*** into a target of electron number density ***n*** and mean excitation potential ***I***, the relativistic version of the formula reads, in SI units:

$$-\left\langle \frac{dE}{dx} \right\rangle = \frac{4\pi}{m_e c^2} \cdot \frac{nz^2}{\beta^2} \cdot \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \cdot \left[\ln\left(\frac{2m_e c^2\beta^2}{I\cdot(1-\beta^2)}\right) - \beta^2\right] \qquad \text{......(4.139)}$$

Where c is the speed of light and ε_0 the vacuum permittivity, $\beta = \frac{v}{c}$, e and m_e the electron charge and rest mass respectively.

Here, the electron density of the material can be calculated by

$$n = \frac{N_A \cdot Z \cdot \rho}{A \cdot M_u},$$

Where **ρ** is the density of the material, ***Z*** its atomic number, ***A*** its relative atomic mass, $\boldsymbol{N_A}$ the ***Avogadro number*** and $\boldsymbol{M_u}$ the Molar mass constant.

In the Figure 4.15 to the right, the small circles are experimental results obtained from measurements of various authors, while the red curve is Bethe's formula. Evidently, Bethe's theory agrees very well with experiment at high energy. The agreement is even better when corrections are applied.

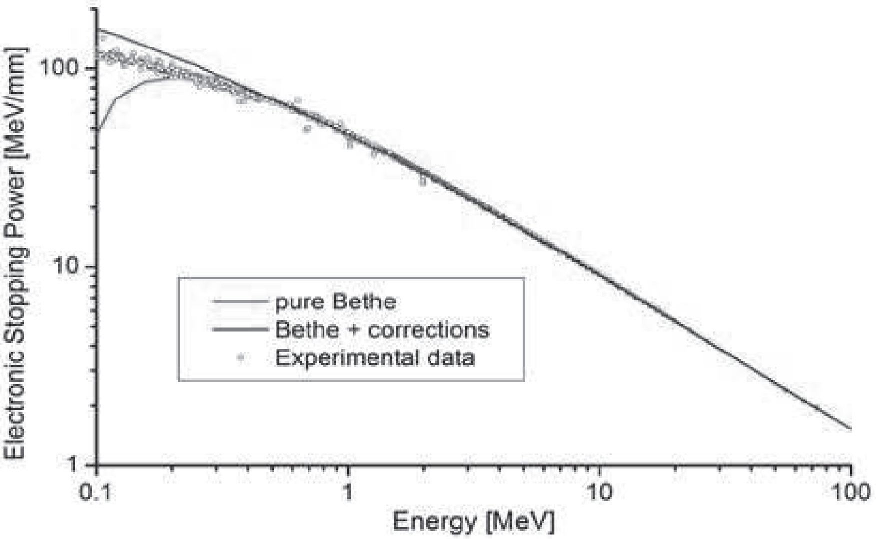

Fig 4.15 Stopping Power of Aluminum for Protons versus Proton Energy, and the Bethe Formula Without (Red) and With Corrections (Blue)

For low energies, i.e., for small velocities of the particle β << 1, the Bethe formula reduces to

$$-\frac{dE}{dx} = \frac{4\pi n z^2}{m_e v^2} \cdot \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \cdot \left[\ln\left(\frac{2m_e v^2}{I}\right)\right]. \qquad \text{.......(4.140)}$$

This can be seen by first replacing **βc** by ***v*** in Equation (4.139) and then neglecting $\boldsymbol{\beta^2}$ because of its small size.

At low energy, the energy loss according to the Bethe formula therefore decreases approximately as $\mathbf{v^{-2}}$ with increasing energy. It reaches a minimum for approximately $E = 3Mc^2$, where M is the mass of the particle (for protons, this would be about at 3000 MeV). For highly relativistic cases $\beta \approx 1$, the energy loss increases again, logarithmically due to the transversal component of the electric field.

4.14 SCATTERING: A WAVE PACKET APPROACH

Scattering is a process in which incident particles (or waves) are affected by interaction with some kind of target. The interaction can affect an incident particle in a number of ways it may change its speed, direction of motion or state of interval excitation. Particles can even be created, destroyed or obsorbed.

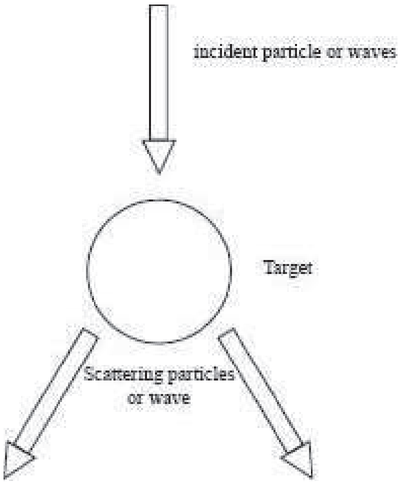

Fig 4.16 *The phenomenon of Scattering*

One dimentional problem in which an incident beam or particle is either transmitted (allow to pass) or reflected) as a result of scattering from a target. Moreover, that target will generally be represent by a fixed potential function, typically a finite well or a finite barrier of the kind indicated in fig 4.17. Finite potential energy barrier of height V_0 can reflect a particle of energ E_0.

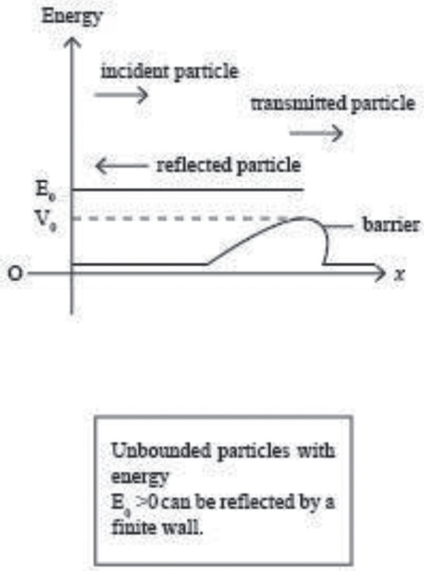

Fig. 4.17 **(*a*)**

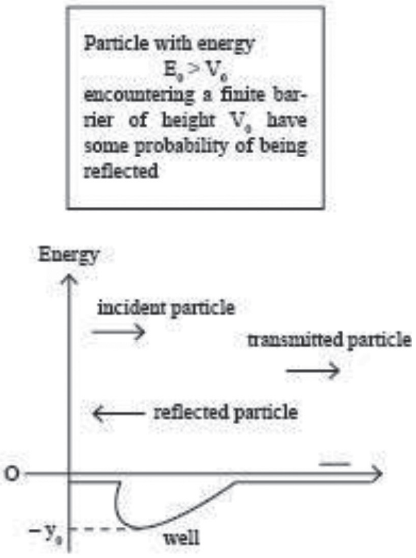

Fig. 4.17 **(*b*)**

Scattering problem needs a temporal description, namely how a wave packet representing the incident particle as t → –∞ behaves as it passes through the region of perturbation and proceeds to t → –∞. However, when there is a steady current of particle in the beam, we often dispense with the temporal description.

Calculate the current of particles at an infinite distance away from the target. This is done by looking for asymptotic solutions of the time-independent Schrodinger equation Since the region the particles are free.

Time Independent Schrodinger Equation

$$\nabla^2\psi(r)+\frac{2\mu}{\hbar^2}\left[E-V(r)\psi(r)\right]=0 \qquad ...(4.141)$$

consider a fixed scattering center which represents the reduce mass of the particle provided the potential energy function depends only on the magnitude of the distance between the two particle $V = V(|r_1 - r_2|)$ Such potentials are known as spherically potentials E represents the energy in the centre of mass system and $r = r_1 - r_2$ represents the relative co-ordinate:

Solution of the Schrodinger equation in the form of an incident plane wave and an outgoing scattering wave

$$\psi(r)\xrightarrow[r\to\infty]{}e^{jkr}+f(\theta)\,\frac{e^{jkr}}{r} \qquad ...(4.142)$$

where $k = kz\ \hat{z}$ representing a unit vector along z axis.

$\underset{r\to\infty}{\mathrm{Lt}}\ r\,V(r) = 0$, short range force

The asymptotic solution of schrodinger equation will be of the form

$$f(\theta)\frac{e^{ikr}}{r}+g(\theta)\frac{e^{-jkr}}{r} \qquad ...(4.143)$$

Second term corresponds to an incoming wave and hence neglected in equation (4.142). Since the potential is assumed to be spherically symmetric; the amplitude of scattered wave. (i.e. the function f) is assured to be independent of the azimuthal angle ϕ.

Multiply the equation (4.142) by appropriate time factor $e^{(-jEt/\hbar)}$, it will be seen that the first term represents a plane wave propagating along the z axis, since $|e^{ikz}|^2 = 1$, the number of particles per unit area per unit time is simply

$$v_\infty=\frac{\hbar k}{m}$$

current density

$$J=\mathrm{Re}\left[\frac{e^{jkr}}{r}f^{\infty}(\theta)\frac{\hbar}{Jm}\nabla\left(\frac{e^{jkr}}{r}f(\theta)\right)\right]$$

or $$J \simeq v_\infty \frac{|f(\theta)|^2}{r^2}\hat{r} \quad \text{...(4.144)}$$

The $1/r^2$ dependence of J implies that the intensity of the scattered wave falls off according to the inverse squares law. The function f (ϕ) describes the angular distribution of the scattered wave and is known as the scattering amplitude.

NOTES

4.14.1 Stationary States and Scattering in One Dimension

The key idea of the stationary state approach is to avoid treating individual particles, and to consider instead the scattering of a steady intense beam of particles, each particles having the same energy E_0. A is not possible to predict the exact behaviour of any particular particle but, of the incident beam is sufficient intense, the result of the scattering will be reflected and transmitted beams with steady intensities that are determined by the reflection and transmission coefficients.

For a one-dimentional beam, the intensity J to be the number of beam particles that pass a given point per unit time. The linear number density n of the beam to be the number of beam particles per unit length.

If all the particle in a beam have the same speed v, the beam intensity is given

$$J = Vn \quad \text{...(4.145)}$$

$$J_{inc} = V_{inc}, \; J_{ref} = V_{ref}\, n_{ref}, \; J_{trans} = V_{trans}\, n_{trans}$$

In stationary state approach, the reflection and transmission coefficient can be expressed in terms of beam intensity ratio, as follow

$$R = \frac{J_{ref}}{J_{inci}}, \qquad \text{and} \qquad T = \frac{J_{trans}}{J_{ine}}$$

If all the incident particles are scattered, and no particles are created or destroyed, it must be the case that

$$J_{inc} = J_{ref} + J_{trans}$$

Dividing both sides by J_{inc} and rearranging gives

$$R + T = 1$$

Schroding's equation is normally used to describe individual particle, rather than beam of particles.

For finite sgnare step (one dimentional scattering lenget) potential energy function

$$V(x) = 0 \text{ for } x \le 0$$

$$V(x) = V_0 \text{ for } x > 0$$

The discontinuous change in the potential energy at x = 0 is of course unrealistic but this is the feature that makes the finite sgnare step simple to treat mathematically. The fact that a sgnare step means that we shall only have to consider two region of the x-axis: Region 1 where $x \le 0$ and region 2 where $x > 0$

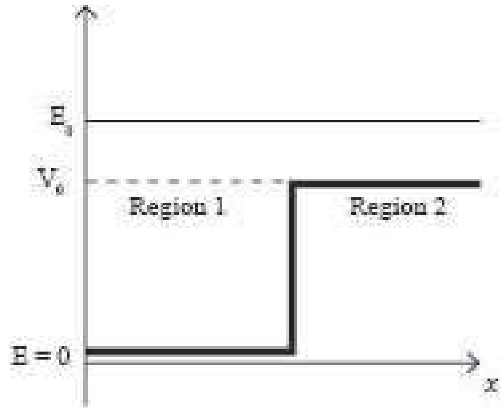

Fig 4.18 *A finite sgnare step of height $V_0 < E_0$*

When a finite sgnare step of height V_o scatters a right ward moving beam in which each particle has energy $E_0 > V_0$ each of the particles will continue moving to the right but will be suddenly showed as it passes the point x = 0. The transmitted particles are slowed because, in the region x > 0, each particles has an increased potential energy and hence a reduced kinetic energy. The intensity of each beam is the product of the linear number density and the speed of the particles in that beam

Schrodinger equation

$$i\hbar\frac{\delta\psi(r,t)}{\delta t} = -\frac{\hbar^2}{2m}\frac{\delta^2\psi(x,t)}{\delta x^2} + V_x\Psi_{(x,t)} \qquad ...(4.146)$$

V_x = Finite square step potential energy function stationary state solution

$$\Psi_{(x,t)} = \Psi_{(x)}e^{iE_0t/\hbar}$$

E_0 = fixed energy of each beam particle solving the time independent schrodingei equations

$$-\frac{\hbar^2}{2m}\frac{\delta^2\Psi}{\delta x^2} + E_0\Psi_{(x)} \text{ for } x \le 0 \qquad ...(4.147)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{\delta x^2} + V_0\Psi_{(x)} = E_0\Psi_{(x)} \text{ for } x > 0 \qquad ...(4.148)$$

A simple rearrangement gives

$$\frac{\delta^2\Psi}{\delta x^2} + \frac{2mE_0}{\hbar^2}\Psi_x = 0 \text{ for } x \le 0$$

$$\frac{\delta^2\Psi}{\delta x^2} + \frac{2m(E_0 - V_0)}{\hbar^2}\Psi_x = 0 \text{ for } x > 0$$

General Solutions

$$\psi_x = Ae^{ik_1x} + Be^{-ik_1x} \text{ for } x \le 0 \text{ Region 1} \qquad ...(4.149)$$

$$\psi_x = Ce^{ik_2x} + De^{-ik_2x} \text{ for } x > 0 \text{ Region 2} \qquad ...(4.150)$$

where A, B, C and D are arbitrary complex constant and the wave number in Region 1 and Region 2 are respectively

$$K_1 = \frac{\sqrt{2mE_0}}{\hbar} \text{ and } K_2 = \frac{\sqrt{2m(E_0 - V_0)}}{\hbar} \qquad ...(4.151)$$

complex exponentials rather than sines and cosines ($e^{ix} = \cos x + i \sin x$)

Equation 4.1459 and 4.150 have interpretation in term of the incident, reflected and transmitted beams.

$$\hat{P}x\, e^{\pm jkx} = -j\hbar \frac{\delta}{\delta x} e^{\pm jkx} = -j\hbar \frac{\delta}{\delta x} e^{\pm jkx} = \pm \hbar e^{\pm jkx}$$

where $\overline{P}_x$ is the momentum operator in the x direction.

It therefore follows that terms proportional to e^{ikx} are associated with particles moving rightward at speed $\hbar k/m$.

These directions of motion can be confirmed by writing down the corresponding stationary state solutions, which take the form

$$\psi_{(x,t)} = Ae^{j(K_1x - \omega t)} + Be^{-j(K_2x + \omega t)} \text{ for } x \le 0 \qquad ...[4.152\text{ (a)}]$$

$$\psi_{(x,t)} = Ce^{j(K_2x - \omega t)} + De^{-j(K_2x + \omega t)} \text{ for } x > 0 \qquad ...[4.152\text{ (b)}]$$

where $\omega = E_0/\hbar$. Identify terms of the form $e^{j(kx-\omega t)}$ as plane wave's travelling in the positive x-direction, while terms of the form $e^{-j(kx+\omega t)}$ are plane wave travelling in the negative x-direction. None of the these waves can be normalised, so they cannot describe individual particles, but describe as steady beam of particles

$\psi_{(x,\,t)}$ describe the state of a single partcle

$|\psi_{(x,\,t)}|^2$ represents the probability density for that particle.

In the steady state approach to scattering however it is assumed that the wave function $\psi_{(x,\,t)}$ describes steady beams of particles with $|\psi_{(x,\,t)}|^2$ interpreted as the number of particles per unit length that is the linear number density of particles.

The wave function is not normalisable, and this corresponds to the fact that the steady beams extend indefinitely to the left and right of the step and therefore contain an infinite number of particles.

Each particle in the beam travels to the right with speed $V_{inc} = \hbar k/m$ and that the linear number density of particles in the beam is

$$n_{inc} = \left|Ae^{j(K_1x-\omega t)}\right|^2 = |A|^2 \left|e^{s(K_1x-\omega t)}\right|^2 = |A|^2$$

The reflected beam in region 1 ($x \le 0$). This beam travels to the left with speed $V_{ref} = \hbar k_1/m$ and has linear number density

$$n_{ref} = |B|^2$$

Equation 4.152 (b), first term on the right represents the transmitted beam in Region 2 ($x > 0$). This beam travels to this right with speed $V_{trans} = \hbar k_2/m$ and has linear number density $n_{trans} = |C|^2$. The second term on the right of equation

4.152(b) would represent a left word moving beam in the region x > 0. On physical grounds, expect these to be any such beam, so its absence by setting D = 0;

Using these interpretations, the beam intensities are

$$J_{inc} = \frac{\hbar k_1}{m}|A|^2,\ J_{ref} = \frac{\hbar k_1}{m}|B|^2,\ J_{tran} = \frac{\hbar k_2}{m}|C|^2$$

Expressions for the reflection and transmission coefficients

$$R = \frac{J_{ref}}{J_{inc}} = \frac{|B|^2}{|A|^2} = \left|\frac{B}{A}\right|^2$$

$$T = \frac{J_{trans}}{J_{inc}} = \frac{k_2|C|^2}{k_1|A|^2} = \frac{k_2}{k_1}\left|\frac{C}{A}\right|^2$$

Expression for the transmission coefficient includes the wave number k_1 and k_2, which are proportional to the speeds of the beams in Regions 1 and 2. The wave numbers cancel in the expression for the reflection coefficient because the incident and reflected beams both travel in the same region. To calculate R and T, need to find the ratio B/A and C/A. To achieve this, eliminate unwanted arbitary constant.

4.14.2 Resonance Tunnelling and Metastable States

Consider an arbitrary but finite length potential 'bump' (formally called a scatter), localised somewhere between point x_1 and x_2, on the Hat potential background, say E = 0

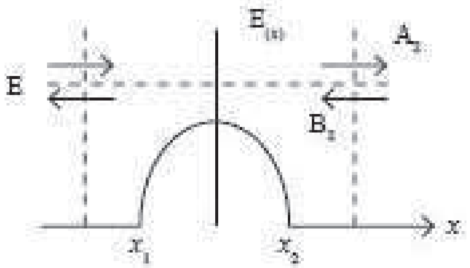

Fig 4.19 *De Broglie wave amplitudes near a one dimentional scatterer*

Schrodinger equation, with a certain energy E, outside the interval $[x_1, x_2]$ is a set of two sinusoidal wave, travelling in the opposite directions.

$$\psi_j = Aje^{jk(x-xj)} + Bj\ e^{-ik(x-xj)} \qquad (\ldots 4.153)$$

j = 1/2 (either 1 or 2)

$$\frac{(\hbar k)^2}{2m} = E$$

Linear Schrodinger equation within the scatterer range ($x_1 < x < x_2$) can provide only linear expression for the tranmitted A_2 and reflected B_1 wave amplitude and the incident wave amplitude A_1 ($B_2 = 0$ incident from the left)

$A_2 = S_{21} A_1$ $\qquad$ S_{11}, S_{21} are certain (Generally complex)

$B_1 = S_{11} A_1$ coefficients

Alternatively, if a wave, with amplitude B_2 is incident on the scatterer from the right (i.e. if $A_1 = 0$), it can induce a transmitted wave (B_1) and a reflected wave (A_2) with amplitude

$B_1 = S_{12} B_2, A_2 = S_2 B_2$

where S_{22}, S_{12} are generally different from S_{12} and S_{21}.

Scattering matrix is linear relation

$$\begin{pmatrix} B_1 \\ A_2 \end{pmatrix} = S \begin{pmatrix} A_1 \\ B_2 \end{pmatrix} \text{ with } S \equiv \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}$$

Double barrier System

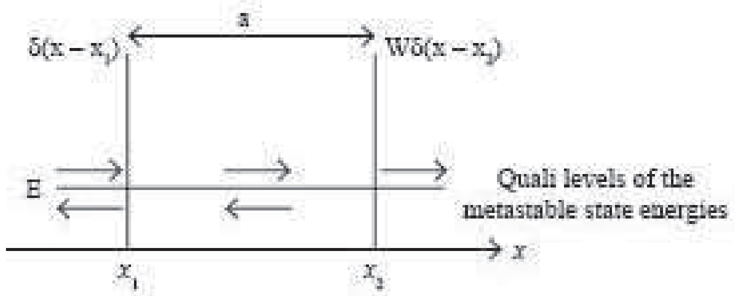

Fig 4.20 : *Double Barrier System*

$$J = \frac{1}{|T_{11}|^2} = \frac{1}{|\propto^2 e^{jka} + (1 - j\propto)^2 e^{jka}|^2}$$

Double layer transparency, the transparency is a π-periodic function of the product ka, reaching its maximum (J = 1) at some point of each period.

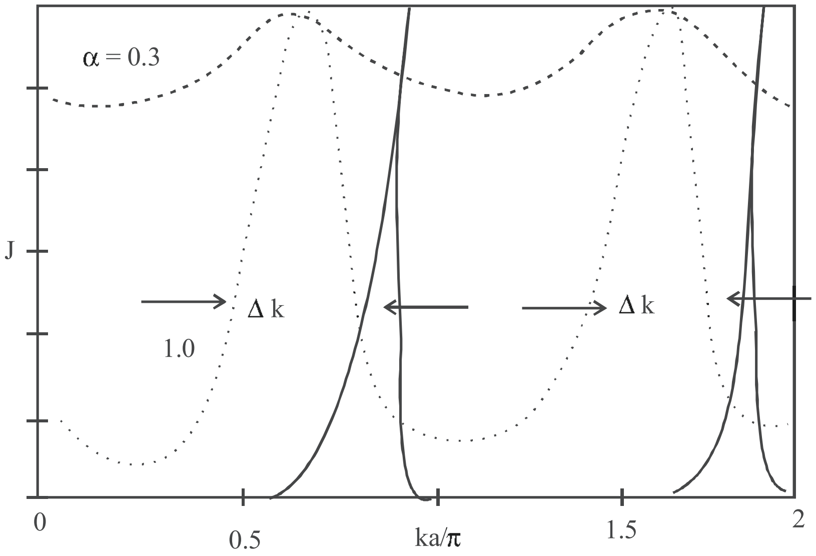

Fig 4.21 : *The system's transparency as a function of* k_a *[Resonance tunneling through a potential well with delta functional wall]*

For a >>> 1, the resonance peaks of transparency are very narrow, reaching their maximum at ka ≈ k_na = nπ where n = 1, 2 ..

Let us assume that the initial state of the particle coincides with one of the stationary states of the infinite wall well of the same size

$$X \alpha \sin k_x x \text{ with } k_x = \frac{\pi n_x}{a_x} \text{ so that } X = \left(\frac{2}{9_x}\right)^{1/2} \sin \frac{\pi_2}{a_x} \text{ with } n_x = 1, 2, \ldots$$

Rectangular potential well one dimensional light function

$$\psi_{(x,\,0)} = \psi_n (x) = \left(\frac{2}{a}\right)^{1/2} \sin [k_n (x - x_1)] \text{ where } k_n = \frac{\pi_n}{a},\ n = 1, 2, 3\ldots \qquad \ldots(4.154)$$

at α → ∞, this is just an eigen state of the system, and from our analysis, the time evolution of its wave function.

$$\psi_{(x,\,t)} = \psi_w (x)\, e^{(j\omega_n t)} = \left(\frac{2}{a}\right)^{1/2} \sin k_n (x - x_1)\, e^{(-j\omega_n t)} \qquad \ldots(4.155)$$

$$\text{With } \omega_n = \frac{En}{\hbar} = \frac{\hbar k_r^2}{2m}$$

We can tell us that the particle remains in the well at all times with constant probability

$$W(t) = W(0) = 1$$

If α is large but finite, the de-Broglie wave would slowly "leak out" from the well, so that W(t) would slowly decreases. Such a state is called "metastable" Generalize equation (4.155) as

$$\psi_{(x,\,t)} = \left(\frac{2w}{a}\right)^{1/2} \sin (k_n (x - x_1)\, e^{(-j\omega_n t)}$$

$$\equiv Ae^{\{j(k_n x - \omega_n t)\}} + Be^{-\{-j(k_n x + \omega_n t)\}} \qquad \ldots(4.156)$$

making the probability of finding the particle in the well equation to W ≤ 1.

$\psi_{(x,\,t)}$ function is the sum of two travelling waves, with equal magnitude of their amplitudes and equal but opposite probability currents

$$|A| = |B| = \left(\frac{W}{2a}\right)^{1/2} \qquad \ldots(4.157)$$

$$I_A = \frac{\hbar}{m} |A|^2\, k_n = \frac{\hbar}{m} \frac{w}{2a} \frac{\pi n}{a} \qquad I_B = -I_A$$

At a >> 1, the delta functional wall's transparency and equals 1/α^2, so that the wave carrying current I_A, incident on the right wall from the inside, induces an outcoming wave outside of the well with the following probability current.

$$I_R = JI_A = \frac{1}{\alpha^2} I_\wedge = \frac{1}{\alpha^2} \frac{\pi n \hbar W}{2ma^2} \qquad \ldots(4.158)$$

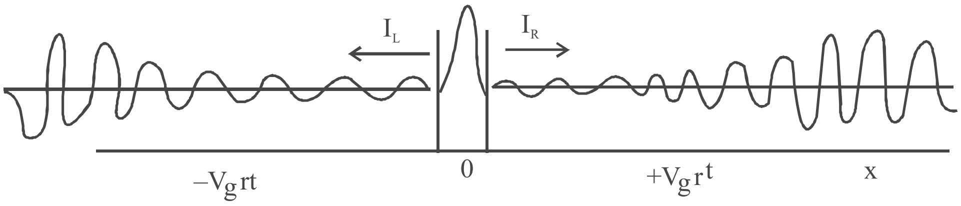

Fig 4.22 *Metastable state's decay in the simple model of a one dimensional potential well formed by two low transparent walls.*

Absolutely Similar

$$I_L = \frac{1}{\alpha^2} I_B = -I_R \qquad \text{...(4.159)}$$

Now combine the one dimensional probability conservation law for the well interior.

$$\frac{dW}{dt} + I_R - I_c = 0$$

Differential equation

$$\frac{dw}{dt} = -\frac{1}{\tau} W \qquad \text{... (4.160)}$$

of the exponextial decay; $W(t) = W(o)\, e^{(-t/\tau)}$,

$$\tau = \frac{ma^2}{\pi n\hbar}\alpha^2 \qquad \text{... (4.161)}$$

It is metalstable state's lifetime.

Wave group vector $V_{gr} = \dfrac{\hbar kn}{m}$

$$= \frac{\pi n\hbar}{ma}$$

General form of the equation (4.161)

$$\tau = \frac{t_a}{J}$$

t_a = attempt time is equal to a/Vgr.

4.15 INTEGRAL REPRESENTATION FOR SCATTERING PHASE SHIFTS

Consider the radial Schrodinger equation for a spherically symmetric potential

$\psi = U\,\psi$, $U = 2\,\mu\,(V_{eff} - E)$ ...(4.162)

where $V_{eff}(R) = V(R) + \dfrac{l(l+1)}{2\mu R^2}$ is the effective potential

μ = reduce mass of the two particles undergoing scattering and E > 0 is energy in the center of mass trans. Atomic units are used throughout.

Assuming that the interaction potential V(R) vanishes faster than R^{-1} asymptotically, the physical solution ψ(R) has the well known asymptotic behaviour.

$$\psi(R) \xrightarrow{R\to\infty} \sin\left(kR - l\frac{\pi}{2} + \delta_t\right) \qquad \text{... (4.163)}$$

which yields the scattering phase shift δ_t for partial wave l. $K = \sqrt{2\mu E}$ is the momentum for the relative motion. The phase shift is usually obtained from the matching condition.

$$\psi(\text{R}) = \text{Af(R)} + \text{Bg (R)} \qquad \text{...(4.164)}$$

where f and g are exact solutions of the radial equations, specified by their asymptotic behaviour,

$$f(R) \xrightarrow{R\to\infty} \sin\left(kR - l\frac{\pi}{2}\right) \qquad \text{...(4.165)}$$

$$g(R) \xrightarrow{R\to\infty} \cos\left(kR - l\frac{\pi}{2}\right) \qquad \text{...(4.166)}$$

From the equations above δ_t = are tan B/A which yield the phase shift modulo π i.e.,

$$\delta t \in \left[-\frac{\pi}{2}, \frac{\pi}{2}\right]$$

Integral representation for the full phase shift

An expression for d_t which does not rely on the explicit evaluation of wave functions instead, the phase shift will be extracted from an R-dependent phase function.

Introduce the envelope function

$$\rho = f^2 + g^2 \qquad \text{...(4.167)}$$

with f and g exact solutions of the radial equation (4.162) obeying the asymptotic behaviour in (4.165) and (4.166), the phase function θ is constructed by integrating

$$\theta' \equiv \frac{d\theta}{dR} = \frac{k}{P} \qquad \text{...(4.168)}$$

θ(R) is defined up to an integration constant which can be chosen freely.

The general solution of the radial equation (4.162) can be represented exactly in terms of p and θ. In particular, the physical solution reads

$$\psi(R) = \sqrt{P(R)\sin[\theta R - \theta(0)]} \qquad \text{...(4.169)}$$

ψ (R) vanishes explicitly at R = 0 while equation (4.165) and (4.166) ensure a key simple asymptotic behaviour for p and θ.

$$p(R) \xrightarrow{R\to\infty} 1 \qquad \text{...(4.170)}$$

$$\theta(R) \xrightarrow{R\to\infty} kR + \text{const.} \qquad ...(4.171)$$

Reduced phase

$$\theta(\text{R}) \equiv \theta(\text{R}) - \text{kR} \qquad ...(4.172)$$

use equation (4.170) and (4.171) in equation (4.169) [Milne's parametrization]

$$\psi(R) \xrightarrow{R\to\infty} \sin\left[kR + \theta(\infty) - \theta(\infty)\right]$$

identical to the asymptotic behaviour of ψ in equation (4.163) consequently, obtain

$$\delta_t - \ell\frac{\pi}{2} = \tilde{\theta}(\infty) - \theta(0) \qquad ...(4.173)$$

Making use of equation (4.172), $\theta(0) = \tilde{\theta}(0)$ and equation (4.168) and in yield $\tilde{\theta}' = \frac{k}{p} - k$. Hence equation (4.173) can be recast as an integral representation

$$\delta_t - \ell\frac{\pi}{2} = \tilde{\theta}(\infty) - \tilde{\theta}(0)$$

$$= k\int_0^\infty dr\left[\frac{1}{p(r)} - 1\right] \qquad ...(4.174)$$

The equation above yield the full phase shift $\left(\delta_t - \ell\frac{\pi}{2}\right)$

Check Your Progress

9. What do you understand by cross section at the resonance?
10. What is infinite potential well?
11. Define the phase shift in scattering theory.
12. State the Born approximation in scattering theory.
13. Mention the uses of Born approximation.
14. What is effective range?
15. What does the Bethe formula describe?

4.16 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The 'Scattering Theory' is significantly used for studying and understanding the scattering of waves and particles in mathematics and physics. Typically the wave scattering corresponds to the collision and scattering of a wave with some material object, for example formation of rainbow is resultant of sunlight scattered by rain drops.
2. The term 'Elastic Scattering' implies that the internal states of the scattering particles do not change, and hence they emerge unchanged from the scattering process.
3. Rayleigh scattering theory refers to the scattering of light off of the molecules of the air, and can be extended to scattering from particles up to about a

tenth of the wavelength of the light. It is Rayleigh scattering off the molecules of the air which gives us the blue sky.

4. When photons are scattered by a material, most of them are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency and wavelength) as the incident photons but different direction. However, a small fraction of the scattered photons (approximately 1 in 10 million) are scattered in-elastically, with the scattered photons having an energy different from, and usually lower than, those of the incident photons—these are Raman scattered photons.
5. When the beam of particles interact with the scattering potential, the incident beam of particles get scattered in all the directions. After leaving the target again they travel in a straight line. The angle is measured between incident and the scattered lines and it is known as scattering angle θ.
6. The scattering cross section gives the idea of the nature of target. It is not equal to the exact spatial area of the target. Usually, cross sections are measured in barns, where 1 barn $= 10^{-24}\ \text{cm}^2$.
7. In the centre of mass coordinate system, the two interacting particles are always at rest. So the coordinate systems move relative to each other and its velocity is equal to the velocity of centre of mass in the laboratory coordinate system. Hence the total momentum is always zero.
8. In scattering experiment the detector is far away from the target. The intensity of scattered wave depends only on θ and ϕ in spherical coordinate, the spherically diverging scattered wave amplitude is denoted by $f(\theta)$ and it is called as scattering amplitude. Scattering amplitude depends on. This can be found using partial wave analysis.
9. The cross section will attain the maximum value. This is known as resonance. The total cross section at the resonance depends on (where, $k = \dfrac{2\mu E}{\hbar^2}$).

   The Breit-Wigner formula will talk about the behaviour of the cross section near resonance.
10. Unlike the infinite potential well, there is a probability associated with the particle being found outside the box. The quantum mechanical interpretation is unlike the classical interpretation, where if the total energy of the particle is less than the potential energy barrier of the walls it cannot be found outside the box. In the quantum interpretation, there is a non-zero probability of the particle being outside the box even when the energy of the particle is less than the potential energy barrier of the walls (cf quantum tunnelling).
11. In scattering theory the phase shift is very important. Phase shift is measured by comparing the incoming wave and the scattered wave. When wave is scattered from the target (potential) there will be a change in the phase, in other words the scattered wave is delayed compared to the incident wave. At high energy for low potential, the phase shift is very small.
12. Generally in scattering theory and in particular in quantum mechanics, the Born approximation consists of taking the incident field in place of the total

field as the driving field at each point in the scatterer.

13. In neutron scattering, the first-order Born approximation is almost always adequate, except for neutron optical phenomena like internal total reflection in a neutron guide, or grazing-incidence small-angle scattering. The Born approximation has also been used to calculate conductivity in bilayer graphene and to approximate the propagation of long-wavelength waves in elastic media. The same ideas have also been applied to studying the movements of seismic waves through the Earth.
14. The limiting value of energy is zero (this limiting value is derived from differential scattering cross section foe s-wave). Thus, as $E \rightarrow 0 \; -f(\theta) = a$, where is called scattering length or effective range.
15. The Bethe formula or Bethe-Bloch formula describes the mean energy loss per distance travelled of swift charged particles (protons, alpha particles, atomic ions) traversing matter (or alternatively the stopping power of the material).

4.17 SUMMARY

- Rayleigh scattering is one commonly known type of scattering which mainly consists of scattering from atmospheric gases, it occurs when the particles causing scattering are smaller in size than the radiation wavelengths in contact with them.
- Scattering, in physics, is defined as a change in the direction of motion of a particle because of a collision with another particle. As defined in physics, a collision can occur between particles that repel one another, such as two positive (or negative) ions, and need not involve direct physical contact of the particles.
- The physicist Ernest Rutherford passed a stream of alpha particles through a thin sheet of gold foil. The alpha particles were emitted by a radioactive material and had enough energy to penetrate an atom; although most passed right through the gold foil, some were deflected in a way that indicated that the scattering was produced by a Coulomb force.
- When two atoms are scattered off one another, one can understand them as being the bound state solutions of some differential equation.
- Scattering by particles similar to, or larger than, the wavelength of light is typically treated by the Mie scattering theory, the discrete dipole approximation and other computational techniques. Rayleigh scattering applies to particles that are small with respect to wavelengths of light, and that are optically ‘soft’ (i.e., with a refractive index close to 1).
- The strong wavelength dependence of the scattering ($\sim\lambda^{-4}$) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths.
- The Rayleigh scattering is mostly seen occurring in nature, and therefore it is considered to be one of the most commonly observed optical phenomena.

- Raman scattering or the Raman effect is the inelastic scattering of a photon by molecules which are excited to higher energy levels. The effect was discovered in 1928 by C. V. Raman and hence named as Raman scattering or the Raman effect.
- The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the material and is independent of the absolute energy of the photon.
- Total cross section and the differential cross section have the dimension of area. If the potential is spherically symmetric, then differential cross section is independent of.
- The scattering cross section gives the idea of the nature of target. It is not equal to the exact spatial area of the target. Usually, cross sections are measured in barns, where.
- Experimental observations are done using laboratory coordinate system. But centre of mass coordinate system reduces the two body problem into one body problem. In these way degrees of freedom reduces by half.
- Thus centre of mass coordinate system is more convenient for the calculation of scattering problem.
- According to the classical scattering theory, let us say particle incident on some scattering centre (we can say target), it comes with some enrgy E and it will get deviated. We can assume that the target is heavy and recoil of target substance is negligible.
- In quantum scattering, waves feel their way around the whole sphere. But in case of classical scattering, the particles can see the head on cross section or a head on surface area.
- By solving the radial part of the Schrödinger equation we can explain the s-wave scattering by an attractive square well potential. Let us consider an equation from the scattering by an attractive square well potential.
- The finite potential well (also known as the finite square well) is a concept from quantum mechanics. It is an extension of the infinite potential well, in which a particle is confined to a ‘Box’, but one which has finite potential ‘Walls’.
- If value of potential is, it is known as repulsive potential and in this case phase shift is negative. If value of potential is, it is known as attractive potential and in this case phase shift is positive.
- The Born approximation is named after Max Born who proposed this approximation in early days of quantum theory development. It is the perturbation method applied to scattering by an extended body. It is accurate if the scattered field is small compared to the incident field on the scatterer.
- The scattering of radio waves by a light styrofoam column can be approximated by assuming that each part of the plastic is polarized by the same electric field that would be present at that point without the column, and then calculating the scattering as a radiation integral over that polarisation distribution.

- For electrons the energy loss is slightly different due to their small mass (requiring relativistic corrections) and their indistinguishability, and since they suffer much larger losses by Bremsstrahlung, terms must be added to account for this.
- Fast charged particles moving through matter interact with the electrons of atoms in the material. The interaction excites or ionizes the atoms, leading to an energy loss of the traveling particle.

4.18 KEY TERMS

- **Scattering:** Scattering occurs when light or other energy waves pass through an imperfect medium, such as air filled with particles of some sort, and are deflected from a straight path. The light is deflected off of its straight path and scatters in many directions.
- **Inelastic scattering:** In inelastic scattering, by contrast, the particles' internal state is changed, which may amount to exciting some of the electrons of a scattering atom, or the complete annihilation of a scattering particle and the creation of entirely new particles.
- **Rayleigh scattering:** It is the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the radiation. Rayleigh scattering does not change the state of material and is, hence, a parametric process.
- **Phase shift:** In scattering theory the phase shift is very important. Phase shift is measured by comparing the incoming wave and the scattered wave. When wave is scattered from the target (potential) there will be a change in the phase.
- **Bethe formula:** The Bethe formula or Bethe-Bloch formula describes the mean energy loss per distance travelled of swift charged particles (protons, alpha particles, atomic ions) traversing matter (or alternatively the stopping power of the material).

4.19 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. What is scattering theory?
2. What does Rayleigh scattering cross-section mean?
3. Who developed Rayleigh scattering?
4. What do you understand by selection rules for Raman scattering?
5. Distinguish between stock and anti-stock lines.
6. State the advantages and disadvantages of Raman scattering.
7. What is scattering angle?

8. What do you understand by centre of mass?
9. What is the impact parameter?
10. Define the resonance scattering.
11. State the effective range theory.

Long Answer Questions

1. Discuss the significance of term scattering theory giving appropriate examples.
2. Explain Rayleigh scattering theory and methods.
3. Describe the selection rules, advantages and disadvantages of Raman scattering.
4. Elaborate on the laboratory and centre of mass system.
5. Describe the scattering by a central potential with help of examples.
6. explain the partial wave analysis and phase shift method by giving examples.
7. Discuss in detail relation between phase shift and logarithmic derivatives.
8. Explain in detail scattering by a deep square well.
9. Describe the sign of the phase shift and Born approximation with relevant examples.

4.20 FURTHER READING

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UNIT 5 RELATIVISTIC QUANTUM MECHANICS

NOTES

Structure

5.0 INTRODUCTION

In general relativity, events are continuous and deterministic, meaning that every cause matches up to a specific, local effect. Classical relativity tells us that motion is relative to the observer's state of motion. However, classical relativity breaks down at the speed of light.

In physics and mathematics, the Lorentz group is the group of all Lorentz transformations of Minkowski spacetime, the classical and quantum setting for all (non-gravitational) physical phenomena. The Klein-Gordon equation is a relativistic version of the Schrödinger equation that describes the behavior of spin less particles. In particle physics, the Dirac equation is a relativistic wave equation derived by British physicist Paul Dirac in 1928. In its free form, or including electromagnetic interactions, it describes all spin-1/2 massive particles, such as electrons and quarks for which parity is a symmetry. A wave function expresses that the three things about the free particle: the energy of the particle, the momentum of the particle, and the probability density of finding the particle at any point.

The theory of hyperfine structure comes directly from electromagnetism, consisting of the interaction of the nuclear multipole moments (excluding the electric monopole) with internally generated fields. In relativistic quantum mechanics, the completely filled, negative-energy electron state that makes up a vacuum. If a negative-energy electron transitions to a positive-energy state, the resulting hole has the properties of a positron. In quantum mechanics, identical particles (also called indistinguishable or indiscernible particles) are particles that cannot be distinguished from one another, even in principle. In quantum mechanics, the exchange operator, also known as permutation operator, is a quantum mechanical operator that acts on states in Fock space.

In particle physics, a bosonis a subatomic particle whose spin quantum number has an integer value (0,1,2 ...). In quantum statistics, Bose-Einstein (B-E) statistics describes one of two possible ways in which a collection of non-interacting, indistinguishable particles may occupy a set of available discrete energy states at thermodynamic equilibrium.

Fermions include all quarks and leptons, as well as all composite particles made of an odd number of these, such as all baryons and many atoms and nuclei. Fermi-Dirac statistics is a type of quantum statistics that applies to the physics of a system consisting of many identical particles that obey the Pauli exclusion principle.

In this unit, you will study about the Relativistic Quantum Mechanics (RQM) and classical relativistic dynamics, Lorentz group, Klein-Gordon equation, Dirac equation, free electron plane wave, hyperfine position theory, hole theory, identical particle, permutation operator and algebra of permutation operator, boson and Bose-Einstein statistics, fermions and Fermi-Dirac statistics.

5.1 OBJECTIVES

- State the Relativistic Quantum Mechanics (RQM) and classical relativistic dynamics
- Know about the Lorentz group
- Understand the Klein-Gordon equation
- Analyse the Dirac equation
- Comprehend the free electron plane wave
- Interpret the hyperfine position theory
- Explain about the hole theory
- Discuss the identical particle
- Describe the permutation operator and algebra of permutation operator
- Elaborate on the boson and Bose-Einstein statistics
- Know about the fermions and Fermi-Dirac statistics

5.2 CLASSICAL RELATIVISTIC DYNAMICS

In physics, Relativistic Quantum Mechanics (RQM) is any Poincaré covariant formulation of Quantum Mechanics (QM). This theory is applicable to massive particles propagating at all velocities up to those comparable to the speed of light c, and can accommodate massless particles. The theory has application in high energy physics, particle physics and accelerator physics, as well as atomic physics, chemistry and condensed matter physics. Non-relativistic quantum mechanics refers to the mathematical formulation of quantum mechanics applied in the context of Galilean relativity, more specifically quantizing the equations of classical mechanics by replacing dynamical variables by operators. Relativistic Quantum Mechanics (RQM) is quantum mechanics applied with special relativity. Although the earlier formulations, like the Schrödinger picture and Heisenberg picture were originally formulated in a non-relativistic background, a few of them (For example, the Dirac or path-integral formalism) also work with special relativity.

Key features common to all RQMs include: the prediction of antimatter, spin magnetic moments of elementary spin 1/ 2 fermions, fine structure, and quantum dynamics of charged particles in electromagnetic fields. The key result is the ***Dirac equation,*** from which these predictions emerge automatically. By contrast, in non-relativistic quantum mechanics, terms have to be introduced artificially into the ***Hamiltonian operator*** to achieve agreement with experimental observations.

The most successful (and most widely used) RQM is relativistic Quantum Field Theory (QFT), in which elementary particles are interpreted as ***field quanta***. A unique consequence of QFT that has been tested against other RQMs is the failure of conservation of particle number, for example in matter creation and annihilation.

The classical relativistic dynamics is made up of two words, which are "classical" and '***Relativistic Dynamics'***. The word classical represents the macroscopic particles in a general sense. Here relativistic dynamics refers to the dynamics (physics) of those particles which moves with the speed comparable to the speed of light.

When the speed of the objects becomes comparable to the speed of light then the mass of the object is no longer a constant and is describes by the famous equation:

$$\mathrm{M{=}Mo}\ \sqrt{1-\frac{v^2}{c^2}}$$

The Einstein's special theory of relativity comes into the picture.

So, at high speeds when v ~ c, such that v=c/2, 3c/5, c/4, 4c/5, c/3, etc. If v=c/100, then it can be treated as non relativistic case.

The conditions for a particle to be treated as a relativistic case are as follows:

When the kinetic energy of a particle or an object is equal to or greater than its rest mass energy:

K.E $e \geq M_o c^2$

When the momentum of the object is greater than the product of the rest mass and the speed of light:

P $e \geq M_o c$

In relativistic dynamics, the relative velocity when the two objects (let 1 and 2) move in the same direction is given by:

$$V_{21} = \frac{v_2 - v_1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

The relativistic momentum equation is given by:

$$P = \frac{M_o v}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Solving this, we then get the value of the speed in terms of momentum i.e.

$$V = \frac{pc}{\sqrt{Mo^2 c^2 + p^2}}$$

The concept of rest mass energy also comes to the notice in relativistic dynamics. An object at rest has the rest mass energy which is given by:

$E = M_o c^2$

And the total energy of the free particle in motion is given by:

$$E = Mc^2 = \frac{M_o c^2}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Here v is the speed of the object with respect to the observer.

The relativistic kinetic energy is given by:

$K = Mc^2 - M_o c^2$

$$K = \frac{M_o c^2}{\sqrt{1 - \frac{v^2}{c^2}}} - M_o c^2$$

Energy momentum relation is given by:

$E = \sqrt{Mo^2 c^4 + p^2 c^2}$ which further gives,

$K = \sqrt{Mo^2 c^4 + p^2 c^2} - M_o c^2$

Which gives a formula for: $p = \frac{1}{c}\sqrt{K\left(K + 2MoC^2\right)}$

We also deal in relativistic dynamics about the expansion of KE in terms of momentum, as follows:

$$\text{KE}= \sqrt{Mo^2c^4 + p^2c^2} - MoC^2$$

$$M_oc^2 \left(1+\frac{p^2}{Mo^2c^2}\right)^{1/2} - Moc^2$$

$$\text{KE}= M_oc^2 \left[\left(1+\frac{p^2}{Mo^2c^2}\right)^{1/2} - 1\right]$$

By binomial theorem:

$$\text{KE}= M_oc^2 \left[1+\frac{1}{2}\frac{p^2}{Mo^2c^2} - \frac{1}{8}\frac{p^4}{Mo^4c^4}\ldots..-1\right]$$

$$\text{KE}= M_oc^2 \left[\frac{1}{2}\frac{p^2}{Mo^2c^2} - \frac{1}{8}\frac{p^4}{Mo^4c^4}\right]$$

$$\text{KE}= M_oc^2 \left[\frac{1}{2}\frac{p^2}{Mo} - \frac{1}{8}\frac{p^4}{Mo^3c^2}\right]$$

So we notice that the relativistic kinetic energy is a sum of a non relativistic term and a lowest/first order correction.

5.3 LORENTZ GROUP

In physics and mathematics, the Lorentz group is the group of all Lorentz transformations of Minkowski space time, the classical and quantum setting for all (non-gravitational) physical phenomena. The Lorentz group is named for the Dutch physicist Hendrik Lorentz.

For example, the following laws, equations, and theories respect Lorentz symmetry:

- The kinematical laws of special relativity
- Maxwell's field equations in the theory of electromagnetism
- The Dirac equation in the theory of the electron
- The Standard Model of particle physics

The Lorentz group expresses the fundamental symmetry of space and time of all known fundamental laws of nature. In general relativity physics, in cases involving small enough regions of space time where gravitational variances are negligible, physical laws are Lorentz invariant in the same manner as that of special relativity physics.

Basic Properties of Lorentz Group

The ***Lorentz group*** is a subgroup of the Poincaré group—the group of all isometries of Minkowski space time. Lorentz transformations are, precisely, isometries that

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leave the origin fixed. Thus, the Lorentz group is an isotropy subgroup of the isometry group of Minkowski space time. For this purpose, the Lorentz group is sometimes called the ***homogeneous Lorentz group*** while the Poincaré group is sometimes called the inhomogeneous Lorentz group. Lorentz transformations are examples of *linear transformations;* general isometries of Minkowski space time are affine transformations. Mathematically, the Lorentz group may be described as the indefinite orthogonal group O(1,3), the matrix Lie group that preserves the quadratic form on R^4.

$$(t, x, y, z) \mapsto t^2 - x^2 - y^2 - z^2$$

This quadratic form is, when put on matrix form (also known as classical orthogonal group), interpreted in physics as the metric tensor of Minkowski space time.

The Lorentz group is a six-dimensional non-compact ***non-Abelian*** real Lie group that is not connected. The four connected components are not simply connected. The identity component (i.e., the component containing the identity element) of the Lorentz group is itself a group, and is often called the restricted Lorentz group, and is denoted $SO^+(1,3)$. The restricted Lorentz group consists of those Lorentz transformations that preserve the orientation of space and direction of time. Its fundamental group has order 2, and its universal cover, the indefinite spin group Spin (1,3), is isomorphic to both the special linear group SL(2, C) and to the symplectic group Sp(2, C). These isomorphisms allow the Lorentz group to act on a large number of mathematical structures important to physics, most notably the spinors. Thus, in relativistic quantum mechanics and in quantum field theory, it is very common to call SL(2, C) the Lorentz group, with the understanding that $SO^+(1,3)$ is a specific representation (the vector representation) of it. The biquaternions, popular in geometric algebra, are also isomorphic to SL(2, C).

The restricted Lorentz group also arises as the point symmetry group of a certain ordinary differential equation.

Restricted Lorentz Group

The ***restricted Lorentz group*** is the identity component of the Lorentz group, which means that it consists of all Lorentz transformations that can be connected to the identity by a continuous curve lying in the group. The restricted Lorentz group is a connected normal subgroup of the full Lorentz group with the same dimension, in this case with dimension six.

The restricted Lorentz group is generated by ordinary spatial rotations and Lorentz boosts (which are rotations in a hyperbolic space that includes a time-like direction). Since every proper, orthochronous Lorentz transformation can be written as a product of a rotation (specified by 3 real parameters) and a boost (also specified by 3 real parameters), it takes 6 real parameters to specify an arbitrary proper orthochronous Lorentz transformation. This is one way to understand why the restricted Lorentz group is six-dimensional.

The set of all rotations forms a Lie subgroup isomorphic to the ordinary rotation group SO(3). The set of all boosts, however, does not form a subgroup, since composing two boosts does not, in general, result in another boost. (Rather, a pair of non-colinear boosts is equivalent to a boost and a rotation, and this relates to Thomas rotation). A boost in some direction, or a rotation about some axis, generates a one-parameter subgroup.

5.3.1 Klein- Gordan Equation

In relativistic quantum mechanics, we use the Klein Gordan equation which is related to the Schrodinger's equation. The Klein-Gordan equation is Lorentz covariant in nature. We can say that the quantized version of the energy- momentum relation depicts the Klein-Gordan equation. One important thing to measure about the Klein-Gordan equation is that it is of second order space time.

The Klein-Gordon equation is a relativistic version of the Schrödinger equation that describes the behavior of spinless particles. The equation has a large range of applications in contemporary physics, including particle physics, astrophysics, cosmology, classical mechanics, etc.

It is represented as follows:

$$\eta^{ab}\partial_a\partial_b \ \Psi - \frac{m^2c^2}{\hbar^2} \Psi = 0$$

Here, η^{ab} is the Minkowski metric.

$\partial_a\partial_b$ is the second order space and time.

But later Schrödinger realized that the Klein Gordan equation is not consistent with the right structure of the hydrogen atom. The main problem for this was due to the spin of the electron which is ½ and has quite different properties. It was Dirac who solved this problem which takes us to our next topic i.e., the Dirac Equation.

H.A. Lorentz introduced transformation equations relating the observations of position and time taken by two observers in two different inertial frames.

Take S, S' two inertial frames of reference such that S' is moving with uniform velocity v along X'-axis relative to S. Let O, O' be two observers in two systems, situated at their origins. If we consider the two sets of axes X, Y, Z and X', Y', Z' parallel, then the choice of the origins of the two systems falls in taking their origins coincident at $t = 0$, $t' = 0$. It is also convenient to take X, X' axes of two systems coincident, so that velocity of S' is permanently along X-axis. Let the two observers O, O' observe the same event at P whose coordinates are (x, y, z, t) w.r.t. S and (x', y', z', t') w.r.t. S' (Refer Figure 5.1).

With these assumptions clearly, points which are at rest relative to S' will move with speed v relative to S in X-direction. Particularly the point at $x' = 0$ will move with speed v in X-direction, i.e., $x' = 0$ will be identical with $x = vt$, so that the first of our transformation equation is

$$x' = \alpha (x - vt) \qquad \text{... (5.1)}$$

where α is a constant to be determined later and vt is the distance traversed by S' in time t along X-axis.

Now velocity of S' being along X-axis only, it follows from symmetry that

$$y' = y \quad \text{and} \quad z' = z \qquad \text{... (5.2)}$$

This set of equations is not complete unless we formulate an equation connecting t' the time measure in S', with the space and time coordinates, i.e., x, y, z, t in S. Due to homogeneity of space and time, t' must depend linearly on t, x, y, z but for reasons of symmetry we assume that t' does not depend on y and z, otherwise two clocks in S'-system in $x' = 0$ plane would appear to disagree as observed from S and hence we take

$$t' = \beta t + \gamma x \qquad \text{... (5.3)}$$

where β and γ are not mere constants but are functions of v and are to be determined along with α.

Let us now assume that the event P is a light signal, produced when both t and t' are zero and when origins of two systems coincide. Also let the light pulse produced at $t = 0$ spread out as a growing sphere such that the radius of wavefront so produced grows with speed c. But the velocity of light in both the systems being the same, i.e., c in all directions, the progress of the spherical wavefront is described by either of the following equations:

$$x^2 + y^2 + z^2 = c^2\, t^2 \qquad \text{...(5.4)}$$

$$x'^2 + y'^2 + z'^2 = c^2 t'^2 \qquad \text{...(5.5)}$$

Substituting values of x', y', z', t' from Equations (5.1), (5.2) and (5.3) to (5.5), we get

$$\alpha^2\,(x - vt)^2 + y^2 + z^2 = c^2\,(\beta t + \gamma x)^2$$

or $(\alpha^2 - c^2\gamma^2)x^2 + y^2 + z^2 - 2xt\,(\alpha^2 v + c^2\beta\gamma) = (c^2\beta^2 - \alpha^2 v^2)t^2$ ... (5.6)

The Equations (5.4) and (5.6) representing the same motion are identical and hence comparison of various coefficients, yields

$$\alpha^2 - c^2\gamma^2 = 1 \qquad \text{... (5.7)}$$

$$\alpha^2 v + c^2\,\beta\gamma = 0 \qquad \text{... (5.8)}$$

$$c^2\beta^2 - \alpha^2 v^2 = c^2 \qquad \text{... (5.9)}$$

Multiplying Equation (5.7) by v^2 and then subtracting Equation (5.8) from it, we have

$$v(1 + c^2\gamma^2) + c^2\beta\gamma = 0 \qquad \text{... (5.10)}$$

Again multiplying Equation (5.7) by v^2 and adding it to Equation (5.9), we get

$$-v^2(1 + c^2\gamma^2) + c^2\beta^2 = 0 \qquad \text{... (5.11)}$$

Now multiplying Equation (5.10) by v and adding it to Equation (5.11), we find

$$\beta^2 - 1 = -v\beta\gamma, \quad \text{i.e.,} \quad \gamma = \frac{1-\beta^2}{v\beta} \qquad \text{... (5.12)}$$

Elimination of γ between Equation (5.10) and Equation (5.12) gives

$$v\left\{1 + c^2\left(\frac{\beta^2 - 1}{v\beta}\right)^2\right\} + c^2\left\{\frac{1-\beta^2}{v}\right\} = 0$$

or $v^2\beta^2 + c^2(\beta^2 - 1)^2 + c^2\beta^2(1 - \beta^2) = 0$

or $\beta^2[v^2 + c^2 - 2c^2] + c^2 = 0$ giving $\beta^2 = \frac{c^2}{c^2 - v^2} = \frac{c^2}{1 - \frac{v^2}{c^2}}$ ... (5.13)

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With the help of Equations (5.13), (5.9) yields (on taking positive roots only)

$$\alpha^2 = \frac{c^2}{c^2 - v^2} = \beta^2 \text{ so that } \alpha = \beta = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \text{... (5.14)}$$

In view of Equations (5.14), (5.8) gives

$$\gamma = \frac{-\alpha^2 v}{c^2 \beta} = \frac{-\alpha v}{c^2} = \frac{-\beta v}{c^2} \quad \text{... (5.15)}$$

From Equations (5.12), (5.14) and (5.15), we get

$$\gamma = \frac{1 - \beta^2}{v\beta} = -\frac{\beta v}{c^2} = -\frac{v}{c^2\sqrt{1 - \frac{v^2}{c^2}}} \quad \text{... (5.16)}$$

Also by Equation (5.8),

$$\alpha^2 = \frac{-c\beta^2\gamma}{v} = \beta^2 = \frac{1}{1 - \frac{v^2}{c^2}} \quad \text{... (5.17)}$$

In view of these results, the transformation Equations (5.1), (5.2), (5.3) become

$$x' = \frac{x - vt}{\sqrt{1 - \frac{v^2}{c^2}}},\ y' = y,\ z' = z \quad \text{and} \quad t' = \frac{t - \frac{vx}{c^2}}{1 - \frac{v^2}{c^2}} \quad \text{... (5.18)}$$

These are known as **Lorentz transformation equations.**

Inversely, we have

$$x = \frac{x' + vt'}{\sqrt{1 - \frac{v^2}{c^2}}},\ y = y',\ z = z' \quad \text{and} \quad t = \frac{t' + \frac{vx'}{c^2}}{1 - \frac{v^2}{c^2}} \quad \text{... (5.19)}$$

These are knwon as **Lorentz inverse transformation equations.**

A look at the Tranformations (5.18) and (5.19) reveals that S has the relative velocity–v w.r.t. S'. This conclusion is not trivial since neither the unit length nor the unit time is directly comparable in S and S'.

In case v is very small then $v/c \to 0$, so that by Equation (5.14), $\beta \to 1$ and then Lorentz transformations reduce to the Galilean transformation, i.e.,

$$x' = x - vt, \quad y' = y, \quad z' = z, \quad t' = t \quad \text{... (5.20)}$$

If $v > c$, the Lorentz transformations give imaginary values of x' and t' leading to an absurdity and hence v cannot be greater than c.

Again if $v << c$ so that $\frac{v^2}{c^2}$ is negligible, the Lorentz transformations take the form

$$x' = x - vt,\ y' = y,\ z' = z \quad \text{and} \quad t' = t - \frac{vx}{c^2} \qquad \text{... (5.21)}$$

In view of the transformations $y' = y$ and $z' = z$ so that

$y^2 + z^2 = y'^2 + z'^2$, Equation (5.4) and (5.5) yield

$$x^2 - c^2t^2 = x'^2 - c^2t'^2 \qquad \text{... (5.22)}$$

We may also write

$$x^2 + (ict)^2 = x'^2 + (ict')^2 \quad \text{where} \quad i = \sqrt{-1} \qquad \text{... (5.23)}$$

Now using the conceptions of four-dimensional geometry and imaginary rotations, we can determine a necessary connection between the two sets of coordinates (x_1, x_2, x_3, x_4) and (x_1', x_2', x_3', x_4').

Setting $x = x_1$, $x' = x_1'$ and $ict = x_4$, $ict' = x_4'$ Equation (5.23) can be written as

$$x_1^2 + x_4^2 = x_1'^2 + x_4'^2 \qquad \text{... (5.24)}$$

Geometrically interpreted if x_1, x_4 and x_1', x_4' form two rectangular sets of coordinate axes, with the same origin, then L.H.S. and R.H.S. of Equation (5.24) separately give the distances of the points (x_1, x_4) and (x_1', x_4') from the same origin. Consequently either the two sets of axes coincide or are inclined at an angle θ (say) with each other. In the later case we can express

$$x_1' = x_1 \cos\theta + x_4 \sin\theta,\ x_4' = -x_1 \sin\theta + x_4 \cos\theta \qquad \text{...(5.25)}$$

Of course, as is evident from Equations (5.24) and (5.25) a circle in original set retains its shape in the rotated set and the coordinates in two sets are connected by circular functions sin θ and cos θ.

If we conceive of an object at rest in S, moving with velocity v w.r.t. S' then we can write $\frac{dx_1}{dt'} = 0$ and $\frac{dx}{dt} = v$, so that

$$\frac{dx_1'}{dx_4'} = \frac{dx_1'}{dx_4} \Big/ \frac{dx_4'}{dx_4} = \frac{\frac{dx_1}{dx_4}\cos\theta + \sin\theta}{-\frac{dx_1}{dx_4}\sin\theta + \cos\theta} = 0$$

or
$$\frac{dx_1}{dx_4} = -\tan\theta \qquad \text{... (5.26)}$$

But when $x = x_1$ and $x_4 = ict$, $\frac{dx}{dt} = v$ gives

$$\frac{dx_1}{dx_4} = \frac{dx_1}{dt} \cdot \frac{dt}{dx_4} = v \cdot \frac{1}{ic} = -\frac{iv}{c} \qquad \text{... (5.27)}$$

Therefore, Equations (5.26) and (5.27) give $\tan\theta = \frac{iv}{c}$ ... (5.28)

Accordingly, $$\frac{\sin\theta}{iv} = \frac{\cos\theta}{c} = \frac{\sqrt{\cos^2\theta + \sin^2\theta}}{\sqrt{c^2 + (iv)^2}} = \frac{1}{c\sqrt{1 - \frac{v^2}{c^2}}}$$

$$\therefore \quad \sin\theta = \frac{iv}{\sqrt{1 - \frac{v^2}{c^2}}} \text{ and } \cos\theta = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}.$$

The substitution of these in Equation (5.25) yields Lorentz transformation equations.

The coordinates x and t in Equation (5.22) may also be related with x', t' by hyperbolic functions such as

$$x' = x \cosh \zeta - ct \sinh \zeta; \; ct' = -x \sinh \zeta + ct \cosh \zeta \qquad \text{... (5.29)}$$

COROLLARY. The above transformations have been derived in a particular case when the frame S' is moving with uniform velocity v along X-axis. We can generalize these results by taking the motion of S' w.r.t. S, along any straight line, so that its velocity

$$\mathbf{v} = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k}$$

where v_x, v_y, v_z are the components of $\mathbf{v}$ along X, Y, Z axes respectively.

Taking $\mathbf{r} = x\mathbf{j} + y\mathbf{j} + z\mathbf{k}$ as the position vector of an event its resolved parts along and perpendicular to $\mathbf{v}$ may be given by $\frac{(\mathbf{r}\cdot\mathbf{v})\mathbf{v}}{v^2}$ and $\mathbf{r} - \frac{(\mathbf{r}\cdot\mathbf{v})\mathbf{v}}{v^2}$.

Denoting them by $\mathbf{P}$ and $\mathbf{Q}$ respectively so that $\mathbf{r} = \mathbf{P} + \mathbf{Q}$ and applying the transformations of Equation (5.18), we have

$$\mathbf{Q}' = \mathbf{Q} = \mathbf{r} - \frac{(\mathbf{v}\cdot\mathbf{r})\mathbf{v}}{v^2} \qquad \text{... (5.30)}$$

And
$$\mathbf{P}' = \frac{\mathbf{P} - \mathbf{v}\,t}{\sqrt{1-\frac{v^2}{c^2}}} = \frac{(\mathbf{r}\cdot\mathbf{v})\mathbf{v} - \mathbf{v}\,t}{\sqrt{1-\frac{v^2}{c^2}}} \qquad \text{... (5.31)}$$

Thus
$$\mathbf{r}' = \mathbf{P}' + \mathbf{Q}' = \mathbf{r} + \frac{(\mathbf{r}\cdot\mathbf{v})\mathbf{v}}{v^2}(\gamma - 1) + \gamma\, vt \qquad \text{... (5.32)}$$

where
$$\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

Also we have the transformation

$$t' = \gamma\left(t - \frac{\mathbf{r}\cdot\mathbf{v}}{c^2}\right) \qquad \text{... (7.33)}$$

Equations (5.32) and (5.33) give the general Lorentz transformations without rotation. Their inverse transformations may be obtained by replacing $\mathbf{v}$ by $-\mathbf{v}$ whence we have

$$\mathbf{r} = \mathbf{r}' + \frac{\mathbf{r}'\cdot\mathbf{v}}{v^2}(\gamma - 1) + \gamma\mathbf{v}t' \text{ and } t = \gamma\left(t' + \frac{\mathbf{r}'\cdot\mathbf{v}}{c^2}\right) \qquad \text{... (5.34)}$$

Example 5.1. *Show that $x^2 + y^2 + z^2 - c^2t^2$ is invariant.*

If (x, y, z, t) and (x', y', z', t) be the coordinates of the same event observed by two observers in frames S and S' where S' is moving with velocity v relative to S, then we have to show that

$$x^2 + y^2 + z^2 - c^2t^2 = x'^2 + y'^2 + z'^2 - c^2t'^2$$

Solution. Lorentz transformations are

$$x' = \beta(x - vt), \; y' = y, \; z' = z \quad \text{and} \quad t' = \beta\left(t - \frac{vx}{c^2}\right)$$

where $\beta = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$

We thus have

$$x'^2 + y'^2 + z'^2 - c^2t'^2 = \beta^2\,(x - vt)^2 + y^2 + z^2 - c^2\beta^2\left(t - \frac{vx}{c}\right)^2$$

$$= \beta^2\left[x^2 + v^2t^2 - 2\,vxt - c^2\left(t^2 + \frac{v^2x^2}{c^4} - \frac{2vtx}{c^2}\right)\right] + y^2 + z^2$$

$$= \beta^2\left(1 - \frac{v^2}{c^2}\right)x^2 - c^2\,t^2\left(1 - \frac{v^2}{c^2}\right)\beta^2 + y^2 + z^2$$

$$= x^2 - c^2t^2 + y^2 + z^2 \quad \because\ \beta = \frac{1}{1 - \frac{v^2}{c^2}}$$

$$= x^2 + y^2 + z^2 - c^2t^2$$

which shows the invariance of $x^2 + y^2 + z^2 - c^2t^2$.

Example 5.2. *Derive Lorentz inverse transformations.*

Lorentz transformations are

$$x' = \beta\,(x - vt),\ y' = y,\ z' = z,\ t' = \beta\left(t - \frac{vx}{c^2}\right)$$

Solution. where $\beta = \dfrac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$.

Solving them for x, y, z we find

$$x = \frac{x'}{\beta} + v\left(t' + \frac{vx}{c^2}\right) = \frac{1}{\beta}\,(x' + vt') + \frac{v^2x}{c^2}$$

or $$\left(1 - \frac{v^2}{c^2}\right) = \frac{1}{\beta}\,(x' + vt'), \quad \text{i.e.,} \quad x = \beta(x' + vt')$$

As such, $t' = \beta\left(t - \dfrac{vx}{c^2}\right)$ gives

$$t = \frac{t'}{\beta} + \frac{v}{c^2}\beta\,(x' + vt') = \frac{t'}{\beta}\left(1 + \frac{v^2}{c^2}\beta^2\right) + \frac{vx'}{c^2}\beta$$

$$= \frac{t'}{\beta}\left[\frac{1 - \frac{v^2}{c^2} + \frac{v^2}{c^2}}{1 - \frac{v^2}{c^2}}\right] + \frac{vx'}{c^2}\beta = \frac{t'}{\beta\left(1 - \frac{v^2}{c^2}\right)} + \frac{vx'}{c^2}\beta$$

$$= \frac{t'}{\beta}\beta^2 + \frac{vx'}{c^2}\beta = \beta\left(t' + \frac{vx'}{c^2}\right)$$

Hence Lorentz inverse transformations are

$$x = \beta\,(x' + vt'),\ y = y',\ z = z',\ t = \beta\left(t' + \frac{vx'}{c^2}\right)$$

5.4 DIRAC EQUATION

He modified the Klein-Gordan equation to his own classic equation known as the *Dirac equation*. He said that by decreasing the space dependent term to first order and by not increasing the time dependent term to the second order, we can find the relativistically-correct wave equation. The equation is written as:

$$i\hbar\gamma^{a}\partial_{a}\Psi\text{-}mc\ \Psi = 0$$

Where, γ^{a} is the Dirac spin matrix and ∂_a is the first order space and time.

5.4.1 Covariant Form of Dirac Equation

For the covariant form of the Dirac equation, Dirac equation can be written more precisely by introducing the four Dirac Gamma matrices:

$$\gamma^{0} \equiv \beta;\ \gamma^{1} \equiv \beta\alpha_x;\ \ \gamma^{2} \equiv \beta\alpha_y;\ \ \gamma^{3} \equiv \beta\alpha_z$$

Where, $\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$; $\alpha_j = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix}$. This is based on the Pauli spin matrices.

Now, pre multiplying the Dirac equation by β, where the Dirac equation is:

$$-i\alpha_x\frac{\partial\Psi}{\partial x} - i\alpha_y\frac{\partial\Psi}{\partial y} - i\alpha_z\frac{\partial\Psi}{\partial z} + m\beta\Psi = i\frac{\partial\Psi}{\partial t}$$

$$i\gamma^{1}\frac{\partial\Psi}{\partial x} + i\gamma^{2}\frac{\partial\Psi}{\partial y} + i\gamma^{3}\frac{\partial\Psi}{\partial z} - m\Psi = -i\gamma^{0}\frac{\partial\Psi}{\partial t}$$

Using the $\partial_\mu = \left(\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$, and this can be written in more compact form as:

$$(i\gamma^{\mu}\partial_{\mu} - m)\Psi = 0$$

5.4.2 Basic Properties of Dirac Matrices

The first and important thing to note about the Dirac Matrices or the Dirac Gamma matrices is that 'Dirac Gamma matrices' are not the four vectors, they are constant matrices which remain invariant under a *Lorentz transformation*. However we can also that the Dirac equation is itself a Lorentz covariant.

The basic properties of Dirac matrices are:

Firstly, for the Dirac equation to be consistent with the Klein-Gordan equation, it requires that:

$$\alpha_x^{\,2} = \alpha_y^{\,2} = \alpha_z^{\,2} = \beta^{2} = 1$$

$$\alpha_j\beta + \beta\alpha_j = 0$$

$$\alpha_j\alpha_k + \alpha_k\alpha_j = 0 \qquad (j \neq k)$$

So the property is:

1. $(\gamma^0)^2 = \beta^2 = 1$

   And, $(\gamma^1)^2 = \beta\alpha_x\beta\alpha_x = -\alpha_x\beta\beta\alpha_x = -\alpha_x{}^2 = -1$

2. The full set of relations is:

   $(\gamma^0)^2 = 1$

   $(\gamma^1)^2 = (\gamma^2)^2 = (\gamma^3)^2 = -1$

   $\gamma^0\gamma^j + \gamma^j\gamma^0 = 0$

   $\gamma^j\gamma^k + \gamma^k\gamma^j = 0 \qquad (j \neq k)$

   This can be expressed as:

   $\{\gamma^\mu, \gamma^\nu\} = \gamma^\mu, \gamma^\nu + \gamma^\nu\gamma^\mu = 2\,g^{\mu\nu}$

3. γ^0 Is Hermitian, since the β is Hermitian.

   The α matrices are also **Hermitian**, giving:

   $\gamma^{1\gamma} = (\beta\alpha_x)^{)} = \alpha_x \quad {}^{)}\beta \quad {}^{)} = \alpha_x\beta = -\beta\alpha_x = -\gamma^1$

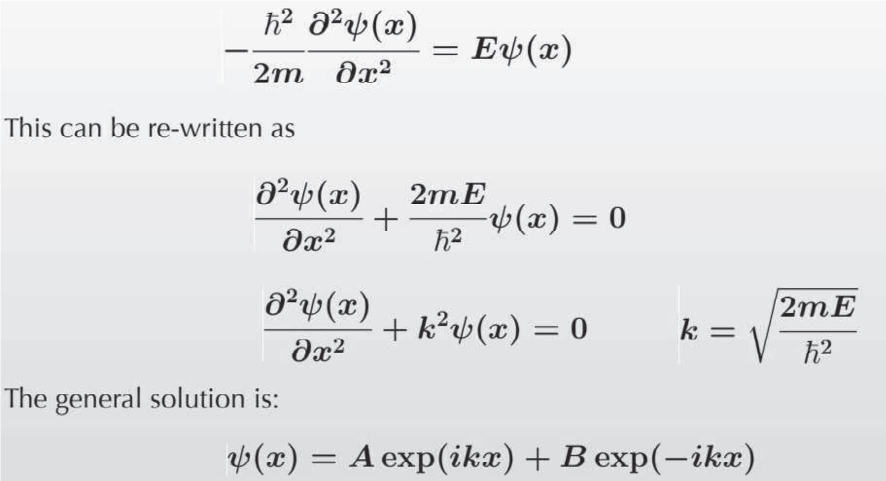
   Hence γ^1, γ^2, γ^3 are **Anti Hermitian**.

   $\gamma^{0\gamma} = \gamma^0,\ \gamma^{0\gamma} = -\gamma^1,\ \gamma^{2\gamma} = -\gamma^2,\ \gamma^{3\gamma} = -\gamma^3$

5.5 THE FREE ELECTRON PLANE WAVES

In *quantum mechanics*, a free particle is defined as any particle (such as, an electron) that does not feel any fore. In such a case, the wave function that describes the free particle is given by a sinusoidal wave and this is referred to as the plane wave. In physics, a *free particle* is a particle that, in some sense, is not bound by an external force, or equivalently not in a region where its potential energy varies. In classical physics, this means the particle is present in a *field-free space*. In quantum mechanics, we will start with some simpler one-dimensional (function of x only), time-independent problems. At one time, such problems were considered.

Although we could use other types of particles in our examples, we will generally use electrons, since they are key in the behavior of nanoelectronic devices. We have already solved this problem. The free electron moves in a potential free region, U = 0. In that case, the time-independent Schrödinger equation is:



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

This can be re-written as

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + k^2\psi(x) = 0 \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The general solution is:

$$\psi(x) = A\exp(ikx) + B\exp(-ikx)$$

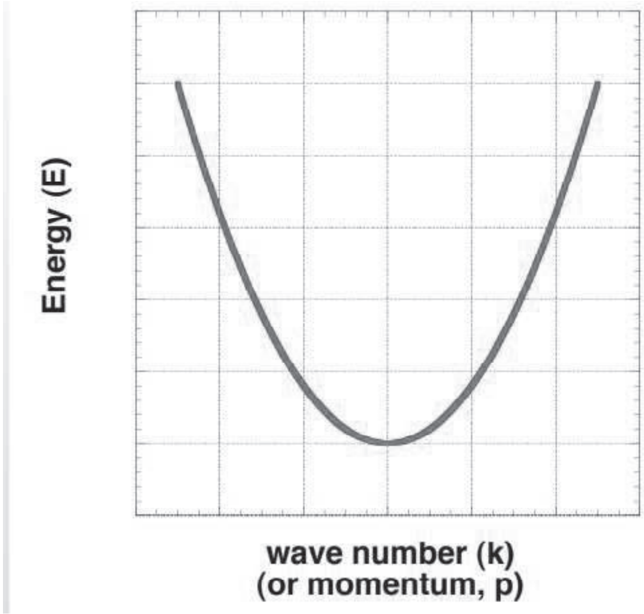
This represents plane waves traveling in the +x (first term) and -x directions.

$$\psi(x) = A\exp(ikx) + B\exp(-ikx) \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

Note that we must include the possibility of travel in either direction. In looking at more specific problems, boundary conditions (or the way that we set up a problem) may let us choose to leave off one term or the other.

$$\nu = \frac{E}{h} \qquad \lambda = \frac{h}{k} = \frac{h}{\sqrt{2mE}}$$

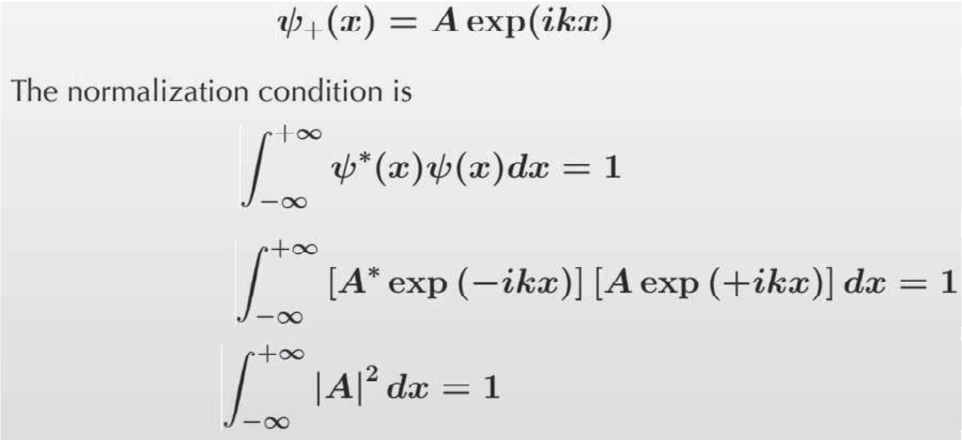
The electron energy can take on any value > 0 — there is no quantization.



$$E = \frac{(\hbar k)^2}{2m}$$

The parabolic E-k (E-p) is indicative of a free electron. This is identical to the classical result.

If we try to complete the problem and normalize the wave function, things get a bit odd, as we had discussed earlier. To see the source of the difficulty more clearly, consider an electron known to be moving in the +x direction, so that we can leave off the second term in the general solution.



$$\psi_+(x) = A\exp(ikx)$$

The normalization condition is

$$\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)dx = 1$$

$$\int_{-\infty}^{+\infty} [A^*\exp(-ikx)]\,[A\exp(+ikx)]\,dx = 1$$

$$\int_{-\infty}^{+\infty} |A|^2\,dx = 1$$

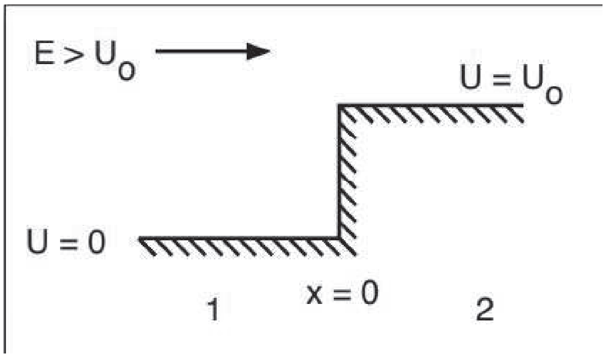
First note that the probability density is a simple constant — there is equal probability that the electron can be at any value of x. This is in line with our notions of a plane wave and the ‘**Uncertainty Principle**’.

The only way that the normalization can be met is if $|\mathbf{A}|^2 \rightarrow \mathbf{0}$. In other words, the amplitude of the wave must be vanishingly small at all points.

In effect, we are saying the electron must be simultaneously everywhere and nowhere. Of course, this is absurd. And it really isn’t a good description of the free electron. The wave function is a valid solution of the S.E., but it fails the basic test of describing a particle that is in some sense localized in space. In order to fix this conundrum, we’ll have to use the superposition principle to add together a collection of valid solutions to create what we call a wave packet. This will also lead us to a consideration of the uncertainty principle.

Electrons Incident on an Energy Step

Now consider an electron incident on a step in the energy. The step goes from a constant region where U = 0 to one with a different constant value of potential energy Uo. The energy of the incident electron is E > Uo.

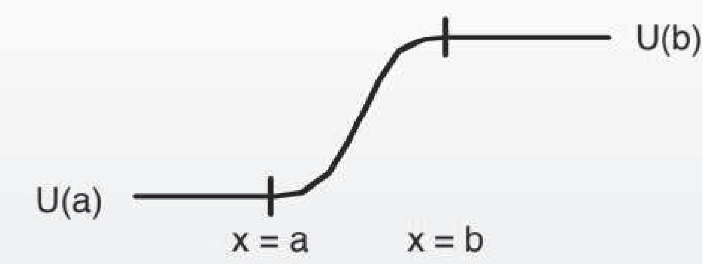


Classically, we would assume that the electron zooms over the step, completely unaware of its presence. When the electron is described by a wave however, things are not that simple.

For instance, we already know the solution in the region where U = 0. (It's a free electron!) And we can probably find the solution for the other region without much trouble. Then we can 'Connect' to the solutions at the interface. So we need to determine the connection rules for step interfaces in 1-D problems. The place to start is with the requirement that the wave function and the derivative of the wave function must be both be continuous. We might assume that these conditions must remain true at the interface.

$$\psi_-(0) = \psi_+(0) \qquad \psi'_-(0) = \psi'_+(0)$$

We can strengthen the argument by looking at the step interface as the limit of a gradual change in potential from one level to another.



Start by writing the Schrödinger Equation (S.E), in a slightly modified form:

$$\psi''(x) = \frac{2m}{\hbar^2}\left[U(x) - E\right]\psi(x)$$

Integrating once from point a to some arbitrary point x

$$\psi'(x) = \psi'(a) + \frac{2m}{\hbar^2}\int_a^x \left[U(y) - E\right]\psi(y)dy$$

In particular, letting $x=b$

$$\psi'(b) = \psi'(a) + \frac{2m}{\hbar^2}\int_a^b \left[U(y) - E\right]\psi(y)dy$$

Integrating a second time from $x = a$ to $x = b$

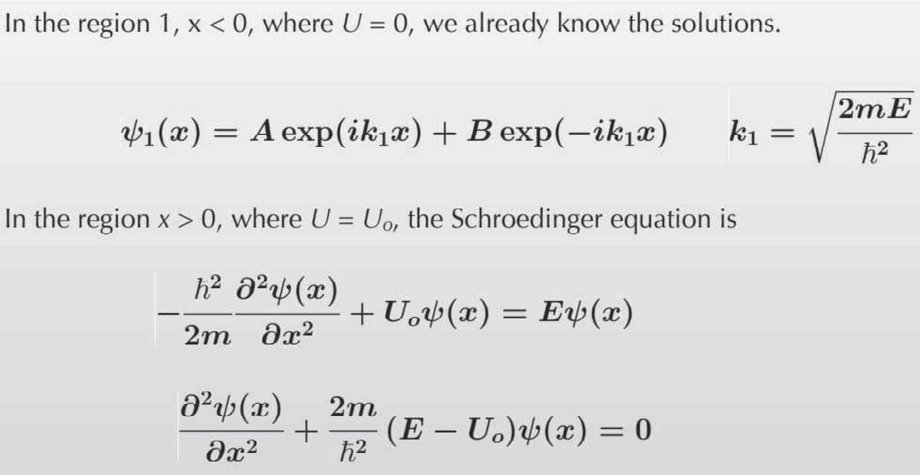
$$\psi(b) = \psi(a) + \psi'(a)\cdot(b-a) + \frac{2m}{\hbar^2}\int_a^b\int_a^x \left[U(y) - E\right]\psi(y)dydx$$

Now, let the gradual change sharpen up to an abrupt change from one level to the other. This means looking at the limit as $b \to a$. In this case, the previous two equations reduce to

$$\psi'(b) = \psi'(a) \qquad \psi(b) = \psi(a)$$

As we expected.

Again, we will find solutions in the two regions of constant potential and then connect them at the interface using our newly found connection rules.



In the region 1, x < 0, where $U = 0$, we already know the solutions.

$$\psi_1(x) = A\exp(ik_1x) + B\exp(-ik_1x) \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

In the region $x > 0$, where $U = U_o$, the Schroedinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U_o\psi(x) = E\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - U_o)\psi(x) = 0$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - U_o)\psi(x) = 0$$

Note that this has general form of the free electron problem, except that the energy factor in the second term is $E - U_o$ instead of just E, as in the free electron case. The solutions should also have the form of plane waves, but with a different value of k. $\psi_2(x) = C\exp(ik_2x) + D\exp(-ik_2x) \qquad k_2 = \sqrt{\frac{2m(E - U_o)}{\hbar^2}}$

In this case, we might be interested in looking at the probability of the electron being reflected or transmitted at the step. Conceptually, the 'Experiment' might go something like this: Send an electron from the left in region 1 towards the step (This is represented by amplitude A.), and look for what is reflected back into region 1 (amplitude B) and transmitted into the other region (amplitude C). This is known as a 'Scattering' problem.

$$\psi_2(x) = C\exp(ik_2x)$$

Also, we are primarily interested in the ratios B/A and C/A, which would represent reflection and transmission amplitudes, respectively. The problem has now been reduced to something manageable. All that is left is to use the connection rules at x = 0 to match the solutions from the two regions.

$$\psi_1(0) = \psi_2(0)$$
$$A + B = C$$

$$\psi_1'(0) = \psi_2'(0)$$
$$ik_1 A - ik_1 B = ik_2 C$$

This gives two equations that can be solved for the two ratios B/A and C/A.

A remarkable result is immediately apparent: Since B/A $\neq$ 0, the electron may be reflected from the step, even though $\boldsymbol{E > U_o}$.

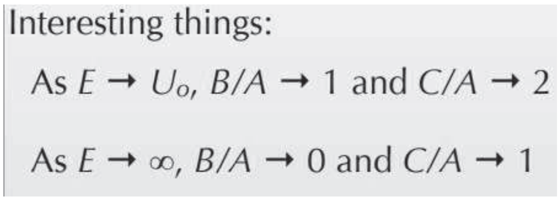
$$B/A = \frac{k_1 - k_2}{k_1 + k_2}$$

$$C/A = \frac{2k_1}{k_1 + k_2}$$

The coefficient ratios can be written in terms of the energies involved.

$$\frac{B}{A} = \frac{\sqrt{E} - \sqrt{E - U_o}}{\sqrt{E} + \sqrt{E - U_o}}$$

$$\frac{C}{A} = \frac{2\sqrt{E}}{\sqrt{E} + \sqrt{E - U_o}}$$



Interesting things:

As $E \to U_o$, $B/A \to 1$ and $C/A \to 2$

As $E \to \infty$, $B/A \to 0$ and $C/A \to 1$

If the 'Barrier' is vanishingly small, it looks like a classical barrier.

5.5.1 Central Potential

In the classical mechanics, the ***potential*** is said to be central if the potential energy is always directed towards or away from a point and it only depends on the distance of particle from that point. The force which generates central potential is given by the expression of:

F= f(r) ($\pm\hat{r}$)

In quantum mechanics, the spherically symmetric potential is called the central potential, where the potential energy is only a function of the distance r from the origin. Some characteristics of the Central potential include:

The Central force giving rise to it is conservative. Total mechanical energy remains conserved.

The angular momentum about the center of force is conserved.

When we deal with the Central potential, then we make use of the spherical coordinates rather than the Cartesian coordinates, since the potential energy is the function of the distance r from the origin. We use the spherical coordinates, where we have:

$x = r\sin\theta\cos\Phi$

$y = r\sin\theta\sin\Phi$

$z = r\cos\theta$

$$\text{So, } r = \sqrt{(x^2+y^2+z^2)},\ \theta = \cos^{-1}\frac{z}{\sqrt{(x^2+y^2+z^2)}},\ \Phi = \tan^{-1}\frac{y}{x}$$

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

This makes the operations a lot easier and we deal with the central potential better.

For an arbitrary potential V (r), we can write:

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\hat{r})$$

Since, it is a central potential, so the potential V is a function of r.

We also study the concept of effective potential under the central potential, which is given by:

$V_{eff} = V(r) + l^2/2mr^2$

Where l is the angular momentum, m is the mass and the r is the distance from the origin.

5.5.2 Free Spherical Waves

To understand the concept of the free spherical waves, we first have to discuss about the free particle, Hamiltonian of which can be written as:

$H = p^2/2m$

The p commutes with itself given $[p_i, p_j]$, also with the Hamiltonian H, so there can be common eigenstates of them. The Hamiltonian also commutes with the Angular momentum operators which are L^2 and L_z. Therefore, we can also say that the Hamiltonian H, L^2 and L_z form a CSCO for a spin less particle. Now if we consider the basis of the eigenstates of the |k, l, m>, we can say that the common eigenstates form a basis, and the wavefunction associated with these are known as the free spherical waves.

We then get into the discussion of the spherical harmonics as follows since that is the way to find the wavefunction associated with these kets |k, l, m> i.e.:

$F(r)\,Y_l^m(\theta, \Phi)$

For a free particle the radial functions F(r) are solutions to the differential equation

$$[-(\hbar^2/(2m))(1/r)(\partial^2/\partial r^2)r + \hbar^2 l(l+1)/(2mr^2)]\,F(r) = E\,F(r)$$

With $\rho = kr$, and $E = \hbar^2k^2/(2m)$ this equation becomes:

$$[(1/\rho)(\partial^2/\partial\rho^2)\rho + 1 - l(l+1)/\rho^2]\,F(\rho) = 0.$$

This is the ***spherical Bessel equation***. Its solutions are the spherical Bessel functions $j(\rho)$ and $n(\rho)$ and linear combinations of both.

5.6 THE HYDROGEN ATOM

A hydrogen atom consists of an electron of charge $-e$, mass m_e and a nucleus having a proton of charge $+e$ and mass m_p. By hydrogen-like atom we mean a one electron atom having a nucleus with Z protons (for example a singly ionized helium atom, a doubly-ionized lithium atom, etc.) For generality we consider a hydrogen-like atom.

If r be distance between the nucleus and the electron then the potential energy function $V(r)$ is given by

$$V(r) = \frac{-1}{4\pi\in_0}\frac{Ze^2}{r} = -k\frac{Ze^2}{r} \qquad \left[k = \frac{1}{4\pi\in_0}\right] \qquad ...(5.35)$$

If E be the total energy of relative motion between the nucleus and the electron then the time independent **Schrödinger equation** for the atom in the centre of mass coordinate system is given by

$$\nabla^2\psi(\vec{r}) + \frac{2m}{\hbar^2}[E - V(r)]\psi(\vec{r}) = 0 \qquad ...(5.36)$$

where

$$m = \frac{m_e(Zm_p)}{m_e + (Zm_p)} \text{ is the reduced mass.}$$

Equation (5.36) expressed in spherical polar coordinate (r, θ, ϕ) is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0$$

...(5.37)

In the above,

$$\psi = \psi(r, \theta, \phi).$$

Using the method of separation of variables we may write

$$\psi = \psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \qquad ...(5.38)$$

We obtain the following three equations

(i) Φ equation: $$\frac{d^2\Phi}{d\phi^2}\ m^2\Phi = 0 \qquad ...(5.39)$$

NOTES

(ii) Θ equation: $$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \qquad ...(5.40)$$

(iii) R (radial) equation: $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[E-v(r)]R-\frac{\lambda}{r^2}R=0 \qquad ...(5.41)$$

In the above, $$\lambda = l(l+1) \qquad ...(5.42)$$

Solution of the Φ equation was obtained earlier and is given by

$$\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi},\ m=0,\pm1,\pm2,... \qquad ...(5.43)$$

Solution of the Θ equation was obtained in earlier and is given by

$$\Theta_{lm}(\theta)=(-1)^m\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos\theta);\quad m>0 \qquad ...(5.44)$$

$$\Theta_{lm}(\theta)=\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos\theta);\quad m\le 0 \qquad ...(5.45)$$

In the above,

$$l=0,1,2,... \qquad ...(5.46)$$

$$m=0,\pm1,\pm2,...,\pm l \qquad ...(5.47)$$

The normalized angular part of the wavefunction is given by

$$\psi_{lm}(\theta,\phi)=\Theta_{lm}(\theta)\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}(-1)^m\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos\theta)\,e^{im\phi} \qquad ...(5.48)$$

Solution of the Radial Equation

Substituting for $V(r)$ given by Equation (5.35) and λ given by Equation (5.42) the radial wave Equation (5.41) becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E-\frac{l(l+1)\hbar^2}{2mr^2}+k\frac{Ze^2}{r}\right]R=0 \qquad ...(5.49)$$

For solving Equation (5.49) let us introduce a dimensionless variable ρ as

$$\rho=\gamma r \qquad ...(5.50)$$

The parameter γ is chosen as

$$\gamma=\sqrt{\frac{-8mE}{\hbar^2}} \qquad ...(5.51)$$

Further let us introduce a constant λ as

$$\lambda=\frac{kZe^2}{\hbar}\sqrt{\frac{m}{-2E}} \qquad ...(5.52)$$

We may note that E is negative for bound states of the atom under consideration and hence both ρ and λ are real.

In terms of ρ and λ, Equation (5.49) becomes

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]R=0 \qquad ...(5.53)$$

Let us first find the *asymptotic solution* of Equation (5.53). It is the solution in the limit ρ (and hence *r*) → ∞. In this limit Equation (5.53) reduces to

$$\frac{d^2R}{d\rho^2}-\frac{1}{4}R=0 \qquad ...(5.54)$$

The two independent solutions of the above equation are

$$R = e^{-\rho/2}$$

And

$$R = e^{+\rho/2}$$

The second solution is not acceptable because as $\rho \to \infty$ $R \to \infty$. Hence the acceptable asymptotic solution is

$$R(\rho) = e^{-\rho/2}$$

In view of the above asymptotic solution, we may write the exact solution of Equation (5.53) as

$$R(\rho) = F(\rho)e^{-\rho/2} \qquad ...(5.55)$$

where $F(\rho)$ is some function of ρ.

Using Equation (5.55) in Equation (5.53) we obtain

$$\rho^2\frac{d^2R(\rho)}{d\rho^2}+\rho(2-\rho)\frac{dF(\rho)}{d\rho}+[\rho\lambda-\rho-l(l+1)]F(\rho)=0 \qquad ...(5.56)$$

We find that when $\rho = 0$

$$l(l+1)\,F(0) = 0$$

or

$$F(0) = 0,\ l\ \pi\ 0 \qquad ...(5.57)$$

Clearly, a power series solution for $F(\rho)$ must not contain a constant term. Hence, we may write the power series solution as

$$F(\rho) = \sum_{k=0}^{\infty} C_k\,\rho^{s+k} \qquad ...(5.58)$$

The above gives

$$\frac{dF(\rho)}{d\rho} = \sum C_k\,(s+k)\rho^{s+k-1} \qquad ...(5.59)$$

$$\frac{d^2F(\rho)}{d\rho^2} = \sum C_k\,(s+k)\,(s+k-1)\rho^{s+k-2} \qquad ...(5.60)$$

Substituting Equations (5.58), (5.59), (5.60) in Equation (5.56) we obtain

$$\sum_k C_k\,(\lambda - 1 - s + k)\,\rho^{s+k-1} + \sum_k C_k\,(s^2 + 2sk + k^2 + s + k - l^2 - l)\rho^{s+k} = 0 \qquad ...(5.61)$$

For the above equation to be valid for all value of ρ, the coefficient of each power of ρ must separately vanish. Equating the coefficient of ρ^s to zero we get

$$C_0(s^2 + s - l^2 - l) = 0$$

Since $C_0\ \pi\ 0$, we get

$$s^2 + s - l^2 - l = 0$$

or

$$(s - l)\,(s + l + 1) = 0$$

The above gives

$$s = l \text{ or } s = -\,(l + 1) \qquad ...(5.62)$$

If $s = -\,(l+1)$, the first term in $F(\rho)$ given by Equation (5.58) becomes C_0 $\rho^{-(l+1)k} = \dfrac{C_0}{\rho^{(l+1)k}}$ which tends to infinity as ρ and hence r tends to zero. We hence get $s = l$. Equating the coefficient of $\rho^{S+k+1} = \rho^{l+k+1}$ in Equation (5.61) to zero we obtain the recurrence relation

$$C_{k+1} = \frac{l + k + 1 - \lambda}{(k+1)\,(k + 2l + 2)}\,C_k \qquad ...(5.63)$$

Using the above relation we can find the coefficients C_1, C_2, C_3, etc., in terms of the coefficient C_0.

For large values of k, Equation (5.63) gives

$$C_{k+1}\ \frac{k}{k^2} = C_k$$

or

$$\frac{C_k + 1}{C_k} = \frac{1}{k} \qquad ...(5.64)$$

We have

$$e^{\rho} = \sum_{k=0}^{\infty} \frac{1}{k!}\rho^k = \sum_{k=0}^{\infty} b_k \rho^k \qquad ...(5.65)$$

where $\quad b_k = \dfrac{1}{k!}$

Clearly $\qquad b_{k+1} = \dfrac{1}{(k+1)!}$

So that $\qquad \dfrac{b_k + 1}{b_k} = \dfrac{k!}{(k+1)!} = \dfrac{1}{k+1}$

For large k we get

$$\frac{b_k + 1}{b_k} = \frac{1}{k} \qquad ...(5.66)$$

$F(\rho)$ given by Equation (5.58) can be written as

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} C_k \rho^k = \rho^l \sum_{k=0}^{\infty} C_k \rho^k \qquad ...(5.67)$$

Using Equation (5.65) we obtain

$$\rho^l e^\rho = \rho^l \sum b_k \rho^k \qquad ...(5.68)$$

In view of the results given by Equations (5.64), (5.66), (5.67) and (5.68) we get

$$F(\rho) = \rho^l e^\rho$$

So that

$$R(\rho) = \rho^l e^\rho e^{-\rho/2} = \rho^l e^{\rho/2} \qquad ...(5.69)$$

$R(\rho)$ given by Equation (5.69) is not acceptable because $R(\rho) \rightarrow \infty$ as ρ and hence $r \rightarrow \infty$. Thus the series governed by the recursion relation given by Equation (5.63) does not lead to an acceptable radial wavefunction unless the series breaks off after a finite number of terms.

5.6.1 Energy Eigenvalues

Let us assume the series to break off after the k^{th} term so that C_{k+1} becomes zero. The recursion formula given by Equation (5.63) then gives

$$l + k + 1 + \lambda = 0$$

or

$$\lambda = l + k + 1 = n \text{ (say)} \qquad ...(5.70)$$

In Equation (5.70), the number k is called the *radial quantum number* which can take values 0, 1, 2, 3,... . The number n is called the total or principal quantum number which can take the values 1, 2, 3,...

From Equation (5.52) we get

$$\lambda^2 = \frac{k^2 Z^2 e^4}{\hbar^2} \frac{m}{(-2E)}$$

Using Equation (5.70) in the above equation we obtain the energy eigenvalues for a hydrogen-like atom to be

$$E_n = \frac{-k^2 m Z^2 e^4}{2\hbar^2 n^2} - \frac{me^4 Z^2}{32\,\pi^2 \in_0^2 \hbar^2 n^2} \qquad ...(5.71)$$

The energy eigenvalues for a hydrogen atom are obtained by putting $Z = 1$ in Equation (5.71). We get

$$E_n = \frac{-me^4}{32\,\pi^2 \in_0^2 \hbar^2 n^2} \qquad \text{...(6.72)}$$

Substituting the values of m, e, ${}_{\text{o}}$ and $\hbar$ we obtain the energy eigenvalues of hydrogen atom to be

$$E_1 = -13.6 \text{ eV}, E_2 = -\,3.4 \text{ eV}, E_3 = -1.51 \text{ eV, etc.}$$

The above values are the same as obtained by Bohr on the basis of old quantum theory.

5.6.2 Radial Wave Function

The infinite series for $F(\rho)$ becomes a polynomial due to the requirement of the series to break off after a finite number of terms.

Let us write

$$F(\rho) = \rho^l L(\rho) \qquad \text{...(5.73)}$$

We then get

$$\frac{dF(\rho)}{d\rho} = \rho^l \frac{dL(\rho)}{d\rho} + l\rho^{l-1} L(\rho) \qquad \text{...(5.74)}$$

$$\frac{d^2F(\rho)}{d\rho^2} = \rho^l \frac{d^2L(\rho)}{d\rho^2} + l\rho^{l-1}\frac{dL(\rho)}{d\rho} + l\rho^{l-1}\frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2}L(\rho)$$

$$q \qquad = \rho^l \frac{d^2L(\rho)}{d\rho^2} + 2l\,\rho^{l-1}\frac{dL(\rho)}{d\rho} + l(l-1)\rho^{l-2}L(\rho) \qquad \text{...(5.75)}$$

Substituting Equations (5.73), (5.74) and (5.75) in Equation (5.56) and simplifying we get

$$\rho \frac{d^2L(\rho)}{d\rho^2} + (2l + 2 - \rho)\frac{dL(\rho)}{d\rho} + (n - l - 1)\, L(\rho) = 0 \text{...(5.76)}$$

If $L \quad /\, ^p\,(\rho)$ be the associated Laguerre polynomial of the order p and degree $(q - p)$ then it satisfies the differential equation

$$\rho \frac{d^2L_q^p(\rho)}{d\rho^2} + (p + 1 - \rho)\frac{dL_q^p(\rho)}{d\rho} + (q - p)\, L_q^p(\rho) = 0 \qquad \text{...(5.77)}$$

If we consider $q = n + l$ and $p = 2l + l$ then Equation (6.76) becomes identical with Equation (5.77) and we can identify $L(\rho)$ as the associated Laguerre polynomial of the order $(2l + 1)$ and degree $(n + l)$, i.e., as $L\,/\,^{2l+1}\,(\rho)$.

We thus obtain the radial wavefunction to be of the form

$$R_{nl}(r) = \rho^l L_{n+l}^{2l+1}(\rho)\, e^{-\rho/2}$$

NOTES

The normalized radial wavefunction is then

$$R_{nl}(r) = N_{nl}\, \rho^l L_{n+l}^{2l+1}(\rho)\, e^{-\rho/2} \qquad \text{...(5.78)}$$

The normalization constant N_{nl} can be obtained from the normalized integral

$$\int_0^\infty R_{nl}^2(r)\, r^2 dr = 1 \qquad \text{...(5.79)}$$

Using $R_{nl}(r)$ given by Equation (5.78) and the orthogonal properties of associated Laguerre polynomials we obtain

$$N_{nl} = \pm\left[\left(\frac{2Zmke^2}{n\hbar^2}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \qquad \text{...(5.80)}$$

Using the result given by Equation (5.80) in Equation (5.78) we obtain

$$R_{nl}(r) = -\left[\left(\frac{2Z}{na_{\mathrm{H}}}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} e^{-\rho/2}\, \rho^l L_{n+l}^{2l+1}(\rho) \qquad \text{...(5.81)}$$

where

$$a_{\mathrm{H}} = \frac{4\pi \in_0 \hbar^2}{me^2} \qquad \text{...(5.82)}$$

Since the reduced mass m is almost the same as the electron mass m_e (for both hydrogen and hydrogen-like atoms), we get

$$a_{\mathrm{H}} = \frac{4\pi \in_0 \hbar^2}{m_e e^2} = a_0 \text{ (A constant)} \qquad \text{...(5.83)}$$

a_0 is identified as the radius of the first circular orbit for the electron in the hydrogen atom called the Bohr radius.

In view of Equation (5.83), the radial wavefunction becomes

$$R_{ne}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right] e^{-\rho/2}\, \rho^l L_{n+l}^{2l+1}(\rho) \qquad \text{...(5.84)}$$

The negative sign for N has been used to make R_{10} positive.

ρ and r are related according to $\rho = \gamma r = \sqrt{\frac{-8mE}{\hbar^2}}\, r$

Substituting for E given by Equation (5.84) we get

$$\rho = \frac{2Z}{na_0}\, r \qquad \text{...(5.85)}$$

NOTES

Equation (5.85) used in Equation (5.81) gives the radial wavefunction for hydrogen-like atom as

$$R_{nl}(r) = -\sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-Z}{na_0}r} \left(\frac{2Zr}{na_0}\right)^l L_{n+1}^{2l+1}\left(\frac{2Zr}{na_0}\right) \quad ...(5.86)$$

Putting $Z = 1$ in the above, the radial wavefunction for hydrogen atom is found to be

$$R_{nl}(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-r}{na_0}} \left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) \quad ...(5.87)$$

Complete Wavefunction

The complete wavefunction is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, \Theta_{lm}(\theta)\, \Phi_m(\phi)$$

where $$\Theta_{lm}(\theta) = \sqrt{\frac{(2l+1)\,(l-|m|)!}{2(l+|m|)!}}\; P_l^m\,(\cos\theta)$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

and $$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{\frac{-Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

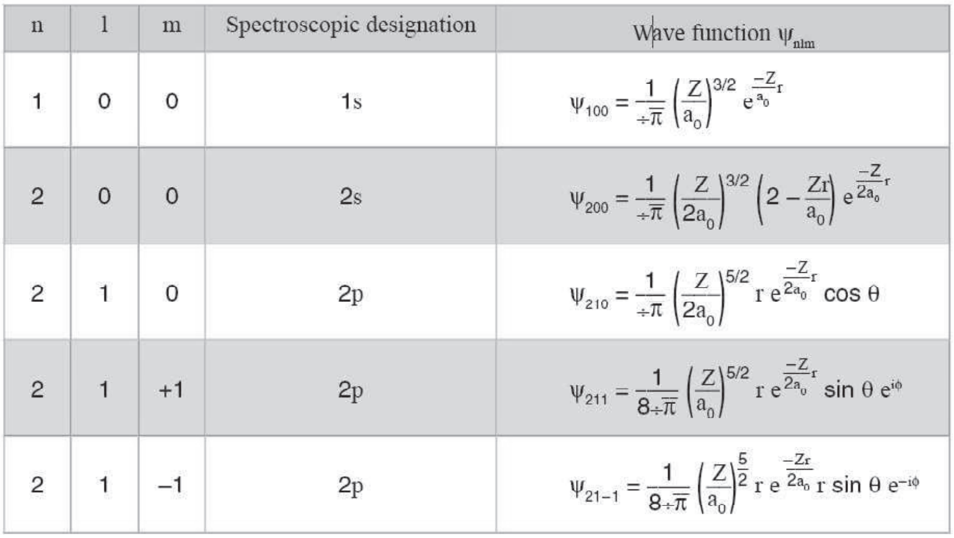
In the above

$n = 1, 2, 3,...$

$l = 0, 1, 2,... (n-1)$

$m = 0, \pm 1, \pm 2,... \pm l.$

The explicit forms of the complete wavefunctions ψ_{nlm}, for some of the values of n, l, m which describe stationary states of the hydrogen-like atom are given below along with the spectroscopic designations of the states.



n	l	m	Spectroscopic designation	Wave function ψ_{nlm}
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{\frac{-Z}{a_0}r}$
2	0	0	2s	$\psi_{200} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{\frac{-Z}{2a_0}r}$
2	1	0	2p	$\psi_{210} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{5/2} r\, e^{\frac{-Z}{2a_0}r} \cos\theta$
2	1	+1	2p	$\psi_{211} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{\frac{-Z}{2a_0}r} \sin\theta\, e^{i\phi}$
2	1	–1	2p	$\psi_{21-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\, e^{\frac{-Zr}{2a_0}} r \sin\theta\, e^{-i\phi}$

Putting $Z = 1$ in the above, we obtain the wavefunctions for the hydrogen atom.

Degeneracy of the Energy Levels

The energy eigenvalues for the hydrogen-like or hydrogen atom depend only on the principal quantum numbers n as is seen from the Equations (5.71) and (5.72). The energy eigenfunctions, however, depend on the quantum numbers n, l and m. We have seen that for a given value of n, l can take values 0 to $n - 1$ and for each of these l values there are $2l + 1$ values of the m from $- l$ to $+ l$. Clearly the energy level defined by the energy eigenvalue E_n is degenerate. The degeneracy is given by

$$D = n^2 \sum_{l=0}^{n-1} (2l+1) = \qquad \text{...(5.88)}$$

The ground state, i.e., the minimum energy state for which $n = 1$ is clearly non-degenerate ($n^2 = 1$). The first excited state for which $n = 2$ is 4-fold degenerate, and so on.

Probability Distribution Function

Let us consider the atom in the state described by the wavefunction $\psi_{nlm}(r, \theta, \phi)$. The probability of finding the electron in the volume element $d\tau = r^2\, dr \sin\theta\, d\theta\, d\phi$ about the point (r, θ, ϕ) is then given by

$$P_{nlm}\, d\tau = |\psi_{nlm}|^2\, d\tau = |\psi_{nlm}|^2\, r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= |R_{nl}(r)|^2\, |Y_{lm}(\theta, \phi)|^2\, r^2 dr \sin\theta\, d\theta\, d\phi$$

Clearly, the probability of finding the electron within a spherical shell of radius r and thickness dr from the nucleus irrespective of its angular position is given by

$$P_{nl}(r)dr = |R_{nl}(r)|^2\, r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

or $$P_{nl}(r)\, dr = 4\pi\, |R_{nl}(r)|^2\, r^2 dr \qquad \text{...(5.89)}$$

In this case, the atom is in the ground state described by the wavefunction,

$$\psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}}\, e^{\frac{-r}{a_0}}$$

The probability of finding the electron at the distance r from the nucleus is according to Equation (5.89) given by

$$P_{10}(r) = \frac{4\pi}{(\pi a_0^3)}\, e^{\frac{-2r}{a_0}}\, r^2 = \frac{4}{a_0^3}\, e^{\frac{-2r}{a_0}}\, r^2 \qquad \text{...(5.90)}$$

For $P_{10}(r)$ to be the maximum we have

$$\frac{d\,P_{10}(r)}{dr} = 0$$

or

$$\frac{d}{dr}\left[\frac{4}{a_0^3}\, e^{\frac{-2r}{a_0}}\, r^2\right] = 0$$

or

$$e^{\frac{-2r}{a_0}}\, 2r - r^2\, e^{\frac{-2r}{a_0}}\, \frac{2}{a_0} = 0$$

or

$$2r - \frac{2r^2}{a_0} = 0$$

or

$$1 - \frac{r}{a_0} = 0 \quad \text{or} \quad \frac{r}{a_0} = 1$$

or

$$r = a_0 \qquad \text{...(5.91)}$$

Thus the electron of the hydrogen atom in the ground state is found with maximum probability at a distance equal to the Bohr radius which is about 0.5 Å from the nucleus.

Equation (5.90) shows that $P_{10} = 0$ at $r = 0$ and also at $r = \infty$. We thus find from the theory of hydrogen atom based on Schrödinger wave mechanics that the position of the electron in the atom is not certain as opposed to Bohr's theory and instead we can say that the electron is found for most of the time around the Bohr radius. The result is consistent with Heisenberg's uncertainty principle.

5.6.3 Properties of the Radial Wave Function of Hydrogen Atom

The radial wavefunctions of the hydrogen atom have the properties shown in the Figure (5.1). We observe the following:

(i) They behave like r^{l} for small r

(ii) They decrease exponentially for large value of r since $L\,/^{\,2l+1}$ is dominated by the highest power r^{n-l-1}.

NOTES

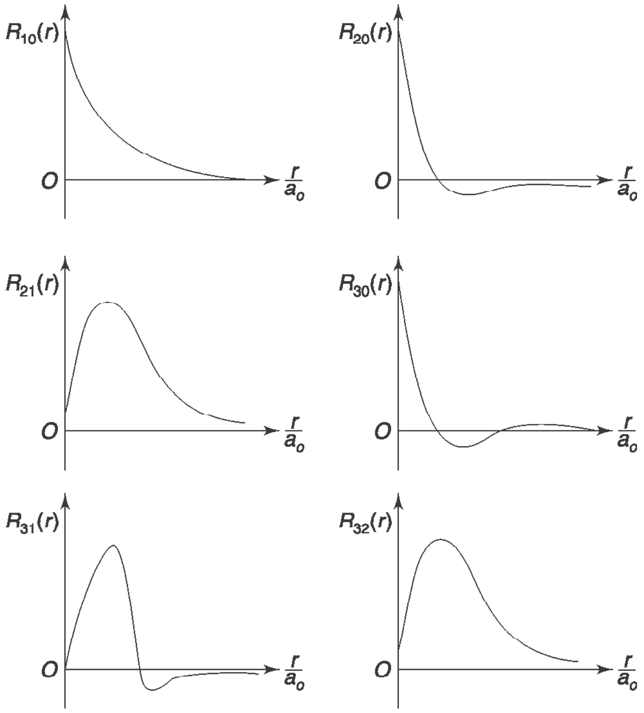


Fig. 5.1 *Radial Wavefunctions of Hydrogen Atom*

(iii) The radial function $R_{nl}(r)$ has $n-l-1$ radial nodes since $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ is a polynomial of degree $n-l-1$.

Check Your Progress

1. What is meant by relativistic quantum mechanics?
2. State the non-relativistic quantum mechanics.
3. What do you understand the classical relativistic dynamics?
4. Define the Lorentz group.
5. What is restricted Lorentz group?
6. State the Klein-Gordon equation.
7. Define the free particle.
8. What do you understand the hydrogen atom?

5.7 LARGE AND SMALL COMPONENTS OF THE DIRAC WAVEFUNCTION

When we study about the interaction of a charge e with an external electromagnetic field **E**, we also consider the:

$$A^{\mu} = (A_0, \vec{A}),$$

$$\mathbf{A^{\mu} = (A_0, A)}$$

This is the four potential, and A^{μ} here is a function of x only.

Using the gauge invariant substitution, we get:

$\hat{p}^{\mu} \to \hat{p}^{\mu} - \frac{e}{c}A^{\mu},$ And here e is the value of the charge of the electron.

Now the transformation of the Dirac Equation is as follows:

$$c\left[i\hbar\frac{\partial}{\partial(ct)} - \frac{e}{c}A_0\right]\psi = \left[c\vec{\alpha}\cdot\left(\hat{p} - \frac{e}{c}\vec{A}\right) + \beta mc^2\right]\psi$$

Or

$$i\hbar\frac{\partial}{\partial t}\psi = \left[c\vec{\alpha}\cdot\left(\hat{p} - \frac{e}{c}\vec{A}\right) + eA_0 + \beta mc^2\right]\psi$$

So, the interaction of the charge with the electromagnetic field is given by the above equation.

$$i\hbar\frac{\partial}{\partial t}\psi = \left(\hat{H} + \hat{H}'\right)\psi,$$

Where the, H' is given by:

$$\hat{H}' = -\frac{e}{c}c\vec{\alpha}\cdot\vec{A} + eA_0 = -\frac{e}{c}\hat{v}\cdot\vec{A} + eA_0,$$

Also, $\hat{v} = c\vec{\alpha}$ here, which is a representation of the classical representation of the velocity operator.

For the non-relativistic limit in the quantum mechanics, we say that the Dirac's equation is reduced to the Schrodinger's wave equation. For that, the case of a positive energy Dirac particle in the presence of an electromagnetic potential is taken into consideration for evaluating the result for the non-relativistic limit, which is:

$$i\hbar\frac{\partial\psi}{\partial t} = \left[c\vec{\alpha}\cdot\left(\hat{p} - \frac{e}{c}\vec{A}\right) + eA_0 + \beta mc^2\right]\psi$$ Where $\hat{p} = -i\hbar\vec{\nabla}$ is for the momentum operator here.

Let us consider:

$$\psi(\vec{x},t) = \begin{bmatrix}\phi(\vec{x},t)\\ \chi(\vec{x},t)\end{bmatrix}$$ Here, the ψ is the 4 component spinor made up of two 2 component spinor which are Φ and X. After we substitute their value into the Dirac equation, we get:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\phi\\ \chi\end{pmatrix} = \begin{pmatrix}c\vec{\sigma}\cdot\left[\hat{p} - \frac{e}{c}\vec{A}\right]\chi\\ c\vec{\sigma}\cdot\left[\hat{p} - \frac{e}{c}\vec{A}\right]\phi\end{pmatrix} + eA_0\begin{pmatrix}\phi\\ \chi\end{pmatrix} + mc^2\begin{pmatrix}\phi\\ -\chi\end{pmatrix} \qquad \text{(a)}$$

If the largest rest mass energy is mc^2, then the solution will be:

$$\begin{bmatrix}\phi(\vec{x},t)\\ \chi(\vec{x},t)\end{bmatrix} = \begin{bmatrix}\phi_0(\vec{x},t)\\ \chi_0(\vec{x},t)\end{bmatrix}e^{-imc^2t/\hbar}$$

Here Φ_o and X_o varies slowly with time. After substituting this non relativistic solution into the Dirac equation gives:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\phi_0\\ \chi_0\end{pmatrix}=\begin{pmatrix}c\vec{\sigma}\cdot\left[\hat{p}-\frac{e}{c}\vec{A}\right]\chi_0\\ c\vec{\sigma}\cdot\left[\hat{p}-\frac{e}{c}\vec{A}\right]\phi_0\end{pmatrix}+eA_0\begin{pmatrix}\phi_0\\ \chi_0\end{pmatrix}-2mc^2\begin{pmatrix}0\\ \chi_0\end{pmatrix}$$

Here, if (Kinetic energy< Rest mass energy), then the X_o varies slowly with time i.e.:

$$|eA_0\chi_0| \ll |mc^2\chi_0|$$

The potential energy will be small in comparison to the rest mass energy, when the electrostatic potential is weak.

With these assumptions, the equation (a) now becomes:

$$0\approx c\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right)\phi_0-2mc^2\chi_0,$$

$$\chi_0=\frac{\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right)}{2mc}\phi_0.$$

So, the X here, which is also the lower component, is known as the 'Small Component' of the Dirac wave function, ψ here and the Φ is the 'Large Component' of the Dirac wave function. In the non-relativistic limit, ψ is approximately v/c less than the Φ.

5.8 PAULI THEORY AS THE NON-RELATIVISTIC LIMIT OF THE DIRAC EQUATION

In the previous section, we talked about the lower component. Now here, in this section, we will talk about the upper component of the equation (a) which becomes:

$$i\hbar\frac{\partial\phi_0}{\partial t}=\frac{\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right)\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right)}{2m}\phi_0+eA_0\phi_0$$

By using a common identity of curl of vectors, we get:

$$\begin{aligned}\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right)\vec{\sigma}\cdot\left(\hat{p}-\frac{e}{c}\vec{A}\right) &= \left(\hat{p}-\frac{e}{c}\vec{A}\right)^2+i\vec{\sigma}\cdot\left[\left(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}\right)\times\left(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}\right)\right]\\ &= \left(\hat{p}-\frac{e}{c}\vec{A}\right)^2-\frac{e\hbar}{c}\vec{\sigma}\cdot(\vec{\nabla}\times\vec{A}),\\ &= \left(\hat{p}-\frac{e}{c}\vec{A}\right)^2-\frac{e\hbar}{c}\vec{\sigma}\cdot\vec{B}.\end{aligned}$$

Then, after applying the identity and performing the experiment, the Dirac equation then becomes:

$$i\hbar\frac{\partial\phi_0}{\partial t} = \left[\frac{\left(\hat{p} - \frac{e}{c}\vec{A}\right)^2}{2m} - \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{B} + eA_0\right]\phi_0$$

So, we successfully get the Pauli equation or in other words, the Pauli's theory as the non-relativistic limit of the Dirac's equation. It is the two component Pauli's equation for the theory of the spins and we also get the description of the spin degrees of freedom. For that, the Φo gives the spin degree of freedom here.

A particle with spin 1/2 with both low and high velocities can be explained by the Dirac's equation though the Pauli's theory and the equation is the non-relativistic limit of the Dirac's equation for the spin ½ particles.

The gyro magnetic factor for electron i.e., g=2 can also be shown by the use of the Pauli's equation and hence the Dirac's equation.

5.9 HYPERFINE POSITIONS THEORY

We know that atoms have their own electronic configuration such as $1s^2$, $2s^2$ and so on. When we have electron transition from higher level to the lower level, and observe them, then due to the spin orbit interaction, instead of a single line, we get more than one line. Due to the total angular momentum J we get J= L±S and for example, for the p orbital, we know that l=1 and s= ½ for an electron, then the J would be 3/2 and ½, so we get two values and we get two levels i.e. $2p_{1/2}$ and $2p_{3/2}$ and that's why we get two lines instead of two lines due to the splitting of the level, which is known as Fine structure. When we discuss about the hyperfine structure, for that we say that the further splitting of the fine structure into more levels is known as the hyperfine structure or hyperfine splitting. The reason behind the formation of the hyperfine positions can be explained as follows:

Firstly, many fine- structure components of the spectral lines when examined under instruments of highest possible resolution are further splitted into components with separation of order of $1 cm^{-1}$, which is much smaller than those of the ordinary multiplet structure. This splitting is called the ***hyperfine structure*** and it is caused by the properties of the atom. For the experimental study, the light source must be giving extremely sharp lines, such as laser.

There are two types of nuclear effects that produce hyperfine structure:

The first is due to the presence of different isotopic species in the element under investigation. The energy levels of the isotopes are slightly displaced relative to each other, producing spectral transitions at slightly different numbers.

The second type of effect arises due to the charged nucleus possesses as spin angular momentum and associated magnetic dipole moment. An interaction between the internal magnetic field produced by the orbital motion of the electrons in the atom and the magnetic dipole moment of the nucleus causes a hyperfine splitting of the spectral terms.

As nuclear magnetic dipole moments are smaller than electronic magnetic dipole moments by 10^3, the hyperfine splitting is smaller than the spin orbit splitting by the same factor.

Isotope effect: Many elements are composed of isotopic atoms. Different isotopes of an element have the same atomic number but they differ from one another in mass.

Since the nuclear mass enters into the Rydberg constant for an atom, different isotopes have slightly different values of Rydberg constant. Correspondingly, the same transitions in different isotopes give rise to slightly different wave numbers. The variation in Rydberg constant is particularly marked in hydrogen. As an example let us calculate the shift for H_β line. For this transition, we have from Balmer's formula:

$$\frac{1}{\lambda_H} = R_H\{(1/2^2)-(1/4^2)\}$$

And, $$\frac{1}{\lambda_0} = R_0\{(1/2^2)-(1/4^2)\}$$

So, $$\frac{\lambda_0}{\lambda_H} = \frac{R\mathrm{H}}{R_O}$$, where R_H is Rydberg constant.

So, we can calculate $\Delta\lambda$ from these to calculate the shift.

The second effect is the more important effect than the first one which is already discussed earlier. The hyperfine structure could be explained when it is assumed that the nucleus possesses an intrinsic spin angular momentum **I** with which a magnetic dipole moment $\boldsymbol{\mu}_\mathrm{I}$ is associated. Just as the in the case of spinning electron, the magnitude of the nuclear angular momentum is:

$$|\mathbf{I}| = \sqrt{\mathrm{I}(\mathrm{I}+1)}\frac{h}{2\pi}$$

Where I is the 'nuclear spin quantum number' which has different values for different mass numbers.

Thus the angular momentum has different magnitudes for different nuclei and also for different isotopes of the same element.

Just as **L, S and J** have quantized components along an axis in space, the component of **I** along the z axis is:

$$\mathrm{I}_z = \mathrm{M}_\mathrm{I}\frac{h}{2\pi}$$

M_I is the nuclear magnetic quantum number. M_I has 2I+1 value.

The motion of the nuclear protons produces a magnetic moment $\boldsymbol{\mu}_\mathrm{I}$ which is proportional to the angular momentum, and which we shall write:

NOTES

$\boldsymbol{\mu}_{\mathbf{I}} = g_I (e/2m_p)\mathbf{I}$

Where e is the charge of the proton,

m_p is the mass of the proton.

g_I is the nuclear g factor.

The magnitude of the nuclear magnetic moment is:

$$\boldsymbol{\mu}_{\mathbf{I}} = g_I (e/2m_p)\sqrt{I(I+1)}\frac{h}{2\pi}.$$

The interaction between **I** and **J** is the cause of the hyperfine splitting, where I is the nuclear spin angular momentum and J is the total angular momentum which we have already studied before.

$$\boldsymbol{\mu}_{\mathbf{I}} = g_I \sqrt{I(I+1)}\frac{eh}{4\pi Mp}.$$

Where, $\frac{eh}{4\pi Mp}$ is the nuclear magneton.

So, $\boldsymbol{\mu}_{\mathbf{I}} = g_I \sqrt{I(I+1)}\,\boldsymbol{\mu}_{\mathbf{N}}$

Since the maximum value of M_I is I, the maximum observable component of μ_I is $g_I I \boldsymbol{\mu}_{\mathbf{N}}$, and is called the nuclear magnetic moment. It is roughly 10^3 times smaller than the electron magnetic moment.

Now we have to understand the Atomic Vector Model: The total angular momentum of the whole atom is the sum of three angular momenta: the electron orbital angular momentum **L**, the electron spin angular momentum **S,** the nuclear spin angular momentum **I**. That is, the total angular momentum is:

F= L+S+I

F= J+I

The interaction between the nuclear magnetic moment and the magnetic field produced by the orbital and spin motions of the atomic electrons couples **I** with **J** and causes these vectors to precess around their resultant **F**.

This precession is, however, about 1000 times slower than that of **L** and **S** about **J**(because nuclear magnetic moment is so much smaller than electron magnetic moment).

Correspondingly, the energy differences are very much smaller.

The quantized values of the total angular momentum **F** are $\sqrt{F(F+1)}\frac{h}{2\pi}$ where the quantum number F can take the values from:

J+1………………………..|J-1|

Giving 2J+1 values if I>=J, or 2I+1 values if I=<J. This means that as a result of I-J interaction, each fine structure J level splits into 2J+1(if I>=J) or 2I+1(if I=<J) hyperfine splitting levels, each characterized by an F value.

The interaction energy is also there, when there is an interaction between the I and J, there is the generation of the interaction energy too. The I-J interaction energy can be shown to be as following:

$E = \frac{1}{2} A'[F(F+1)-I(I+1)-J(J+1)]$

Where A' is a constant.

5.10 HOLE THEORY

The discussion and conclusion regarding the mathematical model of Paul Dirac in relativistic quantum mechanics is contained in the Dirac Hole theory or simply the hole theory during the free particle solution of the Dirac, we also got the negative solutions of the Dirac equation which is expressed by the hole theory given by Dirac. If we look at the atomic spectra of an electron, the part above the $M_o c^2$ is the part of the positive energy continuum and the part below $-M_o c^2$ is the negative energy continuum. So we get to know in the free particle solution of the Dirac equation that there exist both the negative energy and the positive energy continuum. The electron can get to the negative energy continuum by losing energy and due to the presence of infinite negative energy state; the electron can get a lot far in negative energy continuum. This losing of energy by the electron and its transfer to the negative energy continuum is known as the 'Radiation Catastrophe'. If this happens, then there would be no existence of any atom in this universe for which Dirac suggested that the negative continuum is all filled with electrons. All the states of the negative energy continuum are filled with electrons, according to Dirac which prevents the Radiation catastrophe. Further, if an electron from the negative energy continuum wants to go to the positive energy continuum then it should satisfy the equation:

$\hbar w > 2M_o c^2$

When the electron goes to the positive energy continuum by gaining energy of $\hbar w$, then it goes to the positive energy continuum and it creates an electron hole in the negative energy continuum which is of the opposite charge of that of the electron, this process of the formation of an electron and the electron hole is known as the pair creation. Here a pair of a particle and an antiparticle is created, the hole created is in other terms the antiparticle with positive charge.

It can also happen that the electron from the positive energy continuum returns back to the hole in the negative energy continuum and then the process of annihilation takes place which as a whole is known as the pair annihilation, where both the electron and the hole is destroyed and energy i.e. gamma rays persists.

$\mathbf{e^- + e^+ \rightarrow 2c}$

So the hole created is of opposite charge and is the antiparticle of the electron. When we analyze of mass of the antiparticle, firstly we have:

$\hbar w$ = (Energy of electron in positive energy continuum)-(Energy of electron in negative energy continuum)

$$\hbar w = \sqrt{Mo^2c^4 + p^2c^2} - (-\sqrt{Mo^2c^4 + p'^2c^2})$$

$$\hbar \text{ w} = \sqrt{Mo^2c^4 + p^2c^2} + \sqrt{Mo^2c^4 + p'^2\, c^2}$$

$\hbar$ w = $E_e + E_p$, where E_e is the energy of the electron and E_p is the energy of the positron.

NOTES

The rest mass of the positron is same as that of the electron.

Regarding the momentum of the antiparticle i.e. the positron:

Initial total momentum= Final total momentum

$\hbar$ k+ P(momentum of electron in negative energy continuum)= P(momentum of electron in positive energy continuum)

$\hbar$ k = P(electron in positive energy continuum)- P(electron in negative energy continuum)

$\hbar$ k = $P_e + P'_P$

So we saw that the momentum of the positron is negative of the momentum of the electron.

So the Dirac Hole theory is an approach to explain the negative energy solutions of the Dirac equation.

5.10.1 Difficulties with the Hole Theory

The Dirac Hole theory is an approach to explain the negative energy solutions of the Dirac equation, which we already discussed in the previous section. We studied about the Radiation Catastrophe and about the non-existence of any atom in this universe for which Dirac suggested that the negative continuum is all filled with electrons. The illustration is as following Figure 5.2:

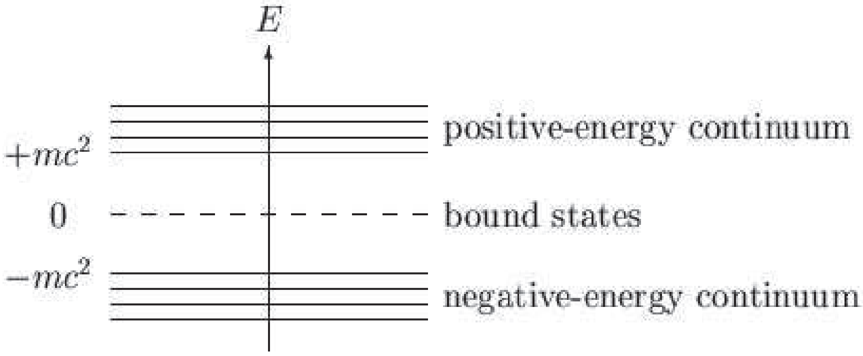


Fig5.2 *Illustration for the Spectrum of Energy Eigenvalues of the Free Particle Dirac Equation*

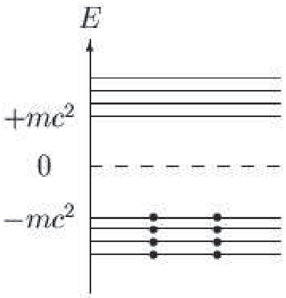


Fig 5.3 *Illustration of the Occupation of the Negative Energy States*

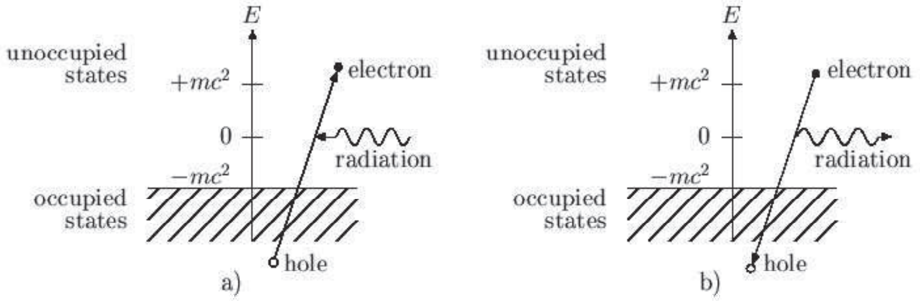
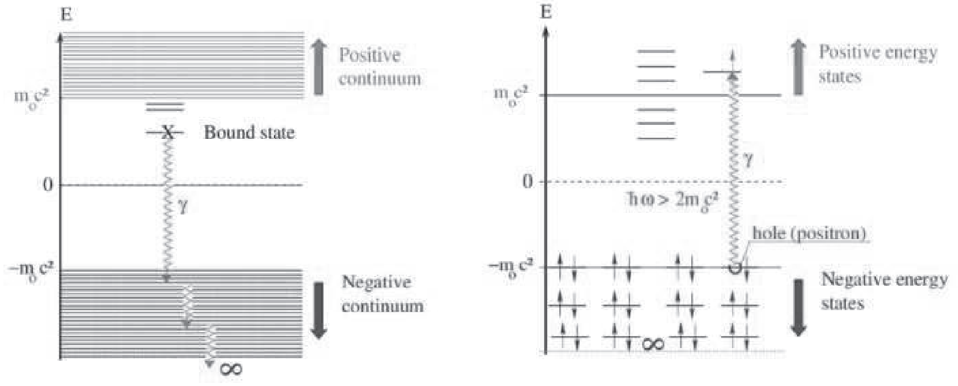


Fig 5.4 *Illustration of the transitions in the hole theory: a) Pair production b) Pair annihilation.*

Illustration of the occupation of the negative energy states, also known as the **Dirac Sea**. This represents the vacuum state (Refer Figure5.3). Then, it was realized that discussion of the hole theory has some difficulties associated with it since it describes the particles that have the charge of both signs i.e. positive and negative which further gives us the many particle theory with whom we were not familiar earlier and now the wave function don't have the simple probability explanation of the one particle theory. With this notion, it can be states also that with many particle theories, the pair production and annihilation of the electron-positron pair should also be taken into consideration.

In the Dirac hole theory, we saw that the vacuum was explained in which the Pauli's exclusion principle played a great role and that is how the hole theory was successful in properly describing the spin ½ particles so the hole theory was a success for the spin ½ particles but it was not able to explain the spin 0 particles for example bosons since bosons do not obey the Pauli's exclusion principle.



a) b)

a) Describes the negative energy continuum which leads to radiation catastrophe.

b) Illustration of the Dirac sea with the creation of the electron-positron pair.

So the conclusion is that we cannot use Dirac's hole theory for the spin ½ particles which is the major drawback of the Hole Theory. But it was one of the successful theories which gave us the explanation of the vacuum and the existence of the antiparticles.

NOTES

5.11 IDENTICAL PARTICLES

Starting with the definition of the identical particles, some obvious points in the definition includes:

The identical particles share the same names. In other words, the electrons and protons are not identical to each other but they are identical to itself, i.e., one electron is identical to another electron and one proton is identical to another proton.

If we have a system of identical particles, then exchanging two particles will lead to exactly same physics.

There is a difference between the classical physics and quantum physics. In classical physics, the identical particles are distinguishable while in quantum physics the identical particles are indistinguishable.

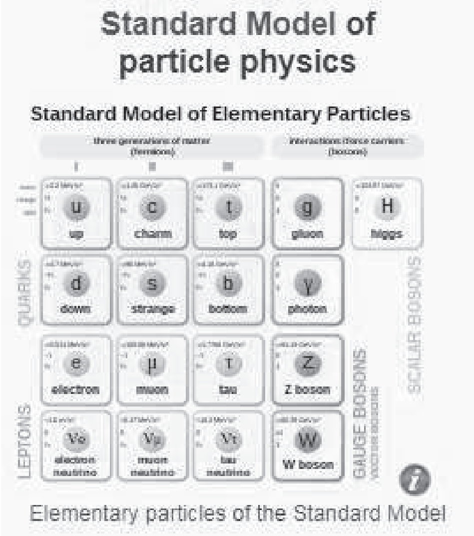
So, two particles are identical particles, when their defining intrinsic properties are the same where the intrinsic properties include: mass, charge and spin.

We can take the examples of electron, muon and positron. All electrons are identical to themselves but they are not identical to muon because the mass of the electron and the muon are different. Again, the positrons are identical to themselves but they are not identical to the electrons because they have different charges i.e. electron has negative charge whereas the positron has positive charge.

It should be noted that the identical particles may be in different states. So exchanging two identical particles does not affect the properties of the system.

For identical quantum particles, when we detect a particle in a region in which the wave packets overlap, we have no way of telling which of the two particles it was. It means that the classical and quantum particles behave in different ways since identical classical particles are distinguishable whereas the identical quantum particles are indistinguishable.

5.11.1 Similar Particles and Symmetrical Representation



We have already studied about the similar particles or the identical particles in previous sections.

So, two particles are similar particles or identical particles, when their defining intrinsic properties are the same where the intrinsic properties include: mass, charge and spin.

We can take the examples of electron, muon and positron. All electrons are identical to themselves but they are not identical to muon because the mass of the electron and the muon are different. Again, the positrons are identical to themselves but they are not identical to the electrons because they have different charges i.e. electron has negative charge whereas the positron has positive charge.

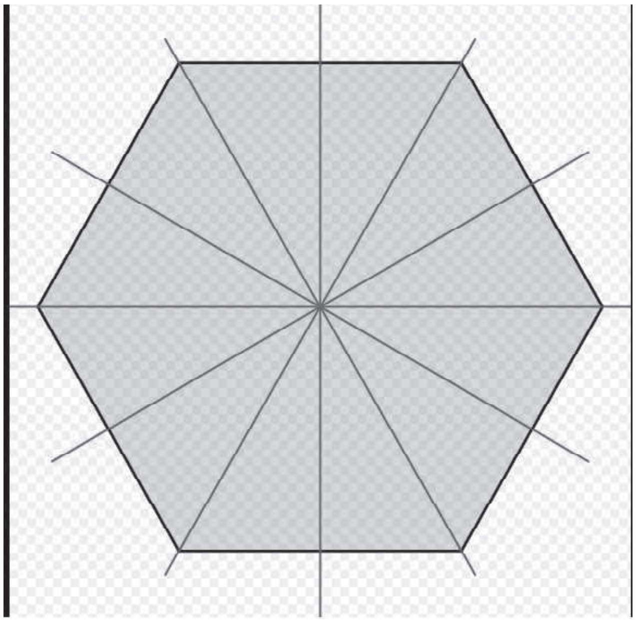


Fig. 5.5 *Symmetries of the Objects*

Symmetrical representation is discussed further in the upcoming topics. A wide view of the symmetrical representation is discussed for the explanation of similar particles and one of the most searched and discussed topics in quantum mechanics.

5.11.2 Permutation Operators

Let us consider two non-identical particles which have the same spin. In other words they have same internal degrees of freedom. Their state space is defined by E= E(1) $\otimes$ E(2).

E(1) and E(2) both are spanned by the same orthogonal basis $\{|u_j>\}$. So the state space is spanned by the basis vectors a follows:

$$\{|1:u_i>\otimes|2:u_j>=|1:u_i;2:u_j>=|u_i,u_j>\}$$

Here, $|1:u_i;2:u_j>\neq|1:u_j;2:u_i>$ unless $u_i=u_j$

We now define the permutation operator P_{21} by noticing its action on the basis vectors.

$$P_{21}|u_i,u_j\rangle=|u_j,u_i\rangle.$$

$$P_{21}^{2}=1,\ P_{21}^{-1}=P_{21}.$$

The elements of P_{21}^{T} and P_{21} matrix are same for different basis vectors.

$$\langle u_i,u_j|P_{21}^{T}|u_{i'},u_{j'}\rangle=\langle u_i,u_j|P_{21}|u_{i'},u_{j'}\rangle=\delta_{ij'}\delta_{i'j}$$

This further explains:

$$P_{21}=P_{21}^{T}=P_{21}^{-1},\ P_{21}P_{21}^{T}=P_{21}^{T}P_{21}=I$$

Here the matrix P_{21} is a Hermitian matrix and unitary too. Therefore, the eigenvalue of P_{21} are real and $P_{21}^{2} = 1$, its eigenvalues are real and of values ±1.

We get a symmetric and an antisymmetric eigenvector too, which are:

$$P_{21}|\psi_S\rangle=|\psi_S\rangle\text{: symmetric eigenvector}$$

$$P_{21}|\psi_A\rangle=-|\psi_A\rangle\text{: anti-symmetric eigenvector}$$

The operators: S= ½ (1+ P_{21}) and A= ½ (1- P_{21}) are the projectors onto the orthogonal subspaces, onto the spaces of symmetric and antisymmetric kets as follows:

$$S^{2}=S,\ S^{T}=S,\ P_{21}S|\psi\rangle=S|\psi\rangle.\ S|\psi\rangle\text{ is symmetric.}$$

$$A^{2}=A,\ A^{T}=A,\ P_{21}A|\psi\rangle=-A|\psi\rangle.\ A|\psi\rangle\text{ is anti-symmetric}$$

$$SA=AS=0,\ S+A=I.$$

Here, the ½ (1+ P_{21}) is called the symmetrizer and ½ (1-P_{21}) is the Anti-symmetrizer and the operators which commutes with the P_{21} are the symmetric observables.

If we consider the three particles, then the basis for the state space is given by:

$$\{|1:u_i\rangle\otimes|2:u_j\rangle\otimes|3:u_k\rangle=|u_i;u_j;u_k\rangle\}$$

Then for three particle system, we define six permutation operators which are P_{123}, P_{321}, P_{231}, P_{132}, P_{321}, and P_{213}.

$$P_{npq}(|1:u_i\rangle\otimes|2:u_j\rangle\otimes|3:u_k\rangle)=(|n:u_i\rangle\otimes|p:u_j\rangle\otimes|q:u_k\rangle)$$

5.11.3 Algebra of Permutation Operators

P_{nlm} gives the values of the quantum numbers of particle 1 to particle *n*, of particle 2 to particle *l*, and of particle 3 to particle *m*.

e.g.: $P_{312}|u_i;u_j;u_k\rangle=|u_j;u_k;u_i\rangle$. (Note: $P_{123}=I$.)

We study about the algebra of another kind of permutation which is known as the transposition. It exchanges two particles. We are able to write any permutation as a product of the transpositions. This is not unique though. In order to write any permutation, we always need an odd number or an even number of permutations. Even parity permutation is the permutation which takes even number of transposition. Odd parity permutation is the permutation which takes odd number of transpositions. All of them define the **Parity of the Permutation**.

For example:

P_{123}, P_{231}, P_{312} are even permutations.
P_{132}, P_{321}, P_{213} are odd permutations.

If we have N number of particles, then the number of permutation operators associated with the N number of particles are N! and the set of permutation operators forms a group.

The elements of this group do not commute in general.

Permutation operators are unitary because of the fact that they are the products of the unitary operators. Let us assume an arbitrary permutation operator P_α where we already know that a symmetric wave function is given by:

$$P_\alpha | \psi_S >= | \psi_S >$$

And the anti-symmetric wave function is given by the following:

$$P_\alpha | \psi_A >= \varepsilon_\alpha | \psi_A >,$$

where $\varepsilon_\alpha = 1$ if $P_\alpha =$ even and $\varepsilon_\alpha = -1$ if $P_\alpha =$ odd

For the space containing N particles, the Symmetrizer and the Anti symmetrizer operators is given by:

$$S = \frac{1}{N!} \sum_\alpha P_\alpha, \quad A = \frac{1}{N!} \sum_\alpha \varepsilon_\alpha P_\alpha$$

$$S^2 = S,\ S^T = S,\ P_\alpha S = S P_\alpha = S.$$

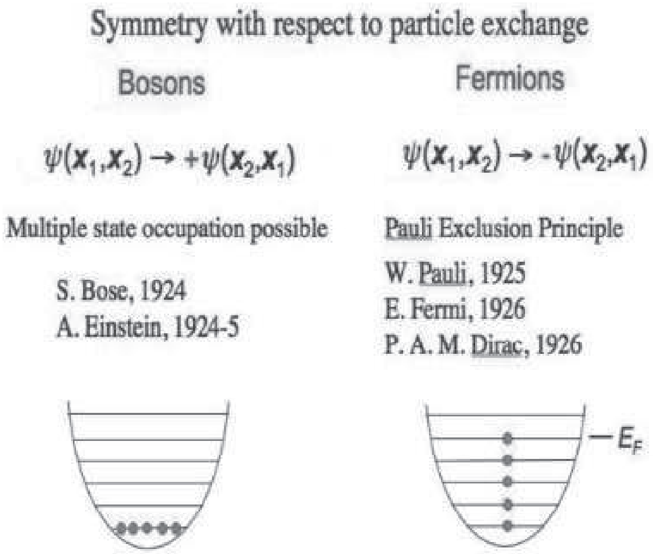
$$A^2 = A,\ A^T = A,\ P_\alpha A = A P_\alpha = \varepsilon_\alpha A.$$

$$SA = AS = 0, \text{ but } S + A \neq I \text{ if } N > 2.$$

Here, the S and A are the projectors onto the orthogonal subspaces.

5.11.4 Symmetrization Postulate

We have studied about the symmetric states, anti-symmetric states, the permutation operators etc but to connect them with quantum mechanics, we need the symmetrization postulate. It is something we cannot derive, so we say that it is a postulate, a kind of axiom in quantum mechanics.



Symmetry with respect to particle exchange

Bosons

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

Multiple state occupation possible

S. Bose, 1924
A. Einstein, 1924-5

Fermions

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

Pauli Exclusion Principle

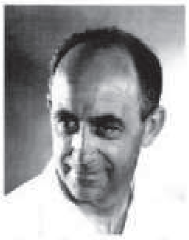
W. Pauli, 1925
E. Fermi, 1926
P. A. M. Dirac, 1926

The postulate is stated as follows:

If we have a system of N identical particles, arbitrary states in $\mathrm{V}^{\blacklozenge N}$ are not the physical states. The physical states are the states that are totally symmetric, and in that case, the particles are called bosons or totally antisymmetric, in which case the particles are called *fermions*.

Symmetrization postulate

Satyendra Nath
Bose
(1894 – 1974)



Enrico Fermi
(1901–1954)

The comments that can be made on symmetrization postulate are:

1. General statement made is that the further statistics or other types of space exist in two dimensions, not in three where we live.
2. The symmetrization postulate gives the statistical definition states for bosons and fermions.
3. The spin-statistics theorem, from where, after analyzing the theorem, we get to know that the particles with spin 0,1,2,…. are bosons and the particles with spin ½, 3/2,. etc., are the ***fermions***.

5.12 BOSON AND BOSE–EINSTEIN STATISTICS

In *particle physics*, a '**Boson**' is a subatomic particle whose spin quantum number has an integer value (0,1,2 ...). Bosons form one of the two fundamental classes of subatomic particle, the other being *fermions*, which have odd half-integer spin (1/2,3/ 2 ...) Every observed subatomic particle is either a boson or a fermion.

Some bosons are elementary particles and occupy a special role in particle physics unlike that of fermions, which are sometimes described as the constituents of 'Ordinary Matter'. Some elementary bosons (for example, gluons) act as force carriers, which give rise to forces between other particles, while one (the Higgs boson) gives rise to the phenomenon of mass. Other bosons, such as mesons, are composite particles made up of smaller constituents.

Outside the realm of particle physics, superfluidity arises because composite bosons (bose particles), such as low temperature helium-4 atoms, follow Bose–Einstein statistics; similarly, superconductivity arises because some quasiparticles, such as Cooper pairs, behave in the same way.

The basis postulates of BE statistics are:

(*i*) The associated particles are identical and *indistinguishable*.

(*ii*) Each energy state can contain any number of particles.

(*iii*) Total energy and total number of particles of the entire system are constant.

(*iv*) The particles have zero or integral spin, *i.e.,* $0\hbar$, $1\hbar$, $5\hbar$, $50\hbar$, etc., where $\hbar$ is the unit of spin.

(*v*) The wave function of the system is symmetric under the positional exchange of any two particles.

Examples: Photon, phonon, all mesons (π, κ, η) etc., these are known as *Bosons***.**

[**Note: Symmetric and Anti-symmetric wave function**

Suppose the allowed wave function for *n*-particles system is $\psi(1, 2, 3, ..., r, s, ... n)$, where the integers within the argument of ψ represent the coordinates of the *n*-particles relative to some fixed orgion. Now, if we interchange the position of any two particles, say, *r* and *s*, the resulting wave function becomes $\psi(1, 2, 3, ..., s, r, ...n)$. The wave function ψ is said to be symmetric when

$$\psi(1, 2, 3, ..., r, s, ...n) = \psi(1, 2, 3, ..., s, r, ...n),$$

and anti-symmetric when

$$\psi(1, 2, 3, ..., r, s, ...n), = -\psi(1, 2, 3, ..., s, r, ...n)]$$

Bose-Einstein Distribution Law

Let N_i number of identical, indistinguishable, non-interacting particles are to be distributed among g_i quantum states each having energy E_i. So, in the *i*th energy level, there are $(N_i + g_i)$ total objects. Keeping the first quantum state fixed, the remaining $(N_i + g_i - 1)$ objects can permuted in $(N_i + g_i - 1)!$ possible ways. But since the particles and the quantum states are indistinguishable, we have to deduct $N_i!$ ways and $(g_i - 1)!$ ways from the all possible ways to get effective number of arrangements. Thus, total number of possible ways of arrangement for the *i*th state is

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad \text{...(5.92)}$$

Hence the total number of ways of the entire distribution of *N* particles in *n* number of energy levels of the system is

$$W = \prod_i^n \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad \text{...(5.93)}$$

where Π denotes the product symbol.

If we assume that N_i and g_i are very large, Equation (5.93) reduces to

$$W = \prod_i^n \frac{(N_i + g_i)!}{N_i!\, g_i!} \qquad \text{...(5.94)}$$

Taking natural logarithm of both the sides of Equation(5.94) we get,

$$\begin{aligned} \ln W &= \sum_i \left[\ln (N_i + g_i)! - \ln N_i! - \ln g_i!\right] \\ &= \sum_i \left[(N_i + g_i) \ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i\right] \qquad \text{...(5.95)} \end{aligned}$$

(using Stirling approximation)

Now, differentiating equation (7.22) to obtain the probable distribution, we get,

$$d(\ln W)_{\max} = \sum_i [\ln (N_i + g_i) - \ln N_i]\, dN_i = 0 \qquad \text{...(5.96)}$$

Also we have other two conditions given by

$$\sum_i dN_i = 0 \text{ (conservation of total no. of particles)} \qquad \text{...(5.97)}$$

$$\sum_i E_i\, dN_i = 0 \text{ (conservation of total energy)} \qquad \text{...(5.98)}$$

Multiplying Equation (5.97) by (–α) and Equation (5.98) by (–β) and then adding with Equation (5.96) we get,

$$\sum_i [\ln (N_i + g_i) - \ln N_i - \alpha - \beta E_i]\, dN_i = 0 \qquad \text{...(5.99)}$$

Since dN_i's are independent of one another, the above equation holds only if,

$$\sum_i [\ln (N_i + g_i) - \ln N_i - \alpha - \beta E_i] = 0$$

Or,

$$N_i = \frac{g_i}{e^{(\alpha + \beta E_i)} - 1} \qquad \text{...(5.100)}$$

Now the Bose-Einstein distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1} \qquad \text{...(5.101)}$$

which represents the probability of finding a boson with energy E_i.

In quantum mechanics we have already established Planck's law of black-body radiation which exactly accounts for the observed energy density in case of a black-body radiation. Here shall re-derive the same Planck's law by using Bose-Einstein statistics. In order to derive this, let us consider a black-body chamber of volume V kept at a constant temperature T and filled with radiant energy that can be considered as an assembly of photons. If the number of photons in the chamber is very large, the spacing between two successive energy levels becomes very small making the energy lavels almost continuous. Thus if the energy of the photons ranges from E to $E + dE$, the number of degnerate states g_i should be replaced by $g(E)dE$ and the total number of photons N_i in these states should be replaced by $N(E)dE$ in the distribution function given by equation (5.100). Thus the total number of photons in the chamber having energy between E to $E + dE$ can be written by the following eqn. (5.100).

The number of photons having energy range between E to $E + dE$ can be written by using Equation (5.100) as given by

$$N(E)dE = \frac{g(E)}{e^{(\alpha+\beta E)} - 1} dE \qquad ...(5.102)$$

where $g(E)dE$ is the number of states of photons having energy between E to $E + dE$. In case of black-body radiation, the total number of particles are not conserved because, photons are absorbed and re-emitted frequently by the walls of the chamber, *i.e.,*

$\sum_i dN_i \neq 0$, which implies $\alpha = 0$. Also it is experimentally established that $\beta = \frac{1}{kT}$, where, $k = 1.38 \times 10^{-23}$ Joule/Kelvin is known as the Boltzmann constant. Thus Equation (5.102) reduces to

$$N(E)dE = \frac{g(E)\,dE}{e^{E/kT} - 1} \qquad ...(5.103)$$

Now the number of quantum states corresponding to the momentum range from p to $p + dp$ is

$$g(E)dE = g_s \frac{4\pi V p^2 dp}{h^3} \qquad ...(5.104)$$

where, g_s is the ***spin-degeneracy* or *duplicity*** of a quantum state. Since a photon has two spin orientations in trensverse direction, $g_s = 2$ for photons.

$$\therefore \qquad g(p)dp = \frac{8\pi V p^2 dp}{h^3} \qquad ...(5.105)$$

The energy of a photon of frequency v is $E = hv$ and so its momentum is $p = hv/c$, where c is the speed of a photon in free space.

$$\therefore \qquad dp = \frac{h}{c} dv \qquad ...(5.106)$$

Substituting the value of p and dp we get the number of quantum states having frequency range between v and $v + dv$ as

$$g(v)dv = \frac{8\pi V}{c^3} v^2 dv \qquad ...(5.107)$$

Hence, expressing Equation (5.102) in terms of v we get,

$$N(v)dv = \frac{g(\nu)d\nu}{e^{h\nu/kT} - 1}$$

$$= \frac{8\pi V}{c^3} \cdot \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \qquad \text{...(5.108)}$$

which represents the number of photons having frequency range between v to $v + dv$ kept in a chamber of volume V at temperature T.

Therefore, the *energy density* (total energy per unit volume) of the photons within frequency range dv is given by

$$u(v)dv = \frac{h\nu}{V} N(v)dv$$

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

Or, $$u(v)dv = \frac{8\pi h}{c^3} \cdot \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \qquad \text{...(5.109)}$$

which is the Planck's law of black-body radiation that we have deduced earlier in quantum mechanics.

5.13 FERMIONS AND FERMI DIRAC STATISTICS

In particle physics, a '**Fermion**' is a particle that follows Fermi–Dirac statistics and generally has half odd integer spin: spin 1/2, spin 3/2, etc. These particles obey the *Pauli exclusion principle*. Fermions include all quarks and leptons, as well as all composite particles made of an odd number of these, such as all baryons and many atoms and nuclei. Fermions differ from bosons, which obey Bose–Einstein statistics. Some fermions are elementary particles, such as the electrons, and some are composite particles, such as the protons. According to the spin-statistics theorem in relativistic quantum field theory, particles with integer spin are bosons, while particles with half-integer spin are fermions.

In addition to the spin characteristic, fermions have another specific property: they possess conserved baryon or lepton quantum numbers. Therefore, what is usually referred to as the spin statistics relation is in fact a spin statistics-quantum number relation.

As a consequence of the Pauli exclusion principle, only one fermion can occupy a particular quantum state at a given time. If multiple fermions have the same spatial probability distribution, then at least one property of each fermion, such as its spin, must be different. Fermions are usually associated with matter, whereas bosons are generally force carrier particles, although in the current state of particle physics the distinction between the two concepts is unclear. Weakly interacting fermions can also display *bosonic behavior* under extreme conditions. At low temperature fermions show super fluidity for uncharged particles and superconductivity for charged particles. Composite fermions, such as protons and neutrons, are the key building blocks of everyday matter. The name fermion was coined by English theoretical physicist Paul Dirac from the surname of Italian physicist Enrico Fermi.

The basis postulates of FD statistics are:

(*i*) Particles are identical and indistinguishable.

(*ii*) Total energy and total number of particles of the entire system is constant.

(*iii*) Particles have half-integral spin, *i.e.,* $\frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{37}{2}\hbar$, etc.

(*iv*) Particles obey Pauli's exclusion principle, *i.e.,* no two particles in a single system can have the same value for each of the four quantum numbers. In other words, a single energy state can contain at best a single particle with appropriate spin.

(*v*) The wave function of the system is anti-symmetric under the positional exchange of any two particles.

Example: Electron, proton, neutron, all hyperons (Λ, Σ, Ξ, Ω) etc., these are known as *Fremions*.

Fermi-Dirac Distribution Law

Consider a system of *N* indistinguishable, non-interacting particles obeying Pauli's exclusion principle. Let $N_1, N_2, N_3, ..., N_i, ..., N_n$ particles in the system have energies $E_1, E_2, E_3, ..., E_i, ..., E_n$, respectively and let g_i is the number of degenerate quantum state in the energy level E_i. According to Pauli's exclusion principle, a single quantum state can be occupied by at best one particle. Since N_i particles are to be distributed among g_i degenerate states ($g_i \geq N_i$) having the same energy E_i, N_i states will be filled up and $(g_i - N_i)$ states will remain vacant. Now g_i states can be arranged in $g_i!$ possible ways. But since the particles and the quantum states are indistinguishable, we have to deduct $N_i!$ ways and $(g_i - N_i)!$ ways from the all possible ways to get effective number of arrangements. Thus, total number of possible ways of arrangement for the *i*th state is

$$W_i = \frac{(g_i)!}{N_i!(g_i - N_i)!} \qquad ...(5.109)$$

Hence the total number of ways for the entire distribution of *N* particles in *n* number of energy levels of the system is

$$W = \prod_i^n \frac{(g_i)!}{N_i!(g_i - N_i)!} \qquad ...(5.100)$$

where Π denotes the product symbol.

Now taking natural logarithm on both sides of Equation (5.100) and applying Stirling approximation, we get,

$$\ln W = \sum_i [\ln g_i - \ln N_i - \ln (g_i - N_i)]$$

$$= \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)] \qquad ...(5.111)$$

Now, differentiating Equation (5.111) to obtain the most probable distribution, we get,

$$d(\ln W)_{\max} = \sum_i [-\ln N_i + \ln (g_i - N_i)] d N_i = 0 \qquad ...(5.112)$$

Considering the conservation of total energy and total number of particles, we can write

$$\sum_i dN_i = 0 \text{ (conservation of total no. of particles)} \qquad ...(5.113)$$

$$\sum_i E_i \, dN_i = 0 \text{ (conservation of total energy)} \qquad ...(5.114)$$

Multiplying Equation (5.113) by α and Equation (5.114) by β and then adding to eqn. (5.112) we get,

$$\sum_i [-\ln N_i + \ln(g_i - N_i) - \alpha - \beta E_i] dN_i = 0 \qquad \text{...(5.115)}$$

NOTES

Since dN_i's are independent of one another, the expression in the bracket in the eqn. (5.115) is zero for each N_i. Thus

$$N_i = \frac{g_i}{e^{(\alpha+\beta E_i)} + 1} \qquad \text{...(5.116)}$$

Hence the Fermi-Dirac distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)} + 1} \qquad \text{...(5.117)}$$

which represents the probability of finding a fermion with energy E_i.

Fermi Distribution at Zero and Non-zero Temperatures

The Fremi-Dirac distribution function is

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)} + 1}$$

Now for the fermions in statistical equilibrium at absolute temperature T, it is found that $\alpha = \frac{-E_F}{kT}$ and $\beta = \frac{1}{kT}$

where, E_F is the *Fremi energy* of the system (*i.e.,* the maximum energy at absolute zero) k is the Boltzmann constant = 1.38×10^{-23} Joule/Kelvin.

Here $\frac{N_i}{g_i}$ is known as the *occupation index*.

Thus, the *F-D* distribution function reduces to

$$(E_i) = \frac{1}{e^{(E_i - E_F)/kT} + 1} \qquad \text{...(5.118)}$$

Now, let us discuss two distinct cases.

Case – 1 (T = 0 K)

$$f(E_i) = 1, \text{ when } E_i < E_F$$
$$= 0, \text{ when } E_i > E_F$$

Thus at $T = 0$ K, $f(E_i)$ is a step function (Refer Fig. 5.6) which implies all the energy states up to $E_i = E_F$ are filled up and the states above E_F are empty.

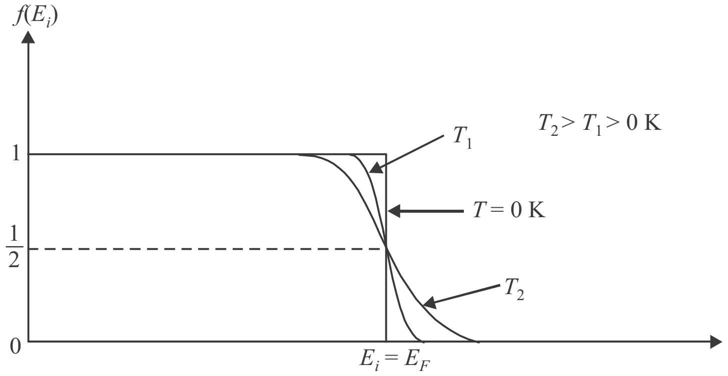


Fig. 5.6 *Plot of Fermi-Dirac distribution function as a function of* E_i

Case – 2 ($T > 0$ K)

As the temperature increases beyond $T = 0$ K, some of the electrons in the level just below the Fermi level go to levels just above E_F resulting a gradual change in the occupation index $f(E_i)$. If $E_i = E_F$, $(E_i) = \frac{1}{e^0 + 1} = \frac{1}{2}$, *i.e.*, at a finite temperatur Fermi energy of a system is that energy for which 50% energy states are filled and 50% states are vacant.

Fermi Energy for Electron Gas in Metals

Metals are characterised by the presence of a good number of free electrons. These electrons move about at random within the metals. While moving the free electrons collide among themselves also encounter with the fixed ion cores. Such behaviour of the free electrons is similar to that of molecules of a gas. Thus metals can be treated as electron gas. Since the electrons have half-integral spin angular momenta and they obey Pauli's exclusion principle, they follow F-D statistics.

Let us consider an electron gas consisting of N electrons occupying volume V. If N is very large, the spacing between two successive energy levels becomes very small making the energy levels almost continuous. Then if the energy of the electrons ranges between E to $E + dE$, the number of degenerate states g_i should be replaced by $g(E)\, dE$ and the total number of electrons N_i in these states should be replaced by $N(E)\, dE$ in the distribution function given by equation (5.116). Thus the total number of electrons in the electron gas having energy between E to $E + dE$ can be written eqn.(5.116) and Equation (5.118) as

$$N(E)dE = \frac{g(E)\,dE}{\exp\left(\frac{E_i - E_F}{kT}\right) + 1} \qquad ...(5.119)$$

Since the electrons have *two* allowed values of spin quantum number $\left(m_s = \pm\frac{1}{2}\right)$, the total number of their allowed states between energy for the energy range E to $E + dE$ can be written following as

$$g(E)dE = 2 \times \frac{1}{h^3}(4\pi V\sqrt{2E}\,m^{3/2})\,dE \qquad ...(5.120)$$

Hence the density of states $g(E)$ for a Fermionic gas is given by

$$g(E) = \frac{1}{h^3}(8\pi V\sqrt{2mE}\,m) \qquad ...(5.121)$$

which shows that $g(E)$ depends only on E for a single type of fermionic gas kept in a fixed volume V.

From Figure (5.6) it is obvious that at $T = 0$ K, all the single-particle state up to energy E_F are filled up. Thus at $T = 0$ K,

$$N(E)dE = \frac{g(E)\,dE}{e^{-\infty} + 1} = g(E)dE \quad [\because\ e^{-\infty} = 0] \qquad ...(5.122)$$

i.e., total number of electrons is equal to the total number of single-particle energy states, hence

$$N = \int_0^{E_F} N(E)\,dE$$

$$= \int_0^{E_F} g(E)\,dE \qquad \text{[using Equation (5.122)]}$$

$$= \frac{1}{h^3}(8\sqrt{2}\pi V m^{3/2}) \int_0^{E_F} E^{1/2}\,dE \qquad \text{[using Equation (5.121)]}$$

Or,
$$N = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} E_F^{3/2} \qquad ...(5.123)$$

which is the expression for the *total number of electrons* in the metal at $T = 0$ K.

Therefore,

$$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad ...(5.124)$$

which is the expression for *Fermi energy* of the electrons in the metal.

If $n = N/V$ denotes the concentration of the electrons in the metal, the Fermi energy of the electrons in the metal is

$$E_F = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} \qquad ...(5.125)$$

which showns that Fermi energy of the electrons depends solely on their *concentration*.

Total Energy at Absolute Zero Temperature

The total energy of electrons at absolute zero ($T = 0$ K) is given by

$$(E_0)_{\text{tot}} = \int_0^{E_F} E.N(E)\,dE$$

$$= \int_0^{E_F} E.g(E)\,dE \qquad \text{[using Equation (5.122)]}$$

$$= \frac{1}{h^3}(8\sqrt{2}\pi V m^{3/2}) \int_0^{E_F} E^{3/2}\,dE \qquad \text{[using Equation (5.121)]}$$

$$= \frac{16\sqrt{2}\pi V m^{3/2}}{5h^3} E_F^{5/2}$$

$$= \frac{3}{5} N E_F \qquad \text{[using Equation (5.123)]} \qquad ...(5.126)$$

which shows *quantum effect because, classically the total energy of a system at absolute zero is nothing but zero*.

The average energy per electron at $T = 0$ K can be written as

$$<E_0> = \frac{(E_0)_{\text{tot}}}{N} = \frac{3}{5} E_F \qquad ...(5.127)$$

which shows that at absolute zero temperature, the average energy per electron is equal to $\frac{3}{5}$ times the Fermi energy.

The ground-state pressure of the system is defined by

$$P_0 = \frac{2E_0}{3V} = \frac{2}{5}nE_F \qquad \text{[using Equation (5.126)]}$$

Substituting for E_F, the foregoing expression takes the form

$$P_0 = \frac{2}{5}\frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3} n^{5/3} \propto n^{5/3}$$

Thus the ground-state pressure of an electron gas at absolute zero solely depends on its concentration.

Fermi Temperature (T_F)

Fermi temperature (T_F) is the temperature equivalent of Fermi energy (F_F) and it is defined as $T_F = \frac{E_F}{k}$, where k (= 1.38 × 10^{-23} Joule/Kelvin) is the Boltzmann constant.

Check Your Progress

9. State the Pauli's theory as the non-relativistic limit of the Dirac's equation.
10. What do you understand by radiation catastrophe?
11. Give the different form of identical particle in classical and quantum physics.
12. Define the boson.
13. What is fermion?

5.14 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Relativistic Quantum Mechanics (RQM) is any Poincaré covariant formulation of Quantum Mechanics (QM). This theory is applicable to massive particles propagating at all velocities up to those comparable to the speed of light c, and can accommodate massless particles.
2. Non-relativistic quantum mechanics refers to the mathematical formulation of quantum mechanics applied in the context of Galilean relativity, more specifically quantizing the equations of classical mechanics by replacing dynamical variables by operators. Relativistic Quantum Mechanics (RQM) is quantum mechanics applied with special relativity.
3. The classical relativistic dynamics is made up of two words, which are 'Classical' and 'Relativistic Dynamics'. The word classical represents the macroscopic particles in a general sense. Here relativistic dynamics refers to the dynamics (physics) of those particles which moves with the speed comparable to the speed of light.
4. The Lorentz group expresses the fundamental symmetry of space and time of all known fundamental laws of nature. In general relativity physics, in cases involving small enough regions of space time where gravitational variances are negligible, physical laws are Lorentz invariant in the same manner as that of special relativity physics.

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5. The restricted Lorentz group is the identity component of the Lorentz group, which means that it consists of all Lorentz transformations that can be connected to the identity by a continuous curve lying in the group. The restricted Lorentz group is a connected normal subgroup of the full Lorentz group with the same dimension, in this case with dimension six.
6. The Klein-Gordon equation is a relativistic version of the Schrödinger equation that describes the behavior of spinless particles. The equation has a large range of applications in contemporary physics, including particle physics, astrophysics, cosmology, classical mechanics, etc.
7. In quantum mechanics, a free particle is defined as any particle (such as, an electron) that does not feel any fore. In such a case, the wave function that describes the free particle is given by a sinusoidal wave and this is referred to as the plane wave.
8. A hydrogen atom consists of an electron of charge – e, mass m_e and a nucleus having a proton of charge + e and mass m_p. By hydrogen-like atom we mean a one electron atom having a nucleus with Z protons.
9. The Pauli's theory as the non-relativistic limit of the Dirac's equation. It is the two component Pauli's equation for the theory of the spins and we also get the description of the spin degrees of freedom. For that, the Öo gives the spin degree of freedom here.
10. The electron can get to the negative energy continuum by losing energy and due to the presence of infinite negative energy state; the electron can get a lot far in negative energy continuum. This losing of energy by the electron and its transfer to the negative energy continuum is known as the 'Radiation Catastrophe'.
11. Identical particle difference between the classical physics and quantum physics. In classical physics, the identical particles are distinguishable while in quantum physics the identical particles are indistinguishable.
12. In particle physics, a 'Boson' is a subatomic particle whose spin quantum number has an integer value (0,1,2 ...). Bosons form one of the two fundamental classes of subatomic particle, the other being fermions, which have odd half-integer spin (1/ 2,3/ 2 ...) Every observed subatomic particle is either a boson or a fermion.
13. In particle physics, a 'Fermion' is a particle that follows Fermi–Dirac statistics and generally has half odd integer spin: spin 1/2, spin 3/2, etc. These particles obey the Pauli exclusion principle. Fermions include all quarks and leptons, as well as all composite particles made of an odd number of these, such as all baryons and many atoms and nuclei.

5.15 SUMMARY

- In non-relativistic quantum mechanics, terms have to be introduced artificially into the Hamiltonian operator to achieve agreement with experimental observations.

- Relativistic dynamics refers to the dynamics (physics) of those particles which moves with the speed comparable to the speed of light.
- In physics and mathematics, the Lorentz group is the group of all Lorentz transformations of Minkowski space time, the classical and quantum setting for all (non-gravitational) physical phenomena. The Lorentz group is named for the Dutch physicist Hendrik Lorentz.
- The Lorentz group is a six-dimensional non-compact non-Abelian real Lie group that is not connected. The four connected components are not simply connected. The identity component (i.e., the component containing the identity element) of the Lorentz group is itself a group, and is often called the restricted Lorentz group, and is denoted $SO^+(1,3)$.
- The restricted Lorentz group also arises as the point symmetry group of a certain ordinary differential equation.
- The set of all rotations forms a Lie subgroup isomorphic to the ordinary rotation group SO(3). The set of all boosts, however, does not form a subgroup, since composing two boosts does not, in general, result in another boost. (Rather, a pair of non-colinear boosts is equivalent to a boost and a rotation, and this relates to Thomas rotation).
- In physics, a *free particle* is a particle that, in some sense, is not bound by an external force, or equivalently not in a region where its potential energy varies.
- In the classical mechanics, the potential is said to be central if the potential energy is always directed towards or away from a point and it only depends on the distance of particle from that point.
- A hydrogen atom consists of an electron of charge – e, mass m_e and a nucleus having a proton of charge + e and mass m_p. By hydrogen-like atom we mean a one electron atom having a nucleus with Z protons.
- A particle with spin 1/2 with both low and high velocities can be explained by the Dirac's equation though the Pauli's theory and the equation is the non-relativistic limit of the Dirac's equation for the spin ½ particles.
- As nuclear magnetic dipole moments are smaller than electronic magnetic dipole moments by 10^3, the hyperfine splitting is smaller than the spin orbit splitting by the same factor.
- When the electron goes to the positive energy continuum by gaining energy of $\hbar w$, then it goes to the positive energy continuum and it creates an electron hole in the negative energy continuum which is of the opposite charge of that of the electron, this process of the formation of an electron and the electron hole is known as the pair creation.
- The Dirac Hole theory is an approach to explain the negative energy solutions of the Dirac equation, which we already discussed in the previous section. We studied about the Radiation Catastrophe and about the non-existence of any atom in this universe for which Dirac suggested that the negative continuum is all filled with electrons.

- The identical particles share the same names. In other words, the electrons and protons are not identical to each other but they are identical to itself, i.e., one electron is identical to another electron and one proton is identical to another proton.
- For identical quantum particles, when we detect a particle in a region in which the wave packets overlap, we have no way of telling which of the two particles it was. It means that the classical and quantum particles behave in different ways since identical classical particles are distinguishable whereas the identical quantum particles are indistinguishable.
- Two particles are similar particles or identical particles, when their defining intrinsic properties are the same where the intrinsic properties include: mass, charge and spin.
- Symmetrical representation is discussed further in the upcoming topics. A wide view of the symmetrical representation is discussed for the explanation of similar particles and one of the most searched and discussed topics in quantum mechanics.
- We study about the algebra of another kind of permutation which is known as the transposition. It exchanges two particles. We are able to write any permutation as a product of the transpositions.
- If we have a system of N identical particles, arbitrary states in $V^{\otimes N}$ are not the physical states. The physical states are the states that are totally symmetric, and in that case, the particles are called bosons or totally antisymmetric, in which case the particles are called fermions.
- Some bosons are elementary particles and occupy a special role in particle physics unlike that of fermions, which are sometimes described as the constituents of 'Ordinary Matter'.
- Fermions include all quarks and leptons, as well as all composite particles made of an odd number of these, such as all baryons and many atoms and nuclei. Fermions differ from bosons, which obey Bose–Einstein statistics.
- In addition to the spin characteristic, fermions have another specific property: they possess conserved baryon or lepton quantum numbers. Therefore, what is usually referred to as the spin statistics relation is in fact a spin statistics-quantum number relation.

5.16 KEY TERMS

- **Relativistic Quantum Mechanics (RQM):** In physics, Relativistic Quantum Mechanics (RQM) is any Poincaré covariant formulation of Quantum Mechanics (QM). This theory is applicable to massive particles propagating at all velocities up to those comparable to the speed of light c, and can accommodate massless particles.
- **Classical relativistic dynamics:** The classical relativistic dynamics is made up of two words, which are 'Classical' and 'Relativistic Dynamics'. The word classical represents the macroscopic particles in a general sense.

Here relativistic dynamics refers to the dynamics (physics) of those particles which moves with the speed comparable to the speed of light.

- **Lorentz group:** The Lorentz group is a subgroup of the Poincaré group—the group of all isometries of Minkowski space time. Lorentz transformations are, precisely, isometries that leave the origin fixed.
- **Boson:** In particle physics, a 'Boson' is a subatomic particle whose spin quantum number has an integer value (0,1,2 ...).
- **Fermion:** In particle physics, a 'Fermion' is a particle that follows Fermi–Dirac statistics and generally has half odd integer spin: spin 1/2, spin 3/2, etc. These particles obey the Pauli exclusion principle.

5.23 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What do you understand by relativistic quantum mechanics?
2. State the classical relativistic dynamics.
3. Define the Lorentz group.
4. Determine the Dirac equation.
5. Give the properties of Dirac matrices.
6. Define the free electron wave.
7. What is central potential?
8. Define the large and small component.
9. State the hyperfine position theory and hole theory.
10. Define the identical particle.
11. What do you understand by algebra of permutation operator?
12. Define the boson and fermions.

Long-Answer Questions

1. Elaborate on the relativistic quantum mechanics and classical relativistic dynamics with relevant examples.
2. Explain in detail about the Lorentz group.
3. Discuss in detail about the Dirac equation and covariant form of Dirac equation.
4. Describe the role of hydrogen atom in quantum mechanics.
5. Analyse the large and small component with relevant examples.
6. Elaborate on the hole theory and its difficulties.
7. Interpret the identical particle with appropriate eamples.
8. Comprehend the permutation operator and algebra of permutation operator.
9. Explain about the boson and Bose-Einstein statistics.
10. Describe the fermions and Fermi-Dirac statistics giving applications.

5.24 FURTHER READING

NOTES

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