# QUANTUM DYNAMICS AND SCATTERING THEORY

## M.Sc. Physics

### FIRST YEAR, SEMESTER-II, PAPER-III

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# *FOREWORD*

***Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.***

***The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.***

***To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.***

***It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.***

***Prof. K. Gangadhara Rao***
*M.Tech., Ph.D.,*
***Vice-Chancellor I/c***
***Acharya Nagarjuna University.***

# Semester-2
# M.Sc. Physics- Syllabus
# 203PH24-QUANTUM DYNAMICS AND SCATTERING THEORY

**Course Objectives:**

- Introduction of Spin and Total angular momentum
- To acquire mathematical skills require developing theory of different pictures.
- To develop understanding of scattering theory
- To offer systematic methodology for the application of molecular quantum mechanical systems

## UNIT-I (Spin and Total angular momentum)

Introduction to spin and total angular momentum, spin angular momentum and Pauli's spin matrices, total angular momentum J, explicit matrices for $J^2$, Jx, Jy & Jz, combination of two angular moment and tensor operator, Clebsch-Gordan coefficients for j1=1/2, j2=1/2 and j1=1, j2=1/2, Wigner-Eckart theorem.

**Learning Outcomes:**

- The students will be able to grasp the concepts of spin and angular momentum, as well as their quantization and addition rules.
- Students will learn the mathematical formalism of Clebsch-Gordan coefficients in quantum theory.

## UNIT II (Quantum dynamics)

Introduction to quantum dynamics, equation of motion in Schrödinger picture and Heisenberg picture, correspondence between the two, correspondence with classical mechanics, application of Heisenberg picture to harmonic oscillator, interaction picture.

**Learning Outcomes:**

- Learn mathematical expressions for Schrödinger picture and their applications.
- Students will learn the application of Heisenberg picture.

## UNIT III (Identical particles)

The indistinguishability of identical particles – the state vector space for a system of identical particles – creation and annihilation operators – continuous one particle system – dynamical variables – the quantum dynamics of identical particle systems.

**Learning Outcomes:**

- Students will learn the physical significance of identical particles.
- The students will be able to grasp the concepts of quantum dynamics of identical particle systems.

## UNIT IV (Scattering Theory)

Introduction of scattering – notion of cross section – scattering of a wave packet – scattering in continuous stream model – Green's function in scattering theory – Born approximation – first order approximation – criteria for the validity of Born approximation, form factor scattering – scattering from a square well potential – partial wave analysis – expansion of a plane wave – optimal theorem – scattering from a square well potential.

**Learning Outcomes:**

- Acquiring knowledge in scattering theory
- Studying the applications of Green's function and Born approximation in Scattering Theory.

## UNIT V (Molecular Quantum Mechanics)

Introduction to molecular quantum mechanics, the Born-Oppenheimer approximation – the hydrogen molecule ion – the valance bond method – the molecular orbital method – Comparison of the methods – Heitler-London method (Ref: Atkins, Chapter-9, 279-294).

**Learning Outcomes:**

- Students will gain the knowledge about the Born-Oppenheimer Approximation
- Learning the significances of Heitler-London method
- Knowing the importance of different methods involved in Molecular Quantum Mechanics

**Course Outcomes:**

- Understand the Spin, Total angular momentum and Clebsch-Gordan coefficients concepts.
- Understand historical aspects of identical particles in quantum mechanics
- Scattering theory will teach them how to use projectiles to infer details about target quantum system.

**Text and Reference Books:**

1. Merzbacher, Quantum Mechanics
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. D Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakurai, Modern Quantum Mechanics
6. Mathews and Venkatesan Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum mechanics by Kakania and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

**(203PH24)**

M.Sc. DEGREE EXAMINATION
Physics
Paper-III- QUANTUM DYNAMICS AND SCATTERING THEORY

Time: Three hours Maximum:70 marks.

All questions carry equal marks.

1 (a) Write the matrix representation of total angular momentum.
(b) Obtain matrix elements for $J_x$, $J_y$ and $J_z$ for ½ system.
OR
(c) Obtain the Clebsch-Gordon coefficients for $j_1 = \frac{1}{2}$ and $j_2 = \frac{1}{2}$ .
(d) Discuss in detail Wigner- Eckart theorem.

2 (a) Obtain the equation of motion in Schrodinger picture.
(b) Discuss how the unitary operator connects the Heisenberg picture and Schrodinger picture.
OR
(c) Obtain the equation of motion using interaction picture.
(d) Obtain the expression for energy levels of harmonic oscillator using Heisenberg picture.

3 (a) Discuss the distinguishability of identical particles.
(b) What are symmetric and anti symmetric wave functions and write the wave functions for three particle system.
OR
(c) What is an operator write about creation and annihilation operators.
(d) Discuss the quantum dynamics of identical particles.

4 (a) Write the theory of scattering in continuous stream model.
(b) Write the validity of Born approximation.
OR
(c) Discuss the theory of partial wave analysis.
(d) Obtain the expression for scattering cross section in case of square Well potential by partial wave method.

5 (a) Discuss in detail Born-Oppenheimer approximation to a molecule.
(b) Outline the theory of Valence bond method of a hydrogen molecule.
OR
(c) Discuss in detail molecular orbital method of a hydrogen molecule.
(d) Write the theory of Heitler-London method of hydrogen molecule.

# CONTENTS

## LESSON-1

# SPIN AND ANGULAR MOMENTUM

## 1.0 Aim and OBJECTIVE

Spin angular momentum represents an intrinsic property of elementary particles, such as electrons with spin quantum number s = 1/2, distinct from orbital angular momentum arising from spatial motion. Total angular momentum J combines spin S and orbital L as J = L + S, crucial for understanding atomic spectra, fine structure, and particle interactions.

### Aim

The primary aim is to unify diverse angular momentum contributions into a single quantum framework obeying su(2) algebra: [J_i, J_j] = iℏε_ijkJ_k. This enables prediction of energy levels, selection rules in transitions, and magnetic properties via Zeeman effects, essential for quantum information, NMR, and condensed matter physics.

### Objectives

- **Quantization and Representation**: Derive $J^2$ eigenvalues $j(j+1)\hbar^2$ and $J_z = m\hbar$ (m = -j to j), constructing explicit matrices (e.g., Pauli for j=1/2) for computations in coupled systems.
- **Coupling Multiple Momenta**: Use Clebsch-Gordan coefficients to couple J1 and J2, forming total J states for multi-electron atoms or spin-orbit interactions.
- **Symmetry Applications**: Apply Wigner-Eckart theorem for tensor operators, factoring matrix elements into angular (Clebsch-Gordan) and reduced parts, simplifying transition amplitudes.
- **Experimental Links**: Connect to Stern-Gerlach experiments verifying spin discreteness and g-factors, bridging quantum to relativistic descriptions in Dirac theory.

Mastery facilitates modeling hyperfine splitting, quantum computing qubits, and particle classification (bosons/fermions by integer/half-integer spin), underpinning quantum field theory foundations. (248 words)

### STRUCTURE

## 1.1 INTRODUCTION TO SPIN AND TOTAL ANGULAR MOMENTUM

Angular momentum plays a central role in both classical and quantum mechanics. In classical physics, angular momentum arises due to the rotational motion of particles or rigid bodies about an axis. In quantum mechanics, however, angular momentum acquires a deeper and more fundamental significance. In addition to the angular momentum associated with the spatial motion of a particle, quantum theory introduces an intrinsic form of angular momentum known as **spin**. The combined effect of orbital angular momentum and spin gives rise to the concept of **total angular momentum**, which governs the behavior of microscopic systems such as electrons, atoms, and nuclei. Understanding spin and total angular momentum is essential for explaining atomic spectra, fine structure, magnetic properties of matter, and selection rules in spectroscopy.

Spin Angular Momentum (**S**):Spin is an intrinsic form of angular momentum possessed by elementary particles (electrons, protons, neutrons, etc.).

It does not arise due to motion in space → purely quantum mechanical.

Properties

Quantized like orbital angular momentum:

$S^2 = \hbar^2 s(s+1)$, $S_z = m_s\hbar$

Quantum number s:

Electron, proton, neutron: $s = 1/2$ ;Photons: $s = 1$; spin-0 nuclei: $s = 0$

**Total Angular Momentum (J):**Total angular momentum is the vector sum of orbital and spin angular momentum: $J = L + S$

**Eigenvalues:** $J^2 = \hbar^2 j(j+1)$, $J_z = m_j\hbar$

**Allowed values of j**

$$J = |l-s|, |l-s| + 1, \ldots, (l+s)$$

**Physical Meaning**

Total angular momentum plays a central role in:

- Fine structure of atomic spectra
- Spin-orbit coupling
- Zeeman effect (interaction with magnetic field)
- Selection rules in spectroscopy

Example (electron in an atom, $s = 1/2$): If $l = 1$,

$$J = 1/2, 3/2$$

These give rise to **doublets** in atomic spectra

### Conclusion

Spin and total angular momentum represent core concepts in quantum mechanics that distinguish it sharply from classical physics. Spin is an intrinsic form of angular momentum inherent to particles, while total angular momentum arises from the vector combination of spin and orbital contributions. Together, they provide a comprehensive framework for understanding atomic structure, spectral features, magnetic behavior, and angular momentum conservation laws. Mastery of these concepts is essential for advanced studies in quantum mechanics, atomic physics, and modern condensed matter physics.

## 1.2 SPIN ANGULAR MOMENTUM AND PAULI'S SPIN MATRICES

**Definition:** In 1920, it was found that orbital quantum properties are unable to explain some observed troubled features, which were observed in the spectra of alkali halides. The spectral lines of alkali like atoms appear doublets which could not be explained by the wave function which is a function of orbital angular momentum alone. The true explanation of the doublet structure ofthe terms of alkali halides is explained by introducing the concept of electron spin. Spin (S) is a vector quantity, with the dimensions of angular momentum. Stern and Gerlach experiment later verified its existence experimentally. The total angular momentum is a sum of orbital angular momentum and the spin of electron.

i.e. $\bar{J} = \bar{L} + \bar{S}$

The characteristic values of the component of the spin in any prescribed direction are $\frac{\hbar}{2}$ & $-\frac{\hbar}{2}$. The spin is measured in the units of $\hbar$ and the characteristic values are reformed to as 1/2 and –1/2 . Now we will see the interpretation of the theory of spin of the electron given by Pauli.

As we have said already, the spin of the electron is represented by the $\bar{S}$ and besides this let us introduce an operator $\sigma$ (known as Pauli's spin operator) such that

$$\bar{S} = \frac{\hbar}{2}\sigma \tag{1}$$

Spin of the electron is also angular momentum as mentioned before. Therefore, it should satisfy the angular momentum commutation relations.

$\bar{S} \; X \; \bar{S} = iS$ In the units of $\hbar$

$$[S_x S_y - S_y S_x] = i\hbar S_z \tag{2}$$

Now introducing (1) and (2), we get

$$\left.\begin{aligned} \sigma_x\sigma_y - \sigma_y\sigma_x &= 2i\sigma_z \\ \sigma_y\sigma_z - \sigma_z\sigma_y &= 2i\sigma_x \qquad (3) \\ \sigma_z\sigma_x - \sigma_x\sigma_z &= 2i\sigma_y \end{aligned}\right\}$$

and $\sigma^{+}{}_{x} = \begin{pmatrix} 0 & a_3^{:*} \\ a_2^{*} & 0 \end{pmatrix}$ All in the units of $\hbar$

The eigen values of $S^2$ are $S(S+1) = 1/2(1/2+1) = 1/4$ (4)

$$\therefore\ S^2 = \frac{\hbar^2}{2}\sigma^2 = \frac{1}{4}\left[\sigma_x^2 + \sigma_y^2 + \sigma_z^2\right] \qquad (5)$$

From the equations (4) and (5) the condition that gives the expectation value of 1/4 is

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$

**spin matrices $\sigma_x, \sigma_y, \sigma_z$**

Let the operator $\sigma_z$ be operated on the ket $|k\rangle$ giving the eigen value a

i.e. $\sigma_z|k\rangle = a|k\rangle$

$\sigma_z^2|k\rangle = a^2|k\rangle$

$\therefore$ a = $\pm 1$

Therefore, there are two eigen values corresponding to in operator $\sigma_z$ which are $\pm 1$.

The matrix representation of these eigen values is a 2X2 matrix.

$$\therefore \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\sigma_x$ :- Since $\sigma_z$ is a 2 x 2 matrix ,$\sigma_x$ *and* $\sigma_y$ should also be 2 x 2 matrices since this has two anti commute.

Let $\sigma_x = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}$

Consider $\sigma_x\sigma_z + \sigma_z\sigma_x = 0$

$$\begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix} = 0$$

$$\Rightarrow \begin{pmatrix} a_1 & -a_2 \\ a_3 & -a_4 \end{pmatrix} + \begin{pmatrix} a_1 & a_2 \\ -a_3 & -a_4 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} 2a_1 & 0 \\ 0 & -2a_4 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \Rightarrow a_1 = a_4 = 0$$

i.e. $\therefore \sigma_x = \begin{pmatrix} 0 & a_2 \\ a_3 & 0 \end{pmatrix}$

$\Rightarrow$ $a_2 = a_3^{:*}$ and $a_3^{:} = a_2^{:*}$

$$\therefore \sigma_x = \begin{pmatrix} 0 & a_2 \\ a_2^* & 0 \end{pmatrix}$$

$$\sigma_x^2 = \begin{pmatrix} 0 & a_2^* \\ a_2 & 0 \end{pmatrix}\begin{pmatrix} 0 & a_2^* \\ a_2 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} a_2 a_2^* & 0 \\ 0 & a_2^* a_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Rightarrow |a_2|^2 = 1$$

We may take a$_2$= exp($i\alpha$)

$$\therefore \sigma_x = \begin{pmatrix} 0 & e^{i\alpha} \\ e^{i\alpha} & 0 \end{pmatrix}$$

$$Similarly\,\sigma_y = \begin{pmatrix} 0 & e^{i\beta} \\ e^{i\beta} & 0 \end{pmatrix}$$

$\sigma_x \sigma_z + \sigma_z \sigma_x = 0$

$$\begin{pmatrix} 0 & e^{i\alpha} \\ e^{-i\alpha} & 0 \end{pmatrix}\begin{pmatrix} 0 & e^{i\beta} \\ e^{-i\beta} & 0 \end{pmatrix} + \begin{pmatrix} 0 & e^{i\beta} \\ e^{-i\beta} & 0 \end{pmatrix}\begin{pmatrix} 0 & e^{i\alpha} \\ e^{-i\alpha} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \exp(i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) \end{pmatrix} + \begin{pmatrix} \exp(i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \exp(i(\alpha-\beta)) + \exp(-i(\alpha-\beta)) & 0 \\ 0 & \exp(i(\alpha-\beta)) + \exp(-i(\alpha-\beta)) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \cos(\alpha-\beta) & 0 \\ 0 & \cos(\alpha-\beta) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$(\alpha-\beta) = \frac{\pi}{2}$$

$$\beta = \alpha + \frac{\pi}{2} \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\alpha = 0; \beta = \frac{-\pi}{2}$$

These matrices are known as Pauli's spin matrices.

$$\sigma_y = \begin{pmatrix} 0 & \exp(-i\frac{\pi}{2}) \\ \exp(i\frac{\pi}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & -i\sin\frac{\pi}{2} \\ i\sin\frac{\pi}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\therefore \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} and \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

## 1.3 TOTAL ANGULAR MOMENTUM J EXPLICIT MATRICES FOR $J^2$, $J_X$, $J_Y$, & $J_Z$

The total angular momentum is defined as J = L ± S and $J_x$, $J_y$, $J_z$ are the components of J. In analogy with the orbital angular momentum operators, we have the relations,

$[J_x, J_y]=i\hbar J_z [J_y, J_z]=i\hbar J_x$

and $[J_z, J_x]=i\hbar J_y$ (1)

J X J= i J (2)

And $[J^2,J]=0$ (3)

$J^2= J^2_x+ J^2_y + J^2_z$

Let us now consider the Eigen value problem of $J_z$ and $J^2$.

Let $\lambda\hbar^2$ and $m\hbar$ are the eigen values of $J^2$ and $J_z$ respectively. To find out the relation between $\lambda$ and m, let us construct new the operators:

**Matrices for $J^2$, $J_x$, $J_y$ and $J_z$**

Matrix element $(J_+)_{m^1 m}$= $\langle \lambda m^1 | J_+ | \lambda_j m \rangle = \sqrt{(j-m)(J+m+1)}\delta_{m^1 m+1}$

Consider j=1/2 then $J^2$ eigen values are $j(j+1)\hbar^2 = 3/4\hbar^2$

$J_z$ eigen values = +1/2 and –1/2 (since (2j+1)=(2*1/2+1=2)

Therefore

$$J^2 = \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$J_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

*similarly* and $J_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

$$J_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & \frac{-\hbar}{2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$J_x = \frac{1}{2}(J_+ + J_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$J_y = \frac{i\hbar}{2}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$J_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

**Physical Significance**

- The explicit matrices allow direct calculation of expectation values and transition amplitudes.
- They are essential in studying **spin systems**, **magnetic resonance**, and **addition of angular momenta**.
- The matrix representation highlights the **non-commuting nature** of angular momentum components.

**Conclusion**

Total angular momentum J is a fundamental conserved quantity in quantum systems with rotational symmetry. Its components obey universal commutation relations and admit finite-dimensional matrix representations. Explicit matrices for $J_2$,$J_x$,$J_y$,$J^2$, $J_x$, $J_y$,$J_2$,$J_x$,$J_y$, and provide a powerful and concrete framework for understanding spin dynamics, atomic structure, and quantum measurements. These representations form the mathematical backbone of modern quantum mechanics and its applications.

## 1.4 COMBINATION OF TWO ANGULAR MOMENT AND TENSOR OPERATOR

In quantum mechanics, many physical systems involve more than one source of angular momentum. Examples include atoms with several electrons, nuclei composed of nucleons, and systems with both orbital and spin angular momenta. To describe such systems correctly, it is essential to understand the **quantum mechanical rules for combining two angular momenta**. Closely connected with this topic is the concept of **tensor operators**, which provide a powerful and systematic way to describe operators that transform under rotations in the same manner as angular momentum states. Together, the theory of angular momentum addition and tensor operators forms a cornerstone of modern quantum mechanics, with wide applications in spectroscopy, atomic structure, nuclear physics, and selection rules.

If two distinct physical systems or two distinct sets of dynamical variables of one system ,which are described in two different vector spaces, are merged ,the states of the composite system are , vectors in the direct product space of the two previously separate vector spaces. If $J_1$ and $J_2$ are the angular momentum of the two physical systems , Then $J= J_1 + J_2$ is the total angular momentum of the entire system. $J_{1x}$ , $J_{1y}$, $J_{1z}$ are the components of $J_1$, $J_{2x}$, $J_{2y}$, $J_{2z}$ components of $J_2$.
$J_x = J_{1x} + J_{2x}$ and so on

Each component of $J_1$ commutes with each component. The total component of J satisfies the angular momentum commutation relations:

$$[J_x,J_y]= i\hbar J_z \ ; \quad [J_y, J_z] = i\hbar J_x \ ; \quad [J_z, J_x]= i\hbar J_y \tag{4}$$

Now, the problem of addition of two angular moment consists of obtaining the eigen values of $J_z$ and $J^2$ and their eigen vectors in terms of the direct products of the eigen vectors of $J_{1z}$ and $J_1^2$ and of $J_{2z}$ and $J^2_2$ . The normalized simultaneous eigen vectors of the four operators $J_1^2$, $J^2_2$, $J_{1z}$ , $J_{2z}$ can be symbolized by the direct product kets.

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle \qquad (5)$$

These constitute a basis in the direct product space . These form a basis in the product space . From this basis , it is desire to construct a new basis with the eigen vectors of $J_z$and $J^2$ .

Corresponding to three angular momentum vectors $J_1$,$J_2$ ,J we have six hermitianoperators . $J^2_1$, $J^2_2$, $J_{1z}$ , $J_{2z}$ ,$J^2$ and$J_z$ out of these $J^2_1$ and $J^2_2$ commute with every component of J and $J^2$also .

i.e. $[J_2, J^2_1] =[ J_2, J^2_2] = [J^2,J^2_1] = [J^2, J^2_2] =0$ (6)

But $J^2$ does not commute with $J_{1z}$ and $J_{2z}$ we therefore have two sets of simultaneous eigen functions. They are

1. $J^2_1$, $J^2_2$, $J_{1z}$ , $J_{2z}$.
2. $J^2_1$, $J^2_2$, $J^2$ ,$J_z$

**Tensor Operator:** A tensor operator is a set of operators that transform under rotation in the same way as classical tensors.

They are labelled by two indices $T^{(k)}$_q:
- k → rank of the tensor
- q = −k, −k+1, …, k → component index

Thus, a tensor operator of rank k has (2k+1) components.

Examples: k = 0 → Scalar operator
k = 1 → Vector operator
k = 2 → Quadrupole operator

**Physical Significance and Applications**

The combined theory of angular momentum addition and tensor operators is indispensable in:

- atomic and molecular spectroscopy,
- nuclear electromagnetic transitions,
- magnetic resonance,
- quantum information theory,
- symmetry-based simplifications of complex quantum systems.

These tools allow physicists to extract physical predictions without solving the full dynamical problem.

**Conclusion**

The combination of two angular momenta is a fundamental problem in quantum mechanics, arising whenever a system possesses multiple angular momentum contributions. The rules governing this combination lead to quantized total angular momentum values and introduce Clebsch–Gordan coefficients as essential mathematical tools. Tensor operators provide a natural language for describing operators that transform under rotations, while the Wigner–Eckart theorem elegantly connects symmetry with observable quantities. Together, these concepts form a powerful and unified framework that underpins much of atomic, nuclear, and molecular physics.

## 1.3 SUMMARY

Spin represents an intrinsic angular momentum of particles like electrons, independent of orbital motion. Total angular momentum J combines orbital L and spin S via $J = L + S$, with its magnitude squared $J^2$ having eigenvalues $j(j+1)\hbar^2$, where j is the total quantum number.

Spin Angular Momentum

Spin angular momentum S for electrons has $s = 1/2$, yielding states $|\uparrow\rangle$ and $|\downarrow\rangle$ with Sz Eigenvalues $\pm\hbar/2$. Pauli spin matrices define S operators: $\sigma_x$ flips spin states, $\sigma_y$ involves imaginary components mixing up and down, and $\sigma_z$ diagonalizes along z-axis

Total Angular Momentum J

J obeys commutation relations like $[J_x, J_y] = i\hbar J_z$, enabling simultaneous $J^2$ and $J_z$ eigenstates $|j, m\rangle$. Matrices are constructed in this basis using raising/lowering operators $J\pm = J_x \pm i J_y$

Total angular momentum J operators have explicit matrix representations in the $|j, m\rangle$ basis, with $J^2$ proportional to the identity matrix scaled by $j(j+1)\hbar^2$. Jz is diagonal with entries $m\hbar$ for $m = -j$ to $+j$, while Jx and Jy are tridiagonal, featuring real and imaginary off-diagonal elements from raising/lowering operators J±

Example for j=1

$Jz = \hbar$ diag(1, 0, -1); $Jx = (\hbar/\sqrt{2})$ off-diagonals connecting adjacent m; Jy similarly with i factors; $J^2 = 2\hbar^2$ identity (3x3).

Combining Angular Momenta

Coupling J1 and J2 produces total J from |J1-J2| to J1+J2, using Clebsch-Gordan coefficients to express coupled states as linear combinations of uncoupled $|m1, m2\rangle$ products

Tensor Operators

These rank-k operators transform irreducibly under rotations, enabling Wigner-Eckart theorem applications for matrix elements split into angular (Clebsch-Gordan) and reduced parts.

## 1.4 TECHNICAL TERMS

Introduction to spin and total angular momentum, Spin angular momentum and Pauli's spin matrices, Total angular momentum J explicit matrices for $J^2$, $J_X$, $J_Y$, & $J_Z$, Combination of two angular moment and tensor operator

## 1.5 SELF ASSESSMENT QUESTIONS

1. Write about the introduction to spin and total angular momentum
2. Explain about the Spin angular momentum and Pauli's spin matrices
3. Explain about the Total angular momentum J explicit matrices for $J^2$, $J_X$, $J_Y$, & $J_Z$,
4. Explain about the Combination of two angular moment and tensor operator

## 1.6 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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# LESSON-2

# WIGNER-ECKART THEOREM

## Aim and Objective

The Wigner-Eckart theorem aims to exploit rotational invariance in quantum systems to simplify calculations of matrix elements for tensor operators acting on angular momentum states. Its primary objective is to factor these elements into a purely geometrical part, given by Clebsch-Gordan coefficients, and an intrinsic dynamical part, the reduced matrix element, which depends only on the tensor rank and initial/final angular momenta but not on magnetic projections.

## Aim

Developed by Eugene Wigner and Carl Eckart, the theorem bridges group representation theory with quantum mechanics. It ensures that under rotations, matrix elements transform predictably, reducing the number of independent computations from (2j+1)(2j'+1)(2k+1) to a single reduced element per tensor component. This leverages SU(2) irreducibility: all orientations relate via Wigner D-matrices or ladder operators.

## Key Objectives

- **Selection Rules**: Enforce $\Delta j \leq k \leq j + j'$ and $\Delta m = q$, automatically vanishing non-allowed transitions without explicit integrals.
- **Computational Efficiency**: Compute one convenient matrix element (e.g., maximum m), extract the reduced value, then scale all others using tabulated Clebsch-Gordan coefficients.
- **Symmetry Exploitation**: Reveal degeneracies; for scalar operators (k=0), elements are m-independent, explaining isotropic energy levels in free atoms.
- **Proof Foundation**: Relies on rotating states and operators, yielding algebraic relations that prove proportionality to CG coefficients, with conventions like Condon-Shortley phases.

## Practical Applications

In atomic physics, it computes dipole (k=1) transition strengths for spectra. Nuclear physics uses it for multipole decays; particle physics for weak currents. Crystal field theory and EPR benefit from vector/tensor forms. Quantum computing employs it for spin operators in qubits. Ultimately, it minimizes numerical effort in multi-particle systems, enhancing predictive power from symmetry alone.

## STRUCTURE OF THE LESSON:

**2.1 CLEBSCH-GORDAN COEFFICIENTS FOR $J_1 = ½$ AND $J_1 = 1, J_2 = ½$**

**2.2 WINGER-ECKART THEOREM**

**2.3 SUMMARY**

**2.4 TECHNICAL TERMS**

## 2.1 CLEBSCH-GORDAN COEFFICIENTS FOR $J_1$ = ½ AND $J_1$ = 1, $J_2$ = ½

### Introduction

In quantum mechanics, the addition of angular momenta is essential for understanding composite systems such as multi-electron atoms, nuclei, and coupled spin systems. When two angular momenta are combined, the resulting total angular momentum states are expressed as linear combinations of product states of the individual angular momenta. The numerical factors appearing in these linear combinations are known as **Clebsch–Gordan (CG) coefficients**. These coefficients play a fundamental role in atomic spectroscopy, spin coupling, selection rules, and transition probabilities.

The basis vectors corresponding to first set of vectors, $J^2_1$, $J^2_2$, $J_{1z}$ , $J_{2z}$. is denoted by

$$|\, j_1 j_2 m_1 m_2 \rangle = |\, j_1 m_1 \rangle |\, j_2 m_2 \rangle \qquad (1)$$

or briefly with $|\, m_1 m_2 \rangle$ and corresponding to the second set, $J^2_1$, $J^2_2$, $J^2$ ,$J_z$

it is given by

$|\, j_1 j_2 jm \rangle$ are briefly by $|\, jm \rangle$

We thus have

$$\left.\begin{aligned}
J_1^2 |\, j_1 j_2 m_1 m_2 \rangle &= j_1 (j_1 + 1)\hbar^2 |\, j_1 j_2 m_1 m_2 \rangle \\
J_{1z} |\, j_1 j_2 m_1 m_2 \rangle &= m_1 \hbar |\, j_1 j_2 m_1 m_2 \rangle \\
J_2^2 |\, j_1 j_2 m_1 m_2 \rangle &= j_2 (j_2 + 1)\hbar^2 |\, j_1 j_2 m_1 m_2 \rangle \\
J_{2z} |\, j_1 j_2 m_1 m_2 \rangle &= m_1 \hbar |\, j_1 j_2 m_1 m_2 \rangle
\end{aligned}\right\} \qquad (2)$$

$$\left.\begin{aligned}
J^2 |\, j_1 j_2 jm \rangle &= j\ (j+1)\hbar^2 |\, j_1 j_2 jm \rangle \\
J_z |\, j_1 j_2 jm \rangle &= m\hbar |\, j_1 j_2 jm \rangle \\
J_1^2 |\, j_1 j_2 jm \rangle &= j_1 (j_1 + 1)\hbar^2 |\, j_1 j_2 jm \rangle
\end{aligned}\right\} \qquad (3)$$

$$J_2^2 |\, j_1 j_2 jm \rangle = j_2 (j_2 + 1)\hbar^2 |\, j_1 j_2 jm \rangle$$

We shall now write the transformation equation between $|\, j_1 j_2 jm \rangle$ and $|\, j_1 j_2 m_1 m_2 \rangle$ as

$$|\, j_1 j_2 jm \rangle = \sum_{m_1 m_2} |\, j_1 j_2 m_1 m_2 \rangle \langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 jm \rangle \qquad (4)$$

Here $j_1$, $j_2$ can be assumed to have fixed values and $m_1$,$m_2$ are variables.

In the above equation, the transformation coefficient

$$\langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j m\rangle = C^{j_1 j_1 j}_{m_1 m_2 m} \tag{5}$$

This is also called **Clebsch-Gordon coefficient** or Wigner coefficient.

**C.G coefficients $j_1=1$ ,$j_2=1/2$.**

The total number of C.G coefficients are $(2j_1+1)(2j_2+1)=6$ .The C.G coefficient matrix is a 6X6 matrix. $m_1$ takes the values 1 0-1 and $m_2$ takes 1/2, -1/2 and mtakes the values $j_1+j_2$ to $|j_1 - j_2|$ i.e. 3/2, 1/2, -1/2, -3/2

j values corresponding to $j_1=1$, $j_2=1/2$.are given by

| m | $m_1$ | $m_2$ | j |
|---|---|---|---|
| $j_1+j_2=3/2$ | $j_1=1$ | $j_2=1/2$ | $m=3/2$ |
| $j_1+j_2-1=1/2$ | $j_1=1$ | $j_2-1= -1/2$ | $j_1+j_2=3/2$ |
| | $j_1-1 =1$ | $j_2 = ½$ | $j_1+j_2-1=1/2$ |
| | $j_1-1=0$ | $j_2-1= -1/2$ | $j_1+j_2=3/2$ |
| $j_1+j_2-2= -1/2$ | $j_1-2 = -1$ | $j_2 = ½$ | $j_1+j_2-1=1/2$ |
| $j_1+j_2-3=-3/2$ | $j_1-2= -1$ | $j_2-1= -1/2$ | $j_1+j_2=3/2$ |

| | | | | | |
|---|---|---|---|---|---|
| j→ 3/2 | 3/2 | 1/2 | 3/2 | 1/2 | 3/2 |
| m→3/2 | 1/2 | 1/2 | 1/2 | 1/2 | 3/2 |

$$\begin{array}{cc} m_1 & m_2 \\ 1 & 1/2 \\ 1 & -1/2 \\ 0 & 1/2 \\ 0 & -1/2 \\ -1 & 1/2 \\ -1 & -1/2 \end{array}
\begin{pmatrix} c_{11} & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{22} & c_{23} & 0 & 0 & 0 \\ 0 & c_{32} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & c_{45} & 0 \\ 0 & 0 & 0 & c_{54} & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix}$$

Now consider

$$|\,jm\rangle\;|\,m_1m_2\rangle\begin{pmatrix}\left|\frac{3}{2}\frac{3}{2}\right\rangle\\ \left|\frac{3}{2}\frac{1}{2}\right\rangle\\ \left|\frac{1}{2}\frac{1}{2}\right\rangle\\ \left|\frac{3}{2}\frac{-1}{2}\right\rangle\\ \left|\frac{1}{2}\frac{-1}{2}\right\rangle\\ \left|\frac{3}{2}\frac{-3}{2}\right\rangle\end{pmatrix}=\begin{pmatrix}c_{11}&0&0&0&0&0\\0&c_{22}&c_{23}&0&0&0\\0&c_{32}&c_{33}&0&0&0\\0&0&0&c_{44}&c_{45}&0\\0&0&0&c_{54}&c_{55}&0\\0&0&0&0&0&c_{66}\end{pmatrix}\begin{pmatrix}\\ \left|1\frac{1}{2}\right\rangle\\ \left|1\frac{-1}{2}\right\rangle\\ \left|0\frac{1}{2}\right\rangle\\ \left|0\frac{-1}{2}\right\rangle\\ \left|-1\frac{1}{2}\right\rangle\\ \left|-1\frac{-1}{2}\right\rangle\end{pmatrix}$$

$$\left|\frac{3}{2}\frac{3}{2}\right\rangle=c_{11}\left|1\frac{1}{2}\right\rangle=c_{11}\left|\frac{3}{2}\right\rangle\left\langle\frac{3}{2}\right|1\frac{1}{2}\right\rangle$$

$$\Rightarrow c\left\langle\frac{3}{2}\frac{3}{2}\right|1\frac{1}{2}\right\rangle=|c_{11}|\left\langle1\frac{1}{2}\right|1\frac{1}{2}\right\rangle$$

$$\left\langle\frac{3}{2}\frac{3}{2}\right|=\left\langle1\frac{1}{2}\right|\Rightarrow c_{11}^2=1\Rightarrow c_{11}=1$$

$$\Rightarrow\left|\frac{3}{2}\frac{3}{2}\right\rangle=c_{11}\left|1\frac{1}{2}\right\rangle$$

$$\left\langle1\frac{1}{2}\right|\frac{3}{2}\frac{3}{2}\right\rangle=c_{11}\left\langle1\frac{1}{2}\right|1\frac{1}{2}\right\rangle$$

$$c_{11}=1$$

Now to find the other coefficients let us apply J- on $\left|\frac{3}{2}\frac{3}{2}\right\rangle$, then we have

$$J_-\left|\frac{3}{2}\frac{3}{2}\right\rangle=(J_{1-}+J_{2-})\left|1\frac{1}{2}\right\rangle$$

i.e.

$$\sqrt{(j+m)(j+m+1)}\,|\,jm-\text{`}1\rangle=\sqrt{(j_1+m_1)(j_1-m_1+1}\,|\,m_1m_2\rangle+\sqrt{(j_2+m_2)(j_2-m_2+1)}\,|\,m_1m_2-1\rangle$$

i.e. $\sqrt{3\left|\frac{3}{2}\frac{1}{2}\right\rangle}=\sqrt{(1+1)}\left|0\frac{1}{2}\right\rangle+\sqrt{1}\left|1\frac{-1}{2}\right\rangle$

$$\left|\frac{3}{2}\frac{1}{2}\right\rangle = \sqrt{\frac{2}{0}}\left|0\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|1\frac{-1}{2}\right\rangle \qquad (6)$$

From the matrix, we have

$$\left|\frac{1}{2}\frac{1}{2}\right\rangle = c_{32}\left|1\frac{-1}{2}\right\rangle + c_{33}\left|0\frac{1}{2}\right\rangle$$

Multiplying the above two equations , we get

$$\left\langle 1\frac{-1}{2}\middle|\frac{3}{2}\frac{1}{2}\right\rangle = 0 = \sqrt{\frac{2}{3}}c^{*}_{33}\left\langle 0\frac{1}{2}\middle|0\frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}c^{*}_{32}\left\langle 1\frac{-1}{2}\middle|1\frac{-1}{2}\right\rangle$$

$$= \sqrt{\frac{2}{3}}c^{*}_{33} + \frac{1}{\sqrt{3}}c^{*}_{32}$$

$$\Rightarrow \frac{c^{*}_{33}}{c^{*}_{32}} = \frac{\frac{1}{\sqrt{3}}}{\frac{-\sqrt{2}}{-\sqrt{3}}} = \frac{c_{33}}{c_{32}}$$

Because they are real coefficients

Now consider equation (3.5.19) and apply J- on both sides, we get

$$J_{-}\left|\frac{3}{2}\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}(J_{1-}+J_{2-})\left|0\frac{1}{2}\right\rangle + (J_{1-}+J_{2-})\frac{1}{\sqrt{3}}\left|1\frac{-1}{2}\right\rangle$$

L.H.S

$$\sqrt{2.2}\left|\frac{3}{2}\frac{-1}{2}\right\rangle$$

R.H.S(1) : $\sqrt{\frac{2}{3}}\sqrt{(1+0)\sqrt{1-0+1}}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\sqrt{1}\left|0\frac{-1}{2}\right\rangle$

$$= \sqrt{\frac{2}{3}}\sqrt{2}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

R.H.S(2): i.e $(J_{1-}+J_{2-})\frac{1}{\sqrt{3}}\left|1\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}}\sqrt{2}\left|0\frac{-1}{2}\right\rangle + 0$

$$\therefore 2\left|\frac{3}{2}\frac{-1}{2}\right\rangle = \frac{2}{\sqrt{3}}\left|-1\frac{1}{2}\right\rangle + 2.\sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

$$\left|\frac{3}{2}\frac{-1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|-1\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0\frac{-1}{2}\right\rangle$$

Again from the matrix

$$\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle = c_{54}\left|0\,\frac{-1}{2}\right\rangle + c_{55}\left|-1\,\frac{1}{2}\right\rangle$$

Multiplying the above two equations, we have

$$\left\langle\frac{1}{2}\,\frac{-1}{2}\middle|\frac{3}{2}\,\frac{-1}{2}\right\rangle = \sqrt{\frac{2}{3}}c_{54}^{*}\left\langle 0\,\frac{-1}{2}\middle|0\,\frac{-1}{2}\right\rangle + \frac{1}{\sqrt{3}}c_{55}^{*}\left\langle -1\,\frac{1}{2}\middle|-1\,\frac{1}{2}\right\rangle$$

$$\Rightarrow \sqrt{\frac{2}{3}}c_{54}^{*} = -\frac{1}{\sqrt{3}}c_{55}^{*}$$

$$\frac{c_{54}^{*}}{c_{55}^{*}} = \frac{\frac{-1}{\sqrt{3}}}{\sqrt{\frac{2}{3}}} = \frac{c_{54}}{c_{55}}\,and$$

$C_{66}$=1,

With this the CG coefficient matrix for $J_1$=1 and $J_2$ = 1/2 are

$$\begin{pmatrix} \left|\frac{3}{2}\,\frac{3}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}\,\frac{1}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{-1}{2}\right\rangle \\ \left|\frac{1}{2}\,\frac{-1}{2}\right\rangle \\ \left|\frac{3}{2}\,\frac{-3}{2}\right\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0 \\ 0 & \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & -\sqrt{\frac{2}{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \left|1\,\frac{1}{2}\right\rangle \\ \left|1\,\frac{-1}{2}\right\rangle \\ \left|0\,\frac{1}{2}\right\rangle \\ \left|0\,\frac{-1}{2}\right\rangle \\ \left|-1\,\frac{1}{2}\right\rangle \\ \left|-1\,\frac{-1}{2}\right\rangle \end{pmatrix}$$

**Physical Applications**

Clebsch–Gordan coefficients for these cases are extensively used in:

- coupling of electron orbital angular momentum (l=1l = 1l=1) with spin (s=12s = \tfrac{1}{2}s=21),
- fine structure of atoms,
- hyperfine interactions,

- nuclear spin coupling,
- quantum information and spin-½ systems.

## 2.2 WINGER-ECKART THEOREM

### Introduction

In quantum mechanics, symmetry principles play a central role in simplifying complex physical problems. Among these, **rotational symmetry** is of fundamental importance in atomic, molecular, and nuclear physics. Physical systems possessing rotational invariance are naturally described using angular momentum theory. However, direct calculation of matrix elements of operators between angular momentum eigenstates often becomes algebraically complicated, especially when the system involves multiple angular momenta.

The **Wigner–Eckart theorem** provides a powerful and elegant solution to this problem. It states that matrix elements of spherical tensor operators can be factorized into a **geometrical part**, which depends only on angular momentum coupling, and a **dynamical part**, which is independent of magnetic quantum numbers. This theorem greatly simplifies calculations of transition probabilities, selection rules, and spectroscopic intensities, and is widely used in atomic, molecular, and nuclear physics.

The Wigner- Eckart Theorem is in general used in calculating the transition probabilities of laser emission transitions. Before going to the proof of the theorem first let us get acquainted with some of the preliminaries used in the theorem.

**Euler angles**

The operator J can be expressed as a unitary operator as a rotation at operator as

$$R_n(\theta)=\exp(-\frac{i(n.J)\theta}{\hbar})\ (\alpha\beta\gamma)=R\ (\alpha)R_y(\chi)R_z(\gamma)=Exp(-\frac{i\alpha J_z}{\hbar})Exp\left(\frac{-i\beta J_y}{\hbar}\right)Exp\left(\frac{-i\gamma J_z}{\hbar}\right)$$

**Rotation Matrix**

Consider R

$$\langle\alpha\beta\gamma|\,jm\rangle=\sum_{m^1}|\,jm^1\rangle\langle jm^1\,|R(\alpha\beta\gamma)|\,jm\rangle$$

$$\langle jm^1\,|R(\alpha\beta\gamma)|\,jm\rangle=\langle jm^1\,|\exp\left(\frac{-i\alpha J_z}{\hbar}\right)\exp\left(\frac{-i\beta J_y}{\hbar}\right)\exp\left(\frac{-i\gamma J_z}{\hbar}\right)\|\,jm\rangle$$

$$=\text{Exp}\left(\frac{-im^1\alpha}{\hbar}\right)\langle jm^1\,|\exp\left(\frac{-i\beta J_y}{\hbar}\right)\|\,jm\rangle\exp\left(\frac{-i\gamma m}{\hbar}\right)$$

$$=\text{Exp}\left(\frac{-im^1\alpha}{\hbar}\right)d^j_{m^1m}\exp\left(\frac{-i\gamma m}{\hbar}\right)=D^j_{m^1m}(\alpha\beta\gamma)$$

Where $d^{j}_{m^1m} = \langle jm^1 | \exp\left(\frac{-i\beta J_y}{\hbar}\right) | jm\rangle$

Therefore

$$R(\alpha\beta\gamma)| jm\rangle = \sum_{m^1=-j}^{j} D^{j}_{m^1m}(\alpha\beta\gamma)| jm^1\rangle$$

$D^{j}_{m^1m}(\alpha\beta\gamma) = \exp(-im^1\alpha) d^{j^1}_{m^1m} \exp(-im\gamma)$ is called rotation matrix.

**The statement of Wignar-Eckart theorem**

$\langle j_2 m_2 | T^k_q | j_1 m_1\rangle = C^{j_1kj_2}_{m_1qm_2} \frac{\langle j_2 \| T^k \| j_1\rangle}{\sqrt{2j_2+1}}$ where $\| T^k \|$ matrix element is called reduced matrix.

**Proof**

$$\langle j_2 m_2 | T^k_q | j_1 m_1\rangle = \langle j_2 m_2 | R^{-1} R T^q_k R^{-1} R | j_1 m_1\rangle = \sum_{m_1^1 m_2 q} \langle j_2 m_2 | T^k_{q^1} | j_1 m_1^1\rangle D^{j_2^*}_{m_2^1 m_2} D^{k}_{q^1 q} D^{j_1}_{m_1^1 m_1}$$

Integrating on both sides, we have

$$\langle j_2 m_2 | T^k_q | j_1 m_1\rangle = \frac{8\pi^2}{2j_2+1} \sum_{m_1^1 q^1 m_2^1} C^{j_1kj_2}_{m_1^1 q^1 m_2^1} C^{j_1kj_2}_{m_1qm_2} \langle j_2 m_2^1 | T^k_{q^1} | j_1 m_1^1\rangle$$

$$\therefore \langle j_2 m_2 | T^k_q | j_1 m_1\rangle = C^{j_1kj_2}_{m_1qm_2} \frac{1}{\sqrt{2j_2+1}} \left\{ \sum_{m_1^1 q^1 m_2^1} \frac{1}{\sqrt{2j_2+1}} C^{j_1kj_2}_{m_1^1 q^1 m_2} \langle j_2 m_2^1 | T^k_{q^1} | j_1 m_1^1\rangle \right\}$$

$$\langle j_2 m_2 | T^k_q | j_1 m_1\rangle = C^{j_1kj_2}_{m_1qm_2} \frac{\langle j_2 \| T^k \| j_1\rangle}{\sqrt{2j_2+1}}$$

**Applications of the Wigner–Eckart Theorem**

The theorem is indispensable in:

- atomic and molecular spectroscopy,
- calculation of transition probabilities,
- nuclear electromagnetic transitions,
- hyperfine structure,
- magnetic resonance,
- particle physics and quantum field theory,
- symmetry-based simplification of many-body problems.

### Advantages of the Wigner–Eckart Theorem

- Reduces computational complexity drastically.
- Makes symmetry properties explicit.
- Provides direct derivation of selection rules.
- Separates physical dynamics from angular geometry.

### Conclusion

The Wigner–Eckart theorem is one of the most powerful results in quantum mechanics, providing a deep connection between symmetry, angular momentum theory, and physical observables. By factorizing matrix elements of tensor operators into a geometrical part and a reduced matrix element, the theorem simplifies calculations and reveals the underlying rotational structure of quantum systems. Its applications span atomic, molecular, nuclear, and particle physics, making it an essential tool for both theoretical understanding and practical computation. Mastery of the Wigner–Eckart theorem is therefore indispensable for advanced studies in quantum mechanics.

## 2.3 SUMMARY

Clebsch-Gordan for Specific Cases

For $J_1 = 1/2$, $J_2 = 1/2$, possible J=1 (triplet, symmetric) and J=0 (singlet, antisymmetric).
$J_1=1/2$ with $J_2=1$ gives J=3/2 and J=1/2, with coefficients determining spin-orbit mixtures like in fine structure.

The Wigner-Eckart theorem provides a powerful factorization for matrix elements of tensor operators between angular momentum states. It separates the angular dependence, captured by Clebsch-Gordan coefficients, from the intrinsic strength given by a reduced matrix element independent of magnetic quantum numbers.

## 2.4 TECHNICAL TERMS

Clebsch-Gordan coefficients for $J_1 = ½$ and $J_1 = 1$, $J_2 = ½$, Winger-Eckart theorem

## 2.5 SELF ASSESSMENT QUESTIONS

1. Explain about the Clebsch-Gordan coefficients for $J_1 = ½$ and $J_1 = 1$, $J_2 = ½$
2. Briefly explain about the Winger-Eckart theorem with proof.

## 2.6 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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## LESSON-3

# QUANTUM DYNAMICS

### 3.0 Aim and Objective

Quantum dynamics aims to describe the time evolution of quantum systems, bridging static energy eigen states to real-time processes like transitions and scattering. Its objective is to predict observable changes, such as spectral lines or reaction rates, using unitary evolution under the Hamiltonian.

Core Principles

Fundamentally, quantum dynamics resolves classical determinism with probabilistic wave mechanics via the Schrödinger equation for state propagation. In the Schrödinger picture, states $|\psi(t)\rangle$ evolve while operators remain time-independent; the Heisenberg picture reverses this, evolving operators to mirror classical Hamilton equations through commutators

Key Objectives

- **Time Evolution**: Govern how superpositions develop, enabling interference and decoherence analysis in open systems.
- **Transition Probabilities**: Compute Fermi's golden rule rates for perturbations, vital for spectroscopy and lasers.
- **Equivalence of Pictures**: Demonstrate Schrödinger, Heisenberg, and interaction pictures yield identical physics, facilitating approximations like time-dependent perturbation theory.
- **Classical Limit**: Via Ehrenfest theorem, show expectation values follow Newton's laws for macroscopic scales.

**STRUCTURE**

## 3.1 INTRODUCTION TO QUANTUM DYNAMICS

Quantum dynamics is the branch of quantum mechanics concerned with the time evolution of quantum systems. While quantum mechanics provides the fundamental laws governing microscopic particles such as electrons, atoms, and molecules, quantum dynamics focuses specifically on how these systems change with time under the influence of internal interactions and external forces. It forms the theoretical backbone for understanding a wide range of physical phenomena, including atomic transitions, molecular vibrations, chemical reactions, scattering processes, and quantum transport.

In classical mechanics, the motion of a system is described by deterministic equations such as Newton's laws or Hamilton's equations, which predict precise trajectories in phase space. In contrast, quantum dynamics replaces classical trajectories with wave functions or state vectors, whose evolution is governed by probabilistic laws. The key objective of quantum dynamics is therefore not to determine exact paths, but to calculate time-dependent probabilities, expectation values, and transition amplitudes.

### Historical Background

The development of quantum dynamics is deeply rooted in the early history of quantum mechanics. In 1926, Erwin Schrödinger formulated the Schrödinger equation, which describes the time evolution of a quantum state. Shortly afterward, Heisenberg, Born, and Dirac developed alternative but equivalent formulations of quantum mechanics. These formulations introduced different ways of describing quantum dynamics, known as the Schrödinger picture, Heisenberg picture, and later the interaction picture.

Early applications of quantum dynamics focused on simple systems such as the hydrogen atom and harmonic oscillator. With advances in computational techniques and experimental tools, the scope of quantum dynamics expanded to include many-body systems, open quantum systems, molecular collisions, and ultrafast processes occurring on femtosecond and attosecond timescales.

### Quantum States and Observables

In quantum dynamics, the complete physical information about a system at a given time is contained in its state. The state may be represented by a wavefunction $\psi(r, t)$ in position space or by an abstract state vector $|\psi(t)\rangle$ in Hilbert space.

Physical quantities such as position, momentum, energy, and angular momentum are represented by operators acting on the state. The measurable value of an observable is obtained through its expectation value, which depends explicitly on time if the system is evolving.

Unlike classical mechanics, where observables have definite values at all times, quantum dynamics predicts only probability distributions, reflecting the inherently probabilistic nature of quantum theory.

### Time-Dependent Schrödinger Equation

The central equation of quantum dynamics is the time-dependent Schrödinger equation (TDSE)

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

Here, $\widehat{H}$ is the Hamiltonian operator, representing the total energy of the system. It typically includes kinetic energy and potential energy terms. The TDSE plays a role analogous to Newton's second law in classical mechanics, determining how the quantum state evolves with time.

If the Hamiltonian is time-independent, the solution of the TDSE can often be expressed as a superposition of stationary states with well-defined energies. If the Hamiltonian is time-dependent, the system exhibits more complex behavior, such as transitions between energy levels.

Stationary and Non-Stationary States

A stationary state is an eigenstate of the Hamiltonian. In such states, the probability density remains constant in time, even though the wavefunction itself acquires a time-dependent phase factor. Stationary states are particularly important because they represent stable configurations of quantum systems, such as atomic orbitals.

In contrast, a non-stationary state is a superposition of two or more stationary states. The time evolution of such states leads to observable phenomena such as quantum beats, oscillations in expectation values, and transitions induced by external perturbations.

Quantum dynamics primarily deals with these non-stationary states, as they reflect the true dynamical behavior of quantum systems

Pictures of Quantum Dynamics

Quantum mechanics allows multiple, mathematically equivalent ways of describing time evolution, known as pictures.

Schrödinger Picture

In the Schrödinger picture, the state vectors evolve in time, while operators corresponding to observables are time-independent (unless they have explicit time dependence). This picture is conceptually simple and widely used in introductory treatments.

Heisenberg Picture

In the Heisenberg picture, operators evolve in time, while state vectors remain fixed. The time evolution of operators is governed by the Heisenberg equation of motion, which resembles classical equations of motion.

Interaction Picture

The interaction picture combines features of both the Schrödinger and Heisenberg pictures. It is particularly useful in systems where the Hamiltonian can be separated into a solvable part and a small interaction. This picture is essential in time-dependent perturbation theory and quantum field theory.

## Time-Dependent Perturbation Theory

Many physically important systems cannot be solved exactly, especially when they interact with external fields. Quantum dynamics addresses this challenge through time-dependent perturbation theory, which treats the interaction as a small correction to an exactly solvable system.

This approach allows the calculation of transition probabilities between quantum states and explains phenomena such as:

* Absorption and emission of radiation

* Atomic and molecular spectroscopy

* Induced transitions by electromagnetic fields

The interaction picture plays a central role in simplifying these calculations.

## Quantum Transitions and Selection Rules

Quantum dynamics provides a framework for understanding transitions between energy levels. These transitions occur when a system interacts with time-dependent perturbations, such as electromagnetic radiation.

Not all transitions are allowed. Selection rules, derived from symmetry considerations and conservation laws, determine which transitions can occur. These rules are essential for interpreting spectroscopic data and understanding the structure of atoms and molecules.

## Many-Body Quantum Dynamics

Realistic quantum systems often consist of many interacting particles. The quantum dynamics of such systems is significantly more complex due to electron–electron interactions, correlations, and collective effects.

Many-body quantum dynamics is crucial for understanding:

* Solids and condensed matter systems

* Superconductivity and magnetism

* Nuclear dynamics

* Quantum gases and Bose–Einstein condensation

Advanced methods such as second quantization and Green’s functions are commonly used in this context.

## Open Quantum Systems

Most quantum systems are not completely isolated but interact with their surroundings. The study of open quantum systems focuses on how environmental interactions lead to decoherence, dissipation, and the emergence of classical behavior.
Quantum dynamics of open systems is vital for:

* Quantum optics
* Quantum information and computation
* Chemical reaction dynamics in solution

These studies bridge the gap between idealized quantum systems and real-world experiments.

Molecular and Chemical Quantum Dynamics

In molecular systems, quantum dynamics explains vibrational motion, rotational motion, and electronic transitions. It also plays a crucial role in understanding chemical reactions, where the motion of nuclei and electrons occurs on comparable timescales.

The concept of potential energy surfaces, derived from quantum mechanics, provides insight into reaction pathways, transition states, and reaction rates.

Modern Applications of Quantum Dynamics

Quantum dynamics is central to many modern scientific and technological fields, including:
* Ultrafast laser spectroscopy
* Quantum control and coherent manipulation of states
* Quantum computing and information processing
* Nanoscience and molecular electronics

Advances in experimental techniques have made it possible to observe and control quantum dynamics in real time, further increasing its importance.

Conclusion

Quantum dynamics is a fundamental and expansive field that describes how quantum systems evolve in time. By replacing classical trajectories with time-dependent wavefunctions and operators, it provides a deep and accurate understanding of microscopic motion and change. From simple atomic systems to complex many-body and open systems, quantum dynamics offers a unifying framework that connects theory with experiment.

As experimental capabilities continue to advance and new quantum technologies emerge, the study of quantum dynamics remains at the forefront of modern physics and chemistry, offering profound insights into the nature of matter, energy, and time**.**

## 3.2 Equation of motion in Schrodinger picture and Heisenberg picture

### Schrodinger Picture:

In this picture the state vectors are time dependent kets and the operators are constant in time. So, the equation of motion is the equation for Ψ:

$$i\hbar \frac{\partial |\psi_s(t)\rangle}{\partial t} = H |\psi_s(t)\rangle \qquad (1)$$

The subscript s indicates Schrodinger picture. One can express the time dependence of $\Psi_s(r,t)$, in the Schrodinger picture, by unitary transformation

$$\Psi_s(r,t) = U(t)\, \Psi_s(r) \qquad (2)$$

with the condition that U(0)=1, then one can write

$\Psi_s(r) = \Psi_s(r,0)$. (3)

Now,

$$\langle \psi_s | \psi_s \rangle = \langle U\psi_s | U\psi_s \rangle = \langle \psi_s | U^\dagger U | \psi_s \rangle = \langle \psi_s | \psi_s \rangle = 1 \text{ if } U^\dagger(t)U(t) = 1$$

Which would imply that if $\Psi_s(r)$ is normalized, $\Psi_s(r, t)$remains normalized at all time ,t, only when U(t) is unitary. From eqans (1) and (2), we have

$$\left[ i\hbar \frac{\partial U(t)}{\partial t} - HU(t) \right] \psi_s(\bar{r}) = 0$$

$$U(t) = U(0)e^{-iHt/\hbar} = e^{-iHt/\hbar} \qquad (4)$$

The corresponding operator equation is

If H does not depend on time, t, then above equation has a solution of the form

$$i\hbar \frac{\partial U(t)}{\partial t} = HU(t)$$

Therefore from eqn (2), we obtain

$$\left| \psi(\bar{r}, t) \right\rangle = e^{-iHt/\hbar} \left| \psi_s(\bar{r}) \right\rangle \qquad (5)$$

From eqn (1) and eqn (5), the time rate of change of the matrix element of an observable $A_s$, with time is given by

$$\begin{aligned} \frac{d}{dt}\langle A_s \rangle &= \frac{d}{dt}\langle \psi_s | A_s | \psi_s \rangle \\ &= \left[ \frac{d}{dt}\langle \psi_s | \right] A_S |\psi_s\rangle + \langle \psi_s | \frac{\partial A_S}{\partial t} |\psi_s\rangle + \langle \psi_s | A_S \left[ \frac{d}{dt} |\psi_s\rangle \right] \\ &= \langle \psi_s | \frac{\partial A_S}{\partial t} |\psi_s\rangle + i\hbar \langle \psi_s | A_s H - HA_s | \psi_s \rangle \\ &= \langle \psi_s | \frac{\partial A_S}{\partial t} |\psi_s\rangle + i\hbar \langle \psi_s | [A_s, H] | \psi_s \rangle \qquad (6) \end{aligned}$$

$$\frac{d}{dt}\langle A_s \rangle = i\hbar \langle \psi_s | [A_s, H] | \psi_s \rangle \qquad (7)$$

If $A_s$ does not depend explicitly on time, first term of the right side of eqn (6) reduces to zero. Then eqn (4.1.6) becomes

Comparing this equation with the equation of motion for the dynamical variables A in classical mechanics, we see that the expectation values of operators obey the same equation of motion in quantum mechanics (Ehrenfest's theorem), provided we identify the commutatory bracket divided by $i\hbar$ with the quantum mechanical Poisson Bracket.

**Heisenberg Picture:**

In this representation, the wave function $\psi_H(\mathbf{r})$ does not change with time while the operators change with time. The subscript H stands for Heisenberg picture. Time-independent state $\psi_H(\mathbf{r})$ is obtained from $\psi_s(\mathbf{r},t)$ by unitary transformation $(U(t)=\exp(-iHt/\hbar))$ i.e.,

$$\psi_H(r) = U^{-1}(t)\psi_s(r,t) \tag{8}$$

Where $\psi_s(\mathbf{r},t)$ is the state vector in Schrodinger picture, and $\psi_H(r)$is in the Heisenberg picture and is independent of time.

The operator in the Heisenberg picture can be written as

$$A_H(t) = U^{-1}(t)A_s U(t) = e^{iHt/\hbar}\, A_s\, e^{-iHt/\hbar}$$

Differentiating this equation with respect to time, we get

$$\begin{aligned}
\frac{d}{dt}A_H &= \frac{d}{dt}\left(e^{iHt/\hbar}A_s e^{-iHt/\hbar}\right)\\
&= \frac{i}{\hbar}\left[HA_H - A_H H\right] + \frac{\partial A_H}{\partial t}\\
&= \frac{i}{\hbar}\left(e^{iHt/\hbar}HA_s e^{-iHt/\hbar}\right) - \frac{i}{\hbar}\left(e^{iHt/\hbar}A_s H e^{-iHt/\hbar}\right) + U^{\dagger}\frac{\partial A_s}{\partial t}U\\
&= -\frac{i}{\hbar}\left[A_H, H\right] + \frac{\partial A_H}{\partial t}\\
&= \frac{1}{i\hbar}\left[A_H, H\right] + \frac{\partial A_H}{\partial t}
\end{aligned} \tag{9}$$

The eqn (9) represents the variation of dynamical variables with time in the Heisenberg picture.

In the interaction Picture the state vector and operators can be represented as

$$\left|\Psi_I(t)\right\rangle \;=\; \exp(iH_{os}t/\hbar)\left|\psi_s(t)\right\rangle$$

$$A_I(t) \;=\; \exp(iH_{os}t/\hbar)\,A_s\,\exp(-iH_{os}t/\hbar)$$

So that the interaction and Heisenberg pictures are the same when $H' = 0$ ( $H'$ represents the explicit time dependence of Hamiltonian). In this case $H_{os} = H_{oI}$

## 3.3 CORRESPONDENCE BETWEEN SCHRODINGER PICTURE AND HEISENBERG PICTURE

In quantum mechanics, we have two fundamental entities, one is the state vector, representing state of the physical system and the other is dynamical operator. We are interested in knowing the time development of these quantities i.e., their equations of motion. In Schrodinger picture, the state vector $\psi_s(t)$, depends on time while operator, say $A_s$, is time independent. Whereas, in Heisenberg representation the operator change with time while the state vector remains constant. As the physical process cannot depend on a particular choice of representation, there must exit some relation between them.

At t = 0, state vector and operator are to be identical in both representations, i.e.,

The Schrodinger state vector at time t, $|\psi_s(r,t)\rangle$ is related to $|\psi_s(r,0)\rangle$ by unitary operator as

$\langle\psi_s(r,t)|\psi_s(r,t)\rangle = \langle\psi_s(r,0)|\psi_s(r,0)\rangle$ due to conservation of probility.

$$|\psi_s(r,0)\rangle = |\psi_H(r)\rangle \qquad \text{and} \qquad A_s = A_H(0).$$

$$|\psi_s(r,t)\rangle = U(t)|\psi(r,0)\rangle$$

$$= U(t)|\psi(r,0)\rangle \qquad (1)$$

Since $|\psi_H\rangle$ does not depend on time, the time differential of the above equation gives

$$i\hbar\frac{\partial|\psi_s(t)\rangle}{\partial t} = i\hbar\frac{\partial U}{\partial t}|\psi_H\rangle \qquad (2)$$

Further, $|\psi_s(t)\rangle$ satisfies the Schrodinger time dependent equation (eqn.1),

so the above equation can be written as

$$H_s|\psi_s(r,t)\rangle = i\hbar\frac{\partial U}{\partial t}|\psi_H(r)\rangle$$

$$\text{or} \qquad H_s U(t)|\psi_s(r,0)\rangle = i\hbar\frac{\partial U}{\partial t}|\psi_H(r)\rangle$$

*Since* $|\psi_H(r)\rangle = |\psi_s(r,0)\rangle$, *the above equation reduces to*

$$H_s U(t) = i\hbar\frac{\partial U(t)}{\partial t} \qquad (3)$$

The solution of eqn is

$$U(t) = \exp(-iH_s t/\hbar) \qquad (4)$$

Where $H_s$ is assumed to be time-independent.

For conservative systems, the Hamiltonian gives the energy of the system. Therefore, inany representation H does not depend on time, so that $H_H = H_s = H$. Since the expectation value

of an operator is the same, irrespective of its representation, so

$$|\psi_s(t)\rangle = e^{-iHt/\hbar}|\psi_H\rangle = U|\psi_H\rangle \qquad (5)$$

$$\langle \psi_H | A_H(t) | \psi_H \rangle = \langle \psi_s(t) | A_s | \psi_s(t) \rangle = \langle \psi_H U^\dagger | A_s | U \psi_H \rangle$$

Therefore,

$$A_H(t) = U^\dagger A_s U \qquad (6)$$

This gives us the relation between any Heisenberg and Schrodinger operators, defining observables. We will now show that the eigenvalues of operators, being the results of physical measurements, must be same in both the representations.

$$|\psi_s\rangle = \sum c_i |u_i^s\rangle \qquad (7)$$

*where* $|u_i^s\rangle$ *are eigenstates* $(i = 1, 2, 3, ...)$ *on which* $A_s$ *is measured*

*to yield eigenvalues* $\lambda_i$*, i.e.,*

Let the state vector in Schrodinger representation be

$$U^\dagger A_s U U^\dagger |u_i^s\rangle = \lambda U^\dagger |u_i^s\rangle$$

$$or \qquad A_H |u_i^H\rangle = \lambda_i |u_i^H\rangle_i \qquad (8)$$

Multiplying both sides by U† with U U† = 1, the above equation becomes

Eqn (8) shows that $\lambda_i'$ s are also the eigenvalues of the operator $A_H$ .Hence the

$$A_s |u_i^s\rangle = \lambda_i |u_i^s\rangle$$

eigenvalues of the operators are the same in Schrodinger and Heisenberg representations. Now, let us show that the probabilities of finding the system in corresponding eigenstates are

$$where \quad U^\dagger A_s U = A_H \qquad and \qquad |u_i^s\rangle = U |u_i^H\rangle$$

same in both representations. For that, consider the eqn (5),

$$|\psi_s\rangle = \sum_i c_i |u_i^s\rangle$$
$$U^\dagger |\psi_s\rangle = \sum_i c_i U^\dagger |u_i^s\rangle$$

Multiplying both sides by U†, we obtain

or

$$|\psi_H\rangle = \sum_i c_i |u_i^H\rangle \qquad (9)$$

In eqn (9), $c_i$ 's give the probabilities of finding the system in the ith eigenstate and the same $c_i$ 's occur as coefficients in eqn (18) also. Therefore, the probabilities of finding the system in the corresponding eigenstates are same in both representations, i.e.,

$$|c_i|^2 = \left|\langle u_i^s | \psi_s \rangle\right|^2 = \left|\langle u_i^H | \psi_H \rangle\right|^2$$

Since two pictures are equivalent, in principle, we can do our calculations using either one of them. However, for a general operator equations of motions in Heisenberg picture is difficult to solve for most systems (there are exceptions) and therefore, we use the Schrodinger picture in which we deal with the more familiar linear differential equations.

Summarizing with the help of metaphor, we can say that the Schrodinger picture rotates the dance floor with the dancers remaining still, while the Heisenberg picture leaves the dance floor alone and lets the dancers rotate.

## 3.4 SUMMARY

Quantum dynamics describes how quantum states evolve over time, governed primarily by the Hamiltonian operator representing total energy. Two equivalent pictures capture this evolution: Schrödinger and Heisenberg.

Schrödinger Picture

States evolve dynamically while operators remain fixed. The state vector |ψ(t)⟩ changes via the time-dependent equation involving the Hamiltonian, preserving probabilities and enabling wave function propagation

Heisenberg Picture

Operators evolve in time while states stay constant, resembling classical mechanics more closely. Operator time dependence follows a commutator-derived equation with the Hamiltonian, facilitating expectation value calculations and symmetry analysis.

Key Equivalence

Both pictures yield identical observables through unitary transformations, with the Schrödinger approach intuitive for state propagation and Heisenberg for operator algebra and Ehrenfest theorem linking to classical limits.

## 3.5 TECHNICAL TERMS

Introduction to quantum dynamics, Equation of motion in Schrodinger picture and Heisenberg picture, Correspondence between Schrodinger picture and Heisenberg picture

## 3.6 SELF ASSESSMENT QUESTIONS

1. Write about the Introduction to quantum dynamics
2. Briefly explain about the Equation of motion in Schrodinger picture and Heisenberg picture
3. Explain about the Correspondence between Schrodinger picture and Heisenberg picture

## 3.7 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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# LESSON-4

# INTERACTION PICTURE

## 4.0 Aim and Objective

Theaim of the interaction pictureistosimplify the solution of the time-dependent Schrödinger equationfor quantum systems whose Hamiltonian consists of asolvable part and asmall interaction (perturbation), especially when the interaction depends explicitly on time.

The interaction picture, also known as the Dirac picture, aims to simplify time-dependent perturbation theory in quantum mechanics by separating free evolution from interaction effects.

### Objectives

1. To separate free evolution and interaction effects
    - The Hamiltonian is written as

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}},$$

2. To simplify time-dependent perturbation theory
    - Leads naturally to the Dyson series.
    - Useful for calculating transition probabilities between quantum states.
3. To place operators and states on equal footing
    - Operators evolve partly in time (as in Heisenberg picture).
    - States evolve partly in time (as in Schrödinger picture).
4. To facilitate calculations in quantum field theory
    - Most scattering theory and Feynman diagram calculations are done in the interaction picture.

**STRUCTURE**

**4.1 CORRESPONDENCE BETWEEN HEISENBERG EQUATION WITH CLASSICAL MECHANICS**

**4.2 APPLICATION OF HEISENBERG PICTURE TO HARMONIC OSCILLATOR**

**4.3 INTERACTION PICTURE**

**4.4 SUMMARY**

**4.5 TECHNICAL TERMS**

**4.6 SELF ASSESSMENT QUESTIONS**

**4.7 SUGGESTED READINGS**

## 4.1 CORRESPONDING BETWEEN HEISENBERG EQUATION WITH CLASSICAL MECHANICS

### Introduction

One of the fundamental requirements of quantum mechanics is that it must reduce to classical mechanics in the appropriate limit. This requirement is known as the **correspondence principle**, originally proposed by Niels Bohr. It ensures the consistency of quantum theory with classical physics for macroscopic systems or in situations involving large quantum numbers. An important manifestation of this principle appears in the **Heisenberg equation of motion**, which governs the time evolution of operators in the Heisenberg picture of quantum mechanics.

The Heisenberg equation exhibits a close formal resemblance to the equations of motion in classical Hamiltonian mechanics. In particular, the quantum mechanical commutator plays a role analogous to the classical **Poisson bracket**. This correspondence provides deep insight into the structure of quantum theory and clarifies how classical laws of motion emerge as limiting cases of quantum dynamics.

In order to get the similarity between Heisenberg equation of motion and corresponding classical equation, we review briefly the structure of classical Hamiltonian theory. Let the Hamiltonian is a function of coordinates and momenta, i.e., H = H ($q_1$, $q_2$, . . .; $p_1$, $p_2$, . . .), and
writing a relation between Hamiltonian and Lagrangian as

$$H(q_1,q_2,...;p_1,p_2,...;t) \;=\; \sum p_i \dot{q}_i - L$$

The variation of Hamiltonian, H, lead to the Hamilton's equations of motion

$$\dot{q} = \frac{\partial H}{\partial p_i} \qquad and \qquad \dot{p} = -\frac{\partial H}{\partial q_i} \qquad\qquad i=1,2,3,...$$

The time dependence of any function of the coordinates, momenta, and the time, calculated

$$\frac{d}{dt}F\left(q_i,p_i,t\right) \;=\; \frac{\partial F}{\partial t} + \sum\left(\frac{\partial F}{\partial q_i}\dot{q}_i \;+\; \frac{\partial F}{\partial p_i}\dot{p}_i\right)$$

$$= \frac{\partial F}{\partial t} + \sum\left(\frac{\partial F}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial F}{\partial p_i}\right)$$

along a moving phase point, is

Here the Hamilton's equations have been used to get the above equation. The Poisson bracket {A, B} of any two functions of the coordinates and momenta is defined as

$$\{A,B\} = \sum\left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} + \frac{\partial B}{\partial q_i}\frac{\partial A}{\partial p_i}\right)$$

In terms of Poisson bracket, the equation of motion for the function F of the dynamical variables becomes

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F,H\}$$

The resemblance between the above equation and Heisenberg equation, suggests that quantum analogs of the classical equations of motion can be found by substituting the commutator bracket divided by iħ for the Poisson bracket,

$$\{A,B\} = \frac{1}{i\hbar}[A,B]$$

and working with the Heisenberg picture.

### Conclusion

The Heisenberg equation of motion represents the quantum mechanical generalization of Hamilton's equations of classical mechanics. Through the close analogy between commutators and Poisson brackets, quantum dynamics mirrors classical dynamics in a precise mathematical sense. The Ehrenfest theorem and explicit examples such as the free particle and harmonic oscillator further reinforce this correspondence. In the classical limit of large quantum numbers or vanishing ħ\hbarħ, the quantum equations of motion reduce seamlessly to their classical counterparts. This correspondence not only validates quantum mechanics but also provides deep insight into the unity and continuity of physical laws across classical and quantum domains.

## 4.2 Application of Heisenberg picture to harmonic oscillator

### Introduction

The quantum harmonic oscillator is one of the most important and exactly solvable problems in quantum mechanics. It serves as a fundamental model for a wide variety of physical systems, including lattice vibrations (phonons), molecular vibrations, electromagnetic field modes, and quantum fields. Because of its simplicity and wide applicability, it provides an ideal framework for illustrating different formulations of quantum mechanics.

Among the various representations of quantum mechanics, the **Heisenberg picture** offers a particularly transparent way of understanding quantum dynamics. In this picture, the **operators evolve in time**, while the **state vectors remain fixed**. The application of the Heisenberg picture to the harmonic oscillator reveals a striking correspondence between quantum and classical motion and highlights the role of operator algebra in determining time evolution. This chapter discusses in detail how the Heisenberg picture is applied to the harmonic oscillator and how its physical properties emerge naturally from this formulation

In the Heisenberg representation the time dependence is assigned to operators leaving the state vector time independent. The Heisenberg equation of motion for an operator is given by

$$i\hbar dA/dt = [A, H]$$

Where A is an operator. He has used this equation of motion to Harmonic oscillator.

Let us consider a linear harmonic oscillator having the Hamiltonian

$H = p^2/(2m) + (1/2)\, k\, x^2$

$= p^2/(2m) + (1/2)\, m\omega^2\, x^2$ (1)

Where p and x are time dependent operators with infinite Hermitian matrices satisfying the

$\left[x, p_x\right] = i\hbar$

commutation relation

The equation of motion for the operator x in the Heisenberg picture is

$$= \frac{1}{2m}[x, p^2] + \frac{1}{2}m\omega^2[x, x^2]$$

$$= \frac{1}{2m}(p[x,p] + [x,p]p)$$

$$= \frac{i\hbar p}{m}$$

or

$$\dot{x} = \frac{p}{m}(2)$$

In the similar way we can write that

$\dot{p}=-m\omega 2x$(3)

Differentiating eqn (2) with respect to t and combining it with eqn (3), we have

$\ddot{x}+\omega 2x=0$(4)

This equation can be written in the matrix form as

$$(\ddot{x})_{kn} + \omega^2 x_{kn} = 0 \qquad (5)$$

The solution of this equation is

$$x_{kn}(t) = x_{kn}(0)\exp(i\omega_{kn}t) \qquad (6)$$

$$\text{where } \omega_{kn} = (E_k - E_n)/\hbar$$

$$\left(\ddot{x}\right) = -w_{kn}^2 x_{kn}(0)\exp(iw_{kn}t) = -w_{kn}^2 x_{kn} \qquad (7)$$

Differentiating the eqn (6) twice with respect to time, we get

$$\left(\omega_{kn}^2 - \omega^2\right)x_{kn}(t) = 0 \quad \text{or} \quad \left(\omega_{kn}^2 - \omega^2\right)x_{kn}(0) = 0 \qquad (8)$$

Substituting eqn (7) in eqn (5), we obtain

It is convenient to derive the relations for the matrix elements, which are independent of time.

$$x_{kn}(0) = 0 \quad \text{if} \quad \omega_{kn} \neq \pm\omega;$$

$$and \quad x_{kn}(0) \neq 0 \quad \text{if} \quad \omega_{kn} = \pm\omega$$

Generalization is not different as similar relations hold for matrices that depend on time. In view of eqn (4.2.8), all matrix elements $x_{kn}(0)$ vanish except those for which the transition frequency $\omega_{kn} = \pm\omega$. Therefore

That is, for a given value of k only two $x_{kn}$elements are non-vanishing and those are n=k+1 and n=k-1:

$$x_{k,k-1} \text{ corresponds to } \omega_{k,k-1} = \frac{E_k - E_{k-1}}{\hbar} = +\omega \qquad (9)$$

and

$$x_{k,k+1} \text{ corresponds to } \omega_{k,k+1} = \frac{E_k - E_{k+1}}{\hbar} = -\omega \qquad (10)$$

The structure of x matrix would then be

$$(x) = \begin{bmatrix} 0 & x_{01} & 0 & 0 & . & . \\ x_{10} & 0 & x_{12} & 0 & . & . \\ 0 & x_{21} & 0 & x_{23} & . & . \\ 0 & 0 & x_{32} & 0 & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix}$$

Similar way the elements of the *p* matrix can be obtained as

$$p_{kn}(0) = im\omega_{kn}x_{kn}(0)$$

In view of eqns (9) and (10), the non-vanishing elements of the $p$ matrix are

$p_{k,k-1} = im\omega x_{k,k-1}$ and $p_{k,k+1} = -im\omega x_{k,k+1}$ (11)

The structure of $p$matrix is

$$p(x) = im\omega \begin{bmatrix} 0 & -x_{01} & 0 & 0 & . & . \\ x_{10} & 0 & -x_{12} & 0 & . & . \\ 0 & x_{21} & 0 & -x_{23} & . & . \\ 0 & 0 & x_{32} & 0 & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix}$$

The Heisenberg equation of motion of an operator allows us to get the structure of the $x$ and $p$ matrices. To get the elements of the $x$ and $p$ matrices, we have to use the fundamental equation of Heisenberg method. The diagonal (k,k) elements of the fundamental

$$(xp)_{kn} - (px)_{kn} = i\hbar$$

commutation relation is

Substituting the matrices for $x$ and $p$ and using matrix multiplication procedures, we get

$$2im\omega \begin{bmatrix} x_{01}x_{10} & 0 & 0 & 0 & . & . \\ 0 & -x_{01}x_{10} + x_{12}x_{21} & 0 & 0 & & \\ 0 & 0 & -x_{12}x_{21} + x_{23}x_{32} & 0 & . & . \\ 0 & 0 & 0 & -x_{23}x_{32} + x_{34}x_{43} & . & \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix} = i\hbar\delta_{kn}$$

Where $\delta_{kn}$ is the unit matrix. Equating the elements on both sides, we have

$$x_{01}x_{10} = \frac{\hbar}{2m\omega}$$

$$x_{12}x_{21} = \frac{2\hbar}{2m\omega}$$

$$.. = ..$$

$$.. = ..$$

$$x_{k,k+1}x_{k+1,k} = \frac{(k+1)\hbar}{2m\omega}$$

$$.. \quad ..$$

$$.. \quad ..$$

Solving this system of equations, Since x is Hermitian, we can write

$$\left|x_{k,k+1}\right|^2 = \frac{(k+1)\hbar}{2m\omega} \qquad or \qquad x_{k,k+1} = \left(\frac{(k+1)\hbar}{2m\omega}\right)^{1/2} \qquad (12)$$

and

$$x_{k-1,k} = \left(\frac{k\hbar}{2m\omega}\right)^{1/2} \qquad (13)$$

From eqns. (11), (12), and (13), we have

$$p_{k,k+1}p_{k+1,k} = \left(-im\omega x_{k,k+1}\right)\left(im\omega x_{k+1,k}\right)$$

$$= \frac{m\omega(k+1)\hbar}{2}$$

*or*

$$p_{k,k+1} = \left(\frac{m\omega(k+1)\hbar}{2}\right)^{1/2}$$

and

$$p_{k,k-1} = \left(\frac{m\omega k\hbar}{2}\right)^{1/2}$$

Now

$(x^2)_{nn}$ = $(xx)_{nn}$ = $\Sigma\, x_{ni}x_{in} = x_{n,n+1}\, x_{n+1,n} + x_{n,n-1}\, x_{n-1,n}$

= (n+1) ħ / (2m ω) +nħ / (2m ω)

= (2n+1) ħ / (2m ω)

and

$(p^2)_{nn}$ = m ω (n+1) ħ / 2 + m ω n ħ / 2 = m ω (2n+1) ħ / 2

Then the Hamiltonian matrix is

$H_{nn}$ = (1/2m) m ω (2n+1) ħ / 2 + m $\omega^2$ (2n+1) ħ / (4 m ω)

= (2n+1)ħ ω / 2

The eigenvalues $E_n$ of the Hamiltonian are given by

$E_n$ = ( n + ½) ħ ω, n = 0,1,2,3, . . . (14)

This is the same as the usual way one can obtain.

Now, one can write the explicit form of the matrices for x(0) and p(0) based on the above equations as

$$x(0) = \left(\frac{\hbar}{2mw}\right)^{1/2} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 \ldots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 \ldots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 \ldots \\ \ldots\ldots & & \ldots & & \ldots \end{pmatrix}$$

and

$$p(0) = \left(\frac{mw\hbar}{2}\right)^{1/2} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & 0 \ldots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & 0 \ldots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 \ldots \\ \ldots\ldots & & \ldots & \ldots & \ldots\ldots \end{pmatrix}$$

We could obtain the energy quantization of the harmonic oscillator results from the application of Heisenberg equation of motion.

**Physical Significance and Applications**

The harmonic oscillator in the Heisenberg picture is fundamental in:

- quantum optics (photons as oscillator modes),
- solid-state physics (phonons),
- molecular spectroscopy (vibrational modes),
- quantum electrodynamics,
- semiclassical approximations and coherent states.

Understanding this formulation is essential for advanced studies in modern physics.

**Conclusion**

The application of the Heisenberg picture to the quantum harmonic oscillator provides deep insight into the dynamical structure of quantum mechanics. By shifting time dependence from states to operators, the Heisenberg formulation reveals a direct and elegant correspondence between quantum and classical motion. The position and momentum operators satisfy equations identical in form to their classical counterparts, while creation and annihilation operators evolve with simple exponential time dependence. This approach not only simplifies calculations but also clarifies the emergence of classical behavior from quantum dynamics. As a result, the harmonic oscillator in the Heisenberg picture stands as a cornerstone example in quantum mechanics and a gateway to more advanced theories.

## 4.3 INTERACTION PICTURE

The interaction picture (also called the Dirac picture) is a formulation of quantum mechanics that lies between the Schrödinger picture and the Heisenberg picture. It is especially powerful for time-dependent perturbation theory and quantum dynamics with interactions.

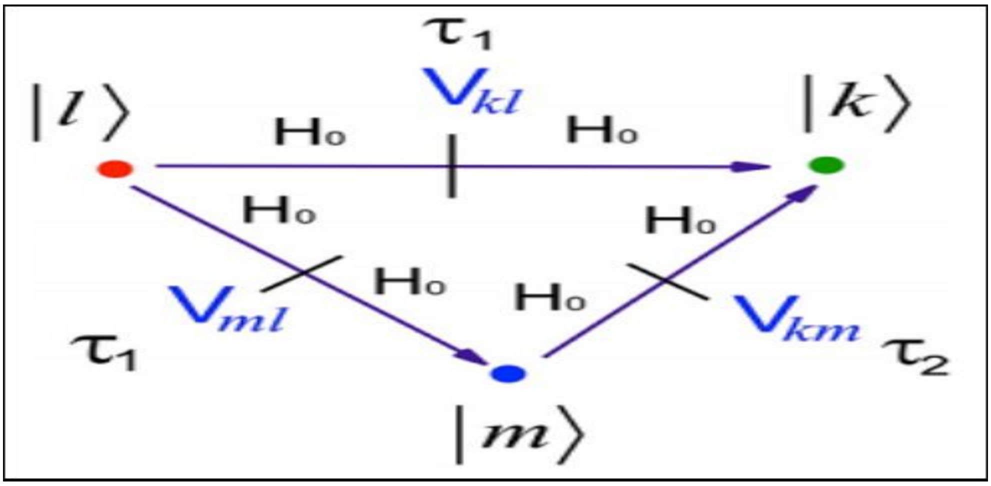

**Fig: 1 Interaction Picture**

### 1. Motivation

In many physical problems, the Hamiltonian can be split as

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}},$$

where:

- $\widehat{H_0}$ is the exactly solvable (free) Hamiltonian

  $\widehat{H_{int}}$is a small interaction or perturbation

The interaction picture treats:

- the free evolution exactly (via $\widehat{H_0}$ )
- the **in**teraction perturbatively (via $\widehat{H_{int}}$ )

### 2. Comparison of Pictures

| **Picture** | **State vectors** | **Operators** |
|---|---|---|
| Schrödinger | Time-dependent | Time-independent |
| Heisenberg | Time-independent | Time-dependent |

| **Picture** | **State vectors** | **Operators** |
|---|---|---|
| Interaction | Time-dependent | Time-dependent |

### 3. Definition of the Interaction Picture

Let $<\psi_S(t)>$ be the Schrödinger picture state.

The **interaction picture state** is defined as:

$$|\psi_I(t)\rangle = e^{\frac{i}{\hbar}\hat{H}_0 t}\,|\psi_S(t)\rangle$$

An operator $\hat{A}$ in the interaction picture is:

$$\hat{A}_I(t) = e^{\frac{i}{\hbar}\hat{H}_0 t}\,\hat{A}_S\,e^{-\frac{i}{\hbar}\hat{H}_0 t}$$

### 4. Time Evolution in the Interaction Picture

The interaction picture state evolves according to:

$$i\hbar\frac{d}{dt}|\psi_I(t)\rangle = \hat{H}_{\text{int}}^{(I)}(t)\,|\psi_I(t)\rangle$$

where the **interaction Hamiltonian** is:

$$\hat{H}_{\text{int}}^{(I)}(t) = e^{\frac{i}{\hbar}\hat{H}_0 t}\,\hat{H}_{\text{int}}\,e^{-\frac{i}{\hbar}\hat{H}_0 t}$$

This equation resembles the Schrödinger equation, but **only the interaction Hamiltonian appears**.

### 5. Time Evolution Operator

The interaction picture evolution operator $\hat{U}_I(t,t_0)$satisfies:

$$i\hbar\frac{d}{dt}\hat{U}_I(t,t_0) = \hat{H}_{\text{int}}^{(I)}(t)\,\hat{U}_I(t,t_0)$$

Its formal solution is:

$$\hat{U}_I(t,t_0) = \mathcal{T}\exp\;-\frac{i}{\hbar}\;{}_{t_0}^{\;t}\;\hat{H}_{\text{int}}^{(I)}(t')\,dt'$$

Here, T is the **time-ordering operator**.

### 6. Dyson Series (Perturbative Expansion)

Expanding the time-ordered exponential gives the **Dyson series**:

$$\hat{U}_I(t,t_0) = 1 - \frac{i}{\hbar} {}_{t_0}^{t} dt_1\, \hat{H}_{\text{int}}^{(I)}(t_1) + \quad -\frac{i}{\hbar} \,{}^{2}\; {}_{t_0}^{t} dt_1 \;\; {}_{t_0}^{t_1} dt_2\, \hat{H}_{\text{int}}^{(I)}(t_1)\hat{H}_{\text{int}}^{(I)}(t_2)$$

This is the foundation of **time-dependent perturbation theory**.

### 7. Physical Significance

The interaction picture:

- Separates **free motion** and **interaction effects**
- Makes perturbative calculations systematic
- Is essential in:
    - Atomic transitions
    - Light–matter interaction
    - Scattering theory
    - Quantum field theory

## 4.4 SUMMARY

The Heisenberg picture establishes a direct bridge between quantum mechanics and classical mechanics, with practical applications to solvable systems and perturbation theory.

Classical Correspondence

The Heisenberg equation $dA/dt = (i/\hbar)[H, A] + \partial A/\partial t$ directly analogs Hamilton's equations, where the commutator $[A, H]/i\hbar$ replaces the Poisson bracket $\{A, H\}$. Ehrenfest's theorem ensures expectation values $\langle x\rangle$ and $\langle p\rangle$ satisfy classical $\dot{x} = \partial H/\partial p$ and $\dot{p} = -\partial H/\partial x$, recovering Newtonian trajectories for coherent states or $\hbar \to 0$ limits. This correspondence validates quantum theory's classical limit while highlighting non-commutativity for microscopic scales.

Harmonic Oscillator in Heisenberg Picture

For $H = p^2/2m + (1/2)m\omega^2x^2$, position and momentum evolve as $x(t) = x(0) \cos(\omega t) + (p(0)/m\omega) \sin(\omega t)$, $p(t) = p(0) \cos(\omega t) - m\omega x(0) \sin(\omega t)$. Ladder operators a(t) = a(0) e^{-iωt} and a†(t) = a†(0) e^{iωt} phase-rotate exactly, preserving commutation $[a, a^\dagger] = 1$ and number eigenstates $|n\rangle$. This mirrors classical sinusoidal motion, ideal for quantum optics and coherent states

Interaction Picture

Splits $H = H_0 + V(t)$: free evolution via $H_0$ governs operators $A_I(t) = e^{i H_0 t/\hbar} A_H(0) e^{-i H_0 t/\hbar}$ and states $|\psi_I(t)\rangle$ via interaction Hamiltonian $V_I(t)$. Time-evolution operator $U_I(t)$ expands as Dyson series $\sum (-i/\hbar) \int V_I(t_1)...V_I(t_n)\, dt$, enabling time-dependent perturbation theory for weak $V(t)$, such as Raman scattering or Rabi oscillations in qubits

These frameworks unify quantum predictions with classical intuition, powering simulations in quantum chemistry and control.

## 4.5 TECHNICAL TERMS

Correspondence with Heisenberg equation with classical mechanics, Application of Heisenberg picture to harmonic oscillator, Interaction picture.

## 4.6 SELF ASSESSMENT QUESTIONS

1. Explain about the Correspondence with Heisenberg equation with classical mechanics
2. Write about the Application of Heisenberg picture to harmonic oscillator
3. Explain about interaction picture

## 4.7 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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## LESSON -5

# IDENTICAL PARTICLES

### 5.0 Aim and Objectives

The aim of this chapter is to understand the quantum mechanical treatment of identical particles and how their indistinguishability affects physical observables. The objectives are to introduce the concepts of symmetric and antisymmetric wavefunctions, study the implications for bosons and fermions, apply the principles to multi-particle systems, and analyse how exchange symmetry influences measurable quantities such as scattering amplitudes and statistical behaviour.

### STRUCTURE OF THE LESSON:

## 5.1THE INDISTINGUISHABILITY OF IDENTICAL PARTICLES

### INTRODUCTION

One of the most profound and fundamentally non-classical features of quantum mechanics is the indistinguishability of identical particles. Unlike classical physics, where particles can always be regarded as distinguishable entities, quantum mechanics imposes a radical and unavoidable constraint: identical particles cannot be distinguished, even in principle. This single idea reshapes our understanding of matter, statistics, and interactions at the microscopic level and lies at the heart of many essential physical phenomena.

In classical mechanics, even if two particles possess exactly the same intrinsic properties—such as mass, charge, and size—they can still be distinguished by tracking their trajectories, initial positions, or histories. Each particle carries an implicit label based on its path through space and time. Quantum mechanics, however, rejects this classical notion. When particles are identical—meaning, they share the same mass, charge, spin, and internal structure—no physical measurement can identify or label them individually. The laws of quantum mechanics therefore require that the description of such particles reflect this fundamental indistinguishability.

This principle has far-reaching consequences. It gives rise to new forms of statistics, governs the structure of atoms and molecules, determines the behavior of solids, and explains phenomena such as the Pauli exclusion principle, degeneracy pressure, Bose–Einstein condensation, superfluidity, and superconductivity. Without indistinguishability, much of modern physics and chemistry would be impossible to understand. It is therefore a cornerstone of quantum theory and a key concept in molecular quantum mechanics.

## Identical versus Distinguishable Particles

### Classical Perspective

In classical physics, particles are always considered distinguishable, even if they are identical in every observable way. For example, consider two identical classical balls. One may label them as particle 1 and particle 2 and follow their positions and velocities as functions of time. Even if the two particles exchange positions, the system is considered to have evolved into a new state because the labels have been exchanged.

This distinguishability is reflected mathematically in classical phase space. Each particle contributes its own coordinates and momenta, and exchanging two particles corresponds to a different point in phase space. Consequently, classical statistical mechanics counts configurations that differ only by particle exchange as distinct microstates. While this approach works well for macroscopic systems, it leads to serious inconsistencies when applied to microscopic particles, such as the Gibbs paradox.

Thus, classical distinguishability is an assumption that ultimately fails at the atomic and subatomic scale.

### Quantum Perspective

Quantum mechanics fundamentally changes this viewpoint. Identical quantum particles cannot be labeled in any physically meaningful way. If two identical particles are exchanged, there is no experiment that can determine whether such an exchange has occurred. Since physical predictions must be independent of unobservable distinctions, the quantum description must treat exchanged configurations as physically identical.

This requirement imposes a strict constraint on the wavefunction of a system of identical particles. The wavefunction must remain either unchanged or change only by a sign when two particles are exchanged. In other words, under the exchange of any two identical particles, the wavefunction must be either:

- Symmetric, or
- Antisymmetric

This symmetry property is not optional—it is a fundamental requirement arising from the indistinguishability of particles.

## Bosons and Fermions

The symmetry of the wavefunction under particle exchange divides all particles in nature into two distinct classes, as dictated by the spin–statistics theorem.

### Bosons

Bosons are particles with integer spin (0, 1, 2, …). Their wavefunctions are symmetric under the exchange of any two particles.

Examples of bosons include:

- Photons
- Phonons
- Helium-4 atoms
- Gluons

- W and Z bosons

Properties of bosons:

- Any number of bosons can occupy the same quantum state.
- They obey Bose–Einstein statistics.
- Their symmetric wavefunctions allow constructive interference between particle states.
- They are responsible for collective quantum phenomena such as:
    - Laser action
    - Superfluidity
    - Bose–Einstein condensation

Because bosons do not exclude one another from quantum states, they can behave coherently on macroscopic scales.

Fermions

Fermions are particles with half-integer spin (1/2, 3/2, …). Their wavefunctions are antisymmetric under the exchange of any two particles.

Examples of fermions include:

- Electrons
- Protons
- Neutrons
- Quarks
- Neutrinos

Properties of fermions:

- No two fermions can occupy the same quantum state.
- They obey Fermi–Dirac statistics.
- The antisymmetric of the wavefunction enforces strong constraints on particle configurations.
- Their behaviour determines the structure and stability of matter.

The antisymmetric nature of fermionic wavefunctions leads directly to one of the most important principles in physics.

Pauli Exclusion Principle

The Pauli exclusion principle states that no two identical fermions can have the same set of quantum numbers. This principle is not an independent assumption but a direct and unavoidable consequence of indistinguishability and antisymmetric.

To see this, consider two fermions placed in the same quantum state. Exchanging the two particles would leave the wavefunction unchanged, since the states are identical. However, antisymmetric requires the wavefunction to change sign under exchange. The only way both conditions can be satisfied simultaneously is for the wavefunction to be zero everywhere, which is physically impossible. Therefore, such a configuration cannot exist.

The Pauli exclusion principle explains:

- The electronic structure of atoms
- The shell structure of atoms
- The periodic table
- Chemical bonding and molecular geometry
- The stability and finite size of matter

Without this principle, electrons would collapse into the lowest energy state, and atoms would not have structure.

## Indistinguishability and Quantum Statistics

Indistinguishability leads naturally to quantum statistics, which differ fundamentally from classical Maxwell–Boltzmann statistics.

### Bose–Einstein Statistics

For bosons:
- Multiple particles may occupy the same energy state.
- At low temperatures, particles tend to accumulate in the lowest available energy level.
- Below a critical temperature, a macroscopic number of particles occupy a single quantum state.

This phenomenon is known as Bose–Einstein condensation, in which quantum effects become visible on a macroscopic scale. It underlies superfluidity and many modern quantum technologies.

### Fermi–Dirac Statistics

For fermions:
- Each quantum state can be occupied by at most one particle.
- At absolute zero, fermions fill energy states up to a maximum value called the Fermi energy.
- Thermal excitation occurs only near the Fermi surface.

Fermi–Dirac statistics determine:
- Electrical conductivity of metals
- Heat capacity of solids
- Properties of semiconductors
- Degeneracy pressure in white dwarf and neutron stars

## Exchange Interaction

Indistinguishability gives rise to the exchange interaction, a purely quantum mechanical effect with no classical analogue. Importantly, this interaction does not arise from a physical force but from the symmetry properties of the wavefunction.

In atoms and molecules, the exchange interaction:
- Explains chemical bonding
- Determines magnetic ordering
- Accounts for ferromagnetism and antiferromagnetism
- Plays a central role in valence bond and molecular orbital theories

Exchange effects are therefore essential for understanding both chemistry and condensed matter physics.

## Indistinguishability in Many-Particle Systems

In systems containing many identical particles, the total wavefunction must be symmetric (bosons) or antisymmetric (fermions) under the exchange of any pair of particles.

For fermions, antisymmetric is conveniently enforced using the Slater determinant, which automatically satisfies the Pauli exclusion principle. This mathematical structure is fundamental in:
- Atomic structure calculations
- Hartree–Fock theory
- Quantum chemistry

- Condensed matter physics

For bosons, symmetric wavefunctions lead to collective states described by mean-field and field-theoretic approaches.

Physical Consequences of Indistinguishability

The indistinguishability of identical particles has profound physical consequences:

1. Stability of Matter
   Without fermionic antisymmetric, matter would collapse.
2. Atomic and Molecular Structure
   Electron configurations and bonding arise from indistinguishability.
3. Thermal and Electrical Properties of Solids
   Conductivity and heat capacity depend on fermionic statistics.
4. Macroscopic Quantum Phenomena
   Superfluidity, superconductivity, and Bose–Einstein condensation depends on bosonic symmetry.

Indistinguishability versus Practical Distinguishability

Quantum indistinguishability is a fundamental principle, not a practical limitation. Even when particles are widely separated, identical particles remain indistinguishable in principle.

However, in certain limits—high temperature or low density—quantum effects become negligible, and particles behave *as if* they were distinguishable. In this regime, classical statistics provides an excellent approximation.

Role in Molecular Quantum Mechanics

In molecular systems, electron indistinguishability is crucial for:

- Constructing correct electronic wavefunctions
- Explaining bonding and antibonding states
- Understanding electron correlation
- Predicting molecular spectra

The requirement of antisymmetric under electron exchange strongly constrains allowed molecular states and shapes chemical behaviour.

## 5.2 THE STATE VECTOR SPACE FOR A SYSTEM OF IDENTICAL PARTICLES

### Indistinguishability of Particles

One of the most fundamental departures of quantum mechanics from classical physics is the principle of indistinguishability of identical particles. In classical mechanics, particles—even if identical in mass, charge, and size—are always considered distinguishable. Each particle follows a definite trajectory in space and time, and by tracing these trajectories one can, at least in principle, label and identify individual particles. Particle labels therefore have physical meaning in classical theory, and exchanging two particles leads to a new configuration in phase space.

Quantum mechanics radically alters this classical picture. Due to the Heisenberg uncertainty principle, particles do not possess well-defined trajectories. Instead, they are described by wavefunctions that give only probabilistic information about their positions and momenta. When particles have identical intrinsic properties such as mass, charge, spin, and internal structure, there exists no physical measurement that can distinguish one particle from another.

Any attempt to label identical quantum particles has no observable consequence and therefore no physical meaning.

As a result, particle labels in quantum mechanics are purely mathematical devices and cannot correspond to experimentally distinguishable features. Exchanging two identical particles must not change any physical prediction. This requirement lies at the heart of quantum statistics and has profound implications for the structure and behaviour of matter at the microscopic scale.

## Total Hilbert Space and Its Limitation

Consider a quantum system consisting of N identical particles. The state of a single particle is described by a Hilbert space $H$. For N particles, the natural mathematical construction of the total Hilbert space is the tensor product of individual single-particle spaces:

$$H_{\text{total}} = H_1 \otimes H_2 \otimes \cdots \otimes H_N$$

Each factor $H_i$corresponds to the state space of the $i$-th particle. This tensor product space contains all possible product states and superpositions of single-particle states and is mathematically complete.

However, this total Hilbert space is larger than the physical state space for a system of identical particles. The reason is that many states in the tensor product space differ only by a permutation of particle labels, which has no physical significance. Since identical particles cannot be distinguished, states that differ only by relabeling particles must represent the same physical situation.

This restriction arises from a fundamental property of the system's Hamiltonian. For identical particles, the Hamiltonian is invariant under any permutation of particle labels. That is, exchanging any two particles leaves the Hamiltonian unchanged. Consequently, the time evolution and measurable quantities must also be invariant under particle exchange.

Therefore, only those states in the total Hilbert space that reflect this permutation symmetry can correspond to physically allowed states. The true physical state space is thus a restricted subspace of the full tensor product space.

## Permutation Operator

To formalize the exchange of particles, we introduce the permutation operator. For two particles $i$and $j$, the permutation operator $P_{ij}$interchanges their states:

$$P_{ij} \ | \cdots, \phi_i, \dots, \phi_j, \dots \ \rangle = | \cdots, \phi_j, \dots, \phi_i, \dots \ \rangle$$

This operator acts on the total Hilbert space and represents the mathematical operation of exchanging the labels of particles $i$and $j$.

The permutation operator has several important properties. Applying the same permutation twice returns the system to its original configuration, which means:

$$P_{ij}^2 = I$$

where $I$is the identity operator. As a consequence, the eigenvalues of the permutation operator can only be $+1$or $-1$.

Since exchanging identical particles has no physical effect, physical states must be eigenstates of the permutation operator. If a state were not an eigenstate, exchanging particles would change the state in a physically observable way, contradicting the principle of indistinguishability.

Thus, the allowed quantum states of identical particles are severely constrained by permutation symmetry.

Symmetrisation Postulate

The constraints imposed by indistinguishability are summarized in the symmetrisation postulate of quantum mechanics. This postulate states that only two types of wavefunctions are physically allowed for identical particles:

1. Symmetric wavefunctions
2. Antisymmetric wavefunctions

No other symmetry behaviour is permitted in nature.

Symmetric States: Bosons

A quantum state is said to be symmetric under particle exchange if it satisfies:

$$P_{ij} \mid \Psi\rangle = +\mid \Psi\rangle$$

Particles described by symmetric wavefunctions are called bosons. Bosons have integer spin (0, 1, 2, …) and obey Bose–Einstein statistics.

Important properties of bosons include:

- Any number of bosons can occupy the same quantum state.
- Their wavefunctions add constructively under exchange.
- They can exhibit collective quantum behaviour on macroscopic scales.

Examples of bosons include photons, phonons, helium-4 atoms, and gauge bosons. Phenomena such as laser action, superfluidity, and Bose–Einstein condensation arise directly from the symmetric nature of bosonic wavefunctions.

Antisymmetric States: Fermions

A quantum state is antisymmetric under particle exchange if:

$$P_{ij} \mid \Psi\rangle = -\mid \Psi\rangle$$

Particles described by antisymmetric wavefunctions are called fermions. Fermions have half-integer spin (1/2, 3/2, …) and obey Fermi–Dirac statistics.

A crucial consequence of antisymmetric is the Pauli exclusion principle. If two fermions occupy the same single-particle state, exchanging them leaves the wavefunction unchanged, but antisymmetric requires a change of sign. The only way both conditions can be satisfied is for the wavefunction to vanish, which is physically forbidden. Therefore, no two identical fermions can occupy the same quantum state.

This principle explains:

- Atomic shell structure
- The periodic table
- Chemical bonding
- The stability and finite size of matter

Construction of Physical States

An arbitrary product state in the total Hilbert space does not, in general, satisfy the symmetry requirements imposed by indistinguishability. To obtain physically allowed states, one must project such states onto the symmetric or antisymmetric subspace.

Symmetrisation for Bosons
For bosons, the physical state is constructed by summing over all permutations of particle labels with equal weight and proper normalization. This symmetrisation ensures that the wavefunction remains unchanged under any particle exchange.

Such states allow multiple particles to occupy the same single-particle state and naturally lead to Bose–Einstein statistics.

Anti symmetrisation for Fermions
For fermions, anti-symmetrisation introduces alternating signs for even and odd permutations. The most convenient way to express antisymmetric states is through the Slater determinant. The Slater determinant automatically ensures antisymmetric and vanishes whenever two particles occupy the same single-particle state, thereby enforcing the Pauli exclusion principle.
This construction is fundamental in:

- Atomic and molecular structure calculations
- Hartree–Fock theory
- Quantum chemistry
- Condensed matter physics

Fock Space Description
In many physical systems, the number of particles is not fixed. Examples include systems where particles can be created or annihilated, such as in quantum field theory or many-body condensed matter systems. In such cases, the tensor product Hilbert space is no longer sufficient.

The appropriate framework is Fock space.
Fock space is defined as the direct sum of all N-particle Hilbert spaces, including the vacuum state:

$$\mathcal{F} = \mathbb{C} \oplus H \oplus (H \otimes H) \oplus (H \otimes H \otimes H) \oplus \cdots$$

For identical particles, only the symmetric (bosons) or antisymmetric (fermions) subspaces of each N-particle sector are included.
Fock space provides:

- A natural description of systems with variable particle number
- A framework for creation and annihilation operators
- Automatic enforcement of particle statistics

It is essential in:

- Many-body quantum mechanics
- Quantum field theory
- Second quantization
- Condensed matter and particle physics

Physical Significance and Consequences
The indistinguishability of particles and the resulting symmetry requirements have profound physical consequences:

1. Stability of Matter
   Without fermionic antisymmetric, electrons would collapse into the lowest energy state.
2. Atomic and Molecular Structure
   Shell structure, bonding, and molecular geometry arise from particle statistics.
3. Thermal and Electrical Properties of Solids
   Conductivity, heat capacity, and magnetism depend on Fermi–Dirac statistics.
4. Macroscopic Quantum Phenomena
   Superconductivity, superfluidity, and Bose–Einstein condensation rely on bosonic symmetry.

## 5.3 CREATION AND ANNIHILATION OPERATORS

In many-particle quantum mechanics, describing a system by explicitly labeling individual particles becomes impractical and physically unnecessary, especially when the particles are identical. Since identical particles are fundamentally indistinguishable, the labeling of particles carries no observable meaning. Instead, it is often far more convenient and physically transparent to describe the system in terms of how many particles occupy each allowed single-particle quantum state.

This approach leads naturally to the occupation number representation, also known as the number representation, which is most conveniently formulated within the framework of Fock space. In this representation, the focus shifts from particle labels to the distribution of particles among available quantum states. Such a description is particularly powerful for systems involving a large or variable number of particles, such as atoms, molecules, solids, and quantum fields.

Fock space provides a unified language for both bosonic and fermionic systems and forms the foundation of second quantization, which is the standard formalism used in modern many-body physics and quantum field theory.

Fock Space and Number States

Fock space is constructed as a direct sum of Hilbert spaces corresponding to different particle numbers. Each basis vector in Fock space is specified by a set of occupation numbers:

$$| n_1, n_2, n_3, \dots \rangle$$

where $n_i$denotes the number of particles occupying the single-particle state labeled by $i$. These basis vectors are called number states or occupation number states.

The allowed values of $n_i$depend on the quantum statistics of the particles:

- For bosons, $n_i = 0,1,2,3, \dots$
- For fermions, $n_i = 0$or 1, reflecting the Pauli exclusion principle

A many-particle quantum state is then represented by specifying the complete set of occupation numbers for all single-particle states. This description automatically incorporates the indistinguishability of particles and the appropriate symmetry requirements.

Creation and Annihilation Operators

The central mathematical objects in the occupation number representation are the creation and annihilation operators. These operators provide a simple and systematic way to build many-particle states from simpler ones and to describe processes in which particles are added to or removed from specific quantum states.

Definition of Creation Operator

The creation operator, denoted by $a_i^\dagger$, creates (adds) one particle in the single-particle state labeled by $i$. When acting on a number state $\mid n_i\rangle$, it increases the occupation number of that state by one:

$$a_i^\dagger \mid n_i\rangle = \sqrt{n_i + 1} \mid n_i + 1\rangle$$

The square-root factor ensures proper normalization of the resulting state and plays a crucial role in preserving the consistency of quantum mechanical probability amplitudes.

Physically, the creation operator represents the act of placing a particle into a specific quantum state, such as adding an electron to an atomic orbital or creating a photon in a particular mode of the electromagnetic field.

Definition of Annihilation Operator

The annihilation operator, denoted by $a_i$, destroys (removes) one particle from the single-particle state $i$. Its action on a number state is given by:

$$a_i \mid n_i\rangle = \sqrt{n_i} \mid n_i - 1\rangle$$

If $n_i = 0$, the annihilation operator yields zero, since it is impossible to remove a particle from an empty state.

The annihilation operator corresponds physically to removing a particle from a given state, such as absorbing a photon or removing an electron from an orbital.

Algebra of Creation and Annihilation Operators

The physical behaviour of many-particle systems is encoded in the algebraic relations satisfied by the creation and annihilation operators. These relations depend on whether the particles are bosons or fermions and reflect the fundamental symmetry properties of their wavefunctions.

Bosonic Operators and Commutation Relations

For bosons, the creation and annihilation operators satisfy commutation relations:

$$[a_i, a_j^\dagger] = a_i a_j^\dagger - a_j^\dagger a_i = \delta_{ij}$$

$$[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0$$

These relations imply that the order in which bosonic operators are applied does not matter, except for the special case involving one creation and one annihilation operator acting on the same state.

The commutation relations allow any number of bosons to occupy the same single-particle state, which is the defining feature of Bose–Einstein statistics. This property leads directly to collective quantum phenomena such as:

- Bose–Einstein condensation
- Superfluidity
- Laser action
- Coherent states of light

The mathematical simplicity of bosonic commutation relations makes bosonic systems particularly amenable to analytical treatment.

Fermionic Operators and Anticommutation Relations

For fermions, creation and annihilation operators obey anticommutation relations:

$$\{a_i, a_j^\dagger\} = a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$

$$\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0$$

These relations imply that exchanging the order of fermionic operators introduces a minus sign. This algebraic structure is a direct mathematical expression of the antisymmetry of fermionic wavefunctions.

A crucial consequence of these anticommutation relations is that:

$$(a_i^\dagger)^2 = 0$$

which means that no more than one fermion can occupy a given single-particle state. This result automatically enforces the Pauli exclusion principle without the need to impose it separately.

Fermionic operators are essential for describing:

- Electrons in atoms and molecules
- Nuclear matter
- Quarks and leptons
- Conducting electrons in solids

Physical Meaning of Operator Algebra

The distinction between commutation and anticommutation relations has profound physical consequences. It determines:

- The allowed occupation numbers
- The statistical behaviour of particles
- The stability and structure of matter

In this way, quantum statistics emerge naturally from the algebra of creation and annihilation operators rather than being imposed as external rules.

**Number Operator**

An important operator constructed from the creation and annihilation operators is the number operator, defined as:

$$\hat{N}_i = a_i^\dagger a_i$$

The number operator measures the number of particles occupying the single-particle state $i$. When acting on a number state, it satisfies the eigenvalue equation:

$$\hat{N}_i \mid n_i\rangle = n_i \mid n_i\rangle$$

Thus, the occupation number $n_i$appears as the eigenvalue of the number operator, confirming the interpretation of $\mid n_i\rangle$as a state with a definite number of particles in state $i$.

The total number operator for the system is given by the sum over all single-particle states:

$$\hat{N} = \sum_i a_i^\dagger a_i$$

This operator plays a central role in distinguishing between systems with fixed and variable particle numbers.

**Second Quantization Formalism**

Creation and annihilation operators form the backbone of second quantization, a formalism in which fields rather than particles are quantized. In this approach:

- Single-particle states define a basis
- Operators create and destroy particles in these states
- Many-particle states emerge naturally

Second quantization offers several advantages:

- Automatic enforcement of particle statistics
- Compact representation of many-body Hamiltonians
- Simplified treatment of interactions
- Natural description of particle creation and annihilation

For example, the Hamiltonian of a many-particle system can often be written compactly in terms of creation and annihilation operators, making calculations more systematic and transparent.

**Applications in Many-Body Physics**

The occupation number representation and second quantization are indispensable in modern physics. They are extensively used in:

1. Many-Body Quantum Mechanics
   To describe interacting systems of electrons, atoms, or nuclei.
2. Quantum Field Theory
   Where particles are interpreted as excitations of underlying quantum fields.
3. Condensed Matter Physics
   In the study of superconductivity, magnetism, and electron correlations.
4. Atomic and Molecular Physics
   For describing electronic structure and correlation effects.
5. Statistical Mechanics
   Where Bose–Einstein and Fermi–Dirac distributions naturally arise.

**Conceptual Advantages of Occupation Number Representation**

The occupation number representation provides a clear and physically meaningful description of quantum systems by:

- Eliminating unphysical particle labels
- Highlighting the role of quantum statistics
- Simplifying calculations involving large numbers of particles
- Providing a natural bridge between quantum mechanics and quantum field theory

It emphasizes that particles are excitations of quantum states, not distinguishable objects following classical trajectories.

## 5.4 CONTINUOUS ONE PARTICLE SYSTEM

In many-particle quantum mechanics, it is often necessary to describe particles moving freely in continuous space rather than occupying a discrete set of energy levels. For such systems, the single-particle states are labeled by continuous variables, most commonly the position ror the momentum p. This situation arises naturally in problems involving free particles, particles in external potentials, electrons in solids, ultracold atomic gases, and quantum fields.

When the single-particle basis is continuous, the occupation number representation based on discrete labels is replaced by a field-theoretic description. In this framework, creation and annihilation operators become field operators, denoted by $\psi^{\dagger}(r)$and $\psi(r)$. These operators create or destroy particles at specific points in space and form the fundamental building blocks of second quantization in the continuous representation.

Definition of Field Operators

The field creation operator $\psi^{\dagger}(r)$creates a particle localized at position r, while the field annihilation operator $\psi(r)$removes a particle from that position. These operators act on states defined in Fock space and allow the description of systems with any number of particles.

Acting on the vacuum state $\mid 0\rangle$, which contains no particles, the field operators satisfy

$$\psi^{\dagger}(r)\mid 0\rangle=\mid r\rangle, \psi(r)\mid 0\rangle=0.$$

Here, $\mid r\rangle$represents a single-particle state localized at position r. The annihilation operator acting on the vacuum gives zero because there is no particle to remove.

Physically, $\psi^{\dagger}(r)$corresponds to the process of adding a particle at point r, while $\psi(r)$represents the removal of a particle from that point. These operators provide a natural and intuitive description of particle dynamics in real space.

Field Operators as Operator-Valued Distributions

It is important to note that field operators are not ordinary operators but operator-valued distributions. The state $\mid r\rangle$is not normalizable in the usual sense, and physical states are obtained by integrating the field operators against suitable wavefunctions. For example, a general single-particle state can be written as

$$\mid \psi\rangle=\int \psi(r)\,\psi^{\dagger}(r)\mid 0\rangle\, dr,$$

where $\psi(r)$is the single-particle wavefunction. This expression demonstrates how the field operator formalism reproduces the standard wavefunction description of quantum mechanics while extending it naturally to many-particle systems.

(Anti)Commutation Relations of Field Operators

The statistical nature of the particles—whether they are bosons or fermions—is encoded in the algebra satisfied by the field operators.

For bosons, the field operators obey commutation relations:

$$[\psi(r), \psi^{\dagger}(r')]=\delta(r-r'),$$
$$[\psi(r), \psi(r')]=[\psi^{\dagger}(r), \psi^{\dagger}(r')]=0.$$

These relations allow multiple bosons to occupy the same position or quantum state, reflecting the symmetric nature of bosonic wavefunctions.

For fermions, the field operators satisfy anticommutation relations:

$$\{\psi(r), \psi^{\dagger}(r')\}=\delta(r-r'),$$
$$\{\psi(r), \psi(r')\}=\{\psi^{\dagger}(r), \psi^{\dagger}(r')\}=0.$$

These relations enforce the Pauli exclusion principle, ensuring that no two fermions can occupy the same quantum state or the same point in space with identical quantum numbers.

The delta function $\delta(r-r')$expresses the locality of the field operators: creation and annihilation at different spatial points are independent, while operators acting at the same point are linked by the statistical rules of the particles.

Physical Significance of Field Operator Algebra

The commutation or anticommutation relations ensure that observable quantities derived from the field operators are consistent with quantum statistics. They guarantee that:

- Bosonic systems exhibit collective behaviour such as Bose–Einstein condensation and superfluidity.
- Fermionic systems obey the exclusion principle, leading to atomic shell structure, electronic band formation, and the stability of matter.

Thus, the statistical behaviour of particles is not imposed artificially but emerges naturally from the algebra of the field operators.

Number Density Operator

An important observable in the continuous representation is the particle number density operator, defined as

$$\hat{n}(r)=\psi^{\dagger}(r)\psi(r).$$

This operator measures the density of particles at position $r$. Its expectation value in a given quantum state gives the probability density of finding a particle at that point in space.

For example, in a single-particle state $|\psi\rangle$, the expectation value of $\hat{n}(r)$reproduces the familiar probability density $|\psi(r)|^2$.

Total Number Operator

The total particle number operator is obtained by integrating the number density operator over all space:

$$\hat{N}=\int \psi^{\dagger}(r)\psi(r)\,dr.$$

This operator counts the total number of particles present in the system. In systems where the particle number is conserved, the Hamiltonian commutes with $\hat{N}$. In other situations, such as in quantum field theory or open quantum systems, the particle number may vary, and $\hat{N}$is not conserved.

Connection to Discrete Representation

The continuous field operators can be expanded in terms of a complete set of single-particle basis functions $\phi_i(r)$:

$$\psi(r)=\sum_i a_i\,\phi_i(r),\psi^{\dagger}(r)=\sum_i a_i^{\dagger}\,\phi_i^{*}(r),$$

where $a_i$and $a_i^{\dagger}$are the annihilation and creation operators in the discrete representation. This expansion shows that the continuous and discrete formulations are completely equivalent and differ only in the choice of basis.

Applications and Importance

Creation and annihilation operators in the continuous representation provide a powerful and natural framework for describing many-particle systems in real space. They are indispensable in:

- Many-body quantum mechanics
- Quantum field theory
- Condensed matter physics
- Atomic, molecular, and optical physics
- Ultracold atomic gases and superfluid's

They allow a compact description of interacting systems, spatial correlations, and particle creation and annihilation processes.

## 5.5 SUMMARY

In quantum mechanics, identical particles are indistinguishable because no experiment can uniquely label particles with the same intrinsic properties. Although the state space of an $N$-particle system is given by the tensor product of single-particle Hilbert spaces, this space is larger than the physical one. Since the Hamiltonian is invariant under particle exchange, only symmetric states for bosons and antisymmetric states for fermions represent physical states.the formalism of creation and annihilation operators is introduced to describe quantum systems containing many particles. Instead of labelling individual particles, the theory uses occupation numbers of single-particle states, which is especially convenient for identical particles. For discrete states as well as continuous one-particle systems, these operators add or remove particles while automatically incorporating Bose–Einstein or Fermi–Dirac statistics.

## 5.6 TECHNICAL TERMS

Indistinguishability of identical particles, the state vector space for a system of identical particles

## 5.7 SELF-ASSESSMENT QUESTIONS

1. State the Indistinguishability of identical particles
2. Describe the state vector space for a system of identical particles
3. Define the creation and annihilation operators.
4. Explain the Creation and Annihilation Operators for a Continuous One- Particle System.

## 5.8 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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## LESSON -6

# QUANTUM DYNAMICAL

### 6.0 Aim and Objectives

The aim of this chapter is to develop a clear understanding of dynamical variables in quantum mechanics and their representation as operators acting on the state vector space. This formulation provides a fundamental link between classical mechanics, where physical quantities are treated as functions of position and momentum, and quantum mechanics, where the same quantities are described by linear operators with well-defined mathematical properties. Through this approach, the chapter establishes the conceptual framework required to describe measurement and dynamics at the microscopic level.

One of the central objectives is to introduce measurable physical quantities as Hermitian operators, emphasizing that Hermiticity guarantees real eigenvalues corresponding to observable measurement outcomes. The distinction between classical variables and quantum operators is examined in detail, highlighting the non-commutative nature of operators and its profound physical consequences. This naturally leads to a discussion of commutation relations, which encode fundamental aspects of quantum behaviour and determine whether different observables can be simultaneously measured.

A key objective of the chapter is to analyze the uncertainty principle as a direct consequence of operator commutation relations. Rather than arising from experimental limitations, uncertainty is shown to be an intrinsic feature of quantum systems, reflecting the structure of the underlying operator algebra. This insight marks a fundamental departure from classical determinism and reshapes the interpretation of physical reality at the quantum scale.The chapter also aims to apply the operator formalism to the time evolution of quantum systems, with particular emphasis on the role of the Hamiltonian operator. The Schrödinger equation is used to describe how quantum states evolve in time and how expectation values of observables can be calculated. Finally, these ideas are extended to multi-particle systems, where operator methods provide a powerful and systematic way to compute physical quantities and describe interactions. Overall, the chapter lays the foundation for advanced studies in quantum dynamics, many-body physics, and quantum statistical mechanics.

### STRUCTURE OF THE LESSON:

**6.1 DYNAMICAL VARIABLES**
**6.2 THE QUANTUM DYNAMICS OF IDENTICAL PARTICLE SYSTEM**
**6.3 SUMMARY**
**6.4 TECHNICAL TERMS**
**6.5 SELF-ASSESSMENT QUESTIONS**
**6.6 SUGGESTED READINGS**

### 6.1 DYNAMICAL VARIABLES

In quantum mechanics, every measurable physical quantity—such as position, momentum, energy, angular momentum, or spin—is referred to as a dynamical variable or observable**.** The treatment of these quantities marks a fundamental departure from classical mechanics. In classical physics, dynamical variables are represented as ordinary functions of the generalized coordinates $x$and momenta $p$, and their values can, in principle, be specified simultaneously and with arbitrary precision.

Quantum mechanics fundamentally alters this viewpoint. Physical quantities are no longer described by numerical functions but by linear operators acting on state vectors in an abstract vector space known as Hilbert space. The physical state of a system is represented by a state vector $\mid \Psi\rangle$, and measurable quantities are extracted through the action of operators on these states.

**Operator Representation of Observables**

In quantum theory, an observable $A$is represented by an operator $\hat{A}$. These operators are required to be Hermitian (self-adjoint) so that their eigenvalues—corresponding to possible measurement outcomes—are real. If $\hat{A}$is a Hermitian operator, then

$$\hat{A}^{\dagger} = \hat{A}.$$

The eigenvalue equation

$$\hat{A} \mid a\rangle = a \mid a\rangle$$

defines the allowed measurement results $a$, while the corresponding eigenstates $\mid a\rangle$form a complete basis for the Hilbert space.

The operator formalism provides a systematic framework to compute:

- **Expectation values**

$$\langle A\rangle = \langle \Psi \mid \hat{A} \mid \Psi\rangle,$$

- **Measurement probabilities**
- **Time evolution of observables and states**

Thus, operators form the core mathematical structure of quantum mechanics.

**Classical View vs Quantum View**

From a conceptual standpoint, the distinction between classical and quantum descriptions of dynamical variables may be summarized as:

- **Classical view:**
  Physical quantities are functions of coordinates $x$and momenta $p$:

$$A = A(x,p).$$

- **Quantum view:**
  Physical quantities are represented by operators acting on the state vector space:

$$x \rightarrow \hat{x}, p \rightarrow \hat{p} = -i\hbar\nabla.$$

The replacement of classical variables by operators introduces non-commutativity, which lies at the heart of quantum behaviour.

**Commutation Relations and Physical Meaning**

Operators in quantum mechanics do not generally commute. The commutation relation between two operators $\hat{A}$and $\hat{B}$is defined as

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

A fundamental example is the canonical commutation relation between position and momentum:

$$[\hat{x}, \hat{p}] = i\hbar.$$

This non-zero commutator directly leads to the Heisenberg uncertainty principle,

$$\Delta x \, \Delta p \geq \frac{\hbar}{2},$$

which places a fundamental limit on the simultaneous measurement of position and momentum. More generally, commutation relations encode deep physical principles and determine:

- Which observables can be simultaneously measured
- The structure of quantum dynamics
- The algebraic properties of physical systems

### Indistinguishability Constraint for Identical Particles

For systems containing identical particles, quantum mechanics introduces an additional and crucial constraint. Identical particles possess the same intrinsic properties (mass, charge, spin), and no measurement can distinguish one particle from another.

As a result:

- Particle labels have no physical meaning
- Physical observables must be invariant under particle exchange
- Dynamical variables must be symmetric under permutation of particle indices

This indistinguishability profoundly affects the structure of the state space and the allowed forms of operators.

### Categorization of Observables in Many-Particle Systems

Dynamical variables in many-particle quantum mechanics are classified according to the number of particles involved.

### One-Body Operators

**One-body operators** describe properties that act independently on each particle and are summed over all particles. Examples include:

- Total kinetic energy
- Total momentum
- Interaction with an external field

### First-Quantized Form

In first quantization, a general one-body operator is written as

$$F_1 = \sum_{i=1}^{N} f(x_i, p_i),$$

where $f(x_i, p_i)$acts only on particle $i$.

### Second-Quantized Form

In second quantization, one-body operators take the form

$$\hat{F} = \sum_{i,j} \langle \phi_i \mid f \mid \phi_j \rangle \, a_i^\dagger a_j,$$

where:

- $a_j$annihilates a particle in state $j$
- $a_i^\dagger$creates a particle in state $i$
- $\langle \phi_i \mid f \mid \phi_j \rangle$are single-particle matrix elements

This formulation greatly simplifies calculations in many-body systems and automatically incorporates particle indistinguishability.

### Two-Body Operators

**Two-body operators** describe interactions between pairs of particles. Typical examples include:

- Coulomb interaction between electrons
- Short-range nuclear forces
- Van der Waals interactions

### First-Quantized Form

The general two-body interaction is written as

$$F_2 = \sum_{i<j} v(x_i, x_j),$$

where $v(x_i, x_j)$depends on the coordinates of two particles.

### Second-Quantized Form

In second quantization, the corresponding operator becomes

$$\hat{V} = \frac{1}{2} \sum_{i,j,k,l} \langle \phi_i \phi_j \mid v \mid \phi_k \phi_l \rangle \, a_i^\dagger a_j^\dagger a_l a_k.$$

The ordering of operators ensures:

- Symmetry for bosons
- Antisymmetric for fermions

Two-body operators are essential for describing correlations, collective behaviour, and interaction-driven phenomena in quantum systems.

### Symmetry and Conservation Laws

A central principle in physics is the intimate connection between symmetry and **conservation laws**, formalized by Noether's theorem. In quantum mechanics:

- **Translational symmetry** → Conservation of linear momentum
- **Rotational symmetry** → Conservation of angular momentum
- **Time-translation symmetry** → Conservation of energy

These symmetries restrict the form of allowed operators, determine selection rules, and simplify the analysis of quantum systems.

### Indistinguishability and the Physical State Space

For a system of $N$identical particles, the total Hilbert space is the tensor product

$$\mathcal{H}_{\text{total}} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots \otimes \mathcal{H}_N.$$

However, not all states in this space are physically meaningful. Only:

- **Symmetric states** (bosons)

- **Antisymmetric states** (fermions)

are allowed. This restriction arises from the requirement that the Hamiltonian be invariant under particle exchange.

This principle governs:

- Quantum statistics
- Allowed transitions
- Correlation effects
- Structure of many-particle wavefunctions

### Time Evolution of Quantum Systems

The time evolution of a quantum system is governed by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \mid \Psi(t)\rangle = \hat{H} \mid \Psi(t)\rangle.$$

For systems of identical particles, the Hamiltonian $\hat{H}$is symmetric under particle permutations. Consequently:

- Bosonic states remain symmetric
- Fermionic states remain antisymmetric

throughout time evolution. This ensures consistency with indistinguishability.

### Hamiltonian Structure in Many-Particle Systems

The total Hamiltonian is generally written as

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i + \sum_{i<j} \hat{V}_{ij},$$

where:

- $\hat{h}_i$: one-body operators (kinetic energy, external fields)
- $\hat{V}_{ij}$: two-body interactions

In second quantization, this structure is compactly expressed using creation and annihilation operators, making it particularly suitable for large systems.

### Observables and Expectation Values

Any physical observable $\hat{O}$must be symmetric under particle exchange. The expectation value in a state $\mid \Psi(t)\rangle$is

$$\langle \hat{O} \rangle = \langle \Psi(t) \mid \hat{O} \mid \Psi(t)\rangle.$$

Such expectation values describe measurable quantities and their evolution in time, including fluctuations and correlations.

### Continuous Systems and Field Operators

For systems with particles moving in continuous space, it is convenient to use field operators $\psi(\mathrm{r}, t)$and $\psi^\dagger(\mathrm{r}, t)$. These operators annihilate or create particles at position r.

The time evolution in the Heisenberg picture is given by

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = [\psi(\mathbf{r}, t), \hat{H}].$$

**Density Operator**

The particle density operator is

$$\hat{n}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r}),$$

which measures the local particle density.

**Hamiltonian in Field Form**

$$\hat{H} = \int d^3r\, \psi^\dagger(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right)\psi(\mathbf{r}) + \frac{1}{2}\int d^3r\, d^3r'\, \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')v(\mathbf{r} - \mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r}).$$

This formulation naturally incorporates interactions, correlations, and quantum statistics.

**Physical Significance**

Field operators and operator methods form the foundation for:

- Bose–Einstein condensation
- Superfluidity and superconductivity
- Collective excitations
- Quantum correlations and entanglement
- Quantum field theory and condensed matter physics

They allow a unified, elegant description of many-particle systems with variable particle number.

## 6.2 THE QUANTUM DYNAMICS OF IDENTICAL PARTICLE SYSTEM

One of the most fundamental departures of quantum mechanics from classical physics lies in the treatment of identical particles. In classical mechanics, particles are always regarded as distinguishable, even if they possess identical intrinsic properties such as mass and charge. One may, at least in principle, label particles by their trajectories, initial positions, or histories. Quantum mechanics radically changes this viewpoint. When particles are identical, meaning they share the same intrinsic properties—mass, charge, spin, and internal structure—it becomes impossible, even in principle, to distinguish one particle from another. This indistinguishability is not a limitation of measurement but a fundamental property of nature.

As a consequence, systems consisting of identical quantum particles exhibit unique and deeply non-classical behaviour. The indistinguishability of particles imposes strict constraints on the mathematical form of the quantum state describing the system. These constraints profoundly influence the dynamics, statistics, and observable properties of many-particle systems and underlie a wide range of physical phenomena in atomic, molecular, condensed matter, and nuclear physics.

Indistinguishability and the Quantum State

In quantum mechanics, the complete physical description of a system is provided by its wavefunction or state vector. For a system of identical particles, this wavefunction must reflect the fundamental fact that exchanging two particles cannot lead to any observable change. If an experiment cannot distinguish whether particle 1 is at position $r_1$and particle 2 at position $r_2$, or vice versa, then the physical predictions of the theory must remain unchanged under such an exchange.

Mathematically, this requirement leads to the symmetry condition on the wavefunction. If $P_{ij}$ denotes the operator that exchanges particles $i$ and $j$, then a physically allowed state $| \Psi\rangle$ must satisfy

$$P_{ij} | \Psi\rangle = \pm| \Psi\rangle.$$

The plus sign corresponds to symmetric wavefunctions, while the minus sign corresponds to antisymmetric wavefunctions. This dichotomy leads directly to the classification of particles into two fundamental classes:

- Bosons, which have integer spin and are described by symmetric wavefunctions.
- Fermions, which have half-integer spin and are described by antisymmetric wavefunctions.

This connection between spin and symmetry is formalized in the spin–statistics theorem, one of the deepest results in quantum theory.

### Consequences of Symmetry Requirements

The requirement of symmetry or antisymmetric under particle exchange has far-reaching consequences. It affects all observable quantities, including:

- Energy spectra, determining allowed and forbidden energy levels.
- Scattering amplitudes, influencing interference patterns and cross sections.
- Statistical distributions, giving rise to Bose–Einstein and Fermi–Dirac statistics.
- Correlation effects, which have no classical analogue.

Understanding these consequences is essential for explaining key physical phenomena such as Bose–Einstein condensation, Fermi degeneracy pressure, exchange interactions, and the stability of matter.

### Indistinguishability and the State Space

Consider a system of $N$ identical particles. The mathematical Hilbert space describing the system is formally given by the tensor product of $N$ single-particle Hilbert spaces:

$$\mathcal{H}_{\text{total}} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots \otimes \mathcal{H}_N.$$

However, this space is larger than the physically meaningful state space. The reason is that the Hamiltonian of a system of identical particles is invariant under permutations of particle labels. Therefore, states that differ only by a permutation of particles represent the same physical situation and must not be counted separately.

As a result, only a restricted subspace of $\mathcal{H}_{\text{total}}$ is physically allowed:

- The symmetric subspace for bosons.
- The antisymmetric subspace for fermions.

This restriction is not optional; it is a fundamental requirement imposed by indistinguishability. It governs the allowed quantum states and determines the structure of many-particle wavefunctions.

### Bosons and Fermions

#### Bosons

Bosons are particles with integer spin (0, 1, 2, …). Their wavefunctions are symmetric under particle exchange:

$$\Psi(\dots, r_i, \dots, r_j, \dots) = \Psi(\dots, r_j, \dots, r_i, \dots).$$

This symmetry allows any number of bosons to occupy the same quantum state. As a result, bosons obey Bose–Einstein statistics. At low temperatures, this leads to macroscopic occupation of the lowest energy state, giving rise to Bose–Einstein condensation, superfluidity, and coherent phenomena such as laser action.

Fermions

Fermions are particles with half-integer spin (1/2, 3/2, …). Their wavefunctions are antisymmetric under particle exchange:

$$\Psi(\dots, r_i, \dots, r_j, \dots) = -\Psi(\dots, r_j, \dots, r_i, \dots).$$

This antisymmetry implies that if two fermions attempt to occupy the same quantum state, the wavefunction vanishes identically. This leads directly to the Pauli exclusion principle, which states that no two identical fermions can have the same set of quantum numbers.

The Pauli principle explains:

- The electronic structure of atoms
- The periodic table
- Chemical bonding
- The stability of matter
- Fermi degeneracy pressure in white dwarfs and neutron stars

Time Evolution of Identical Particle Systems

The quantum dynamics of any system is governed by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \mid \Psi(t)\rangle = \widehat{H} \mid \Psi(t)\rangle,$$

where $\widehat{H}$is the total Hamiltonian of the system. For systems consisting of identical particles, the Hamiltonian must be symmetric under particle permutations. That is,

$$[\widehat{H}, P_{ij}] = 0$$

for all particle exchanges $P_{ij}$.

Because the Hamiltonian commutes with all permutation operators, the symmetry (or antisymmetry) of the wavefunction is preserved during time evolution. If the system begins in a symmetric (bosonic) or antisymmetric (fermionic) state, it will remain in that class for all time. This ensures that all physical predictions—such as probabilities, expectation values, and correlation functions—remain consistent with the principle of indistinguishability.

Hamiltonian Structure for Identical Particles

The Hamiltonian of an interacting system of identical particles typically consists of two parts:

$$\widehat{H} = \sum_{i=1}^{N} \hat{h}_i + \sum_{i<j} \widehat{V}_{ij}\,.$$

Here:

- $\hat{h}_i$represents one-body operators, such as kinetic energy and interaction with external potentials.
- $\widehat{V}_{ij}$represents two-body interaction operators, describing interactions between particle pairs.

This structure reflects the physical reality that particles possess individual kinetic energies and also interact with one another through forces such as Coulomb or short-range interactions.

Second Quantization and Many-Body Dynamics

While the first-quantized formulation is conceptually useful, it becomes cumbersome for systems with many particles. A more powerful and elegant framework is provided by second quantization, in which the Hamiltonian is expressed in terms of creation and annihilation operators.

In this formalism:

- Particle indistinguishability is built in automatically.
- The correct bosonic or fermionic statistics are enforced by commutation or anticommutation relations.
- Calculations of expectation values, correlation functions, and response properties are greatly simplified.

Second quantization is indispensable for the study of large many-body systems and forms the foundation of modern quantum statistical mechanics and quantum field theory.

Observables and Expectation Values

Any physical observable $\hat{O}$describing an identical particle system must itself be invariant under particle exchange. This ensures that measurements do not depend on arbitrary particle labels.

The expectation value of an observable in a time-dependent state $\mid \Psi(t)\rangle$is given by

$$\langle \hat{O}\rangle = \langle \Psi(t) \mid \hat{O} \mid \Psi(t)\rangle.$$

The time dependence of expectation values follows from the system's dynamics and reflects both the interactions and quantum statistics of the particles. Symmetry requirements ensure that statistical properties such as fluctuations and correlations are correctly captured.

Continuous Systems and Field Operators

For systems in continuous space, it is often convenient to adopt a field-theoretic description. In this approach, the basic dynamical variables are the field operators $\psi(\mathrm{r}, t)$and $\psi^{\dagger}(\mathrm{r}, t)$, which annihilate and create particles at position rand time $t$, respectively.

The time evolution of field operators in the Heisenberg picture is governed by

$$i\hbar \frac{\partial \psi(\mathrm{r}, t)}{\partial t} = [\psi(\mathrm{r}, t), \hat{H}].$$

This formulation naturally accommodates systems with variable particle number and automatically incorporates symmetrisation for bosons or antisymmetrisation for fermions.

Physical Significance of Field Operators

Field operator methods provide a unified and powerful framework for describing:

- Bose–Einstein condensation
- Superfluidity and superconductivity
- Collective excitations such as phonons and magnons
- Quantum correlations and entanglement in many-body systems

They form the conceptual bridge between non-relativistic quantum mechanics and quantum field theory.

Key Principles of Quantum Dynamics for Identical Particles

The quantum dynamics of identical particle systems is governed by several fundamental principles:

- The symmetry or antisymmetric of the wavefunction is preserved in time.
- Hamiltonians and observables must be invariant under particle exchange.
- Quantum statistics emerge naturally from indistinguishability.
- Second quantization and field operators provide an efficient and physically transparent description of many-body systems.

So, in the indistinguishability of identical particles is a cornerstone of quantum mechanics and lies at the heart of many of its most striking predictions. By imposing symmetry constraints on the state space and operators, quantum mechanics gives rise to fundamentally new forms of behaviour that have no classical analogue. From the structure of atoms and molecules to the collective phenomena observed in condensed matter systems, the quantum dynamics of identical particles shapes the physical world at every scale.

Understanding these principles is essential for mastering quantum statistical mechanics, many-body physics, and modern theoretical physics as a whole.

## 6.3 SUMMARY

In quantum mechanics, dynamical variables represent measurable physical quantities such as position, momentum, energy, and angular momentum. Unlike classical mechanics, where these quantities are treated as ordinary functions of coordinates and momenta, quantum mechanics represents them by operators acting on state vectors in a Hilbert space. These operators are required to be Hermitian (self-adjoint) so that their eigenvalues, which correspond to possible measurement outcomes, are real and physically meaningful. The operator formalism provides a systematic framework for calculating expectation values, probabilities, and the time evolution of quantum systems.

For a given dynamical variable represented by an operator $\hat{A}$, the measurable values are obtained from the eigenvalue equation $\hat{A} \mid a\rangle = a \mid a\rangle$. In a general quantum state, measurements yield different outcomes with probabilities determined by the projection of the state onto the eigenstates of the operator. Thus, operators form the mathematical backbone of quantum theory and encode the statistical nature of physical measurements.

When dealing with systems of identical particles, additional constraints arise due to the principle of indistinguishability. Identical particles possess the same intrinsic properties and cannot be distinguished by any physical measurement. Consequently, all physical operators, including the Hamiltonian, must be invariant under the exchange of particles. This invariance leads to a fundamental classification of particles into bosons and fermions, according to the symmetry of their quantum states. Bosonic states are symmetric under particle exchange, while fermionic states are antisymmetric.

The symmetry properties of the state space are preserved by the system's quantum dynamics. The time evolution of a quantum system is governed by the Schrödinger equation, $i\hbar\frac{\partial}{\partial t} \mid \Psi(t)\rangle = \hat{H} \mid \Psi(t)\rangle$, where $\hat{H}$is the Hamiltonian operator. For identical particles, the Hamiltonian commutes with permutation operators, ensuring that an initially symmetric or antisymmetric state remains so throughout its evolution. This guarantees that all physical predictions remain consistent with particle statistics.

An equivalent description of dynamics is provided by the Heisenberg picture, in which operators evolve in time according to $i\hbar\frac{d\hat{O}}{dt} = [\hat{O}, \hat{H}]$, while the state vectors remain fixed. This formulation is particularly useful in many-body systems, where the focus is often on the time evolution of observables rather than states.

In continuous systems and many-particle problems, the dynamics is naturally expressed in terms of field operators. The creation and annihilation operators $\psi^\dagger(\mathrm{r}, t)$and $\psi(\mathrm{r}, t)$respectively create and destroy a particle at position rand time $t$. These operators obey commutation relations for bosons and anticommutation relations for fermions, thereby automatically incorporating the correct quantum statistics. Field operators allow a compact and powerful description of observables such as particle density, currents, and correlation functions, and they form the foundation of second quantization.

The symmetry requirements imposed by indistinguishability give rise to several distinctive physical phenomena. For fermions, antisymmetry of the wavefunction leads directly to the Pauli exclusion principle, which forbids more than one fermion from occupying the same quantum state. This principle explains the structure of atoms, the stability of matter, and the behavior of electrons in solids. For bosons, symmetric wavefunctions allow multiple particles to occupy the same state, leading to Bose–Einstein condensation and macroscopic quantum phenomena such as superfluidity.

In addition, exchange interactions arise purely from the symmetry properties of identical particle wavefunctions. These interactions significantly affect energy spectra, correlation functions, and scattering processes in multi-particle systems. As a result, the study of dynamical variables and quantum dynamics in identical particle systems is fundamental to atomic, molecular, and condensed matter physics, providing deep insight into the collective behaviour of quantum matter.

## 6.4 TECHNICAL TERMS

Dynamical variables, The quantum dynamics of identical particle system

## 6.5 SELF-ASSESSMENT QUESTIONS

1. Explain what is dynamical variables.
2. Explain the quantum dynamics of identical particle system.

## 6.6 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

**Prof. G. Naga Raju**

# LESSON- 7

# SCATTERING THEORY

**Aim and Objectives**

The aim of this chapter is to develop a clear and systematic understanding of the fundamental principles of scattering theory, which describes how particles or waves interact with a scattering potential and how these interactions lead to observable physical effects. Scattering processes play a central role in probing the structure of matter, as they provide indirect information about the nature of forces and potentials that cannot be observed directly. This chapter establishes the theoretical framework required to connect microscopic interaction potentials with measurable quantities obtained in experiments.

One of the primary objectives is to introduce the concept of scattering cross sections, including differential and total cross sections, which quantify the probability of particles being scattered into specific directions. These quantities form the basis for comparing theoretical predictions with experimental data. The chapter also examines the scattering of wave packets and contrasts it with the continuous stream model, clarifying how realistic particle beams are described within quantum mechanics and how flux conservation is ensured.

Another important objective is to develop approximate and exact methods for solving scattering problems. The Born approximation is introduced as a perturbative approach applicable when the interaction potential is weak, allowing the scattering amplitude to be expressed in terms of the Fourier transform of the potential. Conditions for the validity of the Born approximation are discussed to highlight its physical limitations. For stronger potentials and lower energies, the chapter presents partial wave analysis, which provides an exact and physically transparent method by decomposing the scattering process into angular momentum components.

The chapter further aims to relate theoretical scattering amplitudes to experimentally observable quantities through concepts such as the optical theorem and phase shifts. By the end of the chapter, the reader gains a coherent understanding of how quantum scattering theory explains experimental observations in atomic, nuclear, and particle physics, and how it serves as a powerful tool for investigating the interaction and structure of physical systems.

**STRUCTURE OF THE LESSON:**

## 7.1 INTRODUCTION OF SCATTERING - NOTION OF CROSS SECTION

In a scattering experiment, one studies the collisions that occur between a beam of incident particles and a target material in order to understand the nature of the interaction between them. A beam consisting of a large number of particles is directed toward a fixed target, and the particles in the beam interact with the constituents of the target as they pass through it. The total number of collisions observed during the course of the experiment is proportional to two important factors: the total number of incident particles in the beam and the number of target particles per unit area encountered along the path of the beam. Hence, increasing either the beam intensity or the target density increases the likelihood of collisions.

In such experiments, the primary task is to count the particles that emerge from the target after the interaction. Not all incident particles undergo scattering. Those particles that do not interact with the target continue their motion essentially undisturbed in the forward direction, maintaining nearly the same momentum and energy as before the collision. On the other hand, particles that do interact with the target experience a change in momentum and are deflected from their original direction of motion. These particles are said to be scattered and emerge at various angles relative to the direction of the incident beam, as illustrated schematically in a typical scattering diagram.

The number of scattered particles is not the same in all directions. In general, the number of particles emerging from the target depends strongly on the direction in which they are observed. To describe this angular distribution quantitatively, the directions of the scattered particles are specified by the polar angle $\theta$ and the azimuthal angle $\varphi$. The detectors measure the number of particles scattered into a small element of solid angle $d\Omega$, where $d\Omega = \sin\theta \, d\theta \, d\varphi$.

The number of particles scattered into this small solid angle element is proportional to a fundamental quantity in scattering theory known as the differential cross section. The differential cross section, denoted by $d\sigma(\theta, \varphi)/d\Omega$, plays a central role in the physics of scattering, as it provides a precise measure of how particles are distributed in angle after the interaction.

By definition, the differential cross section $d\sigma(\theta, \varphi)/d\Omega$ is the number of particles scattered per unit time into the element of solid angle $d\Omega$ in the direction specified by the angles $(\theta, \varphi)$, divided by the incident flux. The incident flux, denoted by J_inc, is defined as the number of incident particles crossing a unit area perpendicular to the beam direction per unit time. It characterizes the intensity of the incoming beam and provides the proper normalization needed to compare results obtained under different experimental conditions.

From this definition, it can be verified that the differential cross section has the dimensions of an area, which justifies the term “cross section.” Physically, it may be interpreted as an effective area that quantifies the probability of scattering into a particular direction. Thus, the differential cross section contains complete information about the angular distribution of scattered particles and forms the basis for analysing and interpreting both classical and quantum mechanical scattering experiments.

$$\frac{d\sigma(\theta,\varphi)}{d\Omega} = \frac{1}{J_{inc}} \frac{dN(\theta,\varphi)}{d\Omega},$$

Here, $J_{\text{inc}}$represents the incident flux, also called the incident current density. It is defined as the number of incident particles crossing a unit area perpendicular to the direction of the beam per unit time, and it characterizes the intensity of the incoming particle beam. From the definition of the differential cross section, $\frac{d\sigma}{d\Omega}$is obtained by dividing the number of particles scattered per unit time into a given solid angle by the incident flux. Dimensional analysis shows that $\frac{d\sigma}{d\Omega}$has the dimensions of an area, which justifies referring to it as a differential cross section.

The relationship between dσ/dΩ and the total cross section σ is obvious:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \frac{d\sigma(\theta,\varphi)}{d\Omega} d\varphi.$$

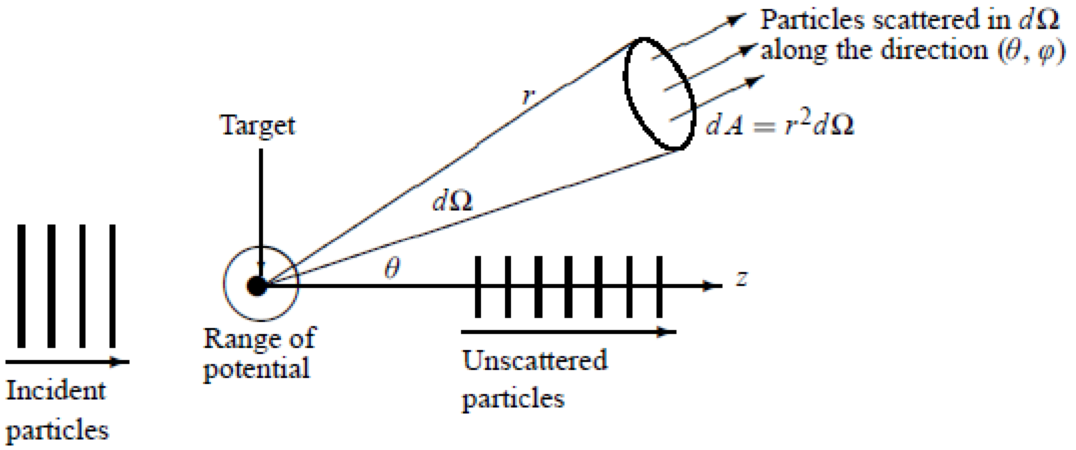


**Figure 1** Scattering between an incident beam of particles and a fixed target: the scattered particles are detected within a solid angle dΩ along the direction (θ,**ϕ**).

Most scattering experiments are performed in the laboratory (Lab) frame, in which the target particles or nuclei are initially at rest, while the incident particles, often called projectiles, are in motion with a well-defined velocity and momentum. In this frame, the experimenter observes the scattering events as the beam of projectiles interacts with the stationary target. Detectors are placed around the target to measure the number and angular distribution of scattered particles. The laboratory frame provides a natural setting for actual experiments because it corresponds to the physical setup in which the target is fixed and the projectile beam is directed towards it. Observations such as particle counts, scattering angles, and energy measurements are typically recorded in this frame.

However, while experiments are performed in the lab frame, theoretical calculations of scattering cross sections are often more conveniently carried out in the centre of mass (CM) frame. In the CM frame, the centre of mass of the system consisting of the incident particle and the target is at rest before the collision and remains at rest after the collision. This simplifies calculations significantly because the total momentum of the system is zero in this frame, allowing one to treat the scattering problem symmetrically. For example, in the CM frame, the magnitudes of the momenta of the two particles before and after the collision are equal for elastic scattering, and the dynamics reduce to a simpler two-body problem. Consequently, many analytical and computational methods, including partial wave analysis and Born approximation, are formulated in the CM frame. This makes it easier to derive expressions for the scattering amplitude, differential cross section, and other observables.

To compare experimental measurements taken in the lab frame with theoretical predictions made in the CM frame, one must carefully transform the relevant quantities between frames. These transformations include converting scattering angles, particle velocities, and momenta from the CM frame to the lab frame, or vice versa. For a two-body elastic collision, the relationship between the scattering angle in the lab frame and the corresponding angle in the CM frame can be derived using vector addition of momenta and the conservation of energy and momentum. Similarly, the velocities of scattered particles in one frame are related to those in the other frame through Galilean transformations in non-relativistic mechanics or Lorentz transformations in relativistic regimes. Understanding these transformations is crucial for interpreting experimental data and ensuring that comparisons between theory and experiment are meaningful.

It is important to note that the total cross section, denoted by $\sigma$, is invariant between the two frames. This invariance arises because the total cross section represents the total number of scattering events that occur, integrated over all angles, and this total number does not depend on the frame of observation. Whether the experiment is observed in the lab frame or analyzed in the CM frame, the overall probability of scattering remains the same, reflecting the physical fact that collisions occur independently of the observer's reference frame.

In contrast, the differential cross section, $\frac{d\sigma}{d\Omega}$, is generally frame-dependent, because the scattering angles themselves are different in the lab and CM frames. The scattering angle $\theta$in the lab frame corresponds to a different direction than the scattering angle in the CM frame, due to the motion of the center of mass. As a result, while the shape of the angular distribution and the number of particles scattered into a given solid angle depend on the frame of reference, the total probability of scattering, integrated over all angles, remains unchanged. Therefore, careful transformation of differential cross sections is essential for comparing theory, usually derived in the CM frame, with measurements made in the lab frame.

In summary, scattering experiments are naturally performed in the lab frame, where the target is at rest and projectiles move towards it. Theoretical calculations are simplified in the CM frame, where the total momentum is zero. Transformations between these frames are necessary to connect theory with experiment. While the total cross section remains invariant between frames, the differential cross section depends on the choice of frame due to differences in scattering angles. Understanding these relationships is fundamental to accurately analysing and interpreting scattering experiments and their theoretical descriptions.

## 7.2 SCATTERING OF WAVE PACKET

### Scattering of a Wave Packet

When a localized wave packet interacts with a potential $V(r)$, the scattering process is described by the time-dependent Schrödinger equation. Unlike a plane wave, which extends infinitely in space and has a single momentum, a wave packet is a superposition of plane waves with different momenta. This superposition allows the wave packet to be localized in space, representing a particle with a finite probability distribution rather than a perfectly delocalized state.

Mathematically, the incident wave packet can be written as

$$\Psi_{\text{inc}}(r,t) = \int a(k)\, e^{i(k\cdot r-\omega_k t)}\, d^3k$$

where $a(k)$is the amplitude corresponding to the momentum $k$, representing the momentum distribution of the packet, and $\omega_k = \frac{\hbar k^2}{2m}$is the energy associated with each plane wave component. The wave packet has a finite width in space, which leads to a spread in momentum space according to the Fourier relationship. A narrower packet in real space corresponds to a wider spread in momentum, and vice versa.

When the wave packet encounters a scattering potential, different momentum components are scattered differently, leading to a modified wavefunction after interaction. The scattered wave is generally a combination of transmitted, reflected, and deflected components, depending on the shape and strength of the potential. Observables such as the scattering probability, differential cross section, and angular distribution can be extracted by analyzing the scattered wave packet.

Wave packet scattering provides a more realistic description of physical particles in experiments compared to idealized plane waves. It allows for the study of time-dependent effects, finite-size effects, and the localization of particles during interactions. Additionally, it connects naturally with experimental measurements, as detectors respond to particles localized in space rather than infinite plane waves. Therefore, understanding wave packet scattering is crucial for bridging theoretical models with realistic scattering experiments.

**Scattered Wave Packet**

In quantum mechanics, a particle is often represented by a localized wave packet rather than an idealized plane wave. This wave packet is a superposition of plane waves with different momenta, allowing it to be localized in space. When such a wave packet interacts with a potential $V(r)$, the scattering process is described by the time-dependent Schrödinger equation, and the total wavefunction of the system after interaction is expressed as:

$$\Psi(r,t) = \Psi_{\text{inc}}(r,t) + \Psi_{\text{sc}}(r,t)$$

Here, $\Psi_{\text{inc}}(r,t)$is the incident wave packet, representing the particle approaching the scattering potential, and $\Psi_{\text{sc}}(r,t)$is the scattered wave packet, representing the particle after interaction with the potential. The scattered component carries information about how the potential has modified the momentum and spatial distribution of the particle.
At large distances from the scattering center ($r \to \infty$), the scattered wave packet assumes an asymptotic form, which can be written as:

$$\Psi_{\text{sc}}(r,t) \sim \frac{e^{ikr}}{r} \int f(\mathbf{k}',\mathbf{k})\, a(\mathbf{k})\, e^{-i\omega_k t}\, d^3k$$

In this expression, $f(\mathbf{k}',\mathbf{k})$is the scattering amplitude, which depends on both the incident momentum $\mathbf{k}$and the potential $V(r)$. The function $a(\mathbf{k})$is the momentum distribution of the incident wave packet, and $\omega_k = \frac{\hbar k^2}{2m}$is the energy associated with each momentum component. The scattering amplitude encodes the effect of the potential on each plane-wave component of the incident packet, including the angular dependence and the strength of scattering.

The scattered wave packet remains localized in space, reflecting the localized nature of the incident particle. However, as time progresses, the packet spreads due to the different momentum components in the superposition. This spreading is a natural consequence of quantum mechanics and is dictated by the Fourier transform relationship between position and momentum space.

**Differential Cross Section for Wave Packets**

The probability for the wave packet to scatter into a solid angle $d\Omega$is given by:

$$\frac{dP}{d\Omega} = \int \mid f(\mathbf{k}', \mathbf{k}) \mid^2 \quad \mid a(\mathbf{k}) \mid^2 \; d^3k$$

This formula accounts for the contribution of each momentum component of the incident wave packet to the scattered wave. For a wave packet that is narrow in momentum space (quasi-monochromatic), the momentum distribution $a(\mathbf{k})$is sharply peaked around a central momentum $\mathbf{k}_0$. In such a case, the integral simplifies, and the differential scattering probability reduces to the familiar plane-wave result:

$$\frac{dP}{d\Omega} \approx \mid f(\mathbf{k}'_0, \mathbf{k}_0) \mid^2$$

This demonstrates that plane-wave scattering formulas, such as those derived from the Born approximation or partial wave analysis, can be applied approximately when the incident wave packet has a narrow momentum spread.

**Physical Interpretation of Scattered Wave Packets**

The wave packet approach provides several key insights into the scattering process that are not captured by idealized plane waves:

1. **Spatial Spread of the Packet:**
   The different momentum components of the wave packet cause it to spread over time. This spreading affects both the temporal duration and the spatial width of the scattered particle, giving rise to finite interaction times during collisions.

2. **Localized Scattering:**
   The scattered wave packet remains localized rather than becoming infinitely extended, preserving the particle-like interpretation of the quantum state. The direction and shape of the outgoing packet depend on the interplay between the incident packet's momentum distribution and the scattering potential.

3. **Applicability of Plane-Wave Formulas:**
   For narrow momentum distributions, the wave packet behaves approximately like a plane wave, allowing the use of standard scattering approximations, including the first-Born approximation and partial wave expansions. This bridge between wave packets and plane waves provides a practical method for connecting theoretical predictions with real experiments.

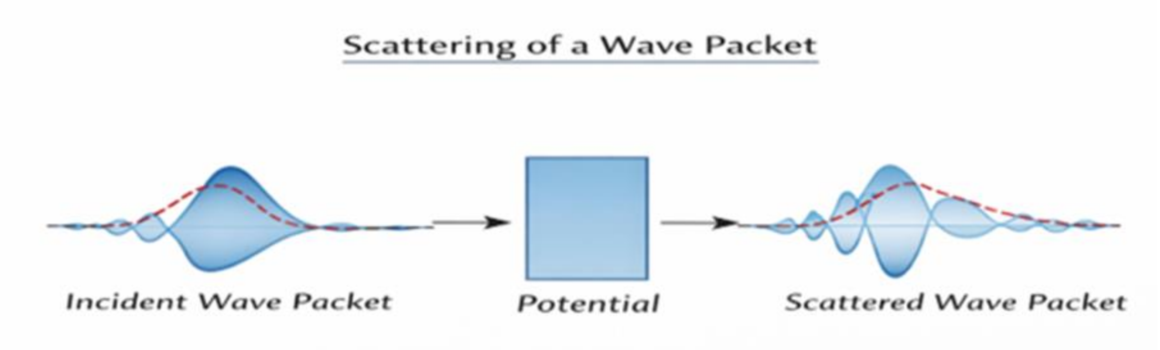
4. **Time-Dependent Behaviour:**
   Wave packet scattering captures the dynamic evolution of the particle, enabling the study of time-dependent phenomena such as tunnelling, resonance effects, and

transient scattering processes. Plane-wave approaches cannot describe these temporal aspects because plane waves are time-independent in terms of probability density.

**Applications of Wave Packet Scattering**

Wave packet scattering is widely used in modern quantum mechanics and experimental physics due to its ability to describe realistic particles:

1. **Electron and Neutron Scattering:**
   In experiments, electrons or neutrons are never perfect plane waves; they have finite spatial extents. Wave packet descriptions account for their localization, coherence properties, and temporal duration, improving the accuracy of theoretical predictions.
2. **Atom and Molecular Collisions:**
   When atoms or molecules collide, their wave packets provide a realistic picture of how interactions occur over finite distances and times, which is essential for calculating reaction rates, collision cross sections, and energy transfer probabilities.
3. **Quantum Optics:**
   Photons in optical experiments are often emitted as localized pulses rather than continuous plane waves. Wave packet theory is crucial for analyzing interference, diffraction, and photon scattering in cavities, waveguides, or free space.
4. **Time-Dependent Quantum Processes:**
   Wave packets allow the study of tunneling dynamics, resonances, and transient phenomena in quantum systems, offering insights into processes that cannot be described with stationary plane waves.
5. **Coherence and Decoherence:**
   The wave packet formalism is essential for understanding coherence effects in scattering, as well as decoherence due to interactions with the environment. It provides a framework for describing how initially localized states evolve and spread during scattering.



## 7.3 SCATTERING IN CONTINUOUS STREAM MODEL

In quantum mechanics, the scattering of particles by a potential is often described using wave mechanics, where the incident particle is treated as a wave interacting with a target. While single-particle plane-wave or wave-packet approaches provide a microscopic description of scattering, many practical experiments involve a large number of identical particles interacting with a target over a period of time. To describe such situations, the continuous stream model (also called the steady-flux model) is particularly useful. In this approach, the incident particle is modelled as a continuous stream or flux of particles moving towards a scattering centre, allowing for a probabilistic interpretation of scattering phenomena and a natural connection with measurable experimental quantities.

**Incident Stream**

In the continuous stream model, the incident beam is considered as a steady flow of particles with a uniform number density $n$and a uniform velocity $v$. The particles are identical, non-interacting before the collision, and the beam is assumed to be collimated such that the particles move in the same direction. The particle flux, $\Phi$, which represents the number of particles passing per unit area per unit time, is expressed as:

$$\Phi = nv$$

Here, $n$is the number of particles per unit volume, and $v$is the speed of the incident particles. The concept of particle flux provides a direct connection between the microscopic motion of particles and macroscopic measurable quantities like counting rates in scattering detectors. The wavefunction of the incident continuous stream is often approximated by a plane wave:

$$\psi_{\text{inc}}(r,t) = e^{i(\mathrm{k}\cdot\mathrm{r}-\omega t)}$$

where kis the wave vector, representing the momentum of the incident particle, and $\omega = \hbar k^2/2m$is the angular frequency corresponding to the particle's energy. This plane-wave description captures the coherent propagation of the incident flux and forms the basis for calculating scattering amplitudes in the quantum mechanical framework.

**Scattering Process**

As the particles in the continuous stream encounter the potential $V(r)$of the scattering center, they interact according to the Schrödinger equation. Each particle in the beam experiences the potential independently, producing a scattered wave that emanates from the scattering center. The scattered wave can be expressed as a spherical wave, whose amplitude depends on the interaction potential and the scattering angle:

$$\psi_{\text{sc}}(r) \sim f(\theta,\phi)\frac{e^{ikr}}{r}$$

Here, $f(\theta,\phi)$is the scattering amplitude, which encodes the angular dependence of scattering and the effect of the potential $V(r)$on the incident particle. The scattered wave is a coherent superposition of contributions from all incident particles, and for a sufficiently dilute beam, each particle's scattering event can be treated independently.

This representation highlights the essential feature of quantum scattering: the outgoing scattered wave carries information about both the incident flux and the potential, and the probability of scattering into a particular direction is proportional to the square of the scattering amplitude.

**Differential Cross Section**

The differential cross section is a central quantity in scattering theory, providing the probability per unit solid angle that a particle is scattered in a given direction. For the continuous stream model, it is defined as:

$$\frac{d\sigma}{d\Omega} = | f(\theta,\phi) |^2$$

This relation connects the microscopic scattering amplitude with an observable probability density. For an incident flux Φ, the number of particles scattered per unit time into a solid angle $d\Omega$is:

$$\frac{dN_{\text{sc}}}{dt} = \Phi\, d\sigma = \Phi \frac{d\sigma}{d\Omega} d\Omega$$

This equation establishes the direct link between the continuous particle flux, the interaction potential, and the measured scattering rates in detectors. By integrating over all solid angles, one obtains the total cross section, which represents the effective area of the target that contributes to scattering:

$$\sigma_{\text{total}} = \int \frac{d\sigma}{d\Omega} d\Omega$$

The total cross section can be interpreted as the sum of all scattering probabilities for particles in the continuous beam, providing a quantitative measure of the interaction strength between the incident particles and the target.

**Physical Interpretation**

The continuous stream model provides a macroscopic and probabilistic picture of scattering processes, bridging the gap between single-particle quantum mechanics and experimental observations. Several key physical insights emerge from this model:

1. Time-Averaged Measurement:
   The model is equivalent to a time-averaged view of many single-particle scattering events. Detectors record an average number of scattered particles per unit time, corresponding directly to the incident flux and the cross section.
2. Connection to Classical Concepts:
   Concepts like flux and impact parameter, familiar from classical mechanics, are naturally incorporated into the quantum description. The particle flux $\Phi = nv$serves as the bridge between microscopic wavefunctions and macroscopic particle currents.
3. Interpretation of Scattering Intensities:
   In beam experiments, the measured scattering intensities (for electrons, neutrons, or photons) can be understood in terms of the continuous stream model. The intensity in a particular direction is proportional to the differential cross section and the incident flux.
4. Bridge Between Micro and Macro:
   The model connects single-particle quantum dynamics with bulk experimental outcomes, allowing theoretical predictions of scattering amplitudes to be directly compared with measured particle counting rates.

**Applications of the Continuous Stream Model**

The continuous stream approach is widely used in experimental and theoretical physics:

1. Electron and Neutron Diffraction:
   Beams of electrons or neutrons are used to probe the structure of crystals and materials. The continuous stream model explains how scattering intensities are related to atomic arrangements and allows extraction of structural information.
2. Light Scattering:
   The scattering of photons by atoms, molecules, or colloidal particles is naturally described using the continuous stream model, which explains angular distributions and intensity patterns observed in experiments.

3. Nuclear and Particle Physics:
   High-energy experiments often involve continuous beams of protons, neutrons, or electrons interacting with targets. The model provides a framework for calculating cross sections and predicting reaction probabilities.
4. Quantitative Analysis of Experimental Data:
   By relating incident flux to scattering events, the model allows accurate determination of differential and total cross sections, which are fundamental parameters in analyzing collisions and interactions in both nuclear and atomic systems.

**Theoretical Implications**
From a theoretical standpoint, the continuous stream model provides an elegant and practical description of scattering in the ensemble limit, where individual particles are treated statistically. This approach also facilitates the application of approximation methods such as:

- Born Approximation: Treating the potential as weak to compute scattering amplitudes for each particle.
- Partial Wave Analysis: Decomposing the scattering amplitude into angular momentum components.
- Time-Dependent Scattering: Modeling wave packets as part of a continuous flux to study the temporal evolution of scattering events.

The continuous stream framework, therefore, serves as a unifying approach that connects single-particle quantum mechanics, statistical interpretations, and experimental observables, enabling a comprehensive understanding of scattering processes.

## 7.4 GREEN’S FUNCTION IN SCATTERING THEORY

In quantum scattering theory, the description of how a particle interacts with a potential is central to understanding observable phenomena such as differential cross sections, total cross sections, and scattering amplitudes. While the Schrödinger equation provides the exact foundation for quantum mechanics, directly solving it for scattering problems can be challenging, particularly when the interaction potential is complicated. To overcome this, the concept of Green’s functions is introduced, providing a powerful and compact mathematical tool for analyzing scattering phenomena. Green’s functions are especially useful in deriving approximate solutions, including the Born approximation, which is widely applied in elastic scattering problems such as electron-atom scattering.

**Schrödinger Equation in Scattering Form**
Consider a particle of mass $\mu$moving in a potential $V(r)$. The time-independent Schrödinger equation describing the particle is:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\psi(r) = E\psi(r)$$

To facilitate scattering calculations, it is convenient to rewrite the Schrödinger equation in a form that separates the free-particle motion from the interaction with the potential. Defining:

$$k^2 = \frac{2\mu E}{\hbar^2}, U(r) = \frac{2\mu}{\hbar^2} V(r)$$

the equation can be rewritten as:

$$(\nabla^2 + k^2)\psi(r) = U(r)\psi(r)$$

Here, the left-hand side represents the free-particle propagation, while the right-hand side encodes the influence of the scattering potential. This separation is fundamental because it allows us to treat the effect of the potential as a perturbation on the free-particle motion.

**Introduction to Green's Functions**

A Green's function is a mathematical construct that provides a solution to an inhomogeneous differential equation with a localized source. For the scattering problem, the Green's function $G(r, r')$is defined as the solution to:

$$(\nabla^2 + k^2)G(r, r') = -4\pi\delta(r - r')$$

where $\delta(r - r')$is the Dirac delta function, representing a point source at position $r'$. The delta function has the property that for any well-behaved function $g(r)$:

$$\int g(r)\delta(r - r')\, dr = g(r')$$

In other words, the delta function "picks out" the value of the function at a specific point. The Green's function thus represents the response of the system to a point source, which can then be used to construct the solution for an arbitrary source term.

**Particular Solution Using Green's Function**

Using the Green's function, one can formally express a particular solution of the inhomogeneous Schrödinger equation as an integral over the potential:

$$\psi(r) = -\frac{1}{4\pi} \int G(r, r')\, U(r')\, \psi(r')\, dr'$$

This integral equation is exact and expresses the wavefunction $\psi(r)$in terms of itself, the interaction potential $U(r')$, and the Green's function $G(r, r')$. To verify that this indeed satisfies the Schrödinger equation, we can operate with $(\nabla^2 + k^2)$on both sides:

$$\left(\nabla^2 + k^2)\psi(r) = -\frac{1}{4\pi} \int (\nabla^2 + k^2)G(r, r')\, U(r')\, \psi(r')\, dr' = \int \delta(r - r')\, U(r')\, \psi(r')\, dr' = U(r)\psi(r\right)$$

This confirms that the integral representation is equivalent to the original differential equation, provided the Green's function satisfies the defining equation.

**General Solution and Homogeneous Term**

The Schrödinger equation also has solutions to the homogeneous equation:

$$(\nabla^2 + k^2)\psi^{(0)}(r) = 0$$

These represent free-particle wavefunctions in the absence of the potential, such as plane waves or spherical waves. Including these solutions, the general solution of the scattering problem can be written as:

$$\psi(r) = \psi^{(0)}(r) - \frac{1}{4\pi}\int G(r,r')\, U(r')\, \psi(r')\, dr'$$

This equation is known as the integral scattering equation. It has several important features:

1. It incorporates both the free motion and the scattering due to the potential.
2. The boundary conditions of the scattering problem are implicitly included in the choice of Green's function.
3. It provides a natural starting point for approximations and numerical solutions.

**Outgoing Green's Function and Boundary Conditions**

In scattering problems, it is important to select a Green's function that satisfies the physical boundary conditions. For elastic scattering, the relevant choice is the outgoing Green's function, which corresponds to a spherical wave radiating away from the scattering center:

$$G(r,r') = \frac{e^{ik|r-r'|}}{|\, r - r'\, |}$$

This ensures that the scattered wave moves outward from the target, consistent with the physical requirement that no waves are incoming from infinity. Using this Green's function, the formal solution becomes:

$$\psi(r) = \psi^{(0)}(r) - \frac{1}{4\pi}\int \frac{e^{ik|r-r'|}}{|\, r - r'\, |}\, U(r')\, \psi(r')\, dr'$$

This integral equation forms the backbone of scattering theory. It elegantly transforms the problem from a differential equation with complex boundary conditions into an integral equation where all boundary conditions are automatically included in the choice of Green's function.

**Advantages of the Integral Formulation**

While integral equations are often more challenging to solve exactly than differential equations, they offer several advantages in scattering theory:

1. Compact Representation:
   The Green's function formulation encapsulates both the potential and the boundary conditions in a single integral.
2. Basis for Approximations:
   The integral equation is ideally suited for perturbative approximations, such as the Born approximation, which is widely used in weak-potential scattering problems.
3. Adaptable to Various Potentials:
   The formalism applies to any potential $U(r)$, whether short-range, long-range, central, or non-central, making it extremely flexible.
4. Direct Relation to Scattering Amplitudes:

The scattering amplitude $f(\theta,\phi)$and differential cross sections can be obtained directly from the integral form, providing a bridge between theory and experiment.

**Connection to the Born Approximation**

The Born approximation arises naturally from the Green's function formulation. In the first-order Born approximation, the wavefunction $\psi(r')$inside the integral is replaced by the incident wave $\psi^{(0)}(r')$, yielding:

$$\psi(r) \approx \psi^{(0)}(r) - \frac{1}{4\pi} \int \frac{e^{ik|r-r'|}}{|\, r - r'\,|} U(r')\, \psi^{(0)}(r')\, dr'$$

This simplification is valid when the potential is weak, so that multiple scattering events are negligible. The resulting scattering amplitude is given by the Fourier transform of the potential, connecting the microscopic interaction with experimentally observable quantities.

## 7.5 SUMMARY

This chapter covered the essentials of quantum scattering theory, which explains how particles interact with potentials and how to quantify these interactions. A key concept is the cross section, which measures the probability of scattering. The differential cross section gives the likelihood of scattering into a specific direction, while the total cross section represents the overall interaction probability, providing a direct link between theory and experiment.

Wave packet scattering describes realistic particles with finite spatial extent and momentum spread. When such a packet interacts with a potential, the scattered wave depends on both the shape of the packet and the interaction, capturing time-dependent effects like spreading and localization. This approach gives a more accurate picture than ideal plane waves and is essential for studying tunneling, collisions, and resonances.

The continuous stream model extends the description to particle beams, treating particles as a steady flux. It connects the scattering amplitude to measurable quantities such as particle flux and scattering rates, allowing a practical interpretation of experimental data.

Finally, Green's functions provide a formal solution to the Schrödinger equation with proper boundary conditions. They allow the scattered wave to be expressed in terms of the incident wave and potential, forming the foundation for approximation methods like the Born approximation. Together, these concepts unify the understanding of elastic and inelastic scattering in quantum systems.

## 7.6 TECHNICAL TERMS

Introduction of Scattering - notion of Cross section, Scattering of Wave packet
Scattering in continuous stream model, Green's function in scattering theory.

## 7.7 SELF-ASSESSMENT QUESTIONS

1. Write the theory of scattering in continuous stream model.
2. Discuss the Green's function in scattering theory.
3. Write the scattering theory of wave packet.

## 7.8 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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# LESSON 8

# BORN-APPROXIMATION

**Aim and Objectives**

The aim of this chapter is to develop a thorough understanding of the Born Approximation, an important method in quantum scattering theory. This approximation provides a practical approach to solving scattering problems when the interaction potential between the incident particle and the target is sufficiently weak. By replacing the exact scattered wave with the incident wave in the integral form of the Schrödinger equation, the Born Approximation simplifies the calculation of scattering amplitudes while preserving the essential physics of the process.

The chapter introduces the first-order Born approximation, which corresponds to the initial iteration of the integral equation, as well as higher-order corrections that account for multiple scattering effects. Explicit expressions for the scattering amplitude and differential cross sections are derived, showing their dependence on the Fourier transform of the potential and the momentum transfer.

A key focus is the criteria for validity, emphasizing that the approximation is reliable when the potential energy is small compared to the kinetic energy of the incoming particle, and higher-order contributions are negligible. The method is then applied to simple, analytically solvable potentials, allowing a direct comparison between theoretical predictions and experimental measurements.

By the end of this chapter, students will understand the utility, limitations, and practical implementation of the Born Approximation, providing a foundation for analysing weak scattering phenomena in atomic, molecular, and nuclear physics.

**STRUCTURE OF THE LESSON:**

## 8.1 BORN -APPROXIMATION

### Introduction

The Born approximation is a fundamental concept in quantum mechanical scattering theory, providing a practical method for calculating the scattering amplitude when an exact solution of the Schrödinger equation is difficult or impossible to obtain. Scattering theory itself is concerned with understanding how particles, such as electrons, neutrons, or atoms, interact with a potential field, such as the electric field of a nucleus or the interatomic potential in molecules. Exact solutions of the time-independent Schrödinger equation are generally available only for a few idealized potentials, such as the Coulomb potential or the square well. For most realistic potentials, an approximate method is required to predict scattering behaviour, and the Born approximation provides one such method.

The Born approximation is particularly useful for weak potentials, where the interaction between the incident particle and the scattering centre perturbs the wavefunction only slightly. This approach converts the complex problem of solving a differential equation into a manageable integral formulation, allowing direct computation of scattering amplitudes, cross sections, and other measurable quantities. Its simplicity and physical transparency make it a cornerstone of scattering theory and a widely used tool in atomic, molecular, and nuclear physics.

**Physical Assumption**

The fundamental assumption underlying the Born approximation is that the scattering potential **V(r)** causes only a small perturbation to the incident wave. In other words, the incident particle essentially “sees” the potential as a minor modification to its motion rather than a strong influence that significantly changes its trajectory. Mathematically, this assumption allows one to replace the exact scattered wavefunction inside the integral form of the Schrödinger equation with the incident plane wave.

Because the potential is weak, the scattered wave is much smaller in amplitude than the incident wave, and the probability of multiple scattering events—where the particle interacts more than once with the potential—is negligible. This assumption also implies that the interaction energy is small compared to the kinetic energy of the particle. Physically, this is often the case for high-energy particles or for potentials that decrease rapidly with distance, such as short-range nuclear or molecular potentials.

This weak-scattering assumption is essential because it allows a first-order perturbative treatment of the scattering problem. Higher-order contributions can be included, but they are usually small and can be neglected in the first approximation. By focusing on the first-order effect, the Born approximation gives an accurate estimate of the scattering amplitude while keeping the calculations tractable.

**Scattering Amplitude**

The **scattering amplitude**, denoted as $f(\theta,\phi)$, is the central quantity in scattering theory. It contains all the information about the angular distribution and intensity of the scattered particles. In the Born approximation, the scattering amplitude is expressed as the Fourier transform of the scattering potential, reflecting how the structure of the potential determines the scattering pattern:

$$f(\theta,\phi) = -\frac{2m}{\hbar^2}\int e^{i\mathbf{q}\cdot\mathbf{r}} V(\mathbf{r}) d^3r$$

Here, $\mathrm{q} = \mathrm{k}_0 - \mathrm{k}$is the momentum transfer vector, representing the difference between the incident momentum $\mathrm{k}_0$and the scattered momentum k. The scattering amplitude depends not only on the potential but also on the angle of scattering, as encoded in q.

This expression highlights the physical interpretation of the Born approximation: the angular distribution of scattered particles is directly related to the spatial structure of the potential. Sharp features in the potential, such as abrupt changes or localized regions, produce wide-angle scattering, while smooth or long-range potentials produce forward-peaked scattering. For spherically symmetric potentials, the integral simplifies, and the scattering amplitude depends only on the magnitude of the momentum transfer, reducing the computational complexity.

The Born approximation therefore provides a direct link between microscopic properties of the potential and macroscopic observables measured in experiments, such as scattering patterns and angular distributions.

**Differential Cross Section**

The differential cross section is defined as the probability of a particle being scattered into a given solid angle $d\Omega$. In the Born approximation, it is obtained as the square of the magnitude of the scattering amplitude:

$$\frac{d\sigma}{d\Omega} = | f(\theta, \phi) |^2$$

This quantity represents a fundamental observable in scattering experiments. It tells us how many particles are scattered per unit solid angle in a given direction relative to the incident beam. Since the scattering amplitude encodes the effects of the potential and the momentum transfer, the differential cross section provides a direct measurable signature of the potential. For spherically symmetric potentials, the differential cross section simplifies further and can often be expressed in analytical forms for simple potentials like square wells or Yukawa potentials. In experimental settings, measuring the angular distribution of scattered particles allows physicists to reconstruct information about the potential, making the Born approximation a practical tool for interpreting experimental data.

The total cross section can then be obtained by integrating the differential cross section over all solid angles:

$$\sigma_{\text{total}} = \int \frac{d\sigma}{d\Omega} d\Omega$$

The total cross section represents the effective "area" of the target that contributes to scattering and is directly related to the overall probability of a scattering event occurring.

**Applications and Limitations**

The Born approximation is widely used in electron-atom scattering, neutron scattering, and X-ray scattering, especially when the interaction is weak or the particles are high in energy. Its simplicity allows for analytical calculations and a clear physical interpretation of experimental results.

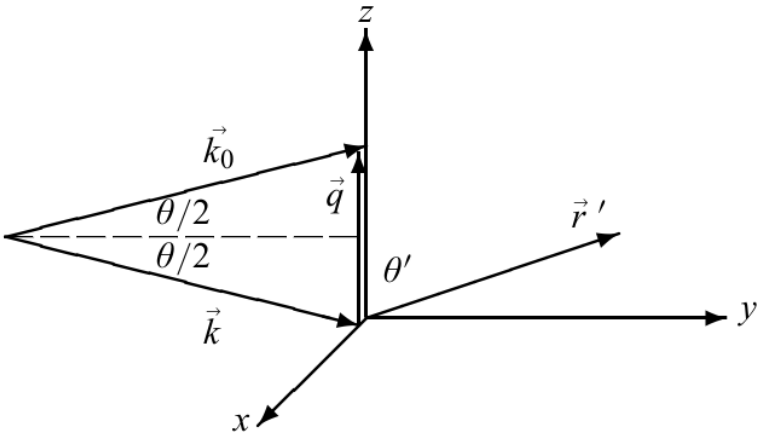
However, the approximation has limitations. It is valid only when the potential is weak and the kinetic energy of the incident particle is sufficiently high. For strong potentials, such as low-energy nuclear interactions or Coulomb scattering at small energies, higher-order contributions cannot be neglected, and the Born approximation may fail. In such cases, alternative methods, such as partial wave analysis, must be used.

## 8.2 FIRST ORDER APPROXIMATION

In quantum scattering, when a particle encounters a potential $V(\mathrm{r})$, its motion is governed by the Schrödinger equation. If the potential is weak, it perturbs the incident particle only slightly, producing a scattered wave that differs only minimally from the incident plane wave. This scenario is addressed by the First-Born Approximation, which provides a practical method to calculate the scattering amplitude under such weak-interaction conditions.

Mathematically, the First-Born Approximation arises as the first-order solution of the integral form of the Schrödinger equation. In this approach, the exact scattered wavefunction inside the integral is replaced by the incident plane wave. This simplification reduces a complex scattering problem to a manageable calculation, allowing the scattering amplitude to be expressed as the Fourier transform of the potential.

The approximation is particularly useful for high-energy particles or short-range potentials, where the first-order contribution dominates and higher-order effects can be neglected. It forms the foundation for understanding differential and total cross sections in many scattering experiments.



Momentum transfer for elastic scattering: $q = |\vec{k}_0 - \vec{k}| = 2k\sin(\theta/2)$, $k_0 = k$.

In quantum mechanics, scattering processes describe the interaction of an incident particle with a potential, which may represent an atom, nucleus, or any localized scattering center. A fundamental approach to solving scattering problems, particularly when the interaction is weak, is the First-Born Approximation. This method simplifies the solution of the Schrödinger equation by assuming that the potential only slightly perturbs the incident particle, allowing the scattered wavefunction to be approximated in terms of the incident plane wave.

Incident Wavefunction

Consider an incident particle moving towards a scattering center. The particle is represented by a plane wave, which is an eigenfunction of the momentum operator:

$$\psi_{\mathrm{inc}}(\mathrm{r}) = e^{i\mathrm{k}_0\cdot\mathrm{r}} \qquad (1)$$

Here, $\mathrm{k}_0$is the incident wave vector, and $\hbar\mathrm{k}_0$is the incident momentum. The plane wave is an idealized representation of a particle with definite momentum and infinite spatial extent, which is a standard starting point in scattering theory. In a more realistic description, one can use a localized wave packet, but the plane-wave assumption simplifies analytical calculations.

Scattered Wavefunction (First Born Approximation)

The total wavefunction for the particle after interacting with a potential $V(\mathrm{r})$can be written as:

$$\psi(\mathrm{r}) = \psi_{\mathrm{inc}}(\mathrm{r}) + \frac{2m}{\hbar^2}\int \frac{e^{ik|\mathrm{r}-\mathrm{r}'|}}{|\,\mathrm{r}-\mathrm{r}'\,|} V(\mathrm{r}')\psi_{\mathrm{inc}}(\mathrm{r}')\, d^3r' \qquad (2)$$

This is the integral form of the Schrödinger equation, where the first term represents the incident plane wave, and the second term accounts for the scattered wave. The integral kernel $e^{ik|\mathrm{r}-\mathrm{r}'|}/|\,\mathrm{r}-\mathrm{r}'\,|$represents a spherical outgoing wave, satisfying the proper boundary condition at infinity.

The First-Born Approximation is obtained by assuming that the potential is weak, so that $\psi(\mathrm{r}')$inside the integral can be replaced by the incident plane wave $\psi_{\mathrm{inc}}(\mathrm{r}')$. This first iteration provides a simple yet accurate solution for weak scattering potentials.

$$\psi(\mathrm{r}) \approx \psi_{\mathrm{inc}}(\mathrm{r}) + \frac{2m}{\hbar^2}\int \frac{e^{ik|\mathrm{r}-\mathrm{r}'|}}{|\,\mathrm{r}-\mathrm{r}'\,|} V(\mathrm{r}')\psi_{\mathrm{inc}}(\mathrm{r}')\, d^3r'$$

Scattering Amplitude

The scattering amplitude $f(\theta,\phi)$is a central quantity in scattering theory. It describes the angular distribution of scattered particles and is directly related to measurable quantities such as differential cross sections. In the First-Born Approximation, the scattering amplitude is expressed as:

$$f(\theta,\phi) = -\frac{2m}{\hbar^2}\int e^{-i\mathrm{k}\cdot\mathrm{r}} V(\mathrm{r})\psi_{\mathrm{inc}}(\mathrm{r})\, d^3r \qquad (3)$$

Substituting $\psi_{\mathrm{inc}}(\mathrm{r}) = e^{i\mathrm{k}_0\cdot\mathrm{r}}$, we obtain:

$$f(\theta,\phi) = -\frac{2m}{\hbar^2}\int e^{i(\mathrm{k}_0-\mathrm{k})\cdot\mathrm{r}} V(\mathrm{r})\, d^3r \qquad (4)$$

Here, $\mathrm{k}_0$and $\mathrm{k}$are the incident and scattered wave vectors, respectively.

Momentum Transfer

Defining the momentum transfer vector:

$$\mathrm{q} = \mathrm{k}_0 - \mathrm{k}$$

the scattering amplitude can be compactly written as:

$$f(\theta,\phi)=-\frac{2m}{\hbar^2}\int e^{i\mathrm{q}\cdot\mathrm{r}}V(\mathrm{r})\,d^3r \qquad (5)$$

This demonstrates a profound result: the scattering amplitude in the Born approximation is the Fourier transform of the potential. The momentum transfer $\hbar$qrepresents the change in the particle's momentum due to the scattering event.

Differential Scattering Cross Section

The differential cross section, which represents the probability of scattering into a specific solid angle, is given by the square of the scattering amplitude:

$$\frac{d\sigma}{d\Omega}=\mid f(\theta,\phi)\mid^2$$

Substituting the Fourier-transformed amplitude:

$$\frac{d\sigma}{d\Omega}=\frac{4m^2}{\hbar^4}\mid\int e^{i\mathrm{q}\cdot\mathrm{r}}V(\mathrm{r})\,d^3r\mid^2 \qquad (6)$$

This general expression forms the basis for calculating cross sections for a variety of potentials, from short-range atomic potentials to long-range Coulomb interactions.

Elastic Scattering

For elastic scattering, the magnitude of the incident and scattered momenta are equal: $\mid \mathrm{k}_0\mid=\mid\mathrm{k}\mid=k$. The momentum transfer is then related to the scattering angle $\theta$by:

$$q=\mid\mathrm{k}_0-\mathrm{k}\mid=2k\sin\frac{\theta}{2}$$

$$q=\sqrt{k_0^2+k^2-2k_0k\cos\theta}=2k\sin\left(\frac{\theta}{2}\right) \qquad (7)$$

This geometrical relation is critical for evaluating the scattering amplitude and cross section for isotropic or spherically symmetric potentials.

Spherically Symmetric Potential

For a spherically symmetric potential, $V(\mathrm{r})=V(r)$, the problem simplifies due to rotational symmetry. Choosing the $z$-axis along q, we have $\mathrm{q}\cdot\mathrm{r}=qr\cos\theta$. The volume integral becomes:

$$\int e^{i\mathrm{q}\cdot\mathrm{r}}V(r)\,d^3r=\int_0^\infty r^2\,V(r)dr\int_0^\pi e^{iqr\cos\theta}\sin\theta d\theta\int_0^{2\pi}d\phi$$

Performing the angular integration yields:

$$\int e^{i\mathrm{q}\cdot\mathrm{r}}V(r)\,d^3r=4\pi\int_0^\infty r^2\,V(r)\frac{\sin(qr)}{qr}\,dr \qquad (8)$$

Scattering Amplitude and Differential Cross Section

The scattering amplitude for a spherically symmetric potential is:

Type equation here.

$$f(\theta)=-\frac{2m}{\hbar^2 q}\int_0^\infty rV(r)\sin(qr)\,dr \qquad (9)$$

Substituting into the formula for the differential cross section, we obtain:

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 m^2}{\hbar^4 q^2}\left[\int_0^\infty r\,V(r)\sin\,(qr)\,dr\right]^2 \qquad (10)$$

This expression shows explicitly that, for spherically symmetric potentials, the differential cross section depends only on the momentum transfer $q$and, therefore, on the scattering angle $\theta$.

Physical Interpretation

The First-Born Approximation provides a clear physical picture:

1. The incident plane wave is only slightly perturbed by the potential, producing a scattered spherical wave.
2. The scattering amplitude is the Fourier transform of the potential, showing how different spatial components of the potential contribute to scattering at different angles.
3. For elastic scattering, the magnitude of momentum is conserved, and the scattering angle determines the momentum transfer.

Validity of the First Born Approximation

The approximation is valid under certain conditions:

- The potential $V(r)$must be weak compared to the kinetic energy of the incident particle.
- Multiple scattering events must be negligible.
- The incident particle energy should be high enough that the first-order term dominates over higher-order contributions.

Under these conditions, the First Born Approximation accurately predicts scattering amplitudes, differential, and total cross sections.

Applications

The First-Born Approximation is widely used in:

- Electron-atom scattering in atomic physics.
- Neutron scattering in condensed matter studies.
- X-ray scattering in crystallography.
- High-energy particle physics, where interactions are weak or short-ranged.

Its simplicity allows straightforward connection between theory and experimental observations, making it a cornerstone of quantum scattering theory.

## 8.3 CRITERIA FOR THE VALIDITY OF BORN APPROXIMATION

The First-Born Approximation provides a simplified solution to scattering problems by assuming that the scattered wave is only a small perturbation to the incident plane wave. However, this approximation is only valid under certain conditions that ensure that higher-order corrections to the wavefunction are negligible. Understanding these conditions is crucial for applying the approximation correctly.

Condition for Validity

The total wavefunction in the First-Born Approximation is given by the integral expression:

$$\psi(\mathrm{r}) = \psi_{\mathrm{inc}}(\mathrm{r}) + \frac{2m}{\hbar^2}\int \frac{e^{ik|\mathrm{r}-\mathrm{r}'|}}{|\,\mathrm{r}-\mathrm{r}'\,|} V(\mathrm{r}')\psi_{\mathrm{inc}}(\mathrm{r}')\, d^3r'$$

For the approximation to be valid, the second term—which represents the scattered wave—must be much smaller than the incident wave $\psi_{\mathrm{inc}}(\mathrm{r})$. Mathematically, this condition is expressed as:

$$|\,\frac{2m}{\hbar^2}\int \frac{e^{ik|\mathrm{r}-\mathrm{r}'|}}{|\,\mathrm{r}-\mathrm{r}'\,|} V(\mathrm{r}')e^{i\mathrm{k}_0\cdot\mathrm{r}'}\, d^3r'\,| \ll |\,\psi_{\mathrm{inc}}(\mathrm{r})\,|^2 \qquad (11)$$

Simplification Using Incident Wavefunction

The incident wavefunction is a plane wave:

$$\psi_{\mathrm{inc}}(\mathrm{r}) = e^{i\mathrm{k}_0\cdot\mathrm{r}}$$

which has unit magnitude ($|\,\psi_{\mathrm{inc}}\,| = 1$). Using this, the validity condition simplifies to:

$$|\,\frac{2m}{\hbar^2}\int \frac{e^{ik|\mathrm{r}-\mathrm{r}'|}}{|\,\mathrm{r}-\mathrm{r}'\,|} V(\mathrm{r}')e^{i\mathrm{k}_0\cdot\mathrm{r}'}\, d^3r'\,| \ll 1 \qquad (12)$$

This inequality provides a general quantitative criterion: the integral of the potential weighted by the phase factor must be small compared to unity.

Elastic Scattering Approximation

For elastic scattering, the incident and scattered momenta have nearly equal magnitudes ($k_0 \approx k$). If the scattering potential $V(r)$is localized, meaning it is significant only near $r = 0$, the integral can be simplified in spherical coordinates:

$$|\,\frac{m}{\hbar^2}\int_0^\infty r\, e^{ikr}V(r)\, dr \int_0^\pi e^{ikr\cos\theta}\sin\theta\, d\theta\,| \ll 1 \qquad (13)$$

Here, the angular integral accounts for the contribution of all directions of scattering, while the radial integral represents the potential's effect over space.

Further Simplification

Performing the angular integration yields a simpler condition:

$$|\,\frac{m}{\hbar^2 k}\int_0^\infty V(r)(\,e^{2ikr} - 1)\, dr\,| \ll 1 \qquad (14)$$

This shows that the dimensionless quantity formed by the ratio of the potential's effect to the incident kinetic energy must be small. The factor $1/k$indicates that higher particle momentum reduces the effect of the potential, making the approximation more accurate.

Physical Interpretation

The energy of the incident particle is purely kinetic:

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

Since $E_i \propto k^2$, the inequalities above imply that the Born Approximation is valid when:

1. High Incident Energy: A larger $k$increases the particle's kinetic energy, making the effect of the potential smaller in comparison.

2. Weak Scattering Potential: The magnitude of $V(r)$must be small enough that the scattered wave remains a perturbation.

In other words, the average interaction energy between the particle and the potential should be much smaller than the particle's kinetic energy. When this condition is satisfied, the particle effectively moves as a free plane wave, and the scattered wave remains a small correction.

## 8.4 FORM FACTOR SCATTERING

In scattering theory, the concept of the form factor is fundamental when the scattering object possesses a finite spatial extent or an internal structure. While idealized point scatterers provide a simple model for basic scattering calculations, real physical systems such as atoms, molecules, nuclei, and nanoparticles have distributed charge or mass densities. These distributions significantly affect the scattering pattern, as each part of the scatterer contributes to the interference of the scattered waves. The form factor is introduced to account for these effects, allowing a quantitative link between the scattering amplitude and the internal structure of the target.

### 1. Scattering Amplitude in the First-Born Approximation

Within the framework of the First-Born approximation, the scattering amplitude for a particle interacting with a weak potential $V(\mathbf{r})$is obtained using the Fourier transform of the potential:

$$f(\mathbf{q}) = -\frac{2m}{\hbar^2}\int e^{i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r})\,d^3r \qquad (1)$$

Here:

- $\mathrm{q} = \mathrm{k}_0 - \mathrm{k}$is the momentum transfer vector,
- $\hbar\mathrm{k}_0$and $\hbar\mathrm{k}$are the incident and scattered momenta, respectively,
- $m$is the mass of the incident particle, and
- $\hbar$is the reduced Planck constant.

Equation (1) shows that the scattering amplitude depends directly on the Fourier components of the potential. This dependence implies that scattering measurements can probe the spatial structure of the target, because the Fourier transform encodes information about the distribution of potential within the object.

**Definition of the Form Factor**

If the scattering potential $V(\mathbf{r})$is proportional to a spatial density distribution $\rho(\mathrm{r})$, such that $V(\mathrm{r}) \propto \rho(\mathrm{r})$, the form factor $F(\mathrm{q})$is defined as:

$$F(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}}\rho(\mathbf{r})\,d^3r \qquad (2)$$

Thus, the scattering amplitude can be expressed in terms of the form factor:

$$f(\mathbf{q}) \propto F(\mathbf{q}) \qquad (3)$$

Consequently, the differential scattering cross section is given by the square of the scattering amplitude:

$$\frac{d\sigma}{d\Omega} = | f(\mathrm{q}) |^2 \propto | F(\mathrm{q}) |^2 \qquad (4)$$

Equation (4) indicates that the measured scattering intensity is directly related to the square of the form factor. Therefore, experimental scattering patterns provide immediate information about the internal distribution of mass or charge in the target. The stronger the variations in the form factor, the more detailed information can be extracted regarding the internal structure.

**Physical Interpretation of the Form Factor**

The form factor has a clear physical meaning. It represents the interference of waves scattered from different regions of the object. Each point inside the scatterer acts as a secondary source of scattered waves. Depending on their relative phases, these waves can interfere constructively or destructively, altering the scattering amplitude observed at a detector.

1. **Small momentum transfer ($q \to 0$)**: All parts of the object scatter coherently, and the form factor approaches the total scattering strength. In this regime, the object behaves approximately like a point scatterer.
2. **Large momentum transfer ($q$ increases)**: The phase differences between waves scattered from different regions become significant, leading to oscillatory behaviour and decay of the form factor. These oscillations carry detailed information about the internal spatial distribution of density or charge.

The form factor, therefore, acts as a bridge between microscopic structure and macroscopic scattering measurements. It encodes the size, shape, and internal features of the scatterer.

**Form Factor for Spherically Symmetric Systems**

In many cases, the scatterer is spherically symmetric, meaning that the density depends only on the radial distance: $\rho(\mathrm{r}) = \rho(r)$. Choosing the z-axis along the momentum transfer vector q, the dot product simplifies to $\mathrm{q} \cdot \mathrm{r} = qr\cos\theta$. The form factor reduces to a one-dimensional radial integral:

$$F(q) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin(qr)}{qr} \, dr \tag{5}$$

Equation (5) is extensively used in nuclear physics, atomic scattering, and small-angle scattering experiments with nanoparticles or molecular clusters. The factor $\sin(qr)/(qr)$arises naturally from the angular integration and accounts for the interference of waves scattered from different radial shells of the object.

**Examples of Spherical Form Factors**

1. **Uniform sphere of radius $R$**:

$$\rho(r) = \begin{cases} \rho_0, & r \le R \\ 0, & r > R \end{cases}$$

This yields:

$$F(q) = 3\rho_0 \frac{\sin(qR) - qR\cos(qR)}{(qR)^3}$$

The scattering amplitude shows oscillatory patterns, with zeros corresponding to destructive interference from different regions of the sphere.

2. **Gaussian density distribution**:

$$\rho(r) = \rho_0 e^{-r^2/2\sigma^2}$$

Then:

$$F(q) \propto e^{-q^2\sigma^2/2}$$

This produces a smooth decay in scattering intensity with increasing $q$, reflecting the gradual decrease in coherence across the distribution.

### Form Factor in Many-Body Systems

For systems containing multiple scatterers, such as liquids, glasses, or powders, the total scattering intensity depends on both the individual particle form factor and the spatial correlations between particles. This is expressed as:

$$I(q) \propto | F(q) |^2 S(q) \qquad (6)$$

where:

- $F(q)$is the form factor of a single particle, and
- $S(q)$is the structure factor, describing positional correlations among particles.

Here, the form factor provides information about the internal structure of individual particles, while the structure factor provides information about the collective arrangement.

### Applications of Form Factor Analysis

1. **X-ray Scattering**:
   Atomic electron density distributions are mapped using X-ray diffraction. The form factor decreases with scattering angle as the effective interference becomes less coherent.
2. **Neutron Scattering**:
   Nuclear densities of atoms or molecules are probed using neutron beams. Isotope-sensitive measurements can differentiate elements with similar electron densities.
3. **Electron Scattering**:
   High-energy electrons probe charge distributions within atoms, molecules, and condensed matter systems.
4. **Nanoparticle and Cluster Scattering**:
   Small-angle scattering experiments reveal particle size, shape, and internal density fluctuations.
5. **Biophysical Applications**:
   Proteins and macromolecules in solution can be characterized using X-ray or neutron scattering, providing structural information without requiring crystallization.

### Interpretation of Experimental Data

The square of the form factor, $| F(q) |^2$, determines the angular distribution of scattering intensity. By measuring intensity as a function of scattering angle (or momentum transfer $q$), experimentalists can extract:

- The overall size of the scatterer, from the decay of intensity at small $q$.
- Internal structure details, from oscillations in intensity at larger $q$.
- Surface or interface features, from deviations from idealized density models.

This makes form factor analysis an essential tool in experimental scattering physics.

## 8.5 SUMMARY

This section discussed the Born approximation, an important method in quantum scattering theory used to obtain approximate solutions when the interaction potential between the incident particle and the target is weak. The approach simplifies the scattering problem by replacing the exact scattered wavefunction with the incident wave, resulting in the first-order Born approximation. This leads to a straightforward expression for the scattering amplitude, which is proportional to the Fourier transform of the scattering potential. From this amplitude, one can directly calculate the differential cross section, representing the probability of scattering into a particular solid angle, as well as the total cross section, which gives the overall scattering probability. The validity of the Born approximation depends on the scattering potential being sufficiently weak and the kinetic energy of the incident particle being relatively high, so that the scattered wave is a small perturbation to the incident wave. Under these conditions, the Born approximation provides a reliable and practical tool for analyzing a wide range of physical scattering phenomena.

## 8.6 TECHNICAL TERMS

Born approximation, first-order Born approximation, validity of the Born approximation.

## 8.7 SELF-ASSESSMENT QUESTIONS

1. Explain the Born Approximation and first order born approximation in the scattering theory.
2. Write the validity of first-Born approximation.

## 8.8 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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## LESSON -9

# SQUARE WELL POTENTIAL

**Aim and objectives**

The aim of this chapter is to study the scattering of particles from a square well potential, which serves as a simple yet powerful model to illustrate the fundamental aspects of quantum scattering. This potential allows us to explore how particles interact with localized attractive or repulsive regions and provides insight into the behavior of realistic scattering systems. The chapter focuses on formulating the Schrödinger equation for a square well potential and solving it to determine the wavefunctions inside and outside the potential region. From these solutions, one can calculate important quantities such as the reflection and transmission coefficients, which quantify the probabilities of particles being reflected or transmitted by the potential. Additionally, the chapter examines scattering phase shifts, differential and total cross sections, and their dependence on energy and potential parameters. By comparing theoretical predictions with experimental scattering data, this model helps develop a deeper understanding of quantum scattering phenomena, resonance effects, and the principles underlying particle-wave interactions.

**STRUCTURE OF THE LESSON:**

## 9.1 SCATTERING FROM A SQUARE WELL POTENTIAL

### Introduction

Scattering theory is a fundamental part of quantum mechanics that describes how an incident particle interacts with a target potential and is deflected as a result of this interaction. It forms the basis for understanding a wide range of phenomena in nuclear physics, atomic physics, and condensed matter systems. Scattering experiments provide critical information about the nature of forces, potentials, and internal structure of the scattering centre.

Among the exactly solvable models in quantum scattering, the square-well potential holds a central place. Despite its simplicity, the square-well potential captures essential features of real physical systems, making it an excellent tool for teaching and research. It allows explicit calculation of key quantities such as phase shifts, differential and total cross sections, and

resonance behaviour. Furthermore, it provides a practical framework to test the validity of approximations such as the Born approximation, which assumes weak scattering potentials**.**
The square-well potential is especially important in low-energy scattering studies, where particles have energies comparable to the potential depth. Examples include neutron scattering from nuclei, electron scattering from atoms, and atom-atom collisions in cold gases. Understanding scattering from the square-well potential also provides insight into more complex potentials, as solutions can often be generalized or serve as a starting point for perturbative or numerical methods.

### Square-Well Potential

The spherically symmetric square-well potential is defined as:

$$V(r) = \begin{cases} -V_0, & r \leq a \\ 0, & r > a \end{cases}$$

where:

- $V_0 > 0$is the depth of the potential well, indicating that the potential is attractive inside the radius $a$.
- $a$is the range of the interaction, which determines the spatial extent of the potential.

Physically, this model represents a particle experiencing a constant attractive force within a certain radius and no interaction outside. It is a simple representation of finite-size scatterers such as nuclei, atoms, or molecules and provides a tractable model for analytic solutions.

### Schrödinger Equation for Scattering

The time-independent Schrödinger equation governs the motion of a particle in the presence of a potential:

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

For scattering states, the particle has positive energy:

$$E = \frac{\hbar^2 k^2}{2m} > 0$$

where $k$is the wave number corresponding to the incident particle momentum.
Due to the spherical symmetry of the potential, it is convenient to express the wavefunction using partial wave expansion, which separates the radial and angular parts. This allows the problem to be reduced to solving a radial differential equation for each angular momentum component.

### Partial Wave Expansion

The total wavefunction is expanded as:

$$\psi(r) = \sum_{l=0}^{\infty} R_l\,(r) P_l(\cos\,\theta)$$

where:

- $l$is the orbital angular momentum quantum number (partial wave index).
- $R_l(r)$is the radial wavefunction for the $l$-th partial wave.
- $P_l(\cos\,\theta)$are the Legendre polynomials, which represent the angular dependence of the wavefunction.

By defining $u_l(r) = rR_l(r)$, the radial Schrödinger equation becomes:

$$\frac{d^2u_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2}V(r)\right]u_l = 0$$

This form separates the effects of angular momentum and the potential, enabling systematic analysis of scattering for each partial wave.

### Solutions of the Radial Equation

### (a) Inside the Well ($r \leq a$)

Inside the potential well, $V(r) = -V_0$. Define the modified wave number:

$$k_1^2 = k^2 + \frac{2mV_0}{\hbar^2}$$

The physically acceptable solution, which is regular at $r = 0$, is expressed in terms of spherical Bessel functions:

$$u_l(r) = A_l j_l(k_1 r)$$

Here, $j_l(x)$are the spherical Bessel functions of the first kind, which are finite at the origin. The constant $A_l$is determined by normalization and matching conditions at $r = a$.

### (b) Outside the Well ($r > a$)

For $r > a$, the potential vanishes ($V(r) = 0$), and the solution is a combination of spherical Bessel and Neumann functions:

$$u_l(r) = B_l[\cos\,\delta_l\, j_l(kr) - \sin\,\delta_l\, n_l(kr)]$$

where:

- $n_l(x)$are spherical Neumann functions (irregular at $r = 0$, but regular at $r > a$).
- $\delta_l$is the phase shift, which contains all information about the scattering process.

The phase shift $\delta_l$arises due to the modification of the wavefunction caused by the potential and plays a central role in determining scattering amplitudes and cross sections.

### Phase Shifts

The phase shifts $\delta_l$are obtained by applying continuity conditions at the boundary $r = a$:

1. Continuity of the wavefunction:

$$u_l^{\text{inside}}(a) = u_l^{\text{outside}}(a)$$

2. Continuity of the derivative:

$$\frac{du_l}{dr}\,|_{\text{inside}} = \frac{du_l}{dr}\,|_{\text{outside}}$$

Solving these equations gives the exact phase shifts for each partial wave. These phase shifts encode the influence of the potential on the scattering process, including constructive or destructive interference effects that manifest as resonances or minima in the scattering cross section.

### s-Wave (Low-Energy) Scattering

At low energies, where $ka \ll 1$, the scattering is dominated by the $l = 0$partial wave (s-wave), as contributions from higher angular momenta are suppressed by the centrifugal barrier.

For $l = 0$, the phase shift is:

$$\delta_0 = ka - \tan^{-1}\left(\frac{k}{k_1}\tan(k_1 a)\right)$$

This simple expression is extremely important in nuclear and atomic scattering. It captures the key physics of low-energy collisions, where particles probe the overall size and depth of the potential rather than its detailed structure.

**Scattering Amplitude**

The scattering amplitude is related to the phase shifts via:

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\, e^{i\delta_l}\sin\,\delta_l\, P_l(\cos\,\theta)$$

For low-energy s-wave scattering, only the $l = 0$term contributes:

$$f(\theta) \approx \frac{1}{k}e^{i\delta_0}\sin\,\delta_0$$

The scattering amplitude determines the angular distribution of scattered particles and is directly measurable in experiments.

**Differential Cross Section**

The differential cross section quantifies the probability of scattering into a solid angle $d\Omega$:

$$\frac{d\sigma}{d\Omega} = |\, f(\theta)\,|^2$$

For s-wave scattering, this simplifies to:

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\sin^2\delta_0$$

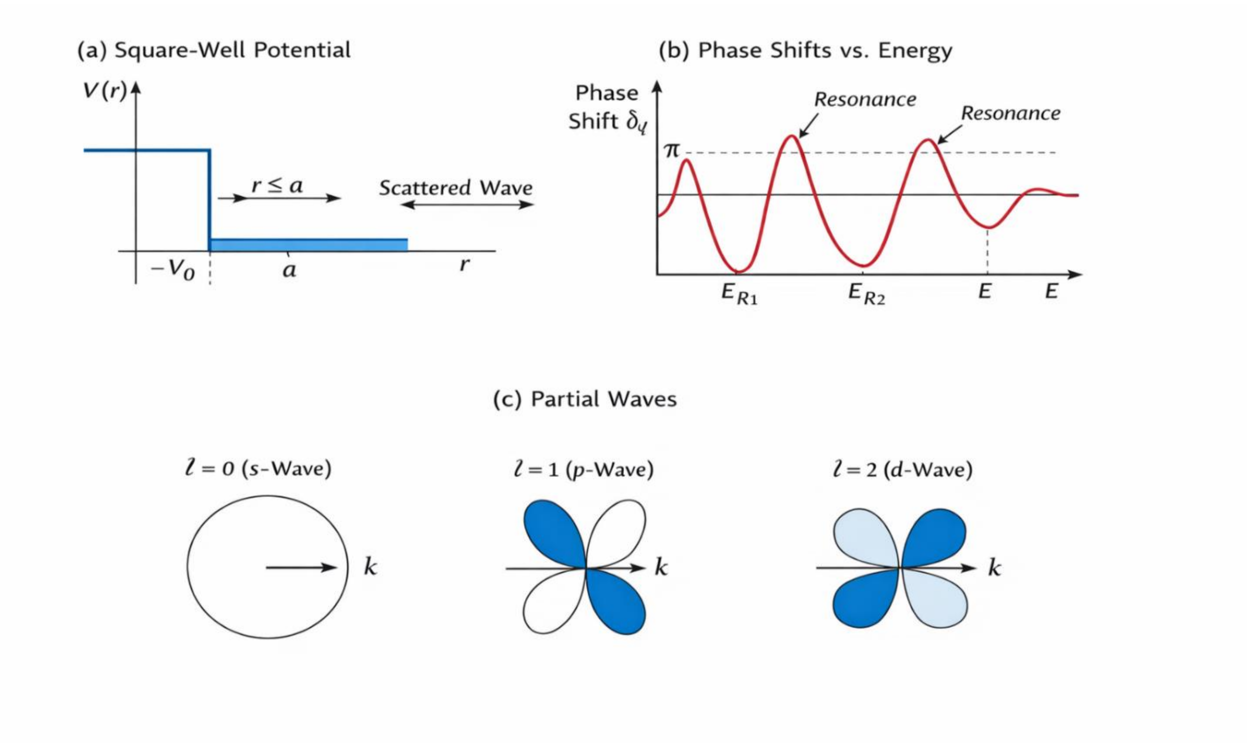
This shows that at low energies, scattering is isotropic, as the differential cross section does not depend on $\theta$. The magnitude of the scattering is controlled by the phase shift, which depends on the potential depth $V_0$and range $a$.

**Physical Interpretation**

The square-well potential illustrates key features of quantum scattering:

1. Phase Shifts ($\delta_l$): Encapsulate the modification of the wave due to the potential and determine all observable scattering properties.
2. Resonances: Occur when $\delta_l$rapidly changes with energy, corresponding to quasi-bound states within the well.
3. Cross Sections: Differential and total cross sections can be calculated exactly, allowing direct comparison with experiments.
4. Low-Energy Scattering: Dominated by s-wave ($l = 0$) contributions, leading to isotropic scattering at low energies.
5. Partial Waves: Higher angular momentum states contribute significantly only at higher energies.

This model also provides a benchmark to test approximations like the Born approximation, which assumes weak scattering potentials. By comparing exact phase shifts and cross sections from the square-well model with Born approximation results, one can assess the conditions under which approximate methods are valid.



### ➢ Total Cross Section

The total scattering cross section measures the overall probability of a particle being deflected by a potential. For a spherically symmetric square-well potential, it is expressed in terms of partial-wave phase shifts $\delta_l$as:

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l$$

At low energies ($ka \ll 1$), scattering is dominated by the s-wave ($l = 0$), simplifying the total cross section to:

$$\sigma \approx \frac{4\pi}{k^2}\sin^2\delta_0$$

### Resonance Scattering

Resonances occur when

$$k_1 a \approx n\pi$$

with $k_1 = \sqrt{k^2 + 2mV_0/\hbar^2}$. At these energies, the particle is temporarily trapped in the potential well, forming a quasi-bound state. Phase shifts change rapidly, and the cross section shows a pronounced peak. Resonances are crucial in nuclear reactions and indicate the energy and lifetime of these states.

Relation to Born Approximation

For weak and shallow potentials, the first Born approximation can estimate scattering. However, for strong potentials or low-energy scattering, it fails, requiring exact partial-wave solutions. The square-well potential provides a clear benchmark to compare approximate and exact methods.

Physical Significance

The square-well model offers insights into:

1. Phase Shifts – Encoding angular distributions and resonance behavior.
2. Low-Energy Scattering – Dominated by s-wave contributions.
3. Resonances – Showing quasi-bound state formation and enhanced cross sections.

As a simple yet exactly solvable model, the square-well potential illustrates fundamental quantum scattering features and serves as a benchmark for more complex potentials in nuclear, atomic, and low-energy particle physics**.**

## 9.2 PARTIAL WAVE ANALYSIS

So far, we have considered only an approximate calculation of the differential cross section where the interaction between the projectile particle and the scattering potential $V(r)$ is considered small compared with the energy of the incident particle. In this section we are going to calculate the cross section without placing any limitation on the strength of $V(r)$.

### Partial Wave Analysis for Elastic Scattering

Partial Wave Analysis for Elastic Scattering

We consider scattering by a spherically symmetric potential $V(r)$. In such cases, the angular momentum of the incident particle is conserved, meaning the particle has the same angular momentum before and after scattering.

The incident plane wave along the $z$-axis is:

$$\phi_{\text{inc}}(\mathrm{r}) = e^{\mathrm{ikr}\cos\theta} = \sum_{l=0}^{\infty} i^l\,(2l+1) j_l(kr) P_l(\cos\,\theta)(1)$$

where $j_l(kr)$ are spherical Bessel functions and $P_l(\cos\,\theta)$ are Legendre polynomials.

The total wavefunction can be expressed as a superposition of angular momentum eigenstates:

$$\psi(\mathrm{r}) = \sum_{lm} c_{lm}\,R_{kl}(r) Y_{lm}(\theta,\phi)$$

Since the potential is central, the system is rotationally invariant about the $z$-axis, so the wavefunction does not depend on the azimuthal angle $\phi$. Therefore, $m = 0$, and the scattered wavefunction reduces to:

$$\psi(r,\theta) = \sum_{l=0}^{\infty} a_l\,R_{kl}(r) P_l(\cos\,\theta) \qquad (2)$$

The radial functions $R_{kl}(r)$ satisfy the radial Schrödinger equation:

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2}\right]\big(rR_{kl}(r)\big) = \frac{2m}{\hbar^2} V(r)\big(rR_{kl}(r)\big) \qquad (3)$$

Each term in the series represents a partial wave, which is a joint eigenfunction of the angular momentum operators $\hat{L}^2$ and $\hat{L}_z$.

Substituting the expansion of the plane wave into the general solution gives the asymptotic form of the wavefunction:

$$\psi(r,\theta) \simeq \sum_{l=0}^{\infty} i^l\,(2l+1)j_l(kr)P_l(\cos\,\theta) + f(\theta)\frac{e^{ikr}}{r} \qquad (4)$$

Here, the scattered wave is represented by the outgoing spherical wave term $f(\theta)e^{ikr}/r$, and the total wavefunction is a combination of the incident plane wave and the scattered wave. This framework forms the basis of partial wave analysis, allowing the scattering amplitude $f(\theta)$to be computed from the phase shifts of each partial wave.

**Partial Wave Analysis: Asymptotic Forms of the Scattered Wave**

In scattering experiments, detectors are located at distances much larger than the target size. Therefore, the measurements correspond to large $r$behavior of the scattered wavefunctions. By comparing the asymptotic forms of the total wavefunction and the partial wave expansion, we can determine the scattering amplitude and hence the differential cross section.

For large $r$, the spherical Bessel function behaves as:

$$j_l(kr) \to \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr}(r \to \infty) \qquad (5)$$

Using this, the asymptotic form of the total wavefunction is:

$$\psi(r,\theta) \to \sum_{l=0}^{\infty} i^l\,(2l+1)P_l(\cos\,\theta)\frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} + \frac{f(\theta)e^{ikr}}{r} \qquad (6)$$

By expressing $\sin\,(kr - l\pi/2)$in terms of exponentials, the wavefunction can be rewritten as:

$$\psi(r,\theta) \to -\frac{e^{-ikr}}{2ikr}\sum_{l=0}^{\infty} i^l\,(2l+1)P_l(\cos\,\theta)$$
$$+\frac{e^{ikr}}{r}\left[f(\theta) + \frac{1}{2ik}\sum_{l=0}^{\infty} i^l\,(-i)^l(2l+1)P_l(\cos\,\theta)\right] (7)$$

To find the asymptotic form of the radial function$R_{kl}(r)$, note that for large $r$, the potential vanishes ($V(r) \to 0$) and the radial equation reduces to:

$$\left(\frac{d^2}{dr^2}+k^2\right)(rR_{kl}(r)) = 0 \quad (8)$$

The general solution is a linear combination of spherical Bessel and Neumann functions:

$$R_{kl}(r) = A_l j_l(kr) + B_l n_l(kr) \quad (9)$$

where the Neumann function asymptotically behaves as:

$$n_l(kr) \to -\frac{\cos\left(kr - \frac{l\pi}{2}\right)}{kr}(r \to \infty) \qquad (10)$$

Hence, the asymptotic form of the radial function is:

$$R_{kl}(r) \to A_l\frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} - B_l\frac{\cos\left(kr - \frac{l\pi}{2}\right)}{kr}(r \to \infty) \qquad (11)$$

For a physical solution, $R_{kl}(r)$ must be finite at the origin. The Neumann function diverges at $r = 0$, so the cosine term is discarded. The radial function is then written in the form:

$$R_{kl}(r) \to C_l \frac{\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)}{kr} (r \to \infty) \quad (12)$$

Here, $\delta_l$is the phase shift introduced by the potential, encoding all information about the scattering in the $l$-th partial wave.
This asymptotic form is crucial for calculating scattering amplitudes, differential cross sections, and understanding the effect of the potential on each partial wave.

**Phase Shift in Scattering**

- The radial function $R_{kl}(r)$for a scattering problem can be written as:

$$A_l = C_l \cos\,\delta_l, B_l = -C_l \sin\,\delta_l \implies C_l = \sqrt{A_l^2 + B_l^2}, \delta_l = -\tan^{-1}\frac{B_l}{A_l}$$

- **Phase shift ($\delta_l$)**:
  - Real angle representing the deviation of $R_{kl}(r)$from $j_l(kr)$due to the potential $V(r)$.
  - Vanishes ($\delta_l = 0$) when $V = 0$, i.e., no scattering.
- Asymptotic form of the wave function for large $r$:

$$\psi(r,\theta) \sim \sum_{l=0}^{\infty} a_l P_l(\cos\,\theta) \frac{\sin\,(kr - l\pi/2 + \delta_l)}{kr}$$

**Distorted Plane Wave**

- The wave function differs from a plane wave due to phase shifts:

$$\psi(r,\theta) \sim -\frac{e^{-ikr}}{2ikr}\sum_{l=0}^{\infty} a_l\, i^l e^{-i\delta_l} P_l(\cos\,\theta) + \frac{e^{ikr}}{2ikr}\sum_{l=0}^{\infty} a_l\,(-i)^l e^{i\delta_l} P_l(\cos\,\theta)$$

Coefficients:

$$a_l = (2l+1) i^l e^{i\delta_l}$$

**Scattering Amplitude**

- Substituting $a_l$into the wave function, the scattering amplitude:

$$f(\theta) = \sum_{l=0}^{\infty} f_l\,(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\, e^{i\delta_l} \sin\,\delta_l\, P_l(\cos\,\theta)$$

**Partial wave amplitude**:

$$f_l(\theta) = \frac{2l+1}{k} e^{i\delta_l} \sin\,\delta_l\, P_l(\cos\,\theta)$$

**Differential and Total Cross Section**

- Differential cross section:

$$\frac{d\sigma}{d\Omega} = \mid f(\theta) \mid^2 = \frac{1}{k^2}\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}(2l+1)(2\,l'+1)e^{i(\delta_l - \delta_{l'})}\sin\,\delta_l \sin\,\delta_{l'} P_l(\cos\,\theta) P_{l'}(\cos\,\theta)$$

Total cross section can be obtained by integrating over solid angle.

1. **Total Cross Section ($\sigma$)**

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = 2\pi \int_0^{\pi} \mid f(\theta) \mid^2 \sin\,\theta\, d\theta$$

2. **Expansion in Partial Waves**

$$f(\theta)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\,e^{i\delta_l}\sin\,\delta_l P_l(\cos\,\theta)$$

Using orthogonality of Legendre polynomials:

$$\int_0^{\pi}P_l\,(\cos\,\theta)P_{l'}(\cos\,\theta)\sin\,\theta\,d\theta=\frac{2}{2l+1}\delta_{ll'}$$

3. **Partial Cross Sections**

$$\sigma=\sum_{l=0}^{\infty}\sigma_l\,,\sigma_l=\frac{4\pi}{k^2}(2l+1)\sin^2\delta_l$$

   - $\sigma_l$corresponds to the contribution from angular momentum $l$.
   - Interference terms vanish when integrated over $\theta$.

4. **Special Case: s-wave Scattering ($l=0$)**

$$f_0=\frac{1}{k}e^{i\delta_0}\sin\,\delta_0,\frac{d\sigma}{d\Omega}=|\,f_0\,|^2=\frac{1}{k^2}\sin^2\delta_0,\sigma=4\pi\,|\,f_0\,|^2=\frac{4\pi}{k^2}\sin^2\delta_0$$

**Forward Scattering Amplitude and Optical Theorem**

$$f(0)=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)(\sin\,\delta_l\cos\,\delta_l+i\sin^2\delta_l)$$

Connection between total cross section and forward scattering:

$$\sigma=\frac{4\pi}{k}\mathrm{Im}f(0)=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\,\sin^2\delta_l$$

This is the **Optical Theorem**: relates total cross section to the imaginary part of forward scattering amplitude.

   - Physical meaning: conservation of particles (probability).

5. **Key Points**
   - For $V=0$, $\delta_l=0\Rightarrow\sigma=0$.
   - Partial wave series converges after finite number of terms except for Coulomb potential.
   - $l=0$dominates at low energies (s-wave).

**Partial Wave Analysis for Inelastic Scattering**

**1. Scattering Amplitude:**

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1)\, f_l(k) P_l(\cos\,\theta)$$

where $P_l$are Legendre polynomials.

**2. Partial Wave Amplitude $f_l(k)$:**

$$f_l(k) = \frac{1}{k} e^{i\delta_l} \sin\,\delta_l = \frac{1}{2ik}(e^{2i\delta_l} - 1) = \frac{1}{2ik}(S_l(k) - 1)$$

with

$$S_l(k) = e^{2i\delta_l}.$$

**No flux loss:**$\mid S_l(k) \mid = 1$

- **With absorption:**$S_l(k) = \eta_l(k) e^{2i\delta_l}$, $0 < \eta_l \leq 1$

**3. Modified Partial Wave Amplitude (with absorption):**

$$f_l(k) = \frac{\eta_l e^{2i\delta_l} - 1}{2ik} = \frac{1}{2k}[\eta_l \sin\,2\delta_l + i(1 - \eta_l \cos\,2\delta_l)]$$

**Scattering amplitude becomes:**

$$\boxed{f(\theta) = \frac{1}{2k} \sum_{l=0}^{\infty} (2l+1)[\eta_l \sin\,2\delta_l + i(1 - \eta_l \cos\,2\delta_l)] P_l(\cos\,\theta)}$$

**4. Elastic Scattering Cross Section:**

$$\sigma_{el} = 4\pi \sum_{l=0}^{\infty} (2l+1) \mid f_l \mid^2 = \frac{\pi}{k^2} \sum_{l} (2l+1)(1 + \eta_l^2 - 2\eta_l \cos\,2\delta_l)$$

**5. Inelastic Scattering Cross Section (flux loss):**

$$\boxed{\sigma_{inel} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)(1 - \eta_l^2)}$$

### 6. Total Cross Section:

$$\boxed{\sigma_{tot} = \sigma_{el} + \sigma_{inel} = \frac{2\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)(1-\eta_l\cos\,2\delta_l)}$$

**Remarks:**

- $\eta_l = 1$→ No inelastic scattering.
- $\eta_l = 0$→ Total absorption, still some elastic scattering in partial waves.
  Sum of elastic and inelastic gives the total scattering cross section.

## 9.3 EXPANSION OF A PLANE WAVE

In scattering theory, states with well-defined momentum are described by plane waves. A plane wave with momentum $\vec{p}$is an eigenfunction of the free-particle Hamiltonian

$$H^0 = \frac{p^2}{2m}.$$

Such a state is denoted by $|\,\vec{p}\rangle$ and represents a particle moving freely with definite momentum.

In the position representation, the plane wave eigenfunction is given by

$$\langle\vec{x}\mid\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}\,e^{i\vec{p}\cdot\vec{x}/\hbar},$$

which represents a wave of constant amplitude extending throughout space.

When the potential depends only on the radial distance, $V(\vec{x}) = V(r)$, the problem becomes spherically symmetric. In this case, it is more convenient to use spherical waves rather than plane waves. Although the momentum operator $\vec{P}$does not commute with angular momentum operators, the Hamiltonian $H^0$commutes with $L^2$ and $L_z$.

Therefore, a common set of eigenstates of $H^0$, $L^2$, and $L_z$can be defined as

$$|\,E\,\ell\,m\rangle,$$

where $E$is the energy, $\ell$the orbital angular momentum quantum number, and $m$its magnetic quantum number (not to be confused with mass).

The spherical wave states form an orthonormal and complete basis of the Hilbert space, satisfying

$$\langle E'\ell'm'\mid E\ell m\rangle = \delta(E'-E)\,\delta_{\ell\ell'}\,\delta_{mm'}.$$

This makes spherical waves particularly useful for analysing scattering from central potentials.

## 9.4 OPTIMAL THEOREM

Optical Theorem

The Optical Theorem is a fundamental result in quantum scattering theory which relates the total scattering cross section to the forward scattering amplitude. It expresses the consequence of probability (flux) conservation in scattering processes.

Statement of the Optical Theorem:
The optical theorem states that the imaginary part of the forward scattering amplitude determines the total cross section:

$$\boxed{\sigma_{\text{total}} = \frac{4\pi}{k} \operatorname{Im} f(0)}$$

where:

- $\sigma_{\text{total}}$is the total scattering cross section
- $k$is the incident wave number
- $f(0)$is the scattering amplitude at zero scattering angle ($\theta = 0$)
- $\operatorname{Im} f(0)$is the imaginary part of the forward amplitude

Physical Meaning:
Although scattering is usually thought of as particles being deflected to non-zero angles, the optical theorem shows that even the forward direction contains information about all scattering events. The reduction in the intensity of the incident beam is due to scattering into all other directions, and this loss appears mathematically as the imaginary part of the forward amplitude.
Thus, the optical theorem connects:

- Forward scattering
- Total probability loss from the incident beam
- Total cross section

**Origin of the Optical Theorem:**
The theorem arises from:

- Conservation of probability (or particle flux)
- The asymptotic form of the scattered wavefunction
- The unitarity of the scattering (S-matrix)

The asymptotic wavefunction is:

$$\psi(\mathrm{r}) \underset{r\to\infty}{\to} e^{ikz} + f(\theta)\frac{e^{ikr}}{r}$$

The interference between the incident plane wave and the scattered spherical wave in the forward direction leads directly to the optical theorem.

**Relation to Differential Cross Section**
The differential cross section is:

$$\frac{d\sigma}{d\Omega} = | f(\theta) |^2$$

The total cross section is obtained by integrating over all angles:

$$\sigma_{\text{total}} = \int | f(\theta) |^2 \, d\Omega$$

The optical theorem provides a shortcut, allowing $\sigma_{\text{total}}$to be determined without performing the angular integration, using only $f(0)$.

**Optical Theorem in Partial Wave Analysis**
The scattering amplitude can be written as:

$$f(\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell + 1)\, e^{i\delta_\ell}\sin\, \delta_\ell P_\ell(\cos\, \theta)$$

At $\theta = 0$, using $P_\ell(1) = 1$:

$$f(0) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{i\delta_\ell}\sin\,\delta_\ell$$

Taking the imaginary part:

$$\operatorname{Im} f(0) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell$$

Hence:

$$\sigma_{\text{total}} = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell$$

This confirms the optical theorem exactly.

**Validity and Importance:**

- The optical theorem is exact and does not depend on the Born approximation
- Valid for elastic and inelastic scattering
- Applies to quantum mechanics, nuclear physics, particle physics, optics, X-ray and neutron scattering

## 9.5 SCATTERING FROM A SQUARE WELL POTENTIAL

### Definition of Square Well Potential

The square well potential is spherically symmetric and defined as

$$V(r) = \begin{cases} -V_0, & r \le a \\ 0, & r > a \end{cases}$$

where $V_0 > 0$is the depth of the well and $a$is its range.

### Radial Schrödinger Equation

The radial motion of a particle in this potential is described by

$$\frac{d^2u_\ell(r)}{dr^2} + [k^2 - \frac{\ell(\ell+1)}{r^2} - \frac{2m}{\hbar^2}V(r)]u_\ell(r) = 0$$

with boundary conditions $u_\ell(0) = 0$and continuity at $r = a$.

### Solution Inside and Outside the Well

- Inside $(r \le a)$: $u_\ell(r) = A_\ell j_\ell(k_1 r)$, where $k_1 = \sqrt{k^2 + \frac{2mV_0}{\hbar^2}}$ and $j_\ell$ is the spherical Bessel function.
- Outside $(r > a)$: $u_\ell(r) = j_\ell(kr) - \tan\,\delta_\ell\, n_\ell(kr)$, where $n_\ell$is the spherical Neumann function and $\delta_\ell$ is the phase shift.

### Phase Shift

Matching the wavefunction and its derivative at $r = a$gives

$$\tan\,\delta_\ell = \frac{kj_\ell(k_1a)j'_\ell(ka) - k_1j'_\ell(k_1a)j_\ell(ka)}{k_1j'_\ell(k_1a)n_\ell(ka) - kn'_\ell(ka)j_\ell(k_1a)}.$$

**Scattering Amplitude**

The scattering amplitude in partial wave expansion is

$$f(\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{i\delta_\ell}\sin\,\delta_\ell P_\ell(\cos\,\theta),$$

where $P_\ell$are Legendre polynomials. At $\theta = 0$, the forward amplitude is

$$f(0) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{i\delta_\ell}\sin\,\delta_\ell$$

and its imaginary part is

$$\mathrm{Im}\, f(0) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell.$$

**Total Cross Section**

The total cross section is obtained as

$$\sigma_{\text{total}} = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell.$$

**Low Energy Scattering**

For low incident energies, the s-wave ($\ell = 0$) dominates, while higher partial waves contribute at higher energies.

**Physical Significance**

The square well potential shows how the depth and range of a potential influence phase shifts, scattering amplitude, and cross sections. It also illustrates resonances, partial wave contributions, and energy dependence. In the weak potential limit, the Born approximation can be applied for simplicity. This model is widely used in quantum mechanics, nuclear physics, and particle physics to study scattering phenomena.

## 9.6 SUMMARY

This chapter discussed key scattering methods including form factor scattering, which accounts for the finite size of the scatterer, and scattering from a square well potential as an exactly solvable model. Partial wave analysis was developed using plane wave expansion into spherical waves, and the optical theorem linked total cross section to forward scattering amplitude.

## 9.7 TECHNICAL TERMS

Form factor scattering, Scattering from a square well potential Partial wave analysis, Expansion of a plane wave, Optimal theorem, Scattering from a square well potential.

## 9.8 SELF-ASSESSMENT QUESTIONS

1. Discuss the theory of partial wave analysis
2. Obtain the expression for scattering cross section in case of square well potential by partial wave method.
3. Explain Optimal Theorem.
4. Explain from Factor scattering.

## 9.10 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

**Prof. Sandhya Cole**

## LESSON-10

# MOLECULAR QUANTUM MECHANICS

**Aim and Objective**

The aim of Molecular Quantum Mechanics is to apply the principles of quantum mechanics to moleculesin order tounderstand, predict, and explain their structure, bonding, spectra, and dynamical behaviorat the atomic and electronic level**.**

**Objectives**

1. To describe electronic structure of molecules
    - Determine allowed electronic energy levels and molecular orbitals.
    - Explain chemical bonding using wavefunctions and operators.
2. To explain molecular spectra
    - Interpret rotational, vibrational, and electronic spectra.
    - Relate spectral lines to quantized energy transitions.
3. To separate electronic and nuclear motion
    - Use the Born–Oppenheimer approximation to simplify the molecular Schrödinger equation.
4. To understand molecular geometry and stability
    - Predict equilibrium bond lengths, bond angles, and molecular shapes.
    - Explain potential energy surfaces and molecular stability.
5. To study molecular dynamics and reactions
    - Analyze vibrational motion, rotations, and reaction pathways.
    - Understand transition states and reaction rates at the quantum level.
6. To explain intermolecular interactions
    - Describe van der Waals forces, hydrogen bonding, and weak interactions.
7. To connect theory with experiments
    - Provide theoretical foundations for spectroscopy, chemical kinetics, and materials science.

**STRUCTURE OF THE LESSON:**

## 10.1 Introduction to quantum mechanics

### Introduction:

Quantum mechanics is the fundamental theory that governs the behavior of matter and radiation at atomic and sub-atomic scales. Unlike classical mechanics, which successfully describes the motion of macroscopic objects, quantum mechanics becomes essential when dealing with systems of very small dimensions such as electrons, atoms, nuclei, and photons.

At these scales, classical concepts like definite position, trajectory, and deterministic motion fail to explain experimental observations. Quantum mechanics provides a new framework based on probabilistic laws and wave–particle duality.

The development of quantum mechanics in the early twentieth century marked a profound revolution in physics. It arose from the inability of classical physics to explain several experimental phenomena, including blackbody radiation, the photoelectric effect, atomic spectra, and the stability of atoms. Today, quantum mechanics forms the foundation of modern physics and plays a crucial role in diverse fields such as solid-state physics, quantum chemistry, nuclear physics, quantum optics, and emerging technologies like quantum computing.

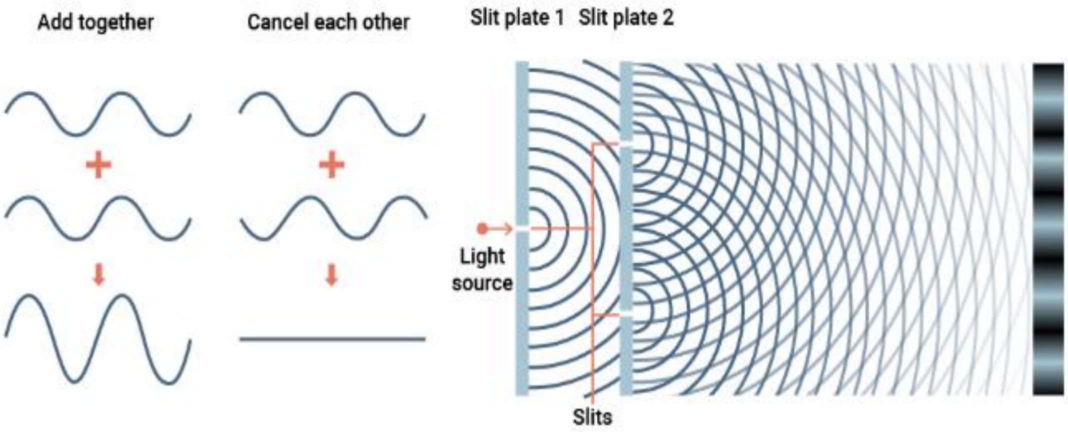


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Fig: 1. Wave Particle Duality

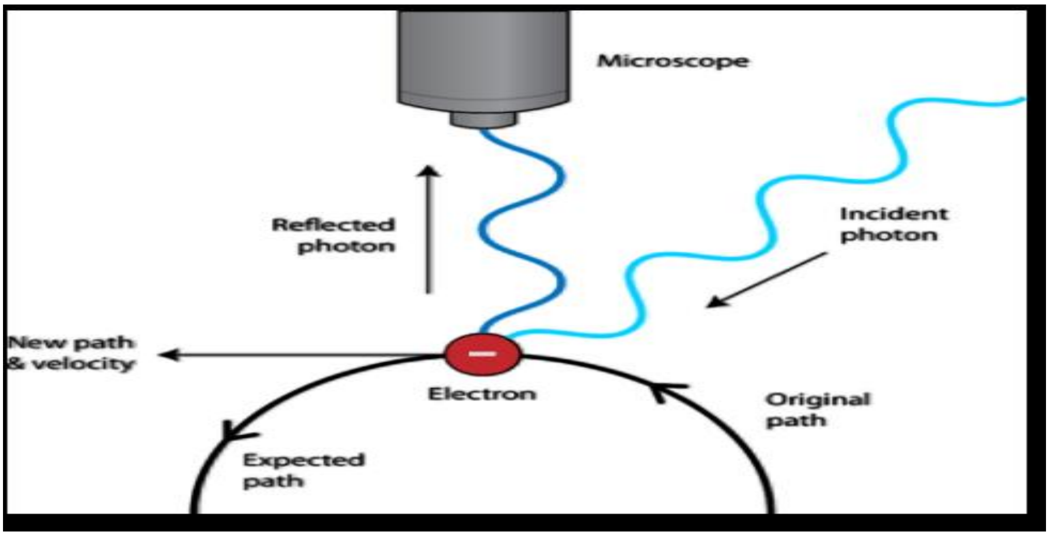

Fig: 2. Heisenberg Uncertainty principle

**Need for Quantum Mechanics**

Several experimental observations could not be explained using classical physics:

- Blackbody radiation
- Photoelectric effect
- Compton scattering

- Atomic line spectra

These failures led to the development of quantum theory in the early twentieth century.

**Key Historical Milestones**

- Planck (1900): Energy is quantized
- Einstein (1905): Light consists of photons
- Bohr (1913): Quantized atomic orbits
- de Broglie (1924): Matter waves
- Schrödinger & Heisenberg (1926): Wave mechanics and matrix mechanics

**Energy Quantization**

According to Planck, energy is not continuous but is exchanged in discrete packets called quanta. The energy of a quantum is given by:

$E = h\nu$

**Wave–Particle Duality**

Louis de Broglie proposed that matter exhibits wave-like properties. The wavelength associated with a particle of momentum p is:

$\lambda = h / p$

**Wave Function and Probability**

In quantum mechanics, the state of a system is described by a wave function $\psi$. The probability density of finding a particle at a given position is given by:

Probability density = $|\psi|^2$

**Schrödinger Equation**

The time-independent Schrödinger equation is the fundamental equation governing non-relativistic quantum systems:

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

**Uncertainty Principle**

Heisenberg's uncertainty principle states that the position and momentum of a particle cannot be simultaneously measured with arbitrary precision:

$$\Delta x\, \Delta p \geq \hbar / 2$$

## Importance and Applications of Quantum Mechanics

Quantum mechanics is essential for understanding and developing modern technologies, including:

- Semiconductors and transistors
- Lasers and LEDs
- Magnetic resonance imaging (MRI)
- Atomic clocks
- Nanotechnology
- Quantum computation and quantum information science

It has transformed not only physics but also chemistry, materials science, and engineering.

## Conclusion

Quantum mechanics represents a fundamental departure from classical physics, introducing new concepts such as wave–particle duality, probabilistic interpretation, and operator-based observables. Born out of the failure of classical theories, quantum mechanics successfully explains phenomena at atomic and subatomic scales and forms the backbone of modern science and technology. Despite its abstract and counterintuitive nature, quantum mechanics provides remarkably accurate predictions and continues to inspire new theoretical and technological developments. A solid understanding of its principles is essential for advanced studies in physics and related disciplines.

## 10.2 THE BORN-OPPENHEIMER APPROXIMATION

Introduction:
The Born–Oppenheimer approximation is one of the most fundamental and widely used approximations in quantum mechanics, particularly in the study of atomic, molecular, and solid-state systems. Proposed in 1927 by **Max Born and J. Robert Oppenheimer**, this approximation provides a practical method for solving the Schrödinger equation for systems containing both nuclei and electrons. Because an exact solution of the full many-body Schrödinger equation is mathematically intractable for most realistic systems, the Born–Oppenheimer approximation plays a crucial role in simplifying the problem while retaining essential physical features.

The key idea of the Born–Oppenheimer approximation is the separation of electronic and nuclear motions based on the large mass difference between nuclei and electrons. Since nuclei are much heavier than electrons, they move much more slowly. This allows the electronic motion to be treated independently of nuclear motion to a very good approximation. As a result, the total wave function of a molecular system can be factorized into electronic and nuclear components. This approximation forms the foundation of molecular quantum mechanics, quantum chemistry, spectroscopy, and computational methods such as Hartree–Fock and density functional theory.

The exact solution of the Schrödinger equation is not possible for light atoms even the simplest molecule $H_2$ consists of these particles. To overcome this difficult we adopt the Born-Oppenheimer approximation.

The Hamiltonian operator for a molecule is

$$\widehat{H =} \hat{T}N + T\hat{e} + V\hat{e}e + V\hat{e}N + VN\hat{N} \qquad \text{…….(1)}$$

Where $\hat{\hat{T}}N$ stands for K.E operators for the electrons $V\hat{e}e$ is the electron –electron repulsion $\hat{V}en$ is the electron-nucleus attractipon term. If the molecule contains k-nuclei and n-electron Then

$$\hat{T}N = -\sum_{i=1}^{k}\frac{1}{2}\nabla i^2$$

$$T\hat{e} = -\sum_{j=1}^{k}\frac{1}{2}\nabla j^2$$

$$V\hat{e}e = \sum_{i}^{n}\sum_{j}^{n}\frac{1}{r_{ij}}$$

$$V\hat{e}N = -\sum_{i}^{n} - \sum_{j}^{k} \frac{2i}{r_{ij}}$$

$$VN\hat{N} = \sum_{i}^{k} - \sum_{j}^{k} \frac{2i2i}{r_{ij}}$$

Since the electrons are much lighter than the nucleus they move much faster in a molecule. The electrons carry out many cycles of motion in the time. The nucleus move a short distance. Therefore we can consider the nucleus to be fixed while the electron move through the whole volume of the molecule. We can now separate the Schrodinger equation for a molecule into two separate equation. One depending upon the electronic motion and the other static nuclear position. This approximation is known as Born-Oppenheimer approximation.

If we take nucleus is fixed in position then 'TN'should be zero and 'VNN' is constant then the Hamiltonian for line electrons would be

$$\hat{H}e = T\hat{e} + V\hat{e}e + V\hat{e}N \qquad \ldots\ldots\ldots (2)$$

Rearranging terms in equ(1) if denoted by 'Hn' are

$\hat{H}n = \hat{T}N + \hat{V}\mathrm{NN}$ …….(3)

So that the Hamiltonian is $H = \hat{H}n + \hat{H}e$

The Schrödinger equation for any electrostatic motion is given by

$$\hat{H}n + \hat{H}e\psi_e = (E_e + E_n)\psi_e$$

$= U\psi_e$ Where U=$E_e + E_n$

Since $E_n$is constant quantity, we can write

$\hat{H}e\psi_e = E_e\psi_e$

Where $E_e$ is the electronic energy $\psi_e$is the corresponding wave function and U is the total energy of the nucleus and electrons

## Applications

The approximation is widely used in:

- Molecular spectroscopy (vibrational and rotational spectra),
- Chemical reaction theory,
- Solid-state physics (phonons),
- Quantum chemistry software packages,
- Understanding molecular structure and bonding.

It provides a conceptual framework for separating electronic, vibrational, and rotational motions in molecules.

## Conclusion

The Born–Oppenheimer approximation represents a cornerstone of modern quantum mechanics and molecular physics. By exploiting the large mass difference between electrons and nuclei, it allows a systematic separation of electronic and nuclear motions, drastically simplifying the many-body Schrödinger equation. The concept of potential energy surfaces arising from this approximation provides deep insight into molecular structure, bonding, and dynamics. Although it has limitations in systems involving strong non-adiabatic effects, the Born–Oppenheimer approximation remains remarkably accurate for a vast range of physical and chemical phenomena. Its success and wide applicability make it one of the most powerful and indispensable tools in theoretical and computational physics.

## 10.3 THE HYDROGEN MOLECULE ION

Introduction

The hydrogen molecule ion, $H_2^+$, is the simplest molecular system, consisting of two protons and one electron. Despite its simplicity, it exhibits essential features of molecular bonding, including electron delocalization, bond formation, and energy splitting. $H_2^+$serves as a fundamental example to understand molecular orbitals, the Born-Oppenheimer approximation, and the quantum mechanical treatment of diatomic molecules.

Schrödinger Equation for $H_2^+$

The time-independent Schrödinger equation for $H_2^+$is:

$$\hat{H}\Psi(\mathrm{r},\mathrm{R}) = E\Psi(\mathrm{r},\mathrm{R})$$

Where:

- r= electron coordinates
- R= internuclear vector
- $\hat{H}$= Hamiltonian for one electron and two nuclei

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A}+\frac{1}{r_B}\right) + \frac{e^2}{4\pi\epsilon_0 R}$$

Where:

- $r_A, r_B$= distances from electron to nuclei A and B
- $R$= internuclear distance

Born-Oppenheimer Approximation

Since nuclei are much heavier than electrons ($m_p \gg m_e$), their motion is slower. The Born-Oppenheimer approximation assumes:

$$\Psi(\mathrm{r},\mathrm{R}) \approx \psi_{\text{electronic}}(\mathrm{r};\mathrm{R}) \cdot \chi_{\text{nuclear}}(\mathrm{R})$$

- Electronic motion is solved first with nuclei fixed.
- Nuclear motion is treated later in the effective potential created by the electron.

Molecular Orbitals: LCAO Approach

The electron in $H_2^+$can occupy molecular orbitals formed as a linear combination of the 1s atomic orbitals of the two hydrogen atoms:

$$\psi_\pm = N[\phi_A \pm \phi_B]$$

- $\psi_+$= bonding orbital (symmetric combination, lower energy)
- $\psi_-$= antibonding orbital (antisymmetric combination, higher energy)
- $N$= normalization constant

Bonding Orbital: Increased electron density between nuclei → stabilizes molecule Antibonding Orbital: Node between nuclei → destabilizes molecule

Energy and Potential Energy Curve

The electronic energy $E_e(R)$depends on internuclear distance $R$. Total energy including nuclear repulsion:

$$E(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0 R}$$

- Equilibrium bond length $R_e$: minimum of $E(R)$
- Bond dissociation energy $D_e$: energy required to separate nuclei infinitely

- Bonding orbital → stable, energy minimum at $R_e \approx 1.06$ Å
- Antibonding orbital → unstable, no bound state

1. Simplest one-electron diatomic molecule → exactly solvable within approximations.
2. Demonstrates covalent bonding via electron delocalization.
3. Basis for understanding molecular orbital theory and larger diatomic systems.
4. Illustrates Born-Oppenheimer approximation and separation of electronic and nuclear motion.

### Importance and Applications

The hydrogen molecule ion plays a crucial role in:

- Understanding molecular bonding,
- Testing quantum mechanical methods,
- Astrophysical chemistry,
- Plasma physics,
- Development of molecular orbital theory.

It serves as a benchmark system for more complex molecules.

### Conclusion

The hydrogen molecule ion, $H_2^+$, is the simplest and most instructive molecular system in quantum mechanics. Through the application of the Born–Oppenheimer approximation and the LCAO method, it provides a clear and quantitative understanding of molecular bonding. The existence of stable bonding and antibonding molecular orbitals demonstrates the purely quantum mechanical origin of chemical bonds. Despite its simplicity, $H_2^+$ captures the essential physics of electron delocalization, potential energy surfaces, and molecular stability, making it a cornerstone of molecular quantum mechanics.

## 10.4 SUMMARY

Molecules in order to understand and predict their structure, bonding, spectra, and dynamics **at** the microscopic level.

Molecules are described by a molecular Schrödinger equation that includes the motion of electrons and nuclei interacting through Coulomb forces. Because this equation is too complex to solve exactly, important approximations are introduced—most notably the Born–Oppenheimer approximation, which separates fast electronic motion from slower nuclear motion.

The electronic structure of molecules is explained using molecular orbitals, formed by the linear combination of atomic orbitals. Solutions of the electronic Schrödinger equation yield quantizedenergy levelsandelectron probability distributions, which determine molecular bonding, stability, and geometry.

Molecular quantum mechanics explains rotational, vibrational, and electronic motions of molecules. Each type of motion has discrete energy levels, leading to characteristic molecularspectra observed in microwave, infrared, and visible/UV regions. Selection rules derived from quantum theory govern allowed transitions.

The theory also provides a quantum description of molecular vibrations and rotations, potential energy surfaces, andreaction dynamics, helping to understand chemical reactions, transition states, and molecular collisions.

Overall, molecular quantum mechanics forms the theoretical foundation of spectroscopy, quantum chemistry, chemical bonding theory, and molecular dynamics, linking experimental observations with fundamental quantum laws.

## 10.5 TECHNICAL TERMS

Introduction to quantum mechanics, The Born-Oppenheimer approximation,The hydrogen molecule ion

## 10.6 SELF ASSESSMENT QUESTIONS

1. Write about the Introduction to quantum mechanics
2. Explain about the the Born-Oppenheimer approximation
3. Briefly explain about the the hydrogen molecule ion

## 10.7 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

**Prof. M. Rami Reddy**

## LESSON -11

# THE VALANCE BOND AND MOLECULAR ORBITAL METHOD

**Aim and Objectives**

The aim of the Valence Bond (VB) and Molecular Orbital (MO) methods is to explain the nature of chemical bonding in molecules using the principles of quantum mechanics and to predict important molecular properties such as structure, stability, bonding characteristics, and spectra. These two theoretical approaches provide a microscopic description of how atoms combine to form molecules by considering the behavior of electrons as wavefunctions rather than as classical particles. By applying quantum mechanical concepts such as orbital overlap, electron spin, and energy quantization, both methods offer a rigorous theoretical framework that goes beyond empirical bonding models and enables a deeper understanding of covalent bonding at the atomic level.

The Valence Bond (VB) method focuses on the concept of localized chemical bonds. According to this approach, a covalent bond is formed when atomic orbitals from two atoms overlap in space, allowing a pair of electrons with opposite spins to be shared between the atoms. The extent of overlap between atomic orbitals determines the strength of the bond, with greater overlap leading to stronger and shorter bonds. VB theory emphasizes the directional nature of bonds, which helps explain molecular shapes and geometries. It accounts for the orientation of bonds in space by introducing the concept of hybridization, where atomic orbitals on the same atom mix to form new hybrid orbitals such as sp, $sp^2$, and $sp^3$. These hybrid orbitals explain linear, trigonal planar, and tetrahedral molecular geometries, respectively, and provide a clear interpretation of observed bond angles in molecules like ethyne, ethene, and methane.

In addition, the VB method explains the pairing of electrons in bonds in accordance with the Pauli exclusion principle and highlights the importance of electron spin in bond formation. It also introduces the idea of resonance, which is used to describe molecules that cannot be represented adequately by a single Lewis structure. In such cases, the actual electronic structure is considered to be a superposition of multiple contributing structures, leading to enhanced stability. VB theory therefore provides valuable insight into bond directionality, localized electron density, molecular geometry, and the relationship between orbital overlap and bond strength. These features make the VB approach particularly useful in understanding the reactivity and bonding patterns of organic molecules.

The Molecular Orbital (MO) method, in contrast, offers a fundamentally different perspective on chemical bonding by treating electrons as delocalized over the entire molecule rather than confined between specific pairs of atoms. In the MO approach, atomic orbitals from all atoms in a molecule combine to form molecular orbitals that extend over the whole molecular framework. These molecular orbitals are obtained using the linear combination of atomic orbitals (LCAO) method and are classified as bonding, antibonding, or non-bonding depending on their energy and electron density distribution. Bonding molecular orbitals concentrate electron density between nuclei and stabilize the molecule, while antibonding orbitals contain nodes between nuclei and destabilize the molecule when occupied.

The MO method provides a quantitative way to determine bond order, which is calculated from the difference between the number of electrons in bonding and antibonding orbitals. This allows prediction of bond strength, bond length, and molecular stability. A higher bond order corresponds to a stronger and shorter bond. The MO approach is particularly powerful in explaining magnetic properties of molecules, such as paramagnetism and diamagnetism, by explicitly showing the presence or absence of unpaired electrons in molecular orbitals. A classic example is the oxygen molecule, $O_2$, whose paramagnetic nature cannot be explained by VB theory but is correctly predicted by MO theory due to the presence of unpaired electrons in antibonding $\pi^*$ orbitals.

Furthermore, the MO method is essential for understanding electronic spectra and transitions, as it provides a clear picture of allowed electronic excitations between molecular orbitals. This makes it highly relevant in spectroscopy, photochemistry, and the study of excited states. The delocalized nature of molecular orbitals also allows the MO approach to successfully describe conjugated systems, aromatic molecules, and extended $\pi$-electron systems, where electrons are spread over several atoms. As a result, MO theory plays a crucial role in explaining the stability of aromatic compounds, color in organic molecules, and the electronic properties of materials.

Together, the VB and MO methods provide a comprehensive and complementary understanding of chemical bonding. While the VB method excels in describing localized bonds, molecular geometry, and hybridization, the MO method offers a broader picture of electron delocalization, molecular stability, magnetic behavior, and spectral properties. By combining insights from both approaches, chemists can connect theoretical predictions with experimental observations such as bond lengths, bond energies, reactivity patterns, and spectroscopic data. Thus, the VB and MO methods together form a complete and powerful framework for interpreting chemical bonding and molecular structure at the quantum mechanical level.

## STRUCTURE OF THE LESSON:

## 11.1 THE VALANCE BOND METHOD

Valence Bond Theory (VBT) is one of the fundamental quantum mechanical models that describe chemical bonding in molecules. Proposed in 1927 by Walter Heitler and Fritz London, VBT was the first attempt to explain chemical bonds using the principles of quantum mechanics. This marked a significant departure from classical ideas of bonding that were based purely on empirical observations, Lewis structures, or chemical intuition. Before the development of VBT, chemists relied on Lewis structures and valence rules, which provided an incomplete picture, especially for explaining bond energies, bond lengths, and molecular stability. Heitler and London's pioneering work focused initially on the hydrogen molecule ($H_2$). They demonstrated that a quantum mechanical treatment of electrons in overlapping atomic orbitals could explain the formation of a stable covalent bond. This approach laid the groundwork for the systematic understanding of covalent bonding in molecules of increasing complexity.

In the VBT framework, a chemical bond forms due to the overlap of atomic orbitals on adjacent atoms. The greater the overlap between orbitals, the stronger the bond. The overlapping orbitals allow electrons to be shared between the two atoms, increasing electron density in the internuclear region and lowering the overall potential energy of the system. This leads to stabilization of the molecule. Mathematically, for the hydrogen molecule, the total wavefunction can be expressed as:

$$\boldsymbol{\Psi = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)}$$

Here, $\psi_A$and $\psi_B$represent the atomic orbitals of atoms A and B, while 1 and 2 denote the two electrons. This symmetric combination increases the probability of finding electrons between the nuclei, forming a covalent bond. In accordance with the Pauli exclusion principle, the electrons in the bond must have opposite spins to ensure that no two electrons occupy the same quantum state. The singlet spin function describing this pairing is:

$$\boldsymbol{\chi_s = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]}$$

This antisymmetric spin combination ensures that the overall wavefunction remains antisymmetric under exchange of electrons, a fundamental requirement for fermions.

The energy of a molecule can be visualized using a potential energy curve as a function of internuclear distance, $R$. At very large distances, the atoms behave independently, and the potential energy approaches zero. As the atoms move closer together, attractive interactions between electrons and nuclei lower the potential energy, while repulsive interactions between electrons and between nuclei increase it. The equilibrium bond length $R_e$occurs at the minimum of this potential energy curve, where the molecule achieves maximum stability. The depth of this minimum, $D_e$, represents the bond dissociation energy, i.e., the energy required to break the bond and separate the molecule into individual atoms. This concept explains why molecules exist at specific bond lengths and why stronger bonds correspond to deeper energy minima**.**

**Key Concepts in VBT**

1. **Wavefunction Superposition:** The overlapping atomic orbitals create a linear combination of wavefunctions, enhancing electron density between the nuclei. This principle is essential in describing localized bonding, where electrons are primarily found between two bonded atoms.
2. **Spin Pairing:** Covalent bonds require electrons in overlapping orbitals to have opposite spins, forming a singlet state that complies with the Pauli exclusion principle.
3. **Potential Energy Curve**: The molecular energy plotted against internuclear distance illustrates bond formation. The depth of the energy minimum indicates bond strength, while the position of the minimum defines the equilibrium bond length.

**Types of Covalent Bonds**

- **Sigma (σ) Bonds:** Formed by head-to-head or end-to-end overlap of atomic orbitals. Examples include H–H bonds (1s–1s overlap), C–H bonds in methane ($sp^3$–1s overlap), and C–C single bonds ($sp^3$–$sp^3$ overlap). Sigma bonds are cylindrically symmetric about the bond axis, relatively strong, and localized.
- **Pi (π) Bonds**: Formed by sideways overlap of p orbitals. Pi bonds are present in double and triple bonds, such as C=C in ethene and C≡C in ethyne. They are weaker, more diffuse, and electrons are delocalized over the bonding region perpendicular to the bond axis.

**Hybridization Theory**

Hybridization is a key concept within VBT that explains molecular geometry and bond angles, which cannot be fully explained by pure atomic orbitals. Hybrid orbitals are formed by mixing atomic orbitals on the same atom to produce new equivalent orbitals oriented to minimize electron pair repulsion.

- **$sp^3$ Hybridization (Tetrahedral Geometry):** Observed in molecules with single-bonded carbon atoms such as methane ($CH_4$) and ethane ($C_2H_6$). One 2s orbital mixes with three 2p orbitals to form four $sp^3$ orbitals arranged tetrahedrally, giving bond angles of approximately 109.5°. Each $sp^3$ orbital forms a sigma bond with another atom's orbital (hydrogen 1s or carbon $sp^3$).
- **$sp^2$ Hybridization (Trigonal Planar Geometry):** Found in molecules with double bonds such as ethene ($C_2H_4$). 1s orbital mixes with two p orbitals to form three $sp^2$ orbitals lying in a plane, with one unhybridized p orbital perpendicular to this plane. The $sp^2$ orbitals form sigma bonds, while the unhybridized p orbitals form a pi bond, giving rise to planar double bonds.
- **sp Hybridization (Linear Geometry):** Present in molecules with triple bonds, such as ethyne ($C_2H_2$). 1s orbital mixes with one p orbital to form two sp orbitals arranged linearly at 180°, while two unhybridized p orbitals form two perpendicular pi bonds along the bond axis.

**Resonance and Delocalization**

VBT also explains resonance, which occurs when a single Lewis structure cannot fully describe electron distribution. In molecules like benzene ($C_6H_6$), electrons are delocalized over six carbon atoms. VBT describes this using a superposition of contributing resonance structures. Resonance stabilizes the molecule and leads to bond lengths that are intermediate between single and double bonds.

**Applications of VBT**

VBT is highly effective in explaining localized bonding, bond strength, bond length, molecular geometry, and hybridization patterns. It can be applied to predict reactivity in organic chemistry, understand molecular stability, and qualitatively explain magnetic properties.

**Limitations**

VBT cannot describe delocalized electrons in conjugated or aromatic systems adequately, nor can it explain Para magnetism in molecules such as $O_2$. Molecular Orbital Theory (MOT) complements VBT by treating electrons as delocalized over the molecule, allowing a more complete understanding of bonding in aromatic compounds, metals, and molecules with unpaired electrons.

**Hybridization in Valence Bond Theory**

| **Hybridization** | **Orbitals Mixed** | **Resulting Orbitals** | **Geometry** | **Ideal Bond Angle** | **Example** |
|---|---|---|---|---|---|
| $sp^3$ | one s, three p | four $sp^3$ | Tetrahedral | 109.5° | Methane, Ethane |
| $sp^2$ | one s, two p | three $sp^2$, one p | Trigonal Planar | 120° | Ethene |
| sp | one s, one p | two sp, two p | Linear | 180° | Ethyne |

In nitrogen and oxygen, **$sp^3$**hybridization also occurs, but some hybrid orbitals contain lone pairs, which causes distortion from the ideal tetrahedral angle (e.g., in ammonia and water).

## 11.2 THE MOLECULAR ORBITAL METHOD

The Molecular Orbital Theory (MOT) is a cornerstone of modern quantum chemistry and a powerful method for understanding chemical bonding in molecules. Developed in the early 20th century by Friedrich Hund and Robert S. Mulliken, MOT was designed to overcome limitations of the Valence Bond Theory (VBT), which treats electrons as localized in bonds between two atoms. While VBT successfully explains many molecular structures and properties, it fails to account for certain phenomena such as the Para magnetism of oxygen, delocalization in conjugated systems, and bonding in molecules with unusual electron configurations. MOT addresses these issues by describing electrons as delocalized over the entire molecule, occupying molecular orbitals (MOs) formed from linear combinations of atomic orbitals (AOs).

Unlike the classical view in VBT, where bonding electrons are confined to the space between two nuclei, MOT considers that the electron density is spread over the entire molecule, giving a polycentric character. This approach allows a more complete description of chemical bonding, electron distribution, and molecular stability, and it provides insights into molecular magnetism, bond order, bond length, and electronic transitions observed in spectroscopy.

### Key Principles of Molecular Orbital Theory

### 1. Formation of Molecular Orbitals

Molecular orbitals are formed by the linear combination of atomic orbitals (LCAO) from the constituent atoms. When two atoms approach each other, their atomic orbitals overlap constructively and destructively to form two molecular orbitals:

1. **Bonding Molecular Orbital:** Constructive interference increases electron density between the nuclei, lowering the energy relative to the separate atomic orbitals. Electrons in bonding orbitals stabilize the molecule. Notation: σ or π.
2. **Antibonding Molecular Orbital**: Destructive interference creates a node between the nuclei, reducing electron density and raising the energy. Electrons in antibonding orbitals destabilize the molecule. Notation: σ* or π*.

For example, in the hydrogen molecule ($H_2$), two 1s atomic orbitals combine to produce one $\sigma_1$s bonding and one *$\sigma_{1s}$ antibonding** orbital. The two electrons occupy the lower-energy $\sigma_1$s orbital, resulting in a stable bond.

The number of molecular orbitals always equals the number of atomic orbitals combined, a principle known as orbital conservation.

### 2. Electron Delocalization

Electrons in atomic orbitals are monocentric, primarily influenced by a single nucleus. In molecular orbitals, electrons are polycentric, meaning they are influenced by all nuclei in the molecule. This delocalization explains properties such as resonance, delocalized bonding in conjugated systems, and unusual magnetic behaviours like Para magnetism in $O_2$, which VBT cannot explain.

### 3. Electron Filling Rules

**Molecular orbitals are filled according to quantum mechanical rules:**

1. **Aufbau Principle:** Electrons occupy molecular orbitals in order of increasing energy. The energy order depends on the type of molecule. For diatomic molecules of elements with atomic numbers less than 8 ($H_2$, $He_2$, $Li_2$, $B_2$, $C_2$, $N_2$), the order is: **σ1s<σ1s∗<σ2s<σ2s∗<σ2pz<π2px=π2py<π2px∗=π2py∗<σ2pz∗**
2. For $O_2$, $F_2$, and $Ne_2$, s-p mixing alters the order slightly: **σ1s<σ1s∗<σ2s<σ2s∗<σ2pz<π2px=π2py<π2px∗=π2py∗<σ2pz∗**
3. **Pauli Exclusion Principle**: A maximum of two electrons can occupy a molecular orbital, with opposite spins**.**
4. **Hund's Rule:** Degenerate orbitals (orbitals of equal energy, e.g., $\pi_2$p_x and $\pi_2$p_y) are singly filled before pairing. This minimizes electron-electron repulsion and stabilizes the molecule.

### 4. Types of Molecular Orbitals

| **Type** | **Interference** | **Energy** | **Electron Density** | **Stability Contribution** | **Notation** |
|---|---|---|---|---|---|
| **Bonding** | **Constructive** | **Lower than AOs** | **High between nuclei** | **Stabilizes molecule** | **σ, π** |
| **Antibonding** | **Destructive** | **Higher than AOs** | **Node between nuclei** | **Destabilizes molecule** | **σ*, π*** |

### 5. Bond Order and Stability

Bond order (B.O.) is a measure of bond strength and stability, defined as:

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

where $N_b$= number of electrons in bonding orbitals, $N_a$= number in antibonding orbitals.

- B.O. > 0 → stable bond
- B.O. = 0 → molecule unstable (e.g., $He_2$)

Bond order correlates with bond length and energy: higher bond order → shorter, stronger bond.

### 6. Magnetic Properties

- Paramagnetic: Molecules with unpaired electrons are attracted to magnetic fields.
- Diamagnetic: Molecules with all paired electrons are repelled by magnetic fields.
- MOT accurately predicts $O_2$ is paramagnetic because two electrons occupy degenerate $\pi^*$ orbitals, whereas VBT incorrectly predicts it as diamagnetic.

### 7. Molecular Orbital Diagrams

Molecular orbital diagrams visually represent the energy levels of AOs and resulting MOs, showing electron distribution and predicting molecular properties.

$H_2$ Example:

- Two 1s atomic orbitals combine → $\sigma_1$s and $\sigma_1$s*
- Two electrons occupy $\sigma_1$s
- Bond order = 1 → single bond

### 8. Oxygen Molecule ($O_2$) MO Diagram

- Total electrons: 16
- Minimal s-p mixing
- $\sigma_{2p}$orbital is lower than $\pi_{2p}$orbitals

Electron Configuration:

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^1(\pi_{2p}^*)^1$$

Bond Order: (10 bonding − 6 antibonding)/2 = 2
Magnetism: Two unpaired electrons → paramagnetic

### 9. Nitrogen Molecule ($N_2$) MO Diagram

- Total electrons: 14
- Significant s-p mixing
- $\sigma_{2p}$orbital lies above $\pi_{2p}$orbitals

Electron Configuration:

$$(\boldsymbol{\sigma}_{\mathbf{1s}})^2(\boldsymbol{\sigma}_{\mathbf{1s}}^*)^2(\boldsymbol{\sigma}_{\mathbf{2s}})^2(\boldsymbol{\sigma}_{\mathbf{2s}}^*)^2(\boldsymbol{\pi}_{\mathbf{2p}})^2(\boldsymbol{\pi}_{\mathbf{2p}})^2(\boldsymbol{\sigma}_{\mathbf{2p}})^2$$

Bond Order: (10 bonding − 4 antibonding)/2 = 3 → triple bond
Magnetism: All electrons paired → diamagnetic

### 10. Energy Level Diagrams and s-p Mixing

- Energy diagrams differ for molecules before and after oxygen.
- s-p mixing occurs in lighter elements ($Li_2$ to $N_2$), altering orbital energies: $\sigma_2$p_z may lie below $\pi_2$p_x and $\pi_2$p_y.
- Explains variations in bond orders and stability.

### 11. Comparison with Valence Bond Theory

- VBT: Electrons localized, explains single bonds and hybridization well.
- MOT: Electrons delocalized, explains Para magnetism, bond order variations, resonance.
- Delocalized MOs are essential for aromatic systems (e.g., benzene), conjugation, and polyatomic molecules.

### 12. Applications of MOT

1. Predicts magnetic properties ($O_2$, NO, $F_2$).
2. Determines bond orders, lengths, and energies.
3. Explains spectroscopic transitions (UV-Vis, IR).
4. Describes resonance and delocalization in aromatic molecules.
5. Clarifies unusual molecules/ions ($O_2^-$, $NO^+$, CO).

### 13. Extension to Polyatomic Molecules

- MOT can be generalized to multiple atoms.
- Atomic orbitals from all atoms combine to form molecular orbitals delocalized over entire molecule.
- Explains bonding in polyatomic ions like $NO_3^-$, $CO_3^{2-}$, and conjugated systems like $C_6H_6$.
- Forms basis for computational chemistry methods**.**

## 11.3 SUMMARY

This chapter focuses on Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT), two fundamental approaches for understanding chemical bonding in molecules using quantum mechanics. Valence Bond Theory describes chemical bonds as localized electron pairs formed by the overlap of atomic orbitals on adjacent atoms. According to VBT, electrons in overlapping orbitals must have paired spins, as dictated by the Pauli exclusion principle, to allow bond formation. The stability of the bond is determined by the potential energy curve, which reaches a minimum at the equilibrium internuclear separation, reflecting the balance between attractive and repulsive forces. VBT also accounts for the directionality of bonds, explaining molecular geometry, and introduces hybridization to describe molecular shapes. In hybridization, atomic orbitals mix to form equivalent hybrid orbitals: $sp^3$ hybridization results in tetrahedral geometry with ideal bond angles of 109.5°, $sp^2$ hybridization leads to trigonal planar geometry with 120° bond angles, and sp hybridization produces linear molecules with 180° bond angles. Lone pairs of electrons can slightly distort these ideal geometries.

Molecular Orbital Theory, developed by Hund and Mulliken, extends the understanding of bonding by considering electrons as delocalized over the entire molecule rather than strictly localized between atoms. MOT uses the Linear Combination of Atomic Orbitals (LCAO) method to construct bonding and antibonding molecular orbitals. Electrons occupy these orbitals according to the Aufbau principle, the Pauli exclusion principle, and Hund’s rule. This approach allows the calculation of bond order, which measures bond strength and stability, and can predict magnetic properties. For example, MOT correctly explains the Para magnetism of oxygen ($O_2$) due to the presence of two unpaired electrons in $\pi^*$ antibonding orbitals, a phenomenon that VBT cannot account for. MOT also helps rationalize the stability of molecules like $N_2$, which has all paired electrons in bonding orbitals, making it diamagnetic.

By integrating the principles of VBT, hybridization, and MOT, one obtains a comprehensive understanding of chemical bonding. VBT explains the formation of localized bonds and electron pairing, hybridization clarifies molecular geometry and bond angles, and MOT accounts for electron delocalization, bond order, and magnetic properties. Together, these theories provide a complete picture of molecular structure, electron distribution, stability, and reactivity, bridging classical chemical intuition with quantum mechanical principles.

## 11.4 Technical terms:

Valence bond theory, Molecular orbital theory

## 11.5 SELF-ASSESSMENT QUESTIONS

1. Briefly explain the of Valence bond method.
2. Explain the Molecular orbital theory.

## 11.6 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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## LESSON - 12

# HEITLER-LONDON METHOD

**Aim and Objectives**

The aim of this study is to critically compare the main quantum mechanical approaches used to describe chemical bonding in molecules, specifically focusing on Valence Bond Theory (VBT), Molecular Orbital Theory (MOT), and the Heitler-London method. These theories provide frameworks for understanding how electrons are distributed in molecules, how chemical bonds form, and how molecular properties such as bond order, magnetism, and stability can be predicted. While VBT emphasizes localized electron pairs and orbital overlap, MOT treats electrons as delocalized over the entire molecule, offering explanations for phenomena that VBT cannot adequately describe. The Heitler-London method, as the earliest quantum mechanical approach to the hydrogen molecule, forms the historical foundation for these theories. By comparing these methods, this study aims to clarify their relative strengths, limitations, and applicability to different molecular systems.

The first objective is to understand the fundamental principles of Valence Bond Theory. VBT describes bonds as localized electron pairs resulting from the overlap of atomic orbitals and incorporates the concepts of hybridization and resonance to explain molecular geometries and bond strengths. It is particularly effective for simple molecules and provides an intuitive visual understanding of bonding, but its limitations become apparent in molecules with delocalized electrons or magnetic properties that cannot be explained by localized electron pairs alone. Understanding these aspects allows one to appreciate both the utility and boundaries of VBT.

The second objective is to study Molecular Orbital Theory, which models electrons as delocalized over the entire molecule. MOT uses the linear combination of atomic orbitals (LCAO) to form bonding and antibonding molecular orbitals and provides a quantitative framework for calculating bond order, predicting magnetic behaviour, and explaining spectral properties. Unlike VBT, MOT successfully accounts for the Paramagnetism of oxygen and other molecules where electrons are not strictly localized. Exploring MOT helps in understanding the advantages of delocalized electron models and their predictive accuracy in complex molecular systems.

The third objective is to analyse the Heitler-London method, which was the first rigorous quantum mechanical treatment of the hydrogen molecule ($H_2$). This method introduces the concept of electron exchange and the importance of antisymmetrization of the wavefunction in bond formation. While computationally intensive, the Heitler-London method provides accurate predictions of molecular energy and bond characteristics for simple systems and forms the basis upon which modern VBT was developed. Studying this method highlights the evolution of bonding theories from the first quantum mechanical attempts to contemporary models.

Another important objective is to compare the predictive capabilities of VBT and MOT. This includes evaluating how each method describes electron distribution, bonding, and antibonding interactions, and assessing their predictions of bond length, bond energy, and magnetic properties in molecules like $H_2$, $O_2$, and $N_2$. While VBT offers a simpler, more intuitive explanation in many cases, MOT provides a more comprehensive approach for systems with delocalized electrons. This comparison allows for informed selection of the appropriate theoretical model depending on the molecule or property under study.

Finally, this study aims to highlight the historical development and practical applications of these theories. Tracing the evolution from Heitler-London to modern VBT and MOT demonstrates the refinement of theoretical models alongside advances in quantum mechanics. Each theory's practical applications in spectroscopy, computational chemistry, and molecular design are evaluated, emphasizing how these models guide our understanding of chemical reactivity, molecular stability, and electronic properties. By integrating insights from all three approaches, the study provides a holistic understanding of chemical bonding, supporting both conceptual clarity and quantitative prediction of molecular behaviour.

## STRUCTURE

## 12.1 COMPARISON OF THE METHODS

Chemical bonding is a central concept in chemistry, and understanding how atoms combine to form molecules is crucial for explaining molecular structure, stability, and properties. Over the past century, two fundamental quantum mechanical models have emerged to describe chemical bonding: Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Both approaches are grounded in quantum mechanics but adopt distinct perspectives on the behavior of electrons within molecules. VBT emphasizes localized electron pairs between atoms, while MOT treats electrons as delocalized across the entire molecule. Together, these theories provide complementary insights into the electronic structure, bonding characteristics, and properties of molecules.

### 1. Conceptual Basis

**Valence Bond Theory (VBT):** VBT, originally developed by Heitler, London, and Pauling, explains bonding as a result of the overlap of atomic orbitals from two atoms to form a covalent bond. In this model, electrons remain largely localized between the atoms they bond, and the strength of a bond is proportional to the extent of orbital overlap. The theory also incorporates concepts such as hybridization, which allows atomic orbitals to mix and form new orbitals that better describe molecular geometries, and resonance, which accounts for delocalization effects in molecules that cannot be represented by a single Lewis structure. The wavefunction of the molecule in VBT is constructed using atomic orbitals of individual atoms, reflecting a strong connection to the electronic structure of isolated atoms.

**Molecular Orbital Theory (MOT):** MOT, developed by Hund and Mulliken, approaches bonding from a delocalized perspective, where electrons are not confined to individual bonds but occupy molecular orbitals (MOs) that extend over the entire molecule. These MOs are constructed as linear combinations of atomic orbitals (LCAO), allowing the formation of bonding and antibonding orbitals. MOT provides a more global description of the molecule's electronic structure, explaining properties such as magnetism, bond order, and electronic transitions that VBT cannot fully address. In contrast to VBT, MOT assigns equal importance to covalent and ionic contributions, giving a more accurate representation of electron distribution in molecules.

**2. Wavefunction Representation**

A key distinction between VBT and MOT lies in how the molecular wavefunction is expressed**.**

- VBT:In the hydrogen molecule ($H_2$), for instance, the wavefunction can be written as:

$$\boldsymbol{\Psi_{\mathrm{VBT}} = c_1\psi_A(1)\psi_B(2) + c_2\psi_A(2)\psi_B(1)}$$

Here, $\psi_A$and $\psi_B$are atomic orbitals centered on atoms A and B, and the terms account for the exchange of electrons between the two nuclei. This form emphasizes the pairing of electrons in a covalent bond and is inherently localized between the two atoms. Ionic contributions, in which both electrons might reside on a single atom, are typically neglected in simple VBT treatments.

- MOT:In contrast, the molecular orbital wavefunction is expressed as**:**

$$\boldsymbol{\Psi_{\mathrm{MOT}} = c_1\psi_A + c_2\psi_B}$$

for each electron, and electrons occupy bonding ($\sigma$) and antibonding ($\sigma^*$) molecular orbitals formed by constructive or destructive interference of atomic orbitals. This representation is delocalized, allowing electrons to be shared across the entire molecule, and naturally includes both covalent and ionic character in the bonding description. MOT thus provides a more versatile framework for describing molecules with complex bonding interactions.

**3. Exchange Integrals**

Another difference between VBT and MOT arises in the treatment of electron exchange:

- VBT:The exchange integral in VBT is given by

$$\boldsymbol{\int \phi_A(1)\phi_B(2)H\phi_B(1)\phi_A(2)d\tau}$$

which represents the simultaneous exchange of two electrons between two atomic orbitals. This integral contributes to the stabilization energy of the covalent bond. It is central to understanding why electron pairing lowers the energy of the system, but its computation becomes increasingly complex for larger molecules.

- MOT**:** In MOT, the exchange integral takes the form

$$\boldsymbol{\int \phi_A(1)\phi_B(2)d\tau}$$

which represents the exchange of a single electron between atomic orbitals. These integral measures the interaction or coupling between orbitals and is used to calculate the energies of bonding and antibonding molecular orbitals. Unlike VBT, MOT inherently incorporates electron delocalization, and exchange interactions are naturally included in the energy levels of the molecular orbitals.

**4. Treatment of Ionic and Covalent Contributions**

VBT and MOT differ significantly in how they handle ionic versus covalent character:

- VBT: The traditional VBT approach focuses on purely covalent bonding, where electrons are localized between atoms. Ionic structures, in which both electrons reside on a single atom, are usually ignored unless explicitly included through resonance.

This simplification works well for molecules dominated by covalent interactions but fails to accurately describe molecules with significant ionic character.

- MOT: MOT treats both covalent and ionic contributions equally, as the molecular orbitals are formed from a combination of atomic orbitals on different atoms. As a result, MOT can naturally explain phenomena like partial ionic character, charge delocalization, and resonance stabilization, providing a more complete picture of bonding in polar molecules and complex systems.

**5. Electron Sharing and Delocalization**

- VBT: In VBT, a single electron is not shared simultaneously by two nuclei; instead, bonding is viewed as localized electron pairing. The bond forms due to the overlap of atomic orbitals, and the electrons remain predominantly confined between the two atoms. This localized view makes VBT intuitive for understanding molecular geometry and simple diatomic molecules but limits its applicability for delocalized systems like conjugated molecules or metals.
- MOT: In MOT, electrons are delocalized and can be simultaneously associated with multiple nuclei. This delocalization explains electronic properties such as Para magnetism, aromaticity, and electronic transitions, which VBT cannot easily account for. For example, MOT correctly predicts that oxygen ($O_2$) isparamagnetic due to the presence of two unpaired electrons in antibonding molecular orbitals, whereas VBT fails to do so**.**

**6. Predictive Power and Applications**

Both VBT and MOT have their strengths and limitations in predicting molecular properties:

- VBT is highly effective for understanding localized bonding, molecular shapes via hybridization, and resonance effects in organic molecules. It provides an intuitive and visual model that is easy to use for explaining covalent structures.
- MOT is more versatile, capable of explaining magnetic properties, bond orders, delocalized electrons, electronic spectra, and molecules with unusual bonding patterns. Its quantitative nature makes it indispensable in computational chemistry, spectroscopy, and the design of molecules with specific electronic properties.
- In practice, modern chemical analysis often uses a combination of both approaches, with VBT providing a simple conceptual framework and MOT providing detailed quantitative predictions.

**7.Historical Context**

The development of these theories also reflects the historical evolution of quantum chemistry:

- The Heitler-London method laid the foundation for VBT by applying quantum mechanics to the hydrogen molecule, introducing electron pairing and exchange interactions.
- VBT further developed these concepts, introducing hybridization and resonance to explain more complex molecules.
- MOT emerged later, providing a more general and mathematically rigorous treatment of electrons in molecules, extending the applicability to delocalized systems and explaining properties that VBT could not.

In summary, Valence Bond Theory and Molecular Orbital Theory represent two complementary approaches to understanding chemical bonding. VBT emphasizes localized electron pairs and covalent interactions, providing intuitive insights into molecular geometry and bonding patterns. MOT, on the other hand, treats electrons as delocalized across the molecule, allowing it to explain magnetic properties, bond order, and electronic spectra. While VBT often simplifies bonding by neglecting ionic contributions, MOT incorporates both ionic and covalent character equally, offering a more complete description of molecules. Together, these theories form the backboneof modern quantum chemistry, providing both qualitative understanding and quantitative tools to predict molecular behaviour.

## 12.2 Heitler-London method

### Introduction

The Heitler–London method, developed in 1927 by Walter Heitler and Fritz London, marked a pivotal moment in the history of quantum chemistry. It was the first rigorous quantum mechanical explanation of chemical bonding, providing a theoretical foundation for what would later become Valence Bond Theory (VBT). Prior to this work, the nature of chemical bonds had been largely understood in classical terms, relying on electrostatic attractions between nuclei and electrons. The Heitler–London method introduced the radical idea that bonding arises not from classical forces alone but from electron exchange and wavefunction symmetry, concepts rooted in the principles of quantum mechanics. This approach was first applied to the hydrogen molecule ($H_2$), the simplest diatomic system, making it an ideal test case for examining how quantum mechanics can describe molecular stability and chemical bonding.

### Historical Context

In the early 20th century, the understanding of atomic structure had advanced significantly due to the work of Bohr, Schrödinger, and Heisenberg, but molecules remained poorly understood. While the Bohr model explained discrete energy levels of isolated atoms, it could not account for chemical bonding or molecular properties. The emerging quantum mechanics framework, particularly the Schrödinger equation, provided a mathematical basis for describing the behaviour of electrons, yet the application to molecules was nontrivial. Heitler and London addressed this challenge by considering the two-electron hydrogen molecule, applying the Schrödinger equation with approximations suitable for molecular systems. Their work demonstrated that electron exchange and wavefunction symmetry could explain bond formation, a concept with no classical analogue. This methodology laid the groundwork for Linus Pauling's Valence Bond Theory and influenced future molecular orbital and quantum chemistry developments.

### Basic Assumptions of the Heitler–London Method

The Heitler–London method relies on several key assumptions that simplify the treatment of molecular bonding while preserving essential quantum mechanical principles:

1. **Electron Contribution**: Each hydrogen atom contributes one electron to bond formation. This allows the simplest molecule, $H_2$, to be treated as a two-electron system, the minimum required to study bonding interactions.
2. **Localization of Electrons**: Electrons are assumed to remain largely associated with their parent nuclei, which corresponds to a localized bond picture. Despite this localization, electron exchange between atoms is explicitly allowed to account for quantum mechanical bonding interactions.
3. **Pauli Exclusion Principle**: The total molecular wavefunction must obey the Pauli exclusion principle, ensuring that it is antisymmetric with respect to the exchange of electron coordinates for fermions (electrons). This antisymmetric leads to spin-dependent energy differences, distinguishing singlet and triplet states.

4. **Neglect of Nuclear Motion**: Initially, the nuclei are assumed to be stationary, following the Born–Oppenheimer approximation, which separates nuclear and electronic motion. This approximation simplifies the calculation of electronic energies without significant loss of accuracy for light molecules such as $H_2$.
5. **Wavefunction Symmetry**: Both possible arrangements of the two electrons must be included because electrons are indistinguishable. This ensures a physically meaningful molecular wavefunction, consistent with quantum principles.

**Atomic Wavefunctions**

Each hydrogen atom is described by a 1s atomic orbital, the simplest solution to the Schrödinger equation for a single electron bound to a proton. Let:

$\psi_A(1)$ represent the 1s orbital of atom A for electron 1,
$\psi_B(2)$ represent the 1s orbital of atom B for electron 2.

Because electrons are indistinguishable, there are two equivalent electron arrangements:

1. Electron 1 in orbital $\psi_A$, electron 2 in $\psi_B$: $\psi_A(1)\psi_B(2)$
2. Electron 1 in orbital $\psi_B$, electron 2 in $\psi_A$: $\psi_A(2)\psi_B(1)$

Both configurations are necessary for constructing a proper molecular wavefunction that accounts for electron indistinguishability.

**Heitler–London Wavefunctions**

The total molecular wavefunction is constructed as a linear combination of the two electron arrangements, leading to two possible states:

**(a) Singlet State (Bonding State)**

In the singlet state, the two electrons have opposite spins, and the spatial part of the wavefunction is symmetric:

$$\Psi_S = \frac{1}{\sqrt{2(1+S^2)}}[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)]$$

Here,

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

is the overlap integral, which quantifies the extent of orbital overlap between atoms A and B. The symmetric combination enhances electron density in the internuclear region, creating an attractive interaction that stabilizes the molecule and leads to bond formation. This bonding state corresponds to the lowest energy configuration, explaining why the $H_2$ molecule is stable.

**(b) Triplet State (Antibonding State)**

In the triplet state, the electrons have parallel spins, requiring an antisymmetric spatial wavefunction:

$$\Psi_T = \frac{1}{\sqrt{2(1-S^2)}}[\psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)]$$

The antisymmetric combination reduces electron density between the nuclei, so repulsion dominates, and no stable bond is formed. This explains why the triplet state of $H_2$ is unstable and why the singlet state is energetically preferred.

### Role of Exchange Interaction

The exchange interaction is central to the Heitler–London method. It arises purely from the quantum mechanical requirement of electron indistinguishability and has no classical analogue. Exchange interaction increases the probability of finding electrons between the nuclei, enhancing electron density in the bonding region and lowering the total energy of the system. This stabilization is the key mechanism behind covalent bond formation. The singlet state benefits from this interaction, while the triplet state, which does not allow symmetric spatial overlap, remains repulsive.

Mathematically, the exchange energy can be expressed as the difference in energy between symmetric and antisymmetric combinations of atomic orbitals. This energy is directly related to the overlap integral, which increases as atomic orbitals come closer, explaining the distance-dependent nature of chemical bonds.

### Energy Expression

The total energy of the $H_2$ molecule is obtained by evaluating the expectation value of the Hamiltonian:

$$E = \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle}$$

The molecular Hamiltonian $\hat{H}$includes contributions from:

- Electron kinetic energy
- Electron–nucleus attraction
- Electron–electron repulsion
- Nucleus–nucleus repulsion

By solving this expression for different internuclear distances (R), one can determine the equilibrium bond length and bond energy of $H_2$. The energy minimization shows that there is an optimal separation $R_e$where attractive and repulsive forces balance, confirming the existence of a stable chemical bond.

### Potential Energy Curve

Plotting the total energy E(R) as a function of internuclear distance yields a potential energy curve:

- At large distances, the electrons are effectively associated with their respective atoms, and the energy approaches that of two isolated hydrogen atoms.
- As atoms approach, electron exchange increases the attractive interaction, lowering energy.
- The minimum of the curve corresponds to the equilibrium bond length $R_e$, and the depth of the minimum represents the bond dissociation energy $D_e$.
- At very short distances, nuclear repulsion dominates, sharply increasing energy.
- This curve provides direct evidence for the stability of the hydrogen molecule and allows quantitative prediction of bond properties, such as length, energy, and vibrational characteristics.

### Extensions and Implications

The Heitler–London method, although applied initially to $H_2$, laid the foundation for Valence Bond Theory, which generalizes electron pairing and orbital overlap to more complex molecules. Key implications include:

1. Localized Bonding: Bonds can be understood as localized electron pairs, a principle widely used in organic and inorganic chemistry.
2. Hybridization: The concept of mixing atomic orbitals to form new directional orbitals (sp, $sp^2$, $sp^3$) emerges naturally from the VBT extension of the Heitler–London approach.
3. Resonance and Delocalization: While Heitler–London treats electrons as localized, it provides the groundwork for incorporating resonance in molecules where electrons are delocalized across multiple atoms.
4. Spin Dependence: Singlet–triplet splitting explains magnetic properties and the preference for certain spin states in molecules.
5. Quantitative Predictions: Though limited to small systems, the method allows estimation of bond lengths, bond energies, and vibrational frequencies with reasonable accuracy.

**Comparison with Molecular Orbital Theory**

While the Heitler–London method provides an intuitive localized picture, Molecular Orbital Theory (MOT) generalizes bonding by delocalizing electrons over the molecule. MOT:

- Accounts for ionic contributions automatically.
- Explains paramagnetism, e.g., $O_2$, which VBT and Heitler–London cannot.
- Provides a framework for molecules with more than two atoms and conjugated systems.

Nonetheless, the Heitler–London method remains foundational, emphasizing the quantum mechanical origin of bonding and introducing exchange interactions, which are fundamental to all covalent bonds.

So, in summary the Heitler–London method represents a milestone in theoretical chemistry. By applying quantum mechanics to the hydrogen molecule, it demonstrated that chemical bonds arise from electron exchange and wavefunction symmetry, not merely classical forces. The method introduced:

- Localized bonding
- Symmetric and antisymmetric wavefunctions
- Exchange interaction as a stabilizing force
- Quantitative energy calculations for molecular stability

Its conceptual framework underpins Valence Bond Theory, influencing the understanding of molecular geometry, bond energies, and electronic structure. While later theories like MOT extend these ideas to delocalized systems, the Heitler–London approach remains a cornerstone of quantum chemical bonding theory, providing insight into the fundamental nature of the chemical bond.

## 12.3 SUMMARY

The study of chemical bonding has been revolutionized by quantum mechanics, with the Valence Bond Theory (VBT), Molecular Orbital Theory (MOT), and the Heitler–London method serving as foundational models. Each approach offers a distinct perspective on how electrons interact to form stable molecules, with unique assumptions, strengths, and limitations.

The Heitler–London method (1927) was the first successful quantum mechanical explanation of bonding. Applied to the hydrogen molecule ($H_2$), it demonstrated that bond formation arises from electron exchange and wavefunction symmetry, rather than purely classical electrostatic forces. The method assumes that each hydrogen atom contributes one electron, which remains largely associated with its parent nucleus, but allows for electron exchange between atoms. The total molecular wavefunction is constructed to obey the Pauli exclusion principle, resulting in a singlet (bonding) and triplet (antibonding) state. The singlet state, with opposite spins, produces a symmetric spatial wavefunction that increases electron density in the internuclear region, leading to a stable bond. The triplet state, with parallel spins, has an antisymmetric spatial wavefunction, reducing electron density between nuclei and preventing stable bonding. The exchange interaction stabilizes the singlet state, and the energy of the molecule is calculated using the expectation value of the Hamiltonian, including kinetic energy, electron–nucleus attraction, electron–electron repulsion, and nuclear repulsion. The resulting potential energy curve illustrates the equilibrium bond length and bond dissociation energy, providing a quantitative description of molecular stability. The Heitler–London method laid the foundation for Valence Bond Theory, which generalizes the concepts of localized electron pairing, hybridization, and resonance to more complex molecules.

Valence Bond Theory (VBT) builds directly on the Heitler–London approach. In VBT, covalent bonds form through the overlap of atomic orbitals, and electrons remain localized between the bonded atoms. Concepts like hybridization explain molecular geometry, while resonance accounts for delocalized bonding in molecules that cannot be represented by a single Lewis structure. VBT provides an intuitive, visual understanding of bonding, making it effective for small molecules and organic systems. However, it often neglects ionic contributions and cannot fully explain phenomena like the Para magnetism of $O_2$.

Molecular Orbital Theory (MOT) offers a complementary perspective, treating electrons as delocalized over the entire molecule. Molecular orbitals are formed as linear combinations of atomic orbitals, resulting in bonding and antibonding orbitals that include both covalent and ionic character. MOT accurately predicts bond order, magnetic behaviour, and electronic spectra, and can describe systems with delocalized electrons, such as benzene, more naturally than VBT. For example, MOT correctly predicts $O_2$ as paramagnetic due to two unpaired electrons in antibonding $\pi^*$ orbitals, whereas VBT and Heitler–London fails in this regard. While more computationally complex, MOT provides a more global and quantitative description of molecular electronic structure.

In summary, the Heitler–London method establishes the quantum mechanical basis for bonding, highlighting the role of electron exchange and wavefunction symmetry. VBT extends this localized approach to explain geometry, hybridization, and resonance in molecules, whereas MOT provides a delocalized framework capable of explaining magnetic properties, bond order, and delocalization phenomena. Together, these models offer a comprehensive understanding of chemical bonding, from the simplest diatomic molecules to complex polyatomic systems, bridging intuitive visualization and quantitative prediction in modern chemistry.

## 12.4 TECHNICAL TERMS

Comparison of the methods
Heitler-London Method

## 12.5 SELF-ASSESSMENT QUESTIONS

1. Distinguish between VBT and MOT.
2. Explain Heitler-London Method

## 12.6 SUGGESTED READINGS

1. Quantum Mechanics – Merzbacher E (John Wiley & Sons, New York)
2. L I Schiff, Quantum Mechanics (Mc Graw-Hill)
3. B Crasemann and J D Powell, Quantum Mechanics (Addison Wesley)
4. A P Messiah, Quantum Mechanics
5. J J Sakural, Modern Quantum Mechanics
6. Mathews and Venkatesan, Quantum Mechanics
7. Quantum Mechanics, R.D. Ratna Raju
8. Quantum Mechanics by Kakani and Chandaliya
9. Atkins P, Molecular Quantum Mechanics, Oup 1996(T)

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